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系统构建无废城市

To Build a Zero-waste City Systematically

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Preface

The International Conference on Waste Management and Technology (ICWMT) initiated by Basel Convention Regional Centre for Asia and the Pacific has been held for 14 times since its inception in 2005, which promotes the knowledge and experience exchanges among the international stakeholders and enhances the technology cooperation among countries. It was jointly organized by Tsinghua University, Solid Waste and Chemicals Management Technology Center, Ministry of Ecology and Environment of the People's Republic of China, United Nations Environment Programme, Basel Convention Regional Centre for Asia and the Pacific (BCRC China).

The ICWMT 15 was virtually held in Beijing, China, from 28th to 30th, June 2020. Themed with "To Build a Zero-waste City Systematically", prominent scholars and government officials were invited to give keynote speeches on the pressing issues of solid waste management, chemicals and circular economy during the conference. The main topics of the conference involve hazardous waste management and risk prevention, recycling and pollution controlling of WEEE, biomass waste treatment and utilization as resources and energy, management and policy of regional chemicals, municipal solid waste classification and disposal technology, remediation of contaminated sites and environmental regulation, integrated utilization of industrial solid waste, circular economy and the development of urban mining, and construction waste disposal & utilization as resource and energy.

Many outstanding articles and abstracts from research institutes and universities, and plenary speeches were received by the ICWMT 15 until June 20th, which can indicate the latest research trend and innovative ideas of current solid waste treatment field and lead the development in this field for the future.

Finally, I would like to thank all the reviewers and authors who devoted a substantial amount of work.

Prof. Jinhui Li

Chairman of Conference

27-06-2020

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Experimental Study on Recovery from sewage sludge for reutilization

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Abstract

With a sharply increase and poor treatment status of sewage sludge in China, it is imperative to explore a green and recyclable strategy with high added value for sludge reutilization instead of landfill or incineration. This study focused on the humic acid in sludge, and creatively discussed its feasibility as soil conditioner and precursor material for supercapacitor. Three extraction and purification approaches were compared by using UV-vis, FTIR and purity determination methods. The results showed that the alkali treatment-ultrafiltration-acid precipitation-centrifugation procedure could increase the hydrosoluble humic acid level by 7.5 times and decrease the heavy metals contents by 17%~67%, meeting the requirements for fertilizer. According to the electrochemical analysis results, the carbonized humic acid originated from sludge had a specific capacitance of 189.7 F g^{-1}, and exhibited excellent long-term cycling performance, which was comparative to other waste- or low-grade coal-derived carbon materials. The recycling of humic acid from sludge for producing soil conditioner or supercapacitor electrode material is a promising reutilization route for the environment-friendly management of sewage sludge.

Keywords: sludge; humic acid; extraction; reutilization

1. Introduction

With the growing proliferation of municipal wastewater treatment plants in compliance with the Water Pollution Control Action Plan, the production of sewage sludge has increased sharply in recent years. According to the Ministry of Housing and Urban-Rural Development of China, by the end of 2017, the amount of dry sludge was up to 10.53 million tons, increasing by an average rate of 13% annually during the last eight years[1]. So, sewage sludge has become one of the key environmental problems in China. At present, sanitary landfill was still the major method for sludge disposal, while incineration and land utilization had a few applications[2]. Anaerobic digestion counted for less than 3% in sewage treatment plants of China, and almost 2/3 of facilities did not work properly[2]. The poor treatment and low-grade disposal of sludge would cause accumulated contamination of hazardous substances in various environmental matrices[3] and a waste of resources in sludge. For example, landfill sites received the biggest portion of sludge-borne mercury, and the amount of mercury ending up in landfill in 2016 was 5.5 tons[4-5]. The content of zinc, lead, cadmium and mercury in the vegetable land soils with long term application of sewage sludge was 3-125 times higher than the corresponding background values[6]. So, there is a strong need to explore environment-friendly and effective technologies for high-value-added resources utilization of sludge instead of simplex disposal.

Sewage sludge is a significant reservoir of humic acid, which could be recycled as a potential resource. Li et al. (2009)[7] extracted humic acid from the dewatered residual sludge for producing liquid fertilizer, which had more nutrition and less heavy metals. Qiao et al. (2014)[8] found that the humic acid-based hierarchical porous carbons were an appropriate precursor for making high-performance supercapacitors. Zhu et al. (2015)[9] explored humic acid as anode materials for lithium ion batteries and sodium ion

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batteries with high storage capacitances. It can be seen from this that the recycling of humic acid originated from sludge as resources for high-value-added reutilization is a plausible and promising strategy for sludge management.

Therefore, with the aim of proposing new route for economical and efficient use of sludge, this study investigated the extraction and purification of humic acid derived from sludge, and discussed the feasibility of humic acid as the soil conditioner or supercapacitor materials. The results would be helpful to the pollution control, reduction, recycling and management of sewage sludge from a new perspective.

2. Materials and methods

2.1. Sampling and chemicals

Excess sludge samples were collected from a large scale municipal sewage treatment plant located in Taiyuan, Shanxi province, in which approximately 16.64×10^4 t/d of sewage is treated by adopting anaerobic-anoxic-oxic technology, and the water content of sludge was around 85% by using the belt pressure dehydration filter. After air-dried and passed through a 20 mesh sieve, the sludge samples were stored in polyethylene bags for further use. Pure humic acid (labeled as HA0) purchased from the International Humic Substances Society (IHSS) was used as reference. All used chemicals were of analytical-reagent grade quality.

2.2. Extraction and purification

Alkali extraction method[10] and the modified IHSS method[11] were used to obtain the humic substances from sludge. Briefly, for the alkali extraction method, sludge samples and 0.2 M NaOH (solid to liquid ratio of 1:50) were mixed thoroughly for 24 h. After centrifugation, the supernatant was acidified to pH=1.0 with 6 M HCl and left to stand for overnight. Then the precipitates were filtered and freeze-dried, labeled as HA1. HA2 was the purified HA1 by using ultrafiltration membrane (5,000Da, 0.3MPa) to concentrate the alkali treated mixture to around 30% before undergoing the same acidification process. HA3 was prepared following the similar procedure of HA2, but the finally precipitates were separated by centrifugation rather than pouring the supernatant directly. As for the modified IHSS method, the sludge samples were pretreated by 0.1 M HCl (S/L, 1:10) for 1 h, and a 0.1 M NaOH solution was used to dissolve the insoluble fraction (S/L, 1:10) for more than 4 h. The alkaline extract was subsequently acidified with a 6.0 M HCl to pH=1.0 and left to stand for 12~16 h to obtain the precipitation of humic acid, labeled as HA4.

2.3. Characterization

HAs solutions were prepared by dissolving the humic materials in 0.1 M $NaHCO_3$ solvent, stirring overnight, and passing through a 0.45-μm filter to remove the undissolved fraction. Ultraviolet and visible spectrophotometry (UV-vis) analysis of the extracted HAs solutions and the 10 times of diluted HA0 solution were recorded on a UV-6000PC spectrophotometer (Shanghai METASH Instruments Co. Ltd., China) in a 1 cm path length quartz cuvette at 220-800 nm. Fourier transform infrared (FTIR) spectra of HAs were recorded on a Perkin Elmer FTIR Spectrum Two spectrometer, covering a wavenumber range of 4000-500 cm^{-1} with a resolution of 1.0 cm^{-1}. The water soluble humic acid content was determined by using the potassium dichromate oxidation method according to the standard of “GB/T 11957-2001”.

2.4. Heavy metals analysis

Total concentrations of As, Cr and Pb in sludge and HA3 were determined by Inductively Coupled Plasma Optical Emission Spectrometer (ICP-MS, Thermo 7000, USA) following digestion with HNO_3-HF-$HClO_4$ (HJ 781-2016).

2.5. Electrode preparation and electrochemical measurements

HA1 and HA3 were carbonized in a horizontal tubular furnace under N_2 flow at 800°C for 1 h with a heating rate of 5°C min^{-1}. After cooling naturally to room temperature and rinsed in distilled water, the carbonized materials were filtered and then dried at 80°C for 24 h. 5 wt.% polytetrafluoroethylene, 10 wt.% acetylene black and 85 wt.% carbonized HAs were fully mixed and grounded in a mortar. Then the slurry was pressed on the nickel foam to form the working electrode, in which approximately 5 mg of prepared materials is contained. A three-electrode system was used for electrochemical tests, in which Hg/Hg_2Cl_2 and Pt foil are chosen as reference electrode and counter electrode, respectively, and the aqueous electrolyte is 6M KOH solution. Galvanostatic charge/discharge (GCD) measurements were performed by a Land Battery Measurement System (Land, PR China) and the applied current densities were ranged from 0.05 to 0.5 A g^{-1}.

3. Results and discussion

3.1. UV-Vis and FTIR

The UV-vis and FTIR spectra of HAs were depicted in Fig. 1. In agreement with HA0, the UV-vis scans of the extracted HAs were featureless as a result of overlapping absorbance of numerous chromophores present in humic substances[12], and exhibited monotonically decrease in absorption from 220 nm to 800 nm. Little shoulders presented between 250 nm and 300 nm of the extracted HAs were characteristics to aromatic or unsaturated compounds[13]. The intensity was observed to steadily decline in order of HA3>HA4>HA2>HA1, indicating a potential enrichment of humic substances due to purification. According to Uyguner and Bekbolet (2005)[14], A250/A365 increases as molecular weight size and aromaticity decrease. A lower A250/A365 value measured in HA3, comparing with HA1, implied an increase of high-molecular-weight fractions in the extracted and purified humic material. The A465/A665 parameter of extracted humic acid amounted 5, 5.8 and 5.7 for HA1, HA4 and HA3, respectively, which pointed to the enrichment of humic acid with oxygen functional groups and aromatic structures in HA3 and HA4[15-16].

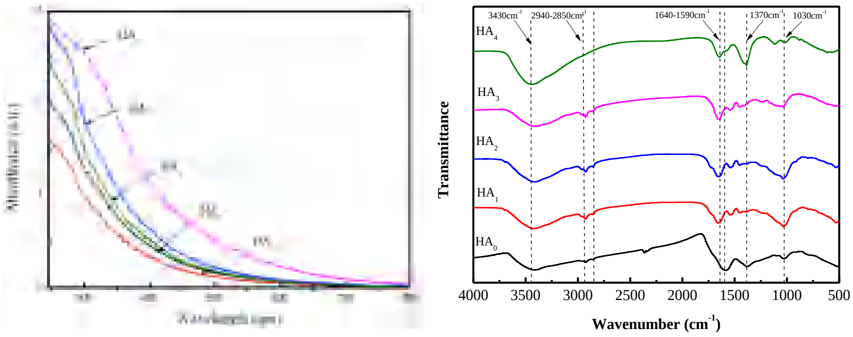

Fig. 1. UV-Vis and FTIR spectra of HAs.

It could be seen from Fig. 1 that, all FTIR spectra showed the same main features of humic substances[17], and no significant changes of characteristic bands were observed between the extracted HAs and HA0. An intense and broad absorption at around 3430 cm^{-1} indicated the presence of O=H stretching and/or N-H stretching of various functional groups[15]. The bands observed between 2850-2940 cm^{-1} were assigned to aliphatic C–H stretching[18], so the stronger absorption in HA1, HA2 and HA3 showed a higher degree of aliphaticity than in HA0 and HA4. According to Amir et al. (2010)[19], the peak at 1660-1600 cm^{-1} in extracted HAs was generally due to aromatic and olefinic C=C, C=O in carboxyl, amide (I), ketone and quinone groups, suggesting the enrichment of them after extraction and purification. A weaker band at around 1370 cm^{-1} in HA1, HA2 and HA3 than in HA0 and HA4 was possibly ascribed to less content of phenols[20].

3.2. Purity

The content of water soluble humic acid in sludge and HAs were shown in Fig. 2. HA3 had the highest humic acid level (15%), followed by HA4, HA2 and HA1, approximately 5~7.5 times higher than the raw sludge sample. This result was also confirmed by mean of UV-vis (see Fig. 1). High purity of humic acid in HAs indicated that the aforementioned extraction methods could enrich the humic substances effectively. Purification by passing through the ultrafiltration membrane and centrifugation could improve the level by 30% and 18%, respectively. A comparative content with HA3 could also be found in HA4 (14%), so, it is reasonable to speculate that the modified IHSS method had the similar enrichment effect with the combined application of alkali extraction, ultrafiltration and centrifugation.

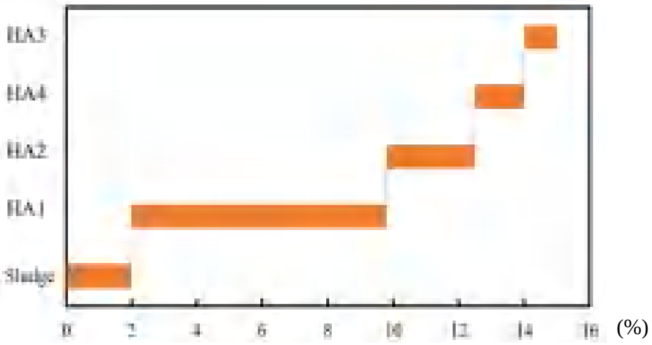

Fig. 2. Water soluble humic acid content in sludge and HAs.

Table 1 summarized the reagents consumption, sludge demand, humic acid purity and operational complexity of the three extraction and purification methods. Even though the hydrosoluble humic acid content in HA4 was significantly higher than that in HA1, more sludge (5 times), alkali and acid (1.8 times), and more complex implementations were needed during the modified IHSS procedure. However, in comparison with HA4, about 5% of alkali and acid could be saved for preparing 1g of HA3, and the humic acid level could be improved by 7%. Based on the comprehensive assessment, the alkali extraction combined with purification method was recommended for humic acid recovery from sewage sludge, so, the subsequent investigation was conducted mainly on HA3.

Table 1. Comparison of the extraction and purification methods to prepare 1g of HA1, HA3 and HA4.

Extracted materials	Raw sludge (*g*)	Alkali and acid consumption (*mmol*)	Hydrosoluble humic acid (*%*)	Operational complexity
HA1	6	140	9.8	Simple (2 steps)
HA3	30	240	15	Complex (3 steps)
HA4	30	252	14	Complex (3 steps)

3.3. Feasibility of the extracted humic acid reutilization

3.3.1. Soil conditioner

Land application of the extracted HA may cause potential detrimental to the environment and health. Sewage sludge is a crucial reservoir of heavy metals, so, the transformation of hazardous substances derived from sludge would lead to long-term contamination in soil. As summarized by Duan et al. (2015)[21], the content of Cr, Pb and As in sewage sludge from different regions in China was in range of 161.4 mg/kg~242.71 mg/kg, 80.63 mg/kg~140.47 mg/kg and 14.2 mg/kg~20.4 mg/kg, respectively, with a pollution index up to 2 (moderate contamination) in comparison with the risk screening values for agricultural land (GB15618-2018). Therefore, it deserves more attention to identify the heavy metals content in humic acid extracted from sludge for reutilizing as the soil conditioner.

As depicted in Fig. 3, the humic acid level in extracted materials has been increased to more than 10%, while the concentration of As, Cr and Pb decreased by 67%, 17% and 19% respectively. It could be seen that, the extraction and purification of HA3 from sewage sludge not only concentrated the organic matter, but also eliminated the hazardous substances. According to the standards for organic fertilizer (NY525-2011) and humic acid organic-inorganic compound fertilizer (T/CHAIA 2-2018), the water soluble humic acid level (>10%) and the three elements contents in HA3 both meet the requirements.

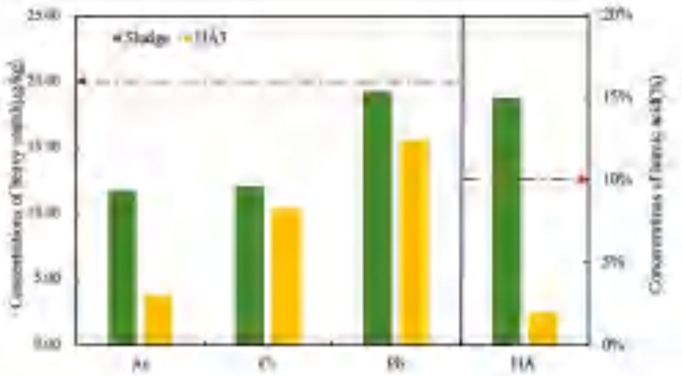

Fig. 3. Concentration of heavy metals and hydrosoluble humic acid in sludge and HA3.

It's worth noting that the concentrations of target heavy metals in sludge were lower than 20 mg/kg, below the limits regulated in standard for organic fertilizer. However, a more than 17% decrease of heavy metals content during extraction and purification could make the application of HA3 in soil more safety and environment-friendly, and the maximum permissible concentrations of heavy metals in sludge could be elevated to 45 mg/kg for As, 180 mg/kg for Cr and 60 mg/kg for Pb.

3.3.2. Electrode materials for supercapacitor

To explore the feasibility of extracted humic acid reused as electrode materials for supercapacitor, the electrochemical performances of the carbonized HA1 and HA3 were measured in a three-electrode system. As shown in Fig. 4, the GCD profiles of samples showed isosceles triangle-like shapes, suggesting their excellent capacitive behaviors. At low current densities (0.05, 0.1 and 0.2 A g^{-1}), the gravimetric capacitances of carbonized HA3 were 189.7 F g^{-1}, 156 F g^{-1} and 144.2 F g^{-1}, respectively, approximately 1.5 times higher than that of HA1. However, as the current density increased to 0.5 A g^{-1}, the capacitance of HA3 decreased to 68.4 F g^{-1}, lower than that of HA1 (83.6 F g^{-1}).

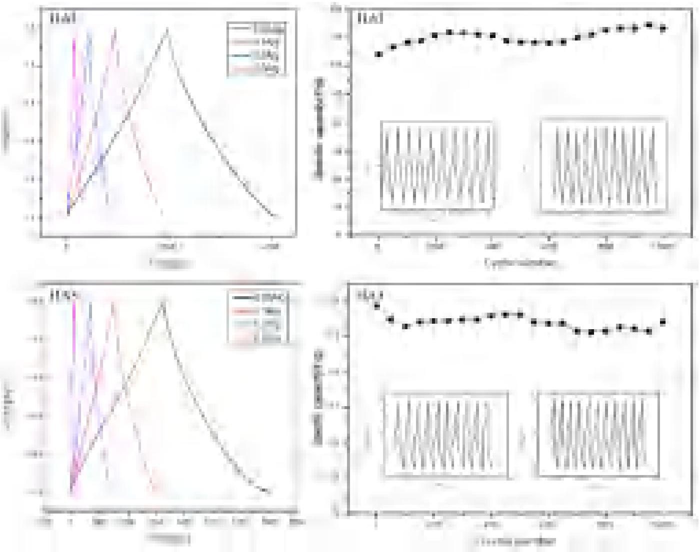

Fig. 4. GCD profiles and cycle stability (at 0.5A g^{-1}) of the carbonized HA1 and HA3 as the electrode materials.

Comparing with other waste-derived carbon materials and the low-grade coal derived graphene-like carbon nanosheets reported previously[22-23], the electrochemical performance of the carbonized humic acid materials extracted from sewage sludge is competitive. After 10,000 cycles at 0.5 A g^{-1}, the carbonized HA1 and HA3 still holds a high capacitance retention more than 90%, confirming the excellent long-term cycling performance. Thus, the extracted humic acid from sludge is a promising precursor material for producing electrode in supercapacitor.

4. Conclusion

This study oriented a promising and effective strategy for sludge reutilization by recycling of humic acid. Comparing with the modified IHSS method, the alkali extraction combined with purification method was more environment-friendly and efficient for producing humic acid from sludge. By adopting the recommended extraction and purification procedure, the water soluble humic acid content increased to more than 10%, and the concentrations of As, Cr and Pb were lower than the threshold values. So, the extracted HA3 has the potential to be processed as the soil conditioner. The supercapacitor with the carbonized HA1 and HA3 electrode exhibited a comparative capacitance and cycling performance, indicating that the humic acid originated from sludge is an appropriate precursor for making high-performance carbons-based supercapacitors.

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Study on the effect of freeze-thaw pretreatment on the dewaterability of municipal sludge

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Abstract

Freeze-thaw pretreatment has been proved to be an effective method to improve the dewaterability of activated sludge. The effects of freeze-thaw temperature and time on EPS distribution, particle size, free water and bound water content of sludge were investigated. The experimental results showed that under the optimal freeze-thaw pretreatment conditions, the content of LB-EPS decreased from 63.7mg/g vs to 18.3mg/g vs, S-EPS increased from 7.1mg/g vs to 75.6mg/g vs, the effect of freeze-thaw pretreatment on TB-EPS is not obvious. The sludge has a significantly larger particle size after freeze-thaw pretreatment, the effect is more obvious at lower freezing temperature and longer freezing time, under the freezing-thaw conditions (-10 °C, 16 h), 373µm particles account for the largest proportion, the volume fraction is about 3.1%, under the freezing-thaw conditions (-20 °C, 40 h) , 409µm particles account for the largest proportion, the volume fraction is about 4.9 % . The DSC measurement found that the bound water which is difficult to be separated mechanically is transformed into free water which is easy to be removed, the content of free water and bound water in the original sludge was 0.604g/g and 4.046g/g, and the free water and bound water content of the sludge after freeze-thaw pretreatment was 1.354g/g and 3.296g/g.
Keywords: freeze-thaw; sludge; EPS; dewaterability

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1. Introduction

The composition of municipal sludge is complex. In addition to containing a large amount of water, there are also various refractory heavy metals and a variety of microorganisms. Municipal sludge dewatering is of major interest to lots of scholars and researchers, but it still continues as a problem for the sludge treatment in the wastewater treatment process. In recent years, there are more and more inorganic, organic polymer and composite flocculants used in sludge chemical treatment, but the recovery of chemicals and the secondary pollution caused by them are still problems to be solved. Many methods and strategies have been developed to strengthen the municipal sludge dewaterability, such as ultrasonic pretreatment[1], thermal pretreatment[2], microwave pretreatment[3], freeze-thaw pretreatment[4] and chemical oxidation[5].

A large number of studies have shown that freeze-thaw pretreatment not only can improve the sludge dewaterability[6] but also can reduce the environmental risk of sludge[7]. This article explores the changes in EPS content of sludge, the effects of freeze-thaw pretreatment on sludge particle size, and the effects of freeze-thaw pretreatment on the distribution of sludge free water and bound water under different freezing temperatures and different freezing times.

2. Materials and methods

2.1. Sludge source

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The sample dewatered sludge used in this experiment was taken from a municipal sewage treatment plant in Nanjing, China. It is a mixed sludge composed of primary settling sludge and remaining sludge, and dehydrated by polyacrylamide quenching and belt filter press. The water content is about 82.3%. The sludge sample is stored at 4℃. The main properties of dewatered sludge are shown in Table 1.

Table 1 Characteristics of the dewatered sludge

pH	Water content（%）	Organic matter content（%）
6.8±0.2	82.3±0.1	48.2±0.5

2.2. Sludge sample treatment

In this study, the sludge was placed in a refrigerator with precise temperature control. The freezing temperatures were set to 0℃, -10℃, -20℃, -30℃, and -40℃. The freezing times were 0h, 8h, 16h, 24h, 32h, 40h, 48h, 56h. The frozen sludge is placed at room temperature to allow it to thaw naturally.

2.3. EPS extraction

EPS fractions from municipal sludge before and after treatment were extracted using a modified heat extraction method[8]. Briefly, the sludge samples were centrifuged at 4000 gravitational acceleration (g) for 15 min, and the supernatant was collected as soluble (S-EPS). The sludge pellet in the tube was then re-suspended to their original volume using 0.05% NaCl solution. The liquor was centrifuged at 4000 g for 10 min and the supernatant was collected as loose bound EPS (LB-EPS). The collected sludge pellet was resuspended to the original volume with 0.05% NaCl solution, then heated at 60℃ for 30 min, and finally centrifuged at 4000 g for 15 min and the supernatant was collected as tight bound EPS (TB-EPS).

2.4. Analysis of sludge particle size

The size distribution of frozen and thawed mud samples and raw mud was measured by laser particle size analyzer.

2.5. Determination of sludge free water and bound water

Determination of free water and bound water in sludge by differential scanning calorimetry (DSC)[9].Given a limit temperature of -60 ° C, and assuming that the bound water is not frozen at this temperature, the sample releases heat to the environment during the freezing process, and this heat is generated by free water. The sludge sample is first cooled from room temperature to -60℃ at a rate of 10℃/min. During this process, the sample will show a significant exothermic peak, and then it will be warmed to room temperature at the same rate. Obvious endothermic peak. Dry the sample in an oven at 103-105 ℃ to determine the total moisture content of the sample. The difference between the sample and the free water is the bound water content. The bound water content calculation formula is shown in (2-1).

$$W_B = W_T - \Delta H / \Delta H_0 \quad (2\text{-}1)$$

W_B—Bound water content（g/g）
W_T—Total water content （g/g）
$\triangle_H$—Heat absorbed by sludge during heating up（kJ/kg）
$\triangle_{H0}$—Standard melting heat of ice, 334.7kJ/kg

3. Results and discussion

3.1. Effect of freeze-thaw pretreatment on sludge EPS

Extracellular polymers (EPS) are important components of sludge flocs. A large number of studies have shown that EPS has an important effect on sludge dewatering performance, settling performance, flocculation performance and surface charge of flocs [10] [11]. The presence of EPS will make the sludge's dewatering performance worse, the EPS package around the bacteria provides a good protection for microorganisms, and the presence of EPS will enhance the stability of sludge flocs. However, the increase of EPS will make more water embedded in sludge flocs, on the one hand, it will increase the combined water content of sludge, on the other hand, it will increase the difficulty of sludge mechanical dewatering. Therefore, the destruction and degradation of EPS is of great significance to promote the release of bound water in sludge. As protein and polysaccharide are the main components of EPS, the effects of different freezing time and temperature on the content of S-EPS, LB-EPS and TB-EPS were investigated by the changes of protein and polysaccharide in EPS, and the mechanism of improving sludge dewatering performance by freeze-thaw pretreatment was described.

Figure 1 shows the effects of different freezing times on protein and polysaccharide content under the conditions of 0℃, -10℃, -20℃, -30℃, and -40℃. Through (a) and (b), it can be found that the freezing temperature has a very obvious effect on the EPS release in sludge. At 0℃, with the increase of freezing time, the content of protein and polysaccharide in S-EPS, LB-EPS and TB-EPS in sludge has no obvious change, which shows that EPS in sludge has no obvious release, but at -10℃， with the increase of freezing time, The content of protein and polysaccharide is increasing, and the content of protein and polysaccharide in LB-EPS is decreasing. Liu[12] found that the content of LB-EPS is negatively related to the dewatering performance of sludge. When the content of LB-EPS is decreasing, the dewatering performance of sludge is obviously improved, which shows that the dewatering performance of sludge is improved under the freezing temperature of -10℃. When the freezing time reached 48h, the content of protein and polysaccharide in LB-EPS decreased to a stable value of 19.3mg/g vs and 3.2mg/g vs.

From (b) and (c), it can be seen that under freezing conditions of -20℃, when the freezing time is 40h, the content of protein and polysaccharide in S-EPS is 60.4mg/g vs and 15.2mg/g vs, the content of protein and polysaccharide in LB-EPS was reduced to stable values of 15.2mg/g vs and 3.1mg/g vs, which indicates that at a lower temperature (-20℃), not only can LB-EPS be released Speed up, and can increase the release of LB-EPS.

Through (c) and (d), it can be found that at -30℃, the final release of LB-EPS in sludge is equivalent to that in -20 ℃. At -30℃, The release of EPS in the sludge reached a maximum at 32h.

From (d) and (e), it can be found that there is no obvious difference between the EPS content change in the sludge at - 40℃ and that at - 30℃, which indicates that the destruction effect of freezing temperature on the EPS of sludge reaches the limit.

Comprehensive analysis of (a), (b), (c), (d) and (e) shows that the effect of freezing temperature and freezing time on TB-EPS content is not obvious, the main reason is that TB-EPS belongs to close combination EPS, and the effect of freeze-thaw pretreatment is not obvious; at the same time, it is found that the total amount of EPS after freeze-thaw pretreatment has increased. According to the study of Chen [13], the effect of freeze-thaw pretreatment causes the cells of the sludge to break down and dissolve the substances in the cells. The main substances in the cell are protein, polysaccharide, DNA, RNA and various ions.

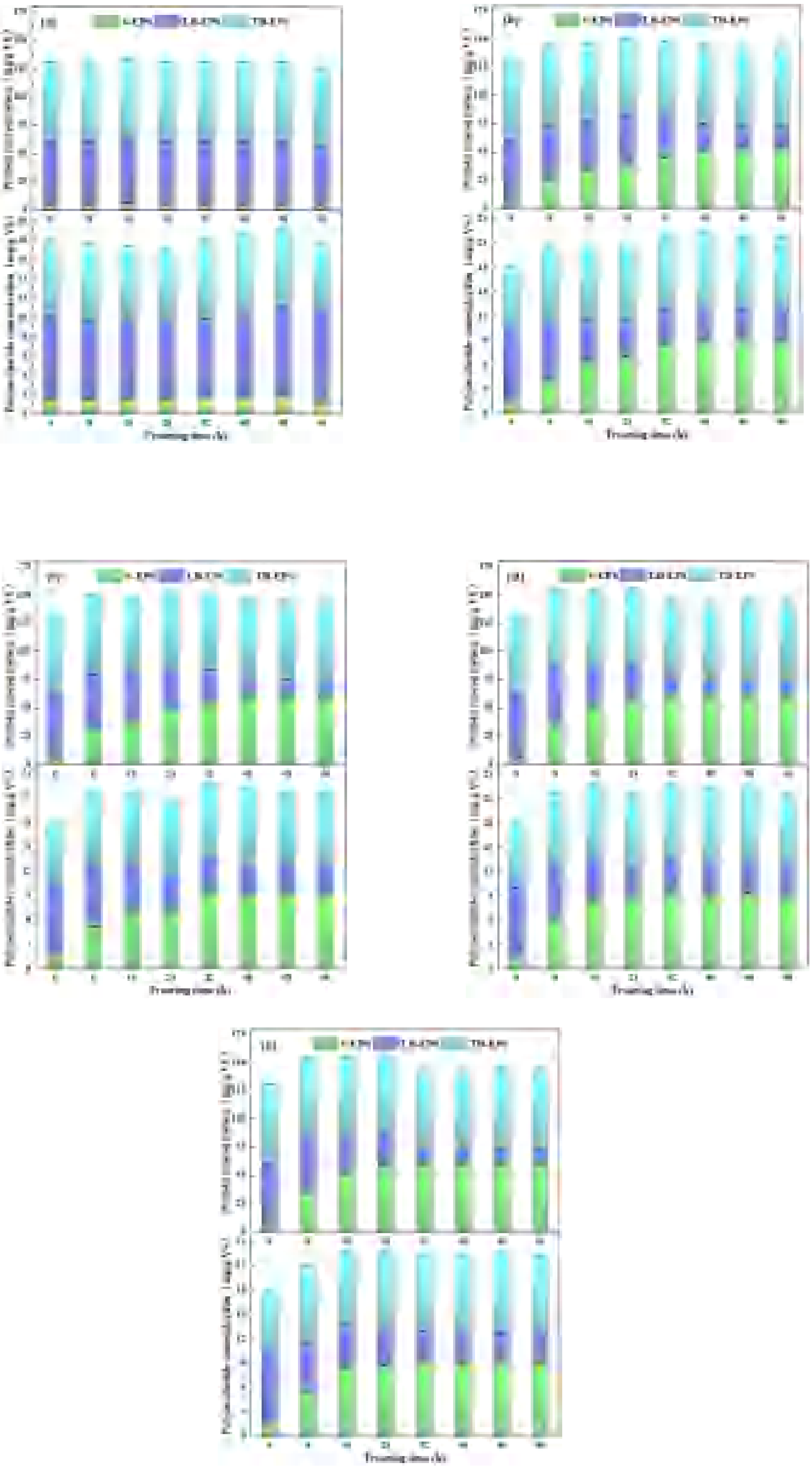

Figure 1 Effect of different freezing time and temperatures on the content of protein and polysaccharide in sludge

3.2. Effect of freeze-thaw pretreatment on sludge particle size

The particle size of municipal sludge has a great influence on its dewatering and sedimentation. Vesilin Martel[14] proposed that during the sludge freezing period, the ice crystal growing repels impurities, dehydrates the solid, and causes the concentrated particles to gather and form large particles. Figure 2 shows the frequency distribution and cumulative distribution curve of the particle size of sludge before and after freezing; it can be seen from Figure 2 that the proportion of particles with the particle size of 146.82 μm in the original sludge is the largest, and the volume fraction reaches about 2.8%. Figure 3 shows the frequency distribution and cumulative distribution curve of sludge particle size under freezing and thawing conditions (- 10℃, 16h), from Figure 3, it can be seen that particles with a particle size of 373 μm account for the largest proportion with a volume fraction of about 3.1%. Figure 4 shows the frequency distribution and cumulative distribution curve of sludge particle size under freezing and thawing conditions (- 20℃, 40h); it can be seen from Figure4 that particles with a particle size of 409 μm account for the largest proportion, with a volume fraction of about 3.9%.

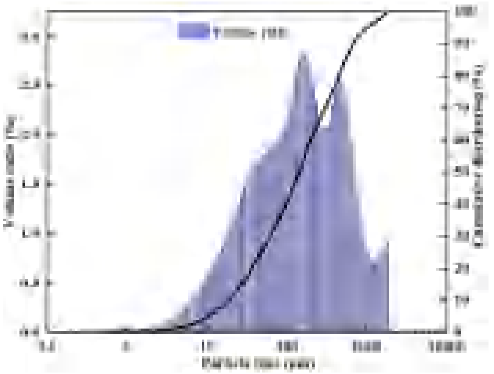

Figure 2 Frequency distribution and cumulative distribution of raw sludge

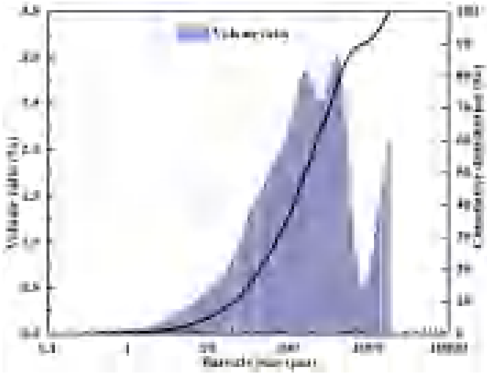

Figure 3 Particle size distribution and cumulative distribution of sludge under freezing and thawing conditions (-10 ° C, 16 h)

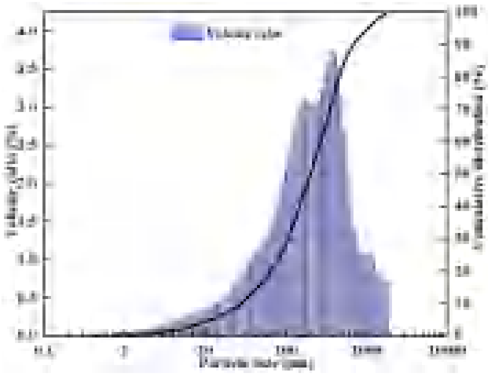

Figure 4 Particle size distribution and cumulative distribution of sludge under freezing and thawing conditions (-20 ° C, 40 h)

3.3. Effect of freeze-thaw pretreatment on the content of free water and bound water in sludge

The experimental results show that for the raw sludge (Figure 5), the sludge releases energy to the environment when the temperature drops between -5℃ to -11 ℃, and an exothermic peak appears. During the temperature rise, the sludge is at An endothermic peak appeared at -1~6℃; for sludge under freeze-thaw pretreatment conditions (Figure 6), during the cooling process between -10 ~ -19 ℃ which an exothermic peak appeared， at -8 ~7℃ an endothermic peak appeared. The free water and bound water content of the raw sludge and the sludge after freeze-thaw pretreatment were calculated according to Formula 2-1, and the results are shown in Figure 7. It can be seen from the figure that the contents of free water and bound water in the raw sludge are 0.604 g/g and 4.046 g/g, respectively, and the contents of free water and bound water in the sludge after freeze-thaw pretreatment are 1.354 g / g and 3.296 g / g; this indicates that the freeze-thaw pretreatment can convert the bound water which is difficult to remove into sludge free water.

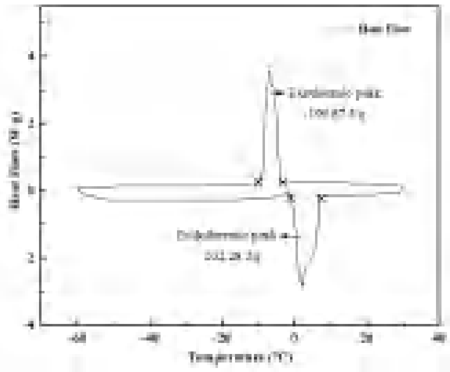

Figure 5 Exothermic and endothermic curves of raw sludge DSC

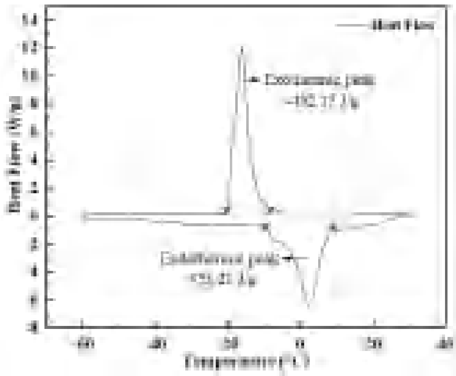

Figure 6 Exothermic and endothermic curves of sludge DSC under freeze and thaw conditions (-20 ° C, 40 h)

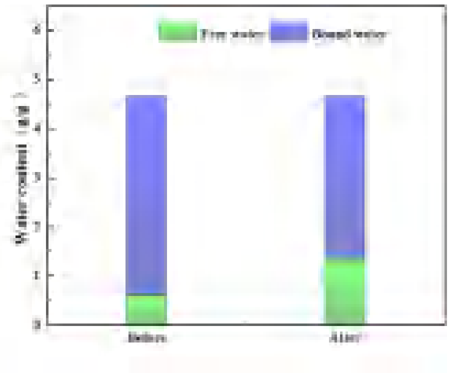

Figure 7 Water content change of sludge before and after freeze-thaw pretreatment

4. Conclusions

Freeze-thaw pretreatment can significantly improve the dewatering performance of sludge. Under the best conditions of freezing and thawing pretreatment, the LB-EPS content decreases to a stable value, the content of LB-EPS decreased from 63.7mg/g vs to 18.3mg/g vs, S-EPS increased from 7.1mg/g vs to 75.6mg/g vs,and the difficult-to-treat bound water is converted into easy-to-handle free water. After the freeze-thaw pretreatment, the EPS of the sludge is destroyed, then a large amount of water, protein, and polysaccharides flow out, which causes the pore size of the sludge to increase significantly. The freezing time is longer this phenomenon becomes more apparent.

Acknowledgements

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Effects of sewage sludge and its biochar on the bioavailability of heavy metal in contaminated soil

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Abstract:

Sewage sludge (SS) as a soil amendment has used to improve soil fertility. However, the negative effects are highly concerned because of its enrichment in both nutrients and contaminants. The pyrolysis of sewage sludge is a technological alternative to product biochar for reducing environmental risk. The objective of this study was to evaluate the effect of SS and its biochars (SSBC) on the bioavailability of Cr, Cu, and Zn in co-contaminated soil through the two-year pot experiment. The result showed the addition of SS and SSBC significantly enhanced the soil pH, EC, and SOM concentrations, compared with the quick and efficient improvement of SS, the amendment of SSBC is a gradual process for soil quality. The acid-extractable fraction of Cr, Cu, and Zn notably decreased by SS and SSBC, as well as the effectiveness of SSBC was superior to SS. The application of SSBC could stabilize three metals, attributing to the acid-extractable fractions of three metals transform to the residual fraction. The results of the pot experiment further indicated the uptake of Cr, Cu, and Zn by radish constantly decreased with SSBC at the rate of 5% and 10%, which was consistent with the decrease of the acid-extractable fraction. The concentration of Cr, Cu, and Zn in the roots of radish reduced 88%, 90%, and 80%, respectively, at a rate of 10% SSBC. The accumulation of Cr, Cu, and Zn in the root of radish gradually reduced with the addition of SS. At the same time, the content of three metals in the shoots slightly increases because of the release of heavy metals in sludge. In conclusion, the addition of SSBC significantly reduced bioavailability of Cr, Cu, and Zn in the contaminated soil, Stabilization of sewage sludge was less effective than its biochar, attributed to higher ash and diversity of surface functional groups in the biochar.

Keywords: Sewage sludge; biochar; soil remediation; heavy metal pollution;

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1. Introduction

Soil heavy metal contamination in China has been an urgency for land utilization and agricultural production safety with large-scale resource exploitation and industrial releases[1, 2]. Hence, Some policies and control strategies have b put into effect on reducing heavy metal pollution and soil remediation[3]. The classified management and risk control of contaminated soil is a priority policy in the action plan, according to the pollution level, which pollution soil is classified into non-pollution and slight pollution as priority protection, light, and moderate pollution, and severe infection. The reality is that slight or light contaminated land will need to farm for food supply in china, so soil remediation becomes a research hotspot to ensure the quality and safety of agricultural products[4]. Several remediation technologies have practiced. Generally, it can be two routes. One of the ways is that metals pollutants thoroughly removed, such as soil washing, electrokinetic extraction, phytoextraction. Another is metals stabilization in soil using various immobilizing materials, which can decrease the mobility and bioavailability of metals [5-7]. To select feasible techniques for safe use of polluted soil, are crucial to considerate remediation cost, the arable property of amended soil, yield and quality of agricultural products, and implementation time[6, 8]. More recently, stabilization of heavy metals have been studied and practiced in agricultural soil, especially, various biomass amendments have attracted widespread attention because these amendments not only can reduce mobility and bioavailability of metals but also enhance soil physicochemical properties and improve plant growth [9-11].

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Biochar as low-cost and varied properties modifier has been studied on the immobility of heavy metal polluted soil in recent years [12-14]. In particular, it is a potential path that reuse of biosolid waste as diversified and inexpensive of feedstock produce biochar, such as crop straw, municipal sludge, livestock manure[15-17]. As a by-product of municipal sewage treatment, sewage sludge disposal has been an environmental burden for the ever-increasing scales of sewage treatment. However, raw sludge contains 70~90% organic substances and nutrients N, P, and K, as available resources, reuse of sewage sludge are economically and sustainable disposal compared to landfilling[18-20]. Several studies investigated that the application of sewage sludge on soil can improve soil fertility [21-23], but the potential risk associated with toxic elements restrict application on soil amelioration. Conversion of sewage sludge to biochar and its use for soil amendment have been proposed as one of the best methods because pyrolysis can eliminate the pathogen, stabilize heavy metal, and retain mineral nutrients [24-26]. Some research showed biochar derived sewage sludge could be a practical approach to reduce heavy metals accumulation into plants and to improve soil chemical and physical properties through short-experiment [27-29]. However, the long-term impact is necessary to study further because structural properties of sewage sludge and its biochar are likely to change in soil over a long period [30, 31], meanwhile the potential leaching risks of immobilized metals need to evaluate.

The aim of this study was to investigate the effect of sewage sludge and its biochar on the bioavailability of Cr, Cu, and Zn through a two-year pot experiment. For this, the speciation changes of three metal in soil with the addition of SS and SSBC were monitored, in the same time, the uptakes of Cr, Cu, and Zn by radish were analyzed. The result can evaluate the long-term effect of sludge and biochar on immobilization of heavy metal in contaminated soil. Moreover, the research results would put insight into whether the pyrolysis of SS, as a sustainable alternative for sludge disposal, is able to guarantee the safe agricultural use of biochar.

2. Materials and methods

2.1. Soil preparation

The experiment soil was collected from 0 to 20cm depth from farmland located in Ganzhou, Jiangxi province. Large roots and stones in original soil were removed, air-dried, and passed through a 2-mm sieve before use in the experiments and further analysis. The solutions of CuSO4·5H2O, ZnSO4, K2Cr2O7 were added into the soil, mixed, and aged for 60 days. The properties of the original soil and simulated pollution soil shown in Table1.

Table 1 Physical and chemical properties of farmland soil and simulated pollution soil

	pH	SOM	Exchangeable Acidity	CEC	Cr	Cu	Zn
		($g\cdot kg^{-1}$)	($cmol\cdot kg^{-1}$)	($cmol\cdot kg^{-1}$)		($mg\cdot kg^{-1}$)	
Original soil	4.79	1.47	6.52	10.21	102.6	34.1	70.9
Simulated soil	4.30	1.32	4.66	9.26	517.6	467	286.5

2.2 Sewage sludge and biochar

Sewage sludge (SS) was collected from Municipal Sewage Treatment Plant in Ganzhou, Jiangxi province. Raw sludge was dried in an oven at 60 °C for several days to a moisture content of about 15%. Biochar was produced by pyrolysis at 400℃ with a heating rate of 10℃/min and residence time 2h under limited oxygen supply[32]. The property of sludge sewage and its biochar in this study were shown in Table 2.

Table 2. physical and chemical properties of SS and SSBC

Property	SS	SSBC
pH (H_2O)	6.63	6.42
Total C (wt%)	17.67	11.79
Total H (wt%)	3.201	0.79

Total N (wt%)	3.17	1.04
Ash (wt%)	56.81	73.39
Organic matter (g kg-1)	50.31	11.32
Cation exchange capacity (c mol kg-1)	34.9	21.1
BET Surface area (m2 g-1)	1.9687	17.36
Total Cr (mg kg-1)	36.9	40.25
Total Cu (mg kg-1)	100.1	101.6
Total Zn (mg kg-1)	12.6	21.35

2.3 Pot treatment

All experiments performed in the greenhouse and last two years (2017-2018). Sewage sludge (SS) and sludge biochar (SSBC) homogeneously mixed with the simulated contamination soil at rates (w/w) of 5% and 10 %, respectively. After the mixture equilibrated for 30 days, a 5kg combination was filled in plastic pots, labeled SS-5%, SS-10%, SSBC-5%, and SSBC-10%. Each treatment replicated three times, simulated contamination soil without amendments set as a control (CK). All treatment soil adjusted to 40 % water-holding capacity (WHC) with deionized water during two years of experiments except plant cultivation. The three-month plant cultivation was carried out from March to May (spring period) and October to December (autumn period) in 2017 and 2018. One hundred seeds of radish per pot were sowed in the pot during the three-month growth period, kept with a natural day/night regimen, and watered as required. After three months, plant samples were harvested, cleaned by deionized water, and dried at 65℃. Aboveground and underground parts of the samples were separated, dried at 105℃, weighed, ground, and passed through a 0.3-mm sieve. The content of copper, zinc, cadmium, and chromium in plants was determined. Meanwhile, soil samples per plot were collected, dried at room temperature, and stored in sample sack after through 0.2mm sieve, to analyze.

2.4 Analysis and determination methods

Standard methods determined the properties of all samples (SS, SSBC, soil, treated soil). Soil pH (water: soil ratio of 1:2.5) was measured in a digital pH meter[33]. Soil organic matter (SOM) was determined by potassium dichromate-ferrous ammonium sulfate titration[34]. Soil exchangeable acid was analyzed according to the method of the Potassium chloride exchange method. soil cation exchange capacity (CEC) was determined by the EDTA-ammonium acetate exchange method[33]. The concentration of Cr, Cu, and Zn in soil were tested by inductively coupled plasma atomic emission spectrometer (ICP-AES) (PerkinElmer, USA) after HNO3-HF-HClO4 digestion process[35]. The speciation of Cr, Cu, and Zn was analyzed by a sequential extraction step of the European Community Bureau of Reference (BCR)[36]. The plants' samples digested by HClO4-HNO3 (1:4), and then the digestion was determined by ICP-AES.

Cr/Cu/Zn fraction was calculated with the following equation:

Take Cr as an example.

$$\text{The change of Cr fraction (\%)} = \frac{\text{The change of each Cr fraction (mg/kg)}}{\text{Total Cr in each soil (mg/kg)}} \times 100$$

Cr/Cu/Zn concentration was calculated with the following equation:

Take Cr as an example.

$$\text{Cr concentration (mg/kg)} = \text{metal of digested sample (mg/L)} \times \text{dilution factor}$$

$$\text{Dilution factor} = \frac{\text{The total volume of the sample (mL)}}{\text{Weigh of soil or plant (g)}}$$

In this study, all reagents were of analytical reagent grade.

2.5 Statistical analysis

The test results were based on the means and standard deviations of three replicates computed using Excel 2016 and Origin 8. Data were dressed as means plus or minus one standard deviation.

3. Results and discussion

3.1 Effects of raw sludge and biochar on soil pH

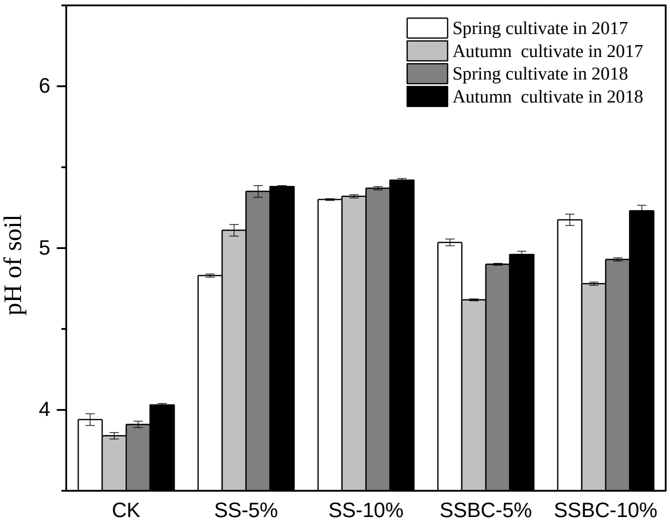


Figure.1 Effects of SS and SSBC on pH value of contaminated soils

The acidity of soil can significantly influence the solubility, migration, and transformation of heavy metals [37, 38]. In two years experiment, the changes in soil pH amended sludge and biochar shown in figure 1. Compared to the un-treatment contaminated soil, the addition of sludge (SS) and biochar (SSBC) can enhance the pH of the soil, and soil pH increased with the increasing amount of sludge and biochar. During two years cultivation experiment, the improvement of SS on soil pH was superior to SSBC, at the end of the experiment, the soil pH with SS-10% reached the maximum value of 5.42, an increase of 1.58 units compared with the untreated soil. The pH of the soil with SSBC was fluctuant during the experiment, in the first cultivation period (spring in 2017), soil pH rapidly increased, and then decreased in the second period (autumn in 2017). However, the soil pH slowly rose in 2018. The alkalinity of the remediation materials plays an essential role in the improvement of soil pH [39]. The pH of SS and SSBC was 6.68 and 6.42, respectively, while the pH of contaminated soil was only 4.3 after SS and SSBC added into soil, the pH of the soil can rapidly increase in the first season of cultivation experiment. However, in the second season, the pH of the soil with SSBC significantly decrease, and then slowly increase following in the third season and the fourth season. The results showed that it took a long time for biochar to recover the acid buffer capacity when the alkalinity of SSBC was consumed.

3.2 Effects of sludge and biochar on soil exchangeable acidity

The effects of sludge and sludge biochar on soil exchangeable acids shown in figure 2. The addition of SS and SSBC significantly reduced soil exchangeable acid compared with the control. Over the two-year experiment, the soil exchange acid decreases firstly, and then increase, kept the lowest value at the end of experiment. In the first cultivation period (spring in 2017), Soil exchangeable acid at the addition of 10%SS dramatically decreased from 5.4cmol/kg to 0.49cmol/kg, and the 10 %SSBC addition of soil also reduced to 2.41 cmol/kg. In the second cultivation period (autumn in 2017), soil exchangeable acid of all treatments significantly increase, and then gradually declined in the next years (2018). At the end of two years cultivation experiment, soil exchangeable acid in soil with 10% SSBC dropped to 0.63cmol/kg, and 0.74 cmol/kg with 10% SS. The oxygen-containing functional groups of biochar can chelate with Al^{3+}, and the essential cation in the ash of biochar, such as calcium, magnesium, and potassium, exchange with Al^{3+} which converted into a less active organic complex state or stable other forms to control the exchangeable acidity of soil[40]. Hence, it is a long and gradual process for biochar derived sewage sludge improving soil acidity.

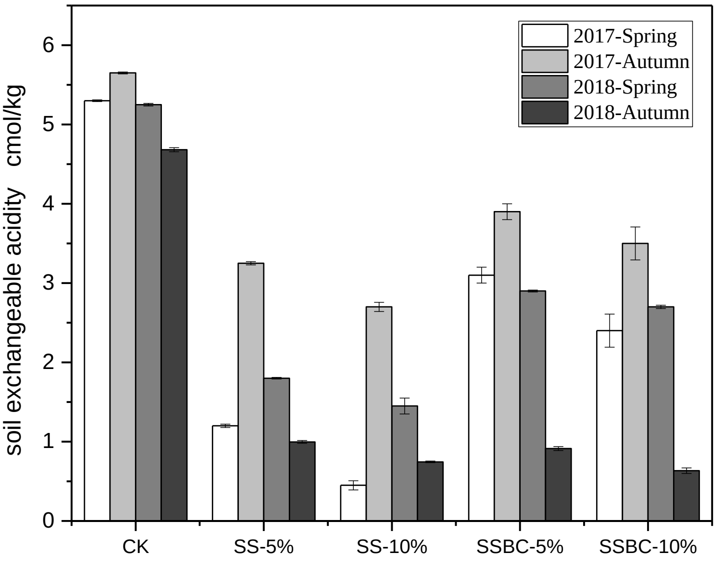


Fig.2 Effect of SS and SSBC on soil exchangeable acidity

3.3 Effects of sludge and biochar on soil organic matter

The effect of SS and SSBC on soil organic matter (SOM) given in figure.3. The addition of SS and SSBC can enhance organic matter of soil, and the increase of SOM consistent with the organic matter content of SS and SSBC in the first year cultivation. The organic matter content of SS was 50.31 g/kg. Still, the organic substances of sludge were continuously decomposed and volatilized by pyrolysis, the organic matter content of SSBC was only 11.32g/kg. Compared to the organic matter of CK (4.19 g/kg), the addition of SS and SSBC continued to increase the content of SOM during the two-year experiment. At the end of the two-year cultivation experiments, the SOM increased to 40.21g/kg in the soil with 10% SS and rose to 41.16g/kg in the soil with 10% SSBC. Although the pyrolysis of sewage sludge reduced the organic matter of biochar, its carbon very slowly released as a carbon sequestration tool [41]. Increasing the temperature of pyrolysis has a negative effect on the organic carbon content. Thus it is crucial to choose an appropriate reaction temperature for biochar application on soil fertilizer[12].

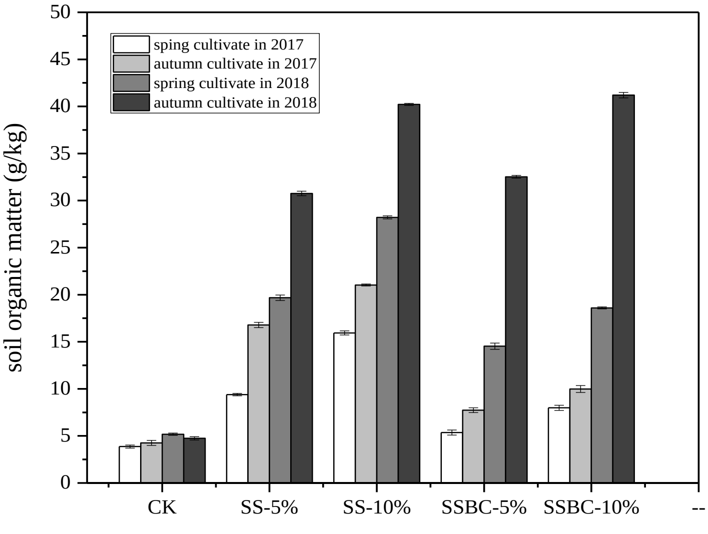


Figure.3 Effect of SS and SSBC on soil organic matter

3.4 Effects of sludge and biochar on soil cation exchange capacity

The change of soil cation exchange capacity (CEC)during the cultivation shown in figure 4. Compared to the untreated soil, the addition of SS and SSBC enhanced the CEC of soil, and the effect of SSBC was better than that of SS. Soil cation exchange capacity increased in the soil amended SS in the first cultivation, which was up to 12.4 cmol/kg at a rate of 10%SS, and then slowly dropped, which was down to 10.27 cmol/kg at 10% SS in the end of the experiment. By contrast, the improvement of SSBC on the CEC of soil continuously promoted, the CEC of soil increased from 13.51 cmol/kg to15.76 cmol/kg, moreover, the CEC in the soil with 10% SSBC significantly increased in the first cultivation. The inorganic mineral of biochar provides abundant cation [42, 43], so the biochar enhances the soil cation exchange capacity because the ash of SSBC reached up to 73.79%. Besides, the surface of biochar is rich in carboxyl group, phenolic hydroxyl group, and other oxygen-containing functional groups, which has a large amount of negative charge, conducive to the adsorption of the cation in soil.

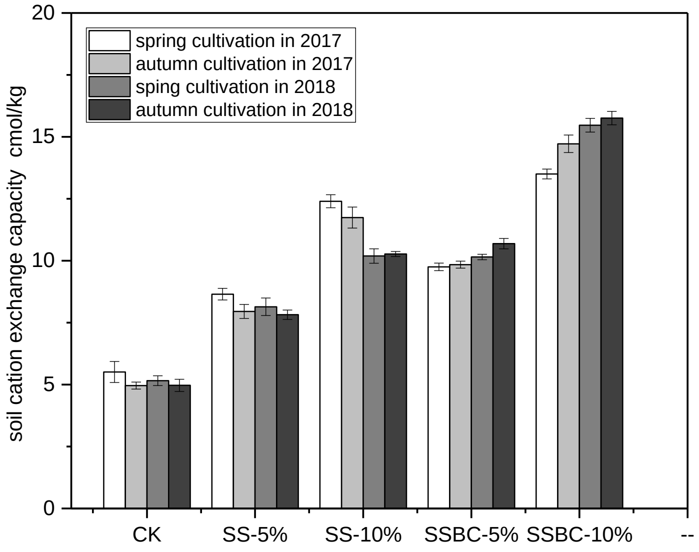
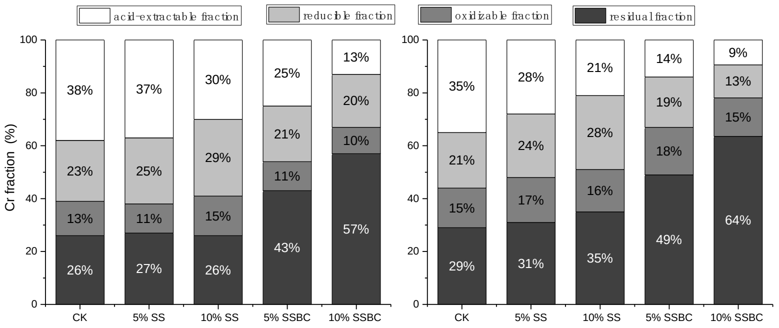


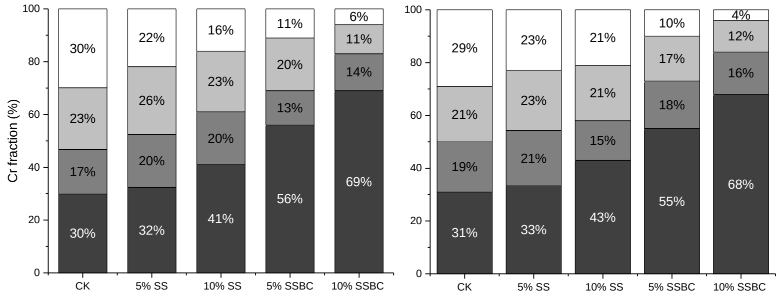
Figure.4 Effects of SS and SSBC on soil cation exchange capacity

3.5. Effect of sludge and biochar on the speciation of heavy metals

The potential toxicity and biological enrichment of heavy metals are closely related to the speciation of heavy metals in soil [44]. During the two-yearexperiment, the speciation change of Cr, Cu, and Zn in soil was analyzed by the BCR method, and the fractions are divided into four fractions, namely, Acid-extractable, Reducible, Oxidizable, and Residual. Moreover, the acid extractable fraction isconsidered as the most active and bioavailability fraction[45]. On the contrary, Residue is not active, long-term stable existence, and challenging to be biological use. The reducible and oxidizable fraction would convert to a more active acid-soluble state under certain conditions[46]. The speciation changes of Cr, Cu, and Zn in soil amended sludge and biochar shown in Fig5, 6, and 7.



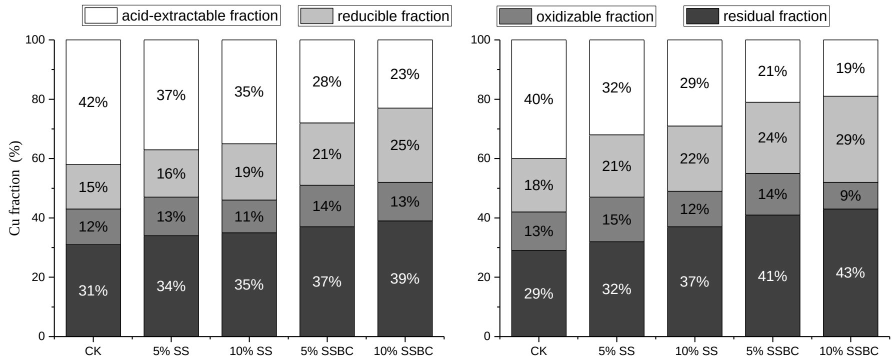
(a) spring pot experiment in 2017 (b) autumn pot experiment in 2017



(c) spring pot experiment in 2018 (d) autumn pot experiment in 2018

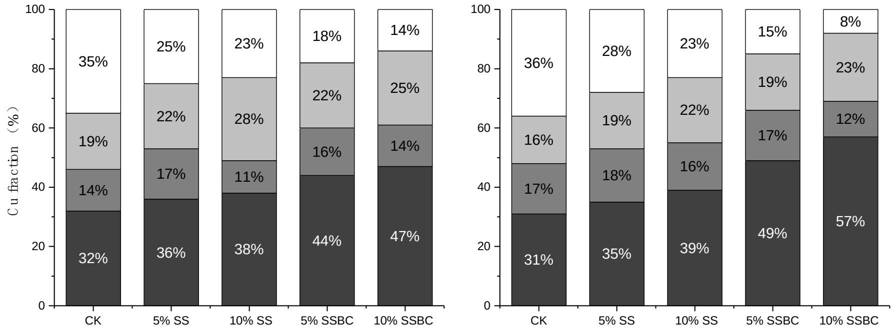
Figure.5 Effects of sludge and biochar on Cr fraction in the soil during incubation

The addition of sludge (SS) and biochar (SSBC) effectively reduce the acid-extractable fraction of Cr in soil(Fig.5)， and the decrease of acid-extractable Cr in soil amended SSBC was superior to SS. By the end of the first year cultivation (2017), compared to untreated soil (35%), the acid-extractable Cr in the soil with 10 %SSBC was down to 9 %. At the same time, the fraction of residual Cr in soil with10% SSBC was significantly increased to 64%, which means the acid-extractable Cr transformed into the residual fraction. In the second year cultivation (2018), the proportion of acid-extractable Cr amended 10% SSBC was down to 4%, and the fraction of residual Cr increased to 68%. The acid-extractable Cr in the soil with SS had been continuing to reduce during the two years experiment. Moreover, the fraction transformation of Cr was ruleless because the raw sludge is complex and amorphous. The results confirmed that Cr immobilization was highly sensitive to functional groups on biochar, which the pyrolysis process of sewage sludge can promote biochar's alkaline, more aromatic carbon structures, and C-O functional groups. The present literature has indicated the adsorption mechanisms of Cr based on complexation with oxygen-containing functional groups such as carboxyl and hydroxyl groups [47, 48].



(a) spring pot experiment in 2017

(b) autumn pot experimnet in 2017

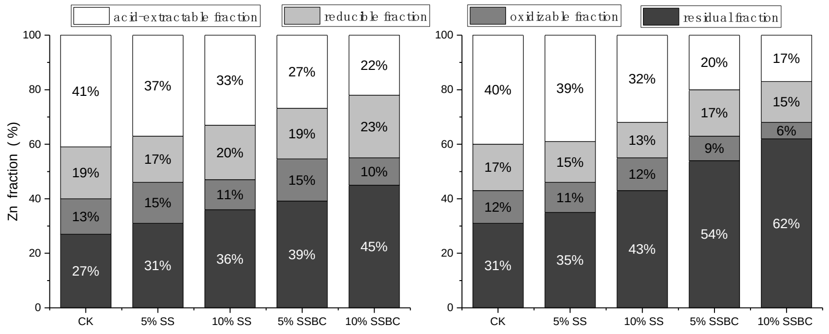


(C) spring pot experiment in 2018

(d) autumn pot experiment in 2018

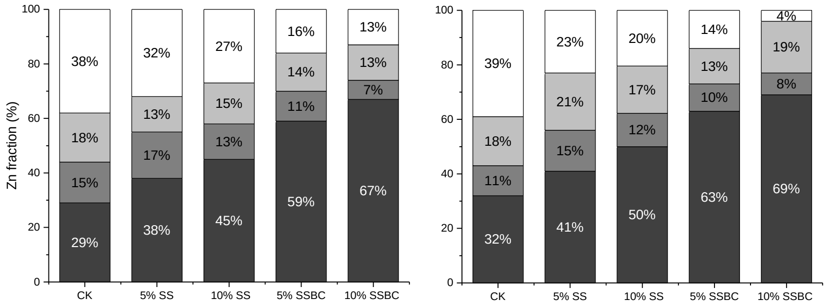
Figure.6 Effects of sludge and biochar on Cu fraction in the soil

The application of sludge biochar (SSBC) could markedly reduce Cu available contents in the contaminated soil because the Cu acid-extractable fraction continuously decreased during the two years experiment (Fig.6). By the end of the first year cultivation(2017), compared to untreated soil (CK) (40%), the acid-extractable Cu in the soil with 10%SSBC was down to 19%, at the same time, the fraction of residual Cu significantly increased to 43%, which mean the acid-extractable Cu transformed to the residual fraction. In autumn 2018, the proportion of acid-extractable was only 8% in the soil with SSBC-10%. Moreover, the residual fraction of Cu significantly increased to 61%. The cultivation experiments showed the remediation effect of SSBC was better than SS, the acid-extractable Cu reduced to 29% in the soil with 10%SS in autumn 2017, compared to the application of 10%SSBC(19%). The proportion of acid-extractable Cu in the soil with 10%SS keep 23% during the whole experiment in 2018, so the stabilization of Cu in polluted soil used sewage sludge is not lasting. The mechanism of Cu remediated biochar is that Cu ion can co-precipitate with carbonate in biochar and adsorb by electrostatic interaction, but it was susceptible to change in pH[49, 50].



(a) spring pot experiment in 2017

(b) autumn pot experiment in 2017



(C) spring pot experiment in 2018

(d) autumn pot experiment in 2018

Figure.7 Effects of sludge and biochar on Zn fraction in the soil

The application of sludge biochar (SSBC) could notably reduce the acid-extractable Zn in the contaminated soil (Fig.6). The proportion of acid-extractable Zn decreased to 17% in the soil added 10% SSBC at the end of pot experiment in 2017, as well as the percent of residual Zn, increased to 62%, which the acid extractable Zn transformed to the residual fraction. By the end of the autumn experiment in 2018, the acid-extractable fraction of Zn in the soil with 10%SSBC reduced to 4%, and the residual Zn increased to 69%. Biochar has a high ash content, alkaline functional groups on the surface, and Zn^{2+} acts with high affinity [51, 52]. Hence, the effect of SSBC on Zn stabilization excelled SS. the proportion of acid-extractable Zn in the soil with 10%SS maintained 32% in the first year(2017). It was only down to 20% in 2018.

The speciation change of Cr, Cu, and Zn in the soil amended sewage sludge and its biochar indicated that the addition of sludge biochar significantly reduced the proportion of acid-soluble fraction, which are easy to release and high bioavailability. Stabilization of sewage sludge on Cr, Cu, and Zn was less active than its biochar, attributed to higher ash and diversity of surface functional groups in the biochar. Biochar binds to heavy metals by increasing pH value, redox potential, adsorption, precipitation or coprecipitation, complexation, and other means to change the morphology of heavy metals[53-55]. Furthermore, the mechanism of Cr, Cu, and Zn boned to biochar determined the transformation of metals speciation. During the two years experiment, the acid-soluble fractions of Cr, Cu, and Zn converted to the residual fraction, which is stable form and unavailable, based on experiment results, and biochar can stabilize Cr, Cu, and Zn in the combined pollution soil.

3.6. Effect of sludge and biochar on the bioavailability of heavy metals

A pot experiment operated to investigate the effect of sewage sludge and its biochar on the bioavailability of heavy metals, and the uptake e of Cr, Cu, and Zn by radish in the amended soil with SS and SSBC was showed on Fig.8,9, and10.

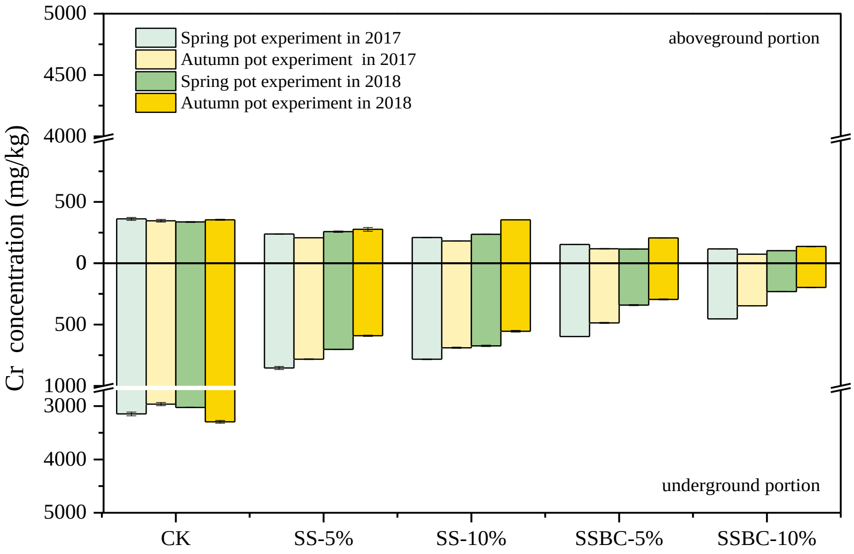


Fig.8 the Cr uptake by radish in the contaminated soil

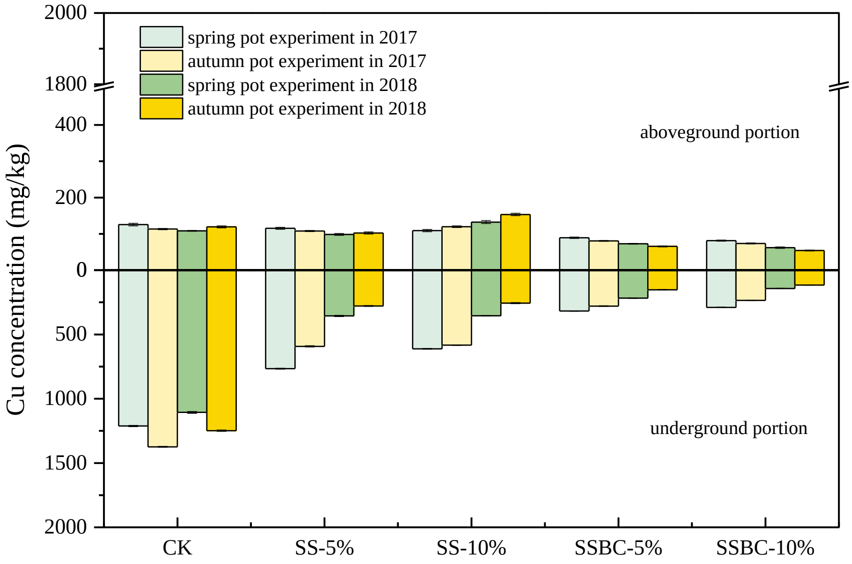


Fig.9 the Cu uptake by radish in the contaminated soil

Over the two-year experiment, the accumulation of Cr, Cu, and Zn in the radish roots were higher than shoots in all the treatments, nevertheless, the addition of SS and SSBC reduced the uptake of Cr, Cu, and Zn by radish compared with the control, and the remediation of SSBC was more effective than SS. the uptake of Cr, Cu, and Zn by radish continually decreased with SSBC at the application rate of 5% and 10%.

At the end of the first-year experiment, the accumulation of Cr, Cu, and Zn with 5% of SSBC decreased to117.65 mg·kg^{-1}, 80.57mg·kg^{-1} and 149.25 mg·kg^{-1} in the shoot of radish, respectively, and were 486.52 mg·kg^{-1}, 279.48 mg·kg^{-1} and 452.26 mg·kg^{-1}in the in the root portion. At the rate of 10% SSBC, the concentrations of Cr, Cu, and Zn in the shoots portion were 73.95 mg·kg^{-1}， 71.54 mg·kg^{-1} and 97.77mg·kg^{-1} respectively, and in the roots portion decreased to 347.16 mg·kg^{-1}， 235.48 mg·kg^{-1}, and 358.36 mg·kg^{-1}, respectively. Compared with the control, the concentration of Cr, Cu, and Zn in the roots of radish which is edible parts reduced 88%, 82%, and 69%, respectively. At the end of the second year experiment, The concentration of Cr, Cu, and Zn in the root of radish decreased to197.79 mg·kg^{-1}, 115.67 mg·kg^{-1}, and 295.93 mg·kg^{-1}, respectively, in the treatments with 10%SSB, compared with the result of the first years experiment, reduced 43%, 51%, and 18%, respectively. By contrast, although the concentration of Cr and Zn in the shoot of radish amended 10% SSBC was lower than the control in the second year experiment, the content of Cr and Zn in the shoot of radish increase 45% and 10% compared with the results of the first year, while the content of Cu decreased by 25%. The decrease of Cr, Cu, and Zn acid-soluble fraction in the soil amended with SSBB was consistent with the content of Cr, Cu, and Zn in the radish.

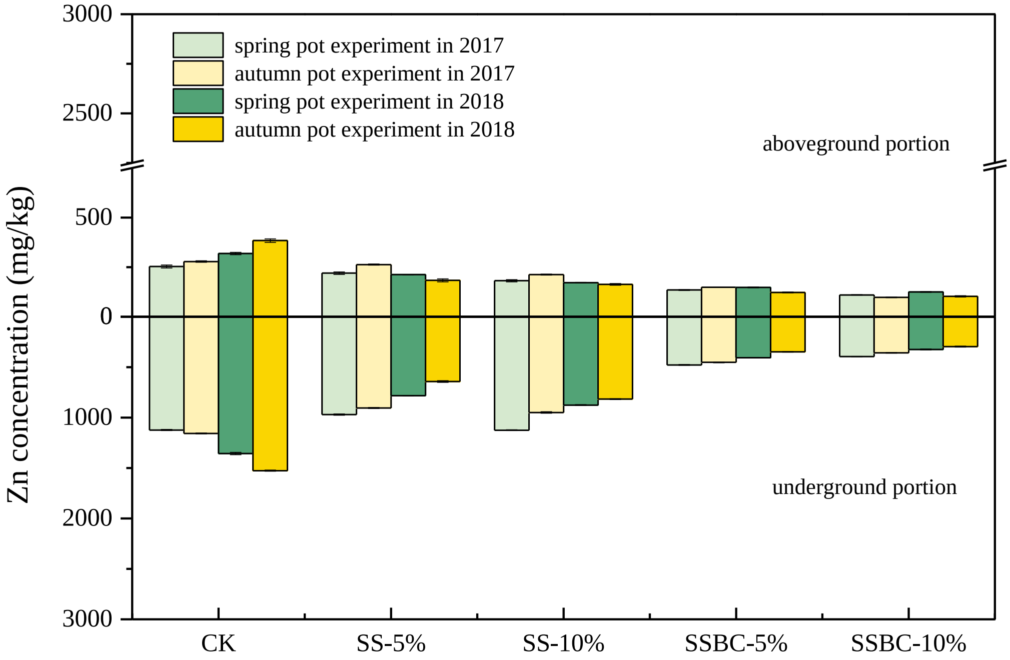


Fig.10 the Zn uptake by radish in the contaminated soil

The accumulation of Cr, Cu, and Zn in the root of radish gradually reduced with the sludge application. Still, the content change of Cr, Cu, and Zn in the shoot were complicated because the release of heavy metal in sludge increases the uptake of heavy metals by radish, and promoted the transport of metals from underground parts to the aboveground parts. At the end of the first-year experiment, compared to the control, the concentration of Cr, Cu, and Zn in the root of radish with 5%SS was reduced 73%, 56%, and 21%, respectively, and 40%, 6% and 4% in the shoot, respectively. However, the content of Cr in the shoot with 5%SS in the second year experiment was 30 % more than the first year. The application amount of sludge accelerated the uptake of heavy metals by the shoot of radish, at a 10% rate of sludge, the content of Cr and Cu in the shoot at the second year experiment was 90% and 28% more than the first year. As a consequence, it will be necessary to evaluate the long-term risk of the release of heavy metals for the application of sludge to soil remediation. However, the uptakes of Cr, Cu, and Zn by radish were below the control treatment.

The conversion of sewage sludge into biochar by pyrolysis is a safer and friendly approach as a soil amendment, overcoming lack of stability, and release of heavy metal. Application of SSBC can significantly reduce the bioavailability of heavy metals Cr, Cu, and Zn in combined pollution soil during the two years experiment, further demonstrates that the effects on bioavailability of Cr, Cu, and Zn are not only due to changes in soil properties, such as pH, CEC, but biochar's highly porous structure, large specific surface area and abundance of functional groups on the surface [56, 57]

4. Conclusions

This study investigated the effects of sewage sludge and its biochar on the bioavailability of Cr, Cu, and Zn in co-contaminated soil by the two-year pot experiment. The results show that the higher addition rate of sewage sludge and its biochar significantly improve the acidity, CEC, and SOM of the contaminated soil, comparing to a quick fix of SS for soil property, the effectiveness of SSBC are long-term and gradually process. The change of Cr, Cu, and Zn speciation indicatied biochar derived sewage sludge can significantly decrease the proportion of acid-soluble fraction which are available speciation by plant. Additionly, the uptake of Cr, Cu, and Zn by radish further demonstrate that the stabilization of SSBC for three metals are more effective than SS. Overall, the pyrolysis of sewage sludge converted into biochar reduces the release risk of heavy metals and may provide a viable option of safe use of sewage sludge for contaminated soil remediation. However, field experiments are needed to confirm the restoration of sludge biochar in combined pollutants in soil.

Acknowledgements

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The Moderating Effect of Perceived Policy Effectiveness on Residents' Waste Classification Intention: A Case in China

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Abstract

Currently, the Chinese government is promoting a policy on waste classification to solve the increasingly serious issue of cities besieged by waste. In this study, we surveyed 351 people in China to examine the moderating effect of perceived policy effectiveness on waste classification by applying a model that incorporates the Theory of Planned Behavior (TPB) as the theoretical basis of the hypotheses. The results showed that the perceived policy effectiveness negatively moderated the relationships between awareness of consequence and waste classification intention, as well as those between attitude and waste classification intention. The study's findings provide potential significant implications for policymakers to develop guidelines and a framework to implement a more effective waste classification policy.

Keywords: waste classification; theory of planned behavior; awareness of consequences; perceived policy effectiveness; China

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1. Introduction

At present, most Chinese cities are suffered by severe environmental pollution, being besieged by waste, which is more extensive, more serious, more far-reaching, and more lasting than the fog and haze. According to the World Bank, China had surpassed the United States as the world's largest waste producer, with an annual output of more than 1 billion tons since 2004. A report by the Ministry of Housing and Urban-Rural Development of China showed that two-thirds of China's cities were besieged by waste, and one-fourth of the cities had no space to build landfills.

The widespread implementation of the waste classification system is related to the improvement of the living environment of nearly 1.4 billion people in China. Following the explicit request at the 14th meeting of the Central Finance and Economics Leading Group on December 21, 2016, to "implement the waste classification system", on June 2, 2019, Chinese Chairman Xi Jinping once again made important instructions on waste classification and profoundly clarified the extreme importance of waste classification for high-quality development of the country, which upgraded waste classification to a national strategy. On July 1, 2019, Shanghai took the lead in entering the era of mandatory waste classification. By the end of 2020, the 46 pilot cities nationwide will have a waste classification and treatment system. Good waste classification at the front end of the residents is the key to mid-end classification collection and transportation, as well as back-end disposal, and resource utilization. It has also become an important way to implement the entire waste classification strategy and solve the dilemma of "waste siege" (Xu et al., 2017a)

The waste classification belongs to the issue of public environmental behavior selection. Previous scholars had examined the explaining effect of TPB(Ajzen,1991) in waste classification or recycling behavior (Garcés, Alberto, Marta, et al.,2002; Oreg and Katz, 2006; Chan and Bishop, 2013; Park and Ha, 2014; Wang, Guo &Wang, et al.,2018b). These studies had also demonstrated policy implications as changing factors to impact the behavior (Wan, Shen & Yu, 2014a; Wang, Zhang & Cao, et al., 2019a). Perceived policy effectiveness is relevant to waste classification (Wan, Shen & Yu, 2014b), however, few studies were empirically tested with the topics in China. In this paper, we propose a conceptual model

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based on an extended TPB model to examine the moderating effects of perceived policy effectiveness that explain waste classification behavior intention. A better understanding of the recycling intention could then be gained for policy formulation.

2. Literature Review and Hypotheses

2.1. Literature review of waste classification intention

The theory of planned behavior (TPB Model) (Ajzen, 1991) is the development of the theory of reasoned action (TRA Model) (Fishbein, 1980). TPB model is an important theoretical model for studying public behavior choice from a micro perspective. The environmental issues like water source protection (Wang et al., 2018a), greenhouse gas emission (Zahedi et al., 2018), tourists' environmental behaviors (Wang et al., 2019a; Ahmad et al., 2020), sustainable transport behavior (Liu et al., 2017) and green product purchase intention (Xu et al., 2019; Bhutto et al., 2019) are all analyzed with TPB model. The TPB model lays the foundation for studying the waste classification intention and related researchers have used the TPB model in the research for analysis (Garcés et al., 2002; Liao et al., 2018; Meng et al., 2019; Tian et al., 2019; Wan et al., 2014b; Wan et al., 2017; Knussen et al., 2004; Chan and Bishop, 2013). As described by Ajzen (Ajzen, 1991), the characteristics of the TPB model that can add variables has provided the research basis for the study of intention and behavior. Many articles that study the intention of waste classification have improved the research model by adding appropriate variables to the basic TPB model.

The TPB model mainly includes three main factors: attitude (ATT), subjective norm (SN), and perceived behavior control (PBC), to predict individual behavioral intentions. **Attitude** is defined as the positive or negative evaluation or cognitive representation of an individual performing a particular behavior. **Subjective norm** refers to the perception of the social pressure that individuals experience when they take a particular behavior, meaning that residents are more willing to implement the behavior when others who are important to them consider waste classification to be effective. **Perceived behavior control** refers to the degree to which an individual is expected to control (or master) when he or she takes a certain behavior (Granco et al., 2019; Ajzen, 1991; Ajzen and Madden, 1986). These three variables in the TPB model have been identified as key predictors of classification intention (Nguyen et al., 2015; Park and Ha, 2014; Wang et al., 2016; Wan et al., 2017; Sidique et al., 2010; Chen and Tung, 2009; Zhang et al., 2019).

Norm Activation Theory (NAT model) assumes that personal norms are a conducive enabler of moral behavior, and the theory focuses on internal determinants (Onwezen et al., 2013; Wang et al., 2019b). **Awareness of consequence** in this study means that individuals can protect their living environment, reduce waste, reduce losses, and set a good example for future generations and their children through the implementation of waste classification. In the exploration of citizens' intention to protect the environment, NAT models are more commonly used (Liu et al., 2017; Zhao et al., 2019; Park and Ha, 2014; Han, 2014; Chen and Tung, 2009). A better perception of the implementation results of waste classification behavior residents can have, their intention to conduct waste classification behavior will be stronger (Davies et al., 2002).

2.2. The moderating effect of perceived policy effectiveness

The TPB model had already been considered as an effective method to explore environmental protection behavior in various research literatures. Previous related studies had also used the model to study the intention of waste classification, and had reached effective conclusions on policy implementation (Knussen et al., 2004; Liao et al., 2018; Nguyen et al., 2015; Tian et al., 2019). In the previous studies, most of the policy recommendations were based on the living environment of the residents, to enhance the publicity and optimize the waste classification facilities of each node.

Value-Belief-Norm theory (VBN) is also an important theory for public environmental behavior research (Oreg and Katz-Gerro, 2006; Fornara et al., 2016). In VBN theory, the **perceived policy effectiveness** has been proved to have a good explanatory power for public environmental behavior intentions such as classifying (Wan et al., 2014a; Wan et al., 2014b). In addition to being a variable that directly affects intention, perceived policy effectiveness may also be a moderator for other variables that affect intention. In other words, an effective policy can be used as an incentive. If people are strongly motivated through policy, their intentions to classify will be increased (Wan et al., 2014b).

Wan.C (Wan et al., 2014b) discussed the role of perceived policy effectiveness as a moderator in recycling behavior in Hong Kong. The study explained that if the people had a positive attitude toward recycling, their intention would decrease if there was no effective policy support. Furthermore, if the individual's attitude towards recycling is still poor under the premise of effective policies, his attitude may not change with the change of policy. The result was also discussed in the study of brand attitudes and purchase intention which motivation was acted as a moderator.

Although attitude has a positive effect on the intention to classify in the TPB model, the moderating role of perceived policy effectiveness between them cannot be ignored. From the analysis, we can propose the following hypothesis:

Hypothesis 1 (H1): Perceived policy effectiveness will have a positive moderating effect on the relationship between attitude and waste classification intention.

In previous related literature, various studies had tested the TPB model and predictors of classifying behavior. In the TPB model, subjective norm is used as an important factor affecting the intention of waste classifying. In addition to the research literature on the waste classification intention, subjective norm was also treated as an important influencing factor in the study of other influencing factors of environmental protection intention (Wang et al., 2018a; Xu et al., 2017b).

However, in the field of health psychology (Trafimow and David, 2000), it was proposed that if the individual had already formed a regular classifying behavior, the impact of subjective norm on the intention to waste classify would be reduced accordingly. Before people learn the knowledge of waste classification and have not formed a good classifying behavior, they will be greatly affected by their relatives and the environment around them. In the process of continuously improving policies and people's comprehensive recycling knowledge, the impact of subjective norms on recycling intention and behavior will decrease accordingly(Wan et al., 2014a). According to this, the following hypothesis is proposed.

Hypothesis 2 (H2): Perceived policy effectiveness will have a negative moderating effect on the relationship between subjective norm and waste classification intention.

Perceived behavior control, as the motivation part of the ultimate classifying behavior in the TPB model (Rosenthal, 2018), requires people to acquire knowledge through autonomous or passive means, so as to transform from motivation to behavior level. Then in the process of passively acquiring classifying knowledge, the effectiveness of policies and social advocacy are the most important. For example, the government can enhance personal PBC by establishing convenient waste classifying facilities, such as the scientific layout of residential waste classifying facilities and the transportation of waste classifying vehicles (Tian et al., 2019). Effective policy implementation will stimulate people's intention to acquire useful waste classification knowledge, thus forming the intention of waste classification. The following hypothesis is proposed.

Hypothesis 3 (H3): Perceived policy effectiveness will have a positive moderating effect on the relationship between perceived behavior control and waste classification intention.

Awareness of consequences can be interpreted as people predicting future development trends through existing policies and surroundings to decide whether to actually implement the behavior (Onwezen et al., 2013). Bamberg and Schmidt (2003) suggested that people would choose behaviors that they think better and easier to implement. External factors would influence the relationship between knowledge and an individual’s behavior (Fiske and Luebbehusen, 1994). If there is a good social atmosphere to strongly support waste classification, the impact of individual perceptions such as active learning of waste classification will be reduced. The effectiveness of policy implementation will significantly reduce uncertainty of people's perception for the results of recycling behavior (Wan et al., 2014b). The following hypothesis is proposed.

Hypothesis 4 (H4): Perceived policy effectiveness will have a negative moderating effect on the relationship between consequence awareness and c waste classification intention.

Based on the aforementioned literature, a conceptual model for this study is presented in Figure 1.

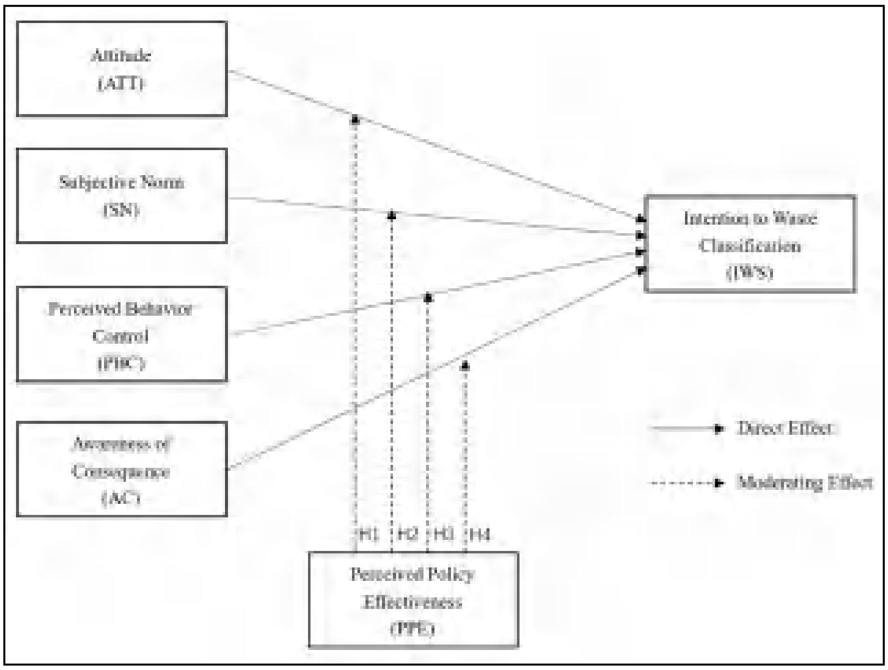

Fig.1. The conceptual framework.

3. Methodology

3.1. Measurement Instruments

In the study, the questionnaire was based on some waste classification literature and the theoretical framework of TPB (Ajzen, 1991; Taylor and Todd, 1995; Wan et al., 2014b; Tonglet et al., 2004). Newly constructed indicators of perceived policy effectiveness were based on China's current policy measures and all the measurement items could be achieved from Appendix A for details.

The questionnaire was divided into two parts. The first part contained the questions for demographic information, including gender, age, income, education level, area of residence, etc. The second part aimed to investigate residents' intention to classify wastes which contained five major independent variables: attitude, subjective norms, perceived behavior control, awareness of consequences, and perceived policy effectiveness. A Likert's seven-level scale was applied to measure respondents' agreement. All the variables ranged from “strongly disagree” (1) to “strongly agree” (7).

3.2. Data Collection

The research object of this study was urban and rural residents in Bengbu City, Anhui Province, China. Bengbu is an important comprehensive industrial base in the Yangtze River delta economics belt. This delta, with only 1% of land and 7% of the population, creates more than 20% of the GDP of China. It is also a national civilized city and a national comprehensive transportation hub city in China. The study adopted the population proportion quota sampling method. To improve the effectiveness of the study, 30 questionnaires were distributed randomly before the official release. Based on the pilot test results, the questionnaire was modified and became the final version.

The questionnaire was distributed from February 1 to February 31, 2020, and 500 questionnaires were collected. Among them, 49 invalid questionnaires with the same answer option were deducted, the left 351 questionnaires were effectively recovered, so the effective questionnaire recovery rate was 87.75%. The gender distribution of the questionnaire was relatively even, of which 49.9% were male and 50.1%

were female. And 44.7% of respondents were between the age of 21 to 35. More details of respondents' profile are shown in Table 1.

Table 1. The demographic results of the respondents.

Variable & Category	**Frequency**	**Percentage (%)**
Gender		
Male	175	49.9
Female	176	50.1
Age (Years old)		
⩽20	23	6.6
21-35	157	44.7
36-50	105	29.9
51-65	46	13.1
⩾65	20	5.7
Monthly Income (RMB)		
⩽5000	209	59.5
5001-10000	98	27.9
10001-15000	26	7.4
⩾15000	18	5.1
Education Level		
Junior high school and below	25	7.1
High school / Secondary school	72	20.5
College / Undergraduate	228	65.0
Postgraduate and above	26	7.4
Living Area		
Urban	232	66.1
Rural	119	33.9

3.3. Data Analysis

Structural equation modeling (SEM) are techniques that include a series of multivariate analysis methods such as regression analysis, factor analysis, and analysis of variance (Joreskog, 1993; Chin, 1998b; Bollen and Long, 1992). It is a statistical model and method for hypothesis testing multivariate analysis (Gefen et al., 2000). Partial least squares (PLS) is a common statistical method of SEM, which can be used to confirm the effectiveness of tool structures and evaluate the structural relationship between these structures (Hair et al., 2014). PLS requires less rigorous requirements about distribution assumptions and a smaller sample size, which is more suitable for theoretical development (Hair et al., 2012; Marko and Jun-Hwa, 2019). In this study, IBM SPSS17.0 and SmartPLS3.0 were used in combination with the SEM.

The analysis included two parts. The first part was the measurement model, which analyzed the reliability and validity of each variable dimension. The second part was the structural model which contained two models. The Model 1 was created to understand the significance of the independent variables (attitude, subjective norms, perceived behavior control, and perceived policy effectiveness) on the dependent variable (intent of waste classification intention) and verified whether the relevant hypotheses were valid. Model 2 used same variables but changed the perceived policy effectiveness as a separate variable into a moderator, to observe the effect of policy effectiveness on residents' waste classification intention.

4. Results

4.1. Measurement model

The study examined the reliability, convergent, and discriminant validity of the indicators, as well as the comprehensive reliability of the indicators to evaluate the PLS measurement model. The following was the process of evaluating the scale.

First, the Cronbach's Alpha and the Composite Reliability (CR) were used to represent reliability. The minimum requirements for the Cronbach's Alpha and Composite Reliability should be greater than 0.7 (Fornell and Larcker, 1981; Chin, 1998b). As shown in Table 2, the Cronbach's Alpha of six variables ranged from 0.74 to 0.91 and the CR values ranged from 0.84 to 0.93, which indicated that the reliability of all the variables was good.

Then the convergent validity could be tested by factor loadings and the Average Variance Extracted (AVE) (Fornell and Larcker, 1981; Chin, 1998b). The minimum factor loading and AVE requirements for each variable should be greater than 0.5. From the table, the factor loadings of all the items ranged from 0.614 to 0.873 and the AVE values ranged from 0.58 to 0.71 which were all suitable for the baseline of 0.5. Besides, the factor loadings for all variables were significant at $p = 0.01$, and greater than 0.6 in the measurement model. The above analyses showed that the reliability and convergent validity of all structures met the requirements.

Table 2. The analysis results of reliability and convergent validity.

Variable	**Item**	**Factor Loadings**	**Cronbach's Alpha**	**CR**	**AVE**
Attitude (ATT)	ATT1	0.767	0.740	0.850	0.660
	ATT2	0.843			
	ATT3	0.821			
Subjective Norm (SN)	SN1	0.859	0.900	0.930	0.710
	SN2	0.873			
	SN3	0.761			
	SN4	0.890			
	SN5	0.833			
Perceived Behavior Control (PBC)	PBC1	0.845	0.820	0.880	0.650
	PBC2	0.820			
	PBC3	0.774			
	PBC4	0.775			
Awareness of Consequence (AC)	AC1	0.822	0.760	0.860	0.670
	AC2	0.820			
	AC3	0.816			
Perceived Policy Effectiveness (PPE)	PPE1	0.768	0.910	0.930	0.680
	PPE2	0.803			
	PPE3	0.805			
	PPE4	0.852			
	PPE5	0.851			
	PPE6	0.860			
Intention to Waste Classification (IWS)	IWS1	0.850	0.780	0.840	0.580
	IWS2	0.696			
	IWS3	0.614			

IWS4	0.851

Based on the above results, the data could be further analyzed. The study tested the discriminant validity by calculating the cross-loadings (Chin, 1998b; Urbach and Ahlemann, 2010; Hair et al., 2014; Henseler et al., 2015). If the loading of each indicator is higher for its particular construct than others, and each constructs' item has the highest load, then the difference validity is high. In Table3, the component scores of each latent variable was higher than all other items, which indicated the study had good discriminant validity.

Table3. The results of discriminant validity analysis.

	ATT	**SN**	**PBC**	**IWS**	**AC**	**PPE**
ATT1	**0.767**	0.547	0.558	0.487	0.547	0.432
ATT2	**0.843**	0.556	0.558	0.439	0.726	0.516
ATT3	**0.821**	0.521	0.514	0.374	0.729	0.489
SN1	0.574	**0.859**	0.578	0.444	0.542	0.575
SN2	0.553	**0.873**	0.645	0.563	0.561	0.561
SN3	0.619	**0.761**	0.650	0.481	0.619	0.526
SN4	0.595	**0.890**	0.607	0.560	0.626	0.609
SN5	0.505	**0.833**	0.560	0.554	0.496	0.539
PBC1	0.488	0.570	**0.845**	0.494	0.499	0.487
PBC2	0.556	0.601	**0.820**	0.482	0.587	0.522
PBC3	0.660	0.629	**0.774**	0.533	0.701	0.567
PBC4	0.460	0.512	**0.775**	0.543	0.462	0.484
IWS1	0.529	0.621	0.617	**0.850**	0.557	0.607
IWS2	0.263	0.302	0.350	**0.696**	0.292	0.308
IWS3	0.214	0.219	0.284	**0.614**	0.223	0.225
IWS4	0.505	0.572	0.568	**0.851**	0.504	0.562
AC1	0.701	0.519	0.542	0.401	**0.822**	0.439
AC2	0.722	0.545	0.607	0.403	**0.820**	0.510
AC3	0.605	0.578	0.574	0.548	**0.816**	0.545
PPE1	0.568	0.498	0.529	0.439	0.581	**0.768**
PPE2	0.539	0.546	0.567	0.454	0.567	**0.803**
PPE3	0.473	0.540	0.536	0.526	0.484	**0.805**
PPE4	0.471	0.557	0.544	0.507	0.490	**0.852**
PPE5	0.433	0.572	0.509	0.572	0.456	**0.851**
PPE6	0.462	0.574	0.503	0.517	0.489	**0.860**

4.2. Structural model

The structural model was generally evaluated by calculating structural paths, t-statistics, and variance (i.e., R^2 value). The study used the bootstrapping method to calculate the significance of the path through 351 cases and 5,000 weighted samples. The bootstrapping was to use the limited sample data to re-establish a new sample that was representative of the distribution of the maternal sample through repeated sampling(Chin, 1998b). Bootstrapping could be used to calculate the accuracy of sample estimates. Table 4 summarized the results of the main and moderating effects (perceived policy effectiveness) in the analysis.

The coefficient of determination (R^2) could be used to explain the model validity which was proposed by Hair, Ringle, and Sarstedt (Hair et al., 2011). R^2 values of 0.25, 0.50, and 0.75 indicate that the model validity is low, medium, and high. The two models' R^2 values ranged from 0.502 to 0.510 in Table 4 showed a certain difference in recycling intention before and after adding perceived policy effectiveness as a moderator.

Before taking perceived policy effectiveness as a moderating effect, the study first considered it as an independent variable and observed as a major factor, and whether it could have a direct effect on the intention to waste classification. Model 1 explained that subjective norm (path coefficient = 0.194, $p < 0.01$) perceived behavior control (path coefficient = 0.280, $p < 0.001$) and perceived policy effectiveness (path = 0.253, $p < 0.001$) would strongly influence the intention to waste classification. After turning the perceived policy effectiveness as a moderator, Model 2 accounted for 51% of the difference in classify intention. The result showed that H1 and H4 were supported (but not H2 and H3). The perceived policy effectiveness had a positive moderating effect between attitude and waste classification intention which the p-value ranged from 0.828 to 0.088. Although the p-value of H1 was not significant, the huge difference indicated that the effect of attitude on waste classification intention would be strengthened by the increasing effectiveness of the government's policy. In addition, the relationship between awareness of consequence and waste classification intention was negatively moderated by perceived policy effectiveness, with a path coefficient of -0.177 and a t-value of 2.223. The results of H4 showed that the more effective a person perceived the policy, the lower the impact of the awareness of consequence on the intention to waste classify. Thus, it explained that the link between awareness of consequence and waste classification intention was negatively moderated by perceived policy effectiveness.

Table 4. Testing results of the main effects and moderating effects of recycling intention.

Constructs	**Model 1**			**Model 2**		
	Path Coefficients	**T value**	**Sig.**	**Path Coefficients**	**T value**	**Sig.**
Attitude	0.025	0.309	0.757	0.018	0.217	0.828
Subjective Norm	0.194	2.665	**	0.205	2.483	*
Perceived Behavior Control	0.280	3.913	***	0.271	3.846	***
Awareness of Consequence	0.061	0.789	0.430	0.041	0.482	0.630
Perceived Policy Effectiveness	0.253	3.977	***	0.267	4.025	***
ATT × PPE				0.148	1.707	0.088
SN × PPE				0.049	0.689	0.491
PBC × PPE				0.021	0.307	0.759
AC × PPE				-0.177	2.223	*
R^2	0.502			0.510		

Note: *p < 0.05; **p < 0.01; ***p < 0.001.

The various validations of the model like c2 were not provided in the PLS calculating program. However, the goodness of fit (GoF) for PLS was proposed as a measure of the predictive relevance of manifest variables (Tenenhaus et al., 2005), and the values 0.10, 0.25, and 0.36 could be interpreted as small, medium, or large effect (Chen and Lin, 2019). The goodness of fit (GoF) of the model in this study was 0.57, so we could conclude that the research model was a good fit.

5. Discussion

From the analysis, we could find out that two moderating effects (i.e. attitude and perceived policy effectiveness; awareness of consequence and perceived policy effectiveness) were efficient, but only one hypothesis was supported. In terms of attitude, unlike related research articles (Liao et al., 2018; Tian et al., 2019; Knussen et al., 2004), the study found that the direct impact of attitudes on waste classification intention was not significant. The possible reason is that Bengbu City, Anhui Province is not China's waste classification implementation city. The local people’s understanding of waste classification is not comprehensive enough, and there is still a certain gap in the implementation of waste classification compared with the cities which were implemented first.

After adding the perceived policy effectiveness as the moderator, the significance between attitude and intention had been greatly improved. This meant after feeling the effects of the policy implementation, the individual's attitude towards waste classification would be improved accordingly, which was conducive to forming the intention of waste classification. So, the enlightenment for us at this point is that people's attitude towards waste classification is closely related to the implementation of policies. Only when the publicity and implementation are truly in place, people will gradually develop the intention and behavior of waste classification.

For awareness of consequences, the performance of policies effectively improved the significance of its intention to classify waste. This showed that by implementing effective policies and achieving good results, the government would improve people’s desired consequences of adopting waste classifying behaviours. With the continuous improvement of policies and the gradual development of residents' waste classification habits, the impact of awareness of consequence on waste classification will decrease.

However, another two hypotheses (i.e. subjective norm and perceived policy effectiveness; perceived behaviour control, and perceived policy effectiveness) were not significant. After adding the perceived policy effectiveness as the moderator, the significances of subjective norm and perceived behaviour control on the intention to waste classification were greatly reduced. The reasonable explanation is that as government policies become more effective, the impact of individual subjective norms and perceived behavioural controls on waste classification will decrease. Once the social environment and policies are completed to meet people's expectations and meet their life requirements, their impact on waste classification will be minimized. Due to the demand for a better life and increased self-control, the impact of one’s social group on their own intention to waste classification may be less important.

5.1. Policy implementation

The above discussion reveals the main challenges and considerations that governments may face when designing and implementing waste separation policies. When people feel that the implementation of the policy is more effective, people’s attitudes toward waste classification will increase but the awareness of consequences will decrease. Furthermore, the direct impact of subjective norms on waste classification is very significant. This represents the need to strengthen social advocacy, and the positive results of universal waste classifying are still necessary. This result contradicts the conclusions drawn in the article (Wan et al., 2014b). It is precisely because China's waste classification industry has just started, the necessary social publicity can effectively promote the gradual implementation of the waste classification policy.

The findings also have implications for policy and plan formulation. In the process of policy implementation, the government should make policies and information open and transparent. The perceived policy effectiveness of residents has improved, the enthusiasm of residents for waste classification will increase as well. People's enthusiasm for waste classification has increased, and the uncertainty of the implementation of this policy in the mind has been gradually eliminated, which can better encourage people to conduct waste classification (Trafimow and David, 2000; Yuan et al., 2016). To strengthen the intention to classify waste, the government also needs high levels of economic incentives to encourage people (Rauwald and Moore, 2002; Liao et al., 2018). At the same time, the government should also adopt a reward or punishment mechanism to regulate the waste classification of residents. Once people develop good waste classification habits, the perception of the results of waste classification implementation will no longer be an important factor (Wan et al., 2014b). This also confirms the findings of the article, that the perceived policy effectiveness has a negative moderating effect between awareness of consequence and waste classification intention.

Secondly, the article proposes that the government should continuously strengthen the construction of waste separation infrastructure to improve the convenience of residents' waste classification. The scientifically planned layout of the front-end classified delivery facilities, the effective operation of the middle-end classified transportation vehicles, and the efficient operation of the dry and wet waste classifying and disposal facilities at the end can finally improve people’s sense of mission and responsibility (Xu et al., 2017a; Liao et al., 2018).

5.2. Limitations and future research

The study also contained some limitations that should be revised in the future. First of all, the sample survey size of the article was still relatively small, which could only represent the influencing factors of waste classification intention in a region. Then, the degree of waste classification implemented in the area selected by the sample was not high, and there were specificities of implementing waste classification policies in each region.

In order to apply the model to different environments and different groups, further research is necessary. To make the research more comprehensive, future research can select two cities with different implementation levels of waste classification policy for comparison. It will be better to gain insights into the effectiveness of perceived policies and recovery goals in different contexts across regions, and better summarize the findings.

6. Conclusions

This study analyzed the moderating effect of perceived policy effectiveness in the waste classification intention model. As a result, the perceived policy effectiveness has a positive impact on attitudes and waste classification intention, and a negative impact on the positive relationship between awareness of consequence and intention, which is different from the conclusions drawn in previous studies (Wan et al., 2014b).

Although the previous literature mostly used the extended TPB model to analyze the waste classification intention, this paper added the variable of perceived policy effectiveness on this basis, conducted research on residents' intention in cities where waste classification has not yet been implemented and drew different conclusions, which is of innovative significance. Residents’ intention in cities that have not implemented waste classification can better help the government understand the real factors, and thus make new breakthroughs in policy design and implementation.

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Appendix A

Constructs	Indicators	Questions
Attitude (ATT)	ATT1	Waste classification is fun.
	ATT2	Waste classification protects the environment.
	ATT3	Waste classification can optimize resource utilization.
Subjective Norm (SN)	SN1	My relatives and friends think the waste classification is right.
	SN2	My relatives and friends support me to classify waste.
	SN3	I will also classify the waste when I see people doing.
	SN4	My relatives and friends think waste classification is important for environmental protection.
	SN5	My relatives and friends suggested that I should classify my waste.
Perceived Behavior	PBC1	I am sure I can classify the waste.
	PBC2	If I want, I will do the waste classification.
	PBC3	I can reduce living environment pollution through waste classification.

Control (PBC)	PBC4	It is easy for me to implement waste classification.
Awareness of Consequence (AC)	AC1	Waste classification can create a better environment for future generations.
	AC2	I protected the environment through waste classification.
	AC3	I reduced the amount of domestic waste through waste classification.
Perceived Policy Effectiveness (PPE)	PPE1	Government-provided waste classifying bins to promote classify.
	PPE2	The government's environmental protection plan has effectively raised public environmental awareness.
	PPE3	Government provides clear guidance on waste classification.
	PPE4	Government advocacy helps citizens understand the importance of waste classification.
	PPE5	Government policies encourage me to classify waste.
	PPE6	Government policies are good for my waste classification.
Intention to Waste Classification (IWS)	IWS1	From now on I will start to classify waste.
	IWS2	I plan to do waste classification next week.
	IWS3	I plan to do waste classification next month.
	IWS4	I will actively promote waste classification to friends and relatives.

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Farmers' Ecological Conservation Intention and Behavior Analysis Based on Theory of Planned Behavior: A Case Study in Min County, China

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Abstract: Farmers' behaviors, littering crop straw and blindly using pesticide or chemical fertilizer, lead to ecological pollution during agricultural production and herbal cultivation. Farmers' ecological protection behaviors play an important role in improving farmland ecological environment. Based on the theory of planned behavior, this study uses the field survey data of 425 Angelica farmers in Min County of Gansu Province. It first empirically analyzed the impact of farmers' behavioral attitudes, subjective norms and perceptive behavior control on their ecological protection intention and behavior in Angelica planting, and then based on the characteristics of head of household, household resource endowment and environmental policy cognition, analyzed the internal factors affecting each variable in TPB structure by using the ordinary least square method. The results show that ecological protection behavior is affected not only by the variables in TPB structure, but also by the education level of householders as well as farmers' awareness of ecological protection policies. Therefore, this study suggests the government should also organize activities to improve the overall comprehensive quality of farmers and guide them to work on green production. Besides, a monitoring mechanism and a reward and punishment mechanism should be established to conduct real-time supervision of farmers' production behaviors.

Keywords: Ecological conservation; Farmers' intention and behavior; Theory of planned behavior; Structural equation model; Min County

1. Introduction

Agro-ecological environment is the fundament for agricultural production. Farmland environmental pollution will lead to serious pollution of cultivated land, affect the quality of agricultural products and hinder the sustainable development of agriculture. Farmland ecological environment pollution has the characteristics of concealment and lag, in order to reduce the pollution problem in agricultural production from the source, the Ministry of Agricultural vigorously advocate that straw should be returned to the field, and that we should prohibit the incineration of straw at will, limit the pollutant emission targets, and formulate environmentally friendly policies such as scientific soil testing and formula fertilization (Yan et al., 2015). The developed countries represented by the United States have also established intermediary organizations such as crop advisers between farmers and the government to provide farmers with information and guidance on ecological protection (Francis et al., 2019). However, due to the lack of ecological protection awareness and common sense in the production process of farmers, the implementation of these policies has not achieved successfully. Farmers' ecological protection behavior refers to the voluntary and environmentally friendly behavior of farmers, including the use of low toxic chemical fertilizers and pesticides, the recycling and reuse of agricultural surplus and other low-pollution behaviors. Farmers are not only the decision makers of agricultural business but also the direct stakeholders of agricultural production. Farmers' irregular behavior in agricultural production is the main cause of farmland ecological environment pollution (Floress et al.， 2018). Therefore, guiding farmers to apply appropriate pesticide and chemical fertilizers in agricultural production and recycling crop straw is a realistic problem to be solved urgently. Farmers' recognition of agricultural ecological environment is the basis of their adoption of environmentally friendly production behaviors in agricultural production (Min et al., 2018), and is an inevitable way to effectively manage the agro-ecological environment as well. Abadi (2018) and Shi et al. (2018) proposed that farmers' ecological protection behavior was not only influenced by behavioral attitudes, subjective norms and perceived behavioral control, but also by the characteristics of household heads, household endowments, exogenous endowments of farmers, scale of operation, level of specialization, and farmers' awareness of low-carbon agriculture. Therefore, only by clarifying the factors affecting farmers' ecological environment protection behavior, can we guide farmers to implement environmentally friendly production and management modes in the agricultural production process and herbal cultivation.

Plastic mulch is used to kill weeds and maintain moisture while Angelica is planted. However, according to the results of field investigation, 95% of the mulch used by farmers was non-degradable, and a large number of used mulch was discarded in the field. In addition, the long-term excessive use of pesticides and chemical fertilizers by farmers for increasing crop yields has contaminated the agro-ecological environment, resulting in the destruction of soil structure, the eutrophication of groundwater quality, and the restriction of land recycling. In this study, it was reasonable and representative to select Min County, the main producing area of Angelica, as the research area for farmers' ecological protection intentions and behavior. The research results can provide a reference for the formulation of ecological environmental protection policies in ecologically fragile areas, and also have important significance for promoting the sustainable development of Angelica industry. Farmers are the basic unit in the cultivation process of Angelica, to realize the sustainable development goals of Angelica cultivation they must fully understand the dominant position of farmers in their production process and stimulate their environmental awareness to the greatest extent. Therefore, it is necessary to carry out new theoretical analysis and empirical research on farmers' ecological protection intentions and behavior problems by using TPB to formulate targeted intervention policies.

The theory of planned behavior is developed on the basis of multi-attribute attitude theory and rational behavior theory, explains the general decision-making process of individual behavior from the perspective of information processing and is considered as one of the most effective social psychology theories for explaining behavior (Ajzen, 1991). In the theory of rational behavior, it is believed that the individual's behavior attitude and subjective norms will have a certain impact on the behavior intention, and the behavior intention has a tendency to adopt a specific behavior for the individual, which can provide a basis for predicting the individual's behavior. Scholars have made great success in using the theory of planned behavior to analyze farmers' intentions and behavior. For example, farmers' intentions and behavior of pesticide application (Wang et al., 2014), farmers' intentions and behavior to save water (Yazdanpanah et al., 2014), farmers' intentions to protect water quality (Floress et al., 2017), and intentions to engage in food safety on farms (Rezaei et al., 2018), intentions to reuse agricultural biomass waste (Jiang et al., 2018).

Fu et al. (2020) points out extensive use of land has put tremendous pressure on the ecosystem and caused a series of ecological problems. By compulsory taxing the inputs of pesticides and fertilizers, and including the environmental costs of excessive use of pesticides and fertilizers into the purchase price, it can protect biodiversity and promote ecological intensive development (Klenjn et al., 2019). Guo and Zhao (2014) used grounded theory to analyze the influencing mechanism of farmers' pro-environment behavior and found that psychological cognition, behavioral cost, social constraints and the status of legal industry would significantly affect farmers' pro-environment behavior, and then built a psychological environment model of cognition, situation, and behavior. Zhang and Li (2017) found that farmers' behavioral attitudes, subjective norms and perceived behavioral attitudes had positive effects on farmers' intentions and behavior for ecological protection. Rezaei et al. (2020) used an extended form of Technology Acceptance Model (TAM) in order to examine the determinants of Iranian 327 tomato farmers' ecological conservation behavior. The results discovered that public behavior attitudes, psychological perceptions, laws and regulations are strong driving forces that directly or indirectly promote their ecological protection behaviors. In addition, farmers' intentions and behavior for ecological protection are also affected by personal characteristics, policy awareness and other factors. However, there is no consensus on the impact of demographic characteristics on farmers' intentions and behavior for ecological protection in existing studies. Farmers of different gender, age and education stage lead to different attitudes and behaviors concerning ecological environment protection (Song, 2010). Existing research shows that age and education level are important factors affecting farmers' willingness and behavior to protect the ecology (Huang et al., 2018; Liu et al., 2019). There are similar studies abroad, for example, Wardropper (2020) conducted a survey of 1,136 residents in an urban and agricultural watershed in the U.S. The results of the study indicated, those with a stronger ecological worldview tended to rate natural areas and processes as more important and agricultural products as less important than respondents with a more anthropocentric worldview. Other individual-level factors relating to livelihood, outdoor recreation, and proximity to lakes, forests and agriculture also plays an important role in the protection of ecosystems. The types of farmers and people's livelihood capital have an important impact on the adaptability of ecological protection policies (Hou et al., 2018). There are differences in farmers' awareness of environmental policy and their environmental protection behavior. It is precisely because of this difference and different influencing factors that there is a deviation between farmers' ecological environment awareness and ecological protection behavior, and a phenomenon of strong cognition and weak behavior has appeared. The reason for this phenomenon is mainly the unbalanced development between economic growth and ecological protection. It is necessary to increase agricultural economic benefits and efficiency by increasing agricultural subsidies (Liu et al., 2020) to achieve green agricultural development.

Through a comprehensive analysis of relevant literature, we can find that the current research has the following limitations: firstly, most scholars involved incorporated psychological factors or demographic variables into the model separately, and analyzed how these indicators affected on farmers' ecological protection intentions or behavior; Secondly, the research on the ecological protection behaviors of farmers is mainly focusing on forest land (e.g. forest areas and conservation areas), and there is a lack of research on farmers' impact, concerning ecological protection intentions and behaviors, during angelica planting process. Therefore, on the basis of the original theory of planned behavior, this paper introduces the three dimensions of household head characteristics, family resource endowment and environmental policy recognition into the model, and explores the influencing factors of farmers' willingness and behavior for ecological protection by analyzing their impact on the variables of TPB structure.

2. Methods and Materials

2.2 Model building

This paper studies the impact of farmers' attitudes, subjective norms and perceived behavior control on their intentions and behavior to protect their ecology, which can be defined as a multi-to-many relationship. Compared with traditional multiple regressions model, structural equation model (SEM) is suitable for dealing with multi-cause and multi-result problems. SEM combines measurement equation with structural equation, and incorporates model errors into the model for analysis. Its greatest feature is to describe the characteristics of latent variables and their relationship through some observation variables (He, 2015). The variables in each dimension of this paper are latent variables, so the structural equation model is adopted; its specific form is as follows:

$$\begin{aligned} X &= \Lambda x\xi + \delta \\ Y &= \Lambda y\eta + \varepsilon \\ \eta &= B\eta + \Gamma\xi + \zeta \end{aligned} \tag{1}$$

where X represents the exogenous latent variable vector, which reflects the indices of farmers' attitudes, subjective norms, and perceived behavioral controls towards ecological protection behavior; Y represents the endogenous latent variable vector, which reflects the indices of farmers' intentions in ecological protection; Λx and Λy represent the correlation coefficient matrices between the exogenous latent variables, the endogenous latent variables and their corresponding observed variables, respectively; ξ represents the exogenous observed variables, referring to their attitudes, subjective norms, and perceived behavioral controls; η represents the endogenous observed variable, referring to their intentions; B represents the coefficient matrix between some endogenous latent variables and other endogenous latent variables, reflecting the mutual influences among the endogenous latent variables; Γ represents the structural coefficient matrix between the endogenous and the exogenous latent variables, reflecting the path coefficients of the exogenous latent variable X on the endogenous latent variable Y; δ and ε represent the measuring error vectors of the exogenous observed variables and the endogenous observed variables, respectively; ζ represents the random error term of the structural equation. According to equation (1), we can construct a structural equation model that affects farmers' intentions and behavior to protect ecology:

$$
\begin{aligned}
y_1 &= \beta_{21} y_2 + \gamma_{11} B1 + \gamma_{12} B2 + \gamma_{13} B3 + \gamma_{14} B4 + \zeta_1 \\
y_2 &= \beta_{31} y_3 + \beta_{41} y_4 + \beta_{51} y_5 + \gamma_{21} IN1 + \gamma_{22} IN2 + \gamma_{23} IN3 + \gamma_{24} IN4 + \zeta_2 \\
y_3 &= \gamma_{31} AT1 + \gamma_{32} AT2 + \gamma_{33} AT3 + \gamma_{34} AT4 + \zeta_3 \\
y_4 &= \gamma_{41} SN1 + \gamma_{42} SN2 + \gamma_{43} SN3 + \gamma_{44} SN4 + \zeta_4 \\
y_5 &= \gamma_{51} PBC1 + \gamma_{52} PBC2 + \gamma_{53} PBC3 + \gamma_{54} PBC4 + \zeta_5
\end{aligned}
\tag{2}
$$

In equation (2), y_1 and y_2 represent endogenous latent variables, including ecological protection behavior and ecological protection intention. y_3, y_4 and y_5 represent exogenous latent variables, including behavior attitude, subjective norm and perceived behavior control; B1-B4, IN1-IN4, AT1-AT4, SN1-SN4 and PBC1-PBC4 represent 20 observation variables. β represents the path coefficient between latent variables, γ is the load coefficient between latent variables and observable variables, and ζ represents residual terms.

Multiple linear regression models can explore the quantitative relationship and the influence degree between multiple explanatory variables and the explanatory variables. This paper sets the OLS model shown in equation (3), and analyzes the impact of household characteristics, family resource endowments and farmers' environmental policy cognition on the variables in the TPB structure.

$$
yi = b_0 + b_1 Gender + b_2 Age + b_3 Education + b_4 Area + b_5 Year + b_6 Eco.cognition + \varepsilon \tag{3}
$$

The meaning of yi (i=1,2,3,4,5) is the same as equation (2); b_0 is intercept parameter; bi (i=1,2,3,4,5,6) is the parameter to be estimated; ε is the interference term.

2.2 Research hypothesis

(1) Behavioral attitude. Behavioral attitudes (AT) are derived from belief sets about the possible outcome of one's own behavior, which are influenced by such factors as belief intensity and outcome assessment (Ajzen, 2001). Behavioral attitude is the extent to which farmers accept or support ecological environmental behaviors. It is the intentions of farmers formed on the basis of values. The forming process of farmers' values is also the forming process of behavioral attitudes. Farmers' attitudes towards certain behaviors will affect their intentions to act, individual behavior attitudes are consistent with the direction of behavior intention (Borges et al., 2014), and the more positive their attitudes, the stronger their intentions to take corresponding actions. In this paper, four items which respectively are “the use of low toxicity and low residue chemical fertilizer is beneficial to the protection of the ecological environment”, “the use of degradable agricultural film is conducive to the protection of the ecological environment”, “recycling of crop straws is beneficial to resource conservation” and “planting pollution-free products is very important for health” (hereinafter referred to as AT1~AT4) are used to measure farmers' attitudes towards ecological environment behavior.

(2) Subjective norms. Subjective norms are the subjective cognition of farmers on social norms or customs, and refer to the social pressure that individuals perceive when deciding whether to perform a particular behavior. Mastrangelo et al. (2014) showed that subjective norms are powerful explanatory factors to explain the intention to conserve forests. Farmers with positive subjective norms usually hold positive attitudes (Bagheri et al., 2019). During Angelica planting, farmers' subjective norms are influenced by the important people or organizations around them. In the theory of planned behavior, it is generally believed that the stronger the behavior subject’s perception of subjective norms, the stronger their intentions to protect ecological environment. In the present paper, four items are used to measure the subjective norms of farmers. They are "the government advocates the use of green pesticides and fertilizers", "my family believes that ecological protection is necessary in production activities", "my neighbors use degradable agricultural membranes", and “my relatives and friends believe that it is good to protect ecological environment” (hereinafter referred to as SN1 ~SN4).

(3) Perceived behavioral control. Perceived behavioral control refers to the feasibility of farmer's subjective recognition of the implementation of ecological behavior. It is the farmers' subjective awareness of the feasibility of implementing ecological protection behavior that can be explained by ability and autonomy. Price and Leviston (2014), Hou and Ying (2015) pointed out that perceived behavior control of behavior can predict and promote people's behavior intention significantly. Mingolla (2019) pointed out that perceived behavioral control plays a most important role in influencing behavioral intentions. Generally speaking, perceived behavior control is positively correlated with behavioral intention (Cui et al., 2017), and the stronger the farmers' perceptual behavioral control is, the stronger their intentions to protect ecological environment will be. In this paper, four items, i.e., “there is subsidy policy for using green pesticides and fertilizers”, “I know what ecological protection behaviors are in the cultivation of Chinese herbal medicines”, “I have other knowledge about ecological protection, and I will do more”, and “I am fully capable of participating in the ecological protection behavior advocated by the government” (hereinafter referred to as PBC1~PBC4), are used to measure the perceived behavioral control of farmers.

(4) Intentions and Behavior to protect ecological environment. As the direct stakeholders of environmental, ecological and social benefits, farmers have inherent demand for ecological protection. The stronger their intentions for ecological protection is, the more likely they will be to use green pesticide fertilizer and recycle crop straw. The theory of planned behavior shows that behavioral intention is the most ideal factor to predict behavior accurately. Most of the current studies were based on the assumption that the farmers' behaviors were positively correlated with their intentions (Daxini et al., 2019), Warren et al. (2016) have found that farmers acknowledge the benefits of behaviors that promote the intention to adoption behaviors. This paper uses "I am willing to participate in ecological protection", "I am willing to participate in ecological protection even without ecological protection subsidies", “I will recommend people around to participate in ecological protection activities” and “I plan to use green chemical fertilizers and pesticides in the next three years” to measure the farmers’ intentions to protect ecological environment; the four items are denoted by IN1~IN4 respectively. Other four items, namely, "I will recycle agricultural and forestry waste such as crop straw", "I will prevent others from damaging the environment", “I will use green pesticides and fertilizers”, and “I will learn the technology of ecological and environmental protection”, are used to measure the ecological protection behavior of farmers; the items are denoted by B1~B4 respectively.

To verify the above hypothesis, this paper constructs a model of influencing factors of farmers' ecological protection intention behavior, and uses structural equation and OLS to analyze it. The structure of the model is shown in Figure 1.

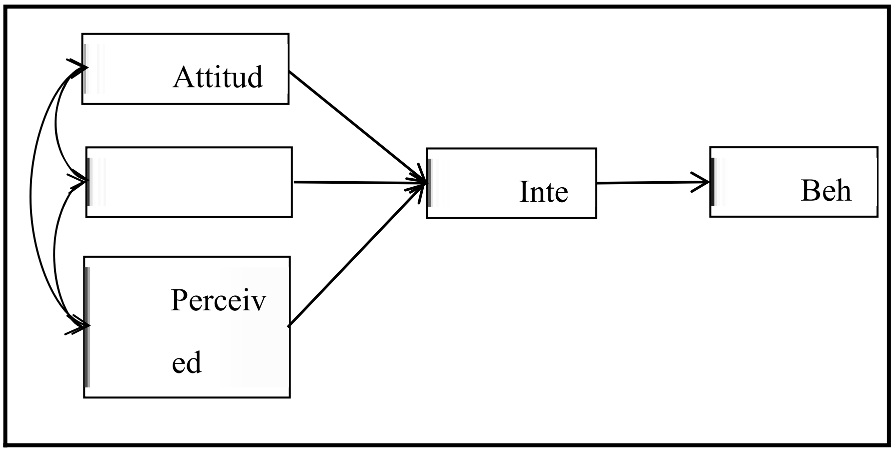

Figure 1 Theoretical model of this study

Combined with the above analysis, the following research hypotheses are proposed：

H1: Behavioral attitude has a positive impact on farmers' intentions to protect ecological environment.

H2: Subjective norms have a positive impact on the intentions to protect ecological environment.

H3: Perceived behavioral control has a positive impact on the intentions to protect ecological environment.

H4: Farmers' intentions to the ecological protection have a significantly positive impact on their ecological behavior.

2.3 Data collection

Min County, a natural disaster-prone mountainous area, is located in the south of Dingxi City, Gansu Province. With the fragile ecological environment, Min County is a key area of ecological protection in China. Within the transition zone from temperate semi-humid to alpine humid climate, Min County has a cold and humid climate which is suitable for planting Chinese medicinal materials like Angelica. In 2017, the planting area of Angelica in Min County exceeded 150,000 mu (a unit of area, a mu=0.0667 hectares); the output accounted for 70% of the total national output of Angelica. The Angelica of Min County was exported to over 20 countries and regions, such as Southeast Asia, Hong Kong, Macao, Taiwan, Europe and the United States. The net income per capital of Angelica in the county reached RMB 2578 in 2016, accounting for 46.8% of the per capital net income of peasants in 2016. Thus, Angelica is one of the main economical sources of the people in Min County.

The questionnaire of this study was designed with reference to the researches on the ecological protection intentions and behavior of farmers (Deng et al., 2016; Yanakittkul and Aungvaraong, 2020), consisting of five parts: characteristics of head of household and family, planting and management of Angelica, knowledge of land ownership, understanding of agricultural policies, and farmers' intentions and behavior during Angelica planting. The 5-Likert scale was used to measure the consent degree of each observation index in the TPB structure: 1=strongly disagree; 2=disagree; 3=partly agree; 4=largely agree; and 5=totally agree.

Considering the educational level of the respondents, as well as to avoid the deviation that may affect the reliability and validity of the data, the questionnaire was completed through face-to-face interviews. First, the members of the research team explained the questions from the questionnaire to the respondents, and then the respondents would answer the questions according to their own real situations. In order to eliminate the influences of the shortages of questionnaire and farmers' misunderstanding on the authenticity and validity of the questionnaire, 30 households in Shili Town and Puma Town of the county were selected for pre-research before the formal investigation. After the preliminary investigation, the questionnaires were revised and improved for the final questionnaire. Intentions Final investigation conducted in five towns with large planting area of Angelica in 2018 (Table 1, Figure 2). A total of 445 questionnaires were obtained in this survey, including 425 valid questionnaires, with an effective rate of 95.51%.

Table 1 Distribution of effective sample areas

Research towns	Number of samples	Percentage (%)	Research towns	Number of samples	Percentage (%)
Puma	85	20%	Qinxu	87	20.5%
Hetuo	82	19.3%	Qingshui	90	21.2%
Zhongzha	81	19.1%			

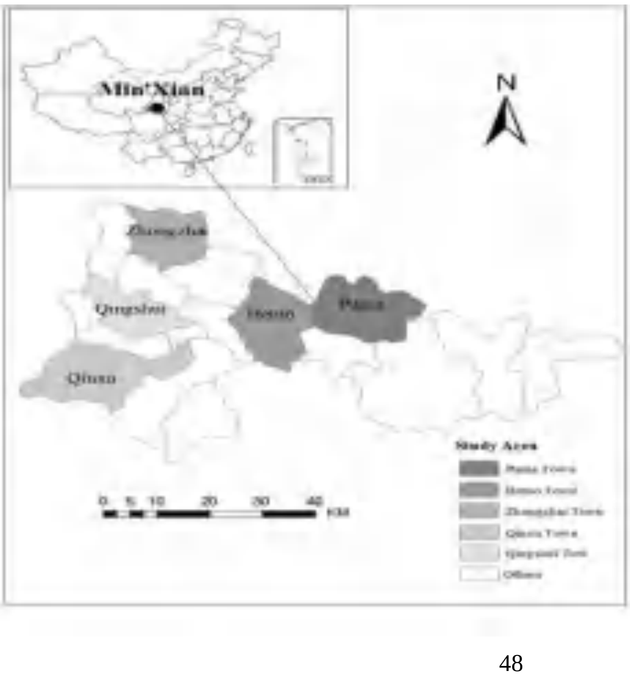

Figure 2 Geographical distribution of study area

3 Results

3.1 Statistical Analysis

3.1.1 Basic Characteristics of Samples

97% of the surveyed families have male household heads (table 2). Their average age is about 50 years old and the average years of schooling is 4.6 years, indicating a low educational level of the surveyed households. The average planting area of Angelica is 4.36 mu, and the average years of planting Angelica is 22.16, indicating that farmers have rich experience. The average score for understanding ecological and environmental laws and policies is 2.44, indicating that farmers' awareness of environmental policies is at a medium level.

Table 2 Basic characteristics of sample data

	Variable	Symbol	Min	Max	Mean	S.E
Household characteristics	Gender of head of household	Gender	0	1	0.97	0.17
	Age of head of household	Age	24	78	49.70	10.80
	Years of schooling	Education	0	18	4.60	4.14
Resource endowment	Planting area of Angelica	Area	0.2	40	4.36	5.28
	Years of planting Angelica	Year	1	60	22.16	13.58
Environmental policy awareness	Understanding of ecological environmental laws and policies	Ecology law	1	5	2.44	0.94

3.1.2 Descriptive Statistics of TPB Structure

The descriptive statistics of the collected data were obtained by SPSS software, AT1, with the largest mean value, indicates that the farmers have a strong understanding of ecological environmental protection and can distinguish which behaviors are good for protecting the ecological environment; the lowest average value is PBC1, indicating that the research area lacks subsidy policies for the use of green pesticides and fertilizers (table 3). The standard deviations of farmer's ecological protection behavioral attitude and protection intentions are both below 1, indicating that farmers' behavioral attitude and protection intentions are relatively at a low level. Nevertheless, the standard deviations of subjective norm, perceived behavioral control, and ecological protection intentions are greater than 1, indicating that the differences of the farmers are significant.

Table 3 Reliability test on TPB structure

		Item	Min	Max	Mean	S.D.
Attitude	AT1	Use low toxicity, low residue fertilizers and pesticides to protect the ecological environment	1	5	4.05	0.876
	AT2	Use of degradable agricultural film helps protect the ecological environment	2	5	3.85	0.821
	AT3	Crop straw recycling is conducive to resource conservation	2	5	3.80	0.822
	AT4	Planting pollution-free products is important for health	1	5	3.95	0.869

Subjective Norm	SN1	The government advocates the use of green pesticides and fertilizers	2	5	3.69	1.140
	SN2	My family believe that ecological protection should be carried out in production activities	2	5	4.01	0.842
	SN3	My neighbors use degradable agricultural film	2	5	3.44	1.084
	SN4	My relatives and friends think that it is good to protect ecological environment	2	5	4.04	0.819
Perceived Behavioral Control	PBC1	Subsidy policy for using green pesticides and fertilizers	1	5	1.86	0.886
	PBC2	I know what behaviors are good for ecological protection in the cultivation of Chinese herbal medicines	1	5	3.08	1.105
	PBC3	I have other knowledges about ecological protection, and I will do more	3	5	4.00	0.752
	PBC4	I am fully capable of participating in the ecological protection activities advocated by the government	2	5	3.75	0.845
Intention	IN1	I am willing to participate in ecological protection	2	5	3.89	0.853
	IN2	I am willing to participate in ecological protection even without ecological protection subsidies	2	5	3.57	0.974
	IN3	I will recommend people around to participate in ecological protection activities	2	5	3.60	0.847
	IN4	I plan to use green fertilizers and pesticides in the next three years	2	5	3.10	0.903
Behavior	B1	I will recycle agricultural and forestry waste such as crop straw	2	5	3.43	0.934
	B2	I will stop others from damaging the environment	1	5	3.07	1.155
	B3	I will use green pesticides and fertilizers	2	5	3.12	1.050
	B4	I will learn eco-friendly technologies	2	5	3.47	0.893

3.2 Model Validation Test

3.2.1 Reliability and Validity Test

The reliability of the questionnaire was tested through the Cronbach's Alpha value Cronbach's Alpha is generally considered to be unreliable below 0.6 and acceptable between 0.6 and 0.7; model simulations are considered good between 0.7 and 0.8 and very good between 0.8 and 0.9. In this paper, SPSS software is used to analyze the reliability of 5 latent variables and 20 observed variables in the model. The results show that the overall reliability of the questionnaire is 0.759. It means that both the questionnaire results and the TPB dimension have high reliability and internal consistency, and the reliability is at a high level, which can meet the research requirements. All the items have been verified through rejection and the results show that all Cronbach's Alpha values are smaller than the overall Cronbach's Alpha value except

AT4, SN3, PBC1, IN4, and B1, indicating that the overall reliability will be reduced if any variable is deleted. In order to improve the overall reliability, the index values of AT4, SN3, PBC1, IN4, and B1 are deleted. Besides, the reliability analysis on the TPB structure is conducted to evaluate the internal consistency of each measurement item. The results of KMO and Bartlett spherical test show that the KMO index value is 0.766, and the Chi-square significant coefficient of Bartlett's spherical test is $p=0.000<0.05$. It suggests that the data measured by this scale could be used for factor analysis.

Table 4 Cronbach's Alpha values for the questionnaire

	Number of items	Cronbach's Alpha
Attitude	3	0.754
Subjective Norm	3	0.636
Perceived behavioral control	3	0.634
Intention	3	0.733
Behavior	3	0.790

3.2.2 Model Simulation Analysis

A structural equation model is constructed and AMOS software for confirmatory factor analysis is used to test the relationship between the predictive factors (attitude, subjective norm, and perceived behavioral control) and the dependent variable (intention). Under the criterion that the acceptable index value $\chi2/df$ <5, RMSEA criterion that the acceptable index value $\chi2/df$ << tentioonfirmatory factor analysis is usdf=1.112, RMSEA=0.016, GFI=0.972, AGFI=0.959, NFI=0.952, RFI=0.939, IFI=0.995, TLI=0.994, and CFI=0.995 (Table 5). Besides, all the index values are within the reasonable range of model, indicating that the structural equation model has a good performance in structural fitting and is relatively scientific.

Table 5 Evaluation index standard and CFA index value of SEM model fit degree

	Fit indices	Norm	Structural model
Absolute fit index	Chi-square	-	92.319
	Chi-square/df	<5	1.112
	RMSEA	<0.08	0.016
	GFI	>.9	0.972
	AGFI	>.9	0.959
Value-added fitness index	NFI	>.9	0.952
	RFI	>.9	0.939
	IFI	>.9	0.995
	TLI	>.9	0.994
	CFI	>.9	0.995

3.3 Fitting Results of Structural Equation Model

The standardized road map (Fig. 3) and the model verification results (Table 6) showed that the influential factors of farmers' behavioral attitudes, subjective norms and perceived behavioral control on their ecological protection intentions are 0.34, 0.56, and 0.13, respectively. The path coefficient of farmers' ecological protection intentions to ecological protection behavior is 0.39. The estimated coefficients of the four critical paths are all positive, and the significance level test is passed. It shows that behavioral attitudes, subjective norms and perceived behavioral control have significantly positive effects on farmers' intentions to protect ecosystem. Therefore, the assumptions H1, H2, H3 and H4 proposed above have been verified.

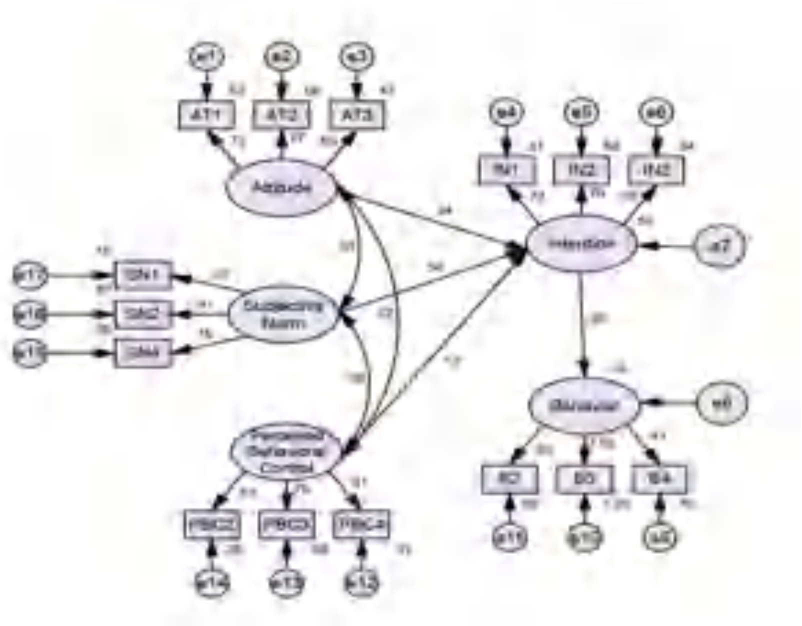

Figure 3 Path diagram of structural equation model

Table 6 Verification results of model hypothesis

	Estimate	C.R.	Hypothetical Test
Attitude → Intention	0.342***	4.903	Support H1
Subjective Norm → Intention	0.559***	7.187	Support H2
Perceived Behavioral Control → Intention	0.129**	1.982	Support H3
Intention → Behavior	0.394***	5.555	Support H4

Note: ***, **, *, significant at 1%, 5% and 10%, respectively.

3.4 Impact effect analysis

In addition to the path coefficients, the intrinsic relationship between the latent variables can be thoroughly analyzed through the direct, indirect, and total effects among variables. The direct effects of behavioral attitudes, subjective norms and perceived behavioral control on farmers' intentions to protect ecosystem are 0.342, 0.559 and 0.129, respectively (Table 7). That is to say, farmers' subjective norms have the greatest impact on their intentions to protect ecological environment, which indicates that the social pressure perceived by farmers plays a key role in their intentions for ecological protection during planting. Specifically, the indirect effects of behavioral attitudes, subjective norms and perceived behavioral control on ecological protection behavior are 0.135, 0.220 and 0.051, respectively. Correspondingly, the indirect effects of subjective norms on ecological protection behavior are also the largest. It shows that farmers' ecological protection behaviors are more likely to be affected by people around them. The direct effect of ecological protection intentions on ecological protection is 0.394, which indicates that intention is the basis for influencing behaviors. In the process of angelica planting, it is one of the paths to promote ecological protection behavior to guide the green production of farmers with ecological protection intentions with the correct method, and it is also the key to sustainable agricultural development.

Table 7 The effects of different variables on ecological protection the intention and behavior

	Intention	Behavior

Variable	Direct Effects	Indirect Effects	Total Effects	Direct Effects	Indirect Effects	Total Effects
AT	0.342		0.342		0.135	0.135
SN	0.559		0.559		0.220	0.220
PBC	0.129		0.129		0.051	0.051
IN				0.394		0.394

3.5 Impacts of Other Factors on the Internal Structure of TPB

During Angelica planting, women have a stronger intentions for ecological protection than men; the education levels of household heads have a positive impact on farmers' subjective norms and ecological protection behavior; the ages of household heads have no significant impacts on the variables; the area of planting Angelica has a significant negative impact on farmers' subjective norms; the years of Angelica planting have a significant positive impact on farmers' attitudes, subjective norms and perceived behavior control; farmers' understanding of ecological environment laws and policies not only influences their attitudes and perceived behavior control, but also positively affects their ecological protection behavior significantly (Table 8).

Table 8 Estimation results of model

	AT		SN		PBC		IN		B	
	B	Sig.	B	Sig.	B	Sig.	B	Sig.	B	Sig.
Gender	-0.037	0.895	-0.399	0.154	-0.214	0.443	-0.605	0.032^{**}	0.113	0.685
Age	-0.006	0.192	-0.001	0.859	-0.003	0.480	-0.005	0.281	0.004	0.380
Education	0.000	0.979	0.020	0.099^{*}	0.013	0.285	-0.002	0.898	0.024	0.042^{**}
Area	0.005	0.615	-0.023	0.015^{**}	-0.004	0.631	-0.011	0.250	0.001	0.919
Year	0.011	0.003^{***}	0.006	0.087^{*}	0.012	0.001***	0.004	0.245	0.000	0.907
Ecology Law	0.157	0.003^{***}	-0.006	0.906	-0.148	0.004^{***}	0.034	0.520	0.193	0.000^{***}

4. Discussions

4.1 Impacts of AT, SN and PBC on Ecological Protection Intentions and Behavior

Based on the micro-survey data of 425 households in Min County, Gansu Province, this paper empirically analyzed the impacts of farmers' behavior attitude, subjective norms and perceived behavior control on their intentions and behavior for ecological protection during Angelica planting by using structural equation model. Behavioral attitude, subjective norm and perceived behavioral control all have significant positive effects on farmers' intentions to protect ecological environment. The impact from top to bottom is subjective norm, behavioral attitude, and perceived behavioral control; and the corresponding effects are 0.559, 0.342 and 0.129, respectively. The variables have indirect effects on farmers' ecological protection behavior. The influence degree from top to bottom is subjective norm, behavioral attitude, and perceived behavioral control; the corresponding effects are 0.220, 0.135 and 0.051, respectively. As an intermediary variable, the intentions for ecological protection have a direct impact on farmers' ecological protection behavior; the effect is 0.394, means farmers' intentions for ecological protection can promote their ecological protection behavior to a large extent. Among the above results, subjective norms have the greatest impact on farmers' ecological protection intentions and behavior, which is consistent with the research conclusion of Deng et al. (2016), It shows that the relative attitudes of relatives and friends around ecological environmental protection greatly affect the intentions and behavior of farmers on ecological protection. The possible reason is that relatives and friends are still the main source of information for farmers to obtain agricultural production information, and present a certain partnership effect in agricultural production. Therefore, their behavior is more susceptible to the influence of surrounding people. Secondly, behavioral attitudes also have a greater impact on farmers 'ecological protection intentions and behaviors, which is consistent with the research conclusion of Hammes et al. (2016). As the main body of agricultural production, farmers' attitudes to ecological protection more easily affect their behaviors. The influence of perceived behavior control on farmers' ecological protection intentions and behavior is relatively weak, which is consistent with the research conclusion of Zhang and Li (2017), It shows that farmers have weak perception and control ability of their ecological protection intentions and behavior, The possible reason is that the surveyed farmers have a low level of education. In the process of Angelica planting, they mainly rely on the experience passed down from their ancestors. Farmers' low level of mastery of modern science and technology leads to their inability to assess whether their behavior is scientific.

4.2 Impacts of Other Factors on the Internal Structure of TPB

In this paper, OLS is used to analyze the impact of household owner's basic characteristics, household resource endowment, and farmers’ awareness of ecological environment policy on the variables in TPB structure. During Angelica planting, women have a stronger intention to protect the environment, mainly due to the existing family labor division. For instance, most women work in farming while men go out to work which leads women pay more attention on ecological protection intentions. The education level of householders has a positive effect on subjective norm and ecological protection behavior. Because farmers who with more educational experience who usually have a stronger ability to learn and accept new knowledge. For instance, some respondents know that increasing the application amount of pesticides and chemical fertilizers will lead to the decline of soil fertility, thereby reducing crop production. Therefore, they are more willing to accept eco-friendly behavior and learn new technologies for ecological environmental protection.

The planting area of Angelica has a significant negative effect on subjective norms, which is consistent with the results of Hou et al. (2012). She proposed that the larger the cultivated land area, the weaker the farmers' intentions to participate in rural ecological environment governance. This reason may be that the scale effect of pro-environmental behavior is not significant. Furthermore, it is found from field research that farmers with a large area of Angelica are generally expert at planting Angelica and they have developed their particular modes of Angelica planting. Therefore, it is rather difficult for them to adapt to other different pro-environment production modes. The planting years indicates that farmers with more experience in planting Angelica have a stronger awareness of ecological environment protection, not only because high soil fertility requirement but also more expertise need.

Farmers' understanding of ecological environment laws and policies not only affects their behavior attitudes and perception behavior control, but also influences the ecological protection behavior directly and positively. And the coefficient is positive, which is consistent with the research conclusion of Zhang et al. (2018). It means that the more farmers know about the policy of ecological environment protection, the clearer they will become about the actions conducive to ecological environmental protection, and the more likely they will be to have environmental friendly behaviors such as recycling crop straw, preventing others from destroying the environment, and littering agricultural waste. Therefore, it is suggested to further strengthen the publicity of ecological protection concepts and ecological protection laws and policies, organize skill training conductive to environmental protection, improve farmers' awareness of environmental protection, and guide farmers to establish ecological environmental protection values. Moreover, it is suggested to affirm the positive effect of pesticides and chemical fertilizers on crops, promote scientific fertilization technology like soil testing and formula fertilization, appropriately motivate farmers to use green pesticides and chemical fertilizers, and guide farmers to develop good fertilization habits.

5. Conclusions and Policy Implications

During Angelica planting, farmers have a strong awareness of ecological environment protection. However, this strong cognition has not been completely transformed into a strong ecological protection behavior. The three variables, behavior attitude, subjective norm, and perceived behavior control of farmers, have significant positive effects on their intentions to protect ecosystem, and have indirect effects on their ecological protection behavior. Among them, subjective norm has the greatest impact. The characteristics of household heads, the endowment of household resources and farmers' awareness of ecological protection policies have significant effects on the internal structure of TPB. Among them, the years of Angelica planting and policy cognition significantly affect the behavior attitude and perceived behavior control of farmers. Educational level as well as the planting area and years of Angelica influences farmers' subjective norms significantly; women's intentions for ecological protection is stronger; ecological protection behavior is affected not only by the variables in TPB structure, but also by the education level of householders as well as farmers' awareness of ecological protection policies.

From farmers' own endowment resources and cognition, this paper investigated the influencing factors of each dimension in TPB structure, and provided a new perspective for analyzing farmers' ecological protection intentions and behavior through the theory of planned behavior. Farmers' intentions to protect ecosystem can promote ecological protection behavior to a great extent, however, there is a gap between farmers' awareness of ecological protection and their ecological protection behavior, which is influenced by factors such as gender, age and education level. The conclusion shows that farmers' subjective norms have the greatest impact on farmers' ecological protection intentions and behavior in the investigated area, which indicates that the pressure of rural groups has a high binding and influence on farmers' behavior.

Therefore, while increasing the publicity of ecological protection policies, the government should also organize activities such as planting experience sharing and skill training to improve the overall comprehensive quality of farmers and guide them to green production. Secondly, it is necessary to give full play to the demonstration and leading role of village cadres, capable people in the village, and agricultural parks, and encourage farmers to use green pesticides and chemical fertilizers and degradable mulch in the process of Angelica planting, improve the quality of agricultural products, recycle crop straws, and ease agricultural non-point source pollution. Finally, a monitoring mechanism and a reward and punishment mechanism should be established to conduct real-time supervision of farmers' agricultural production behaviors, report and punish abuse of pesticides and fertilizers, and reward farmers who continue to protect the agricultural ecological environment and green production behavior. It should be pointed out that due to different types of crops and regional differences, the ecological protection intentions and behavior of farmers in the process of angelica production may not be representative of all types of agricultural production. The main points of ecological environmental protection construction in various regions must fully consider agricultural production and regional difference.

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The 15th International Conference on Waste Management and Technology (ICWMT 15)

Institutional Reform and Innovation of Hazardous Waste Environmental Management in the Background of "Zero-Waste City" Construction

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Abstract

Environmental management of hazardous waste is an important aspect of ecological civilization construction and ecological environmental protection. It is also an important part of the pollution prevention and control battle. The policy-driven characteristics of hazardous waste environmental management determine that institutional innovation should be focused on in the background of "Zero-waste City" construction. Based on the analysis of China's institutional system of hazardous waste environmental management, this paper discusses the obstacles of the current management system, and by combining the pilot work that has been carried out in relevant provinces, proposes the suggestions on the institutional reform and innovation of environmental management of hazardous waste in the background of "Zero-waste City" construction.

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Keywords: Zero-waste city; Hazardous waste; Institutional obstacles; Institutional innovation

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1. Introduction

The Party Central Committee and the State Council highly value the work of ecological environment protection and solid waste management. In December 2018, the State Council issued the "Zero-waste City" Construction Pilot Program, which aims to deepen the comprehensive management of solid waste from the city level, and vigorously promote the reduction of solid waste generation, resource utilization, and harmless disposal. The original intention and goal of "Zero-waste City" construction is to explore the establishment of an institutional, technical, market, and supervision system [1]. Among them, the innovation of the institutional system is the basis. However, "11 + 5" pilot cities and regions still have doubt about the specific innovative practices and paths. This paper introduces the feasible practices and experiences such as formulation of local policies and regulations and innovation on supervision practices, which could be learned by the pilot cities to deepen the construction of "Zero-waste City".

2. Current hazardous waste environmental management institutional system in China

The environmental management of hazardous waste in China began in the early 1990s. Through the implementation of the Basel Convention on the Control of Transboundary Movements of Hazardous Wastes and their Disposal, and by drawing on the experience of the United States, the European Union, and other countries and regions, an institutional system of environmental management for hazardous waste has been was established. Since 1995, China has promulgated laws and regulations such as the Law on the Prevention and Control of Environmental Pollution by Solid Wastes, the Regulations on the Management of Medical Wastes, and the Measures for the Management of Hazardous Waste Business Permits. 8 management institutions such as hazardous waste identification, management plan, declaration

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registration, transfer document, operating permits, emergency plans, markings, and export approvals, as well as 13 standards, 17 technical specifications, and 6 technical guidelines has been released. A relatively complete institutional system for environmental management of hazardous wastes was established, covering management of the entire process of generation, storage, utilization and disposal of hazardous waste.

At present, the Ministry of Ecology and Environment is promoting the revision of the Measures for the Management of Hazardous Waste Business Permits, the Measures for the Management of Hazardous Waste Transfer Orders, and the National Hazardous Waste List, and the formulation and revision of policies and standards for pollution control such as hazardous waste incineration and medical waste treatment and disposal.

3. Problems remaining in institutional system of hazardous waste environmental management in China

3.1 Local administrative regulations restrict the development of hazardous waste utilization and disposal industry

Since 2017, in the context of frequent illegal transfer and dumping of hazardous waste across regions, Hebei, Jiangsu, Henan, Anhui, Hunan, and Ningxia provinces have successively introduced regulations for management of the hazardous waste transfer across provinces. These regulations strictly control transfer of hazardous waste from other provinces for incineration and landfilling, which to some extent, has intensified the contradiction of structural, phased, and regional shortages of centralized disposal capacity for hazardous wastes, and is not conducive to the development of the hazardous waste utilization and disposal industry.

3.2 Obstacles existed in the hazardous waste collection permit system

With the increase of the amount of hazardous waste generated in China and the advancement of refined environmental management, the existing collection permit system has been unable to meet the collection needs of hazardous waste generators and utilization and disposal enterprises. The Measures for the Management of Hazardous Waste Business Permits stipulates that the hazardous waste collection and management permit can only engage in the collection and management activities of waste mineral oil and waste cadmium nickel batteries. It places obstacles in the collection of hazardous waste from social sources and hazardous waste from small or scattered sources by restricting the effective collection of hazardous waste.

3.3 Incomplete standard system for the utilization and disposal of hazardous waste

At present, with the exception of comprehensive incineration, landfilling, and utilization of a few types of hazardous wastes, there is no supporting standard or specification for most types of the hazardous waste utilization and disposal. The lack of standard or specification has led to restricted utilization of hazardous waste and high disposal cost.

3.4 Lack of rigid institutional constraints for utilization and disposal of hazardous waste on-site by generators

The utilization and disposal of hazardous waste in China mainly include two methods, which are utilization and disposal by generators and by the treatment units. At present, the utilization and disposal of hazardous waste on-site by generators is the main method. According to statistics, in 2018, about two-thirds of the total amount of hazardous waste generation was utilized or disposed by generators in China. Due to the inadequate implementation of declaration registration system for the utilization and disposal of hazardous waste by generators, some hazardous waste generators illegally transferred and dumped hazardous waste under the guise of on-site utilization and disposal, posing a great threat to the ecological and environmental safety, and to the human health.

3.5 Refined management of hazardous waste restricted by Environmental Impact Assessment system

The Environmental Impact Assessment (EIA) failed to give full play to the source prevention effectiveness, and the description related with hazardous waste was inconsistent with the actual situation. Quite a number of enterprises' EIA documents have the problems of inaccurate identification of the sources of hazardous waste, and inadequate management measures. With lack of corresponding error correction mechanisms, the types, quantities and utilization and disposal methods of hazardous waste within the scope of management differ greatly from the actual situation. It is leading to the following two consequences. First, the EIA document not only is incapable of providing technical support for the supervision of hazardous waste, but has also help an enterprise for illegal disposal of hazardous waste. Second, the law enforcement officials at the primary level of environmental protection departments use the information that does not conform to the actual situation as the technical support for supervision, and they cannot effectively find the illegal problems of hazardous waste treatment, which is difficult to promote the refined management of hazardous waste.

4. Suggestions on China’s hazardous waste environmental management regulations

4.1 Innovate hazardous waste supervision methods and strengthen regional joint prevention and management

Fully implement the electronic transfer document system of hazardous waste to have the timely information of hazardous waste transfer. Explore the pilot project of hazardous waste business permit exemption for the "point-to-point" utilization of hazardous waste. Strengthen in-depth cooperation in regional joint prevention and control, and promote the establishment of a hazardous waste disposal system with “general matching of capabilities within provinces, coordination and cooperation among provinces and nationwide coordination of special categories”. For example, Department of Ecology and Environment of Sichuan Province and Chongqing Ecology and Environment Bureau signed the Chongqing and Sichuan Province Hazardous Waste Cross-Province Transfer Cooperation Agreement. Guangdong Provincial Government and the Government of the Guangxi Zhuang Autonomous Region signed the Agreement on Joint Prevention and Control of Illegal Transfer of Hazardous Waste across Guangdong and Guangxi Province.

4.2 Establish multi-style collection mode and improve the hazardous waste collection system

Implement the Extended Producer Responsibility and promote qualified generators to rely on sales outlets to collect hazardous waste generated during the use of their products [2]. For example, lead battery manufacturers conduct centralized collection and interregional transfer pilot work of waste lead battery. According to the distribution characteristics of hazardous waste generation sources, organize the pilot work of centralized collection and storage of hazardous waste to alleviate the problems of collection and disposal of hazardous waste effectively. Shanghai has promulgated the Administrative Measures for the Centralized Collection Platform for Hazardous Waste of Small and Micro Enterprises in the Shanghai Industrial Park to promote the construction of key hazardous waste disposal facilities and the hazardous waste collection platform for small and micro enterprises.

4.3 Improve relevant standards and specifications for hazardous waste, and promote the utilization of hazardous waste

Based on the basic principles of environmental risk prevention and control throughout the entire process, formulate secondary pollution control requirements for hazardous waste disposal processes and environmental protection requirements for resource utilization processes by industry and category, stipulate limits for the content of toxic and hazardous substances in resource utilization products, and promote safe utilization of hazardous waste. For example, the Solid Waste and Chemicals Management Technology Center of the Ministry of Ecology and Environment, together with other units, is proceeding with the development of technical specifications for the pollution control of disposal of typical hazardous wastes such as waste catalysts, waste packaging material, and waste acids.

4.4 Accelerate the reform of the pollutant discharge permit system and improve the efficiency of solid waste supervision

The Solid Waste Law (Revised Draft) (draft for comments) has proposed that the State implements an industrial solid waste discharge permit system, and it is recommended to ensure that this clause is retained in the follow-up review process. Accelerate the study of related supporting management measures and technical specifications. Cover solid waste in the pollutant discharge permit system, and collect the information of hazardous waste generation, utilization, transfer, storage, and disposal. For example, Hainan Province issued the Hainan Province Pollutant Discharge Permit Management Regulations. For the first time in the form of local legislation, it clearly proposes that the department of ecology and environment shall specify the requirement from the perspectives of water, atmosphere, soil, solid waste, noise, and other environmental management elements in order to implement systematic, scientific, and rule-of-law management.

4.5 Strengthen the source control of EIA and establish an error correction mechanism

New construction projects shall strictly implement the Guidelines for Environmental Impact Assessment of Hazardous Waste in Construction Projects. Promote the technical check and random inspection of environmental impact assessment documents for construction projects in key industries related to hazardous waste. If the types, quantities, and disposal methods of hazardous waste in long-term operation enterprises is seriously inconsistent with the original EIA document, error correction and rectification shall be adopted in accordance with the circumstances, such as post-environmental impact assessment, environmental impact assessment revision, or re-approval. Establish an effective linkage mechanism for the approval of hazardous waste business permits, the EIA and the pollutant discharge permits. For example, Chongqing has taken the lead in establishing a coordination mechanism for pollutant discharge permits of hazardous waste disposal construction project and hazardous waste operation permits to achieve simultaneous submission of materials and simultaneous approval.

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New Organic Leaching and Recycling of Gold, Nickel and Copper in Waste Printed Circuit Boards

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Abstract

Electronic waste is considered as one of the fastest-growing urban solid waste. The printed circuit board is the core component of electronic products. The printed circuit board contains a lot of valuable metals such as gold, nickel, copper and so on, and has a high value of recovery. In this paper, trichloroisocyanuric acid was used as the leaching agent to efficiently leach gold, nickel and copper from the golden finger part of waste printed circuit boards. The effects of leaching agent concentration, leaching time, leaching temperature and pH on the leaching efficiency were experimentally studied. During the study, it was found that the best leaching yield of gold (65.15%)、nickel (53.69%) and copper (55.53%) was achieved when the concentration of trichloroisocyanuric acid was 25 mM, the leaching time was 10 h, the temperature was 30˚C, and the pH was 1. In this study, an organic leaching agent was used to extract metals from waste printed circuit boards, and it will provide technical supports for organic leaching and recycling of metals.

Keywords: Waste printed circuit board, the golden finger part, gold, trichloroisocyanuric acid, organic leaching, metal recovery

1. Introduction

With the rapid development of technology, the elimination rate of electronic equipment has gradually increased. As the core component of electronic products, printed circuit boards are discarded in large quantities as electronic products are eliminated. According to relevant data, China produces 1.1 million tons of waste electrical appliances each year, of which 3% are waste printed circuit boards[1]. Kaya[2] found that approximately 1.5 million tons of waste printed circuit boards were discarded each year. Printed circuit boards contain toxic and hazardous substances such as polyvinyl chloride and halogen flame retardants, and heavy metals such as lead, cadmium, and chromium that pollute the environment. These heavy metals are enriched in the environment, increasing the environmental toxicity level[3]. If the waste printed circuit board is discarded in the environment without treatment, it will undoubtedly cause serious environmental pollution and even threaten human health. But the waste printed circuit board is not useless, it contains precious metals, such as gold, silver, palladium, etc., as well as other metals like copper and nickel large content. These metals, especially precious metals, are not rich in nature. For example, if the gold content of gold ore is above 2 g/t, the gold ore has a mining

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value. It is worth noting that the gold content in waste printed circuit boards is 80-1500 g/t, which reveals that waste printed circuit boards have much higher economic value than mining[4]. Consequently, e-waste, which is called ‘urban mines’ is a good secondary resource for obtaining precious and base metals. What’s more, recycling those metals in waste printed circuit boards can not only reduce environmental pressure, but also alleviate the pressure of resource shortage.

Domestic and foreign metal recycling technologies in waste printed circuit boards include mechanical processing technology, pyrometallurgy technology, hydrometallurgy technology, and biometallurgy technology. Generally, a combination of multiple technologies with one as the dominant technique is employed to recover metals in the actual processing process. The general process of mechanical recycling technology is disassembly-crushing-decomposition, which mainly utilizes the physical properties between metals and non-metals such as density, magnetic force, conductivity and other differences, to separate these two kinds of sections [5]. However, during mechanical processing, it will cause a lot of waste of precious metals as well as the release of heavy metals, and the separation of metals and non-metals may not achieve. pyrometallurgy technology uses high temperature to separate metals from non-metals[6]. However, during the refining process, it will cause the loss of precious metals and the generation of toxic and harmful gases, and will endanger the environment and human health[7]. It has high requirements for equipment such as a gas recovery treatment device, which is not suitable for long-term use in the market. Biometallurgy technology has the advantages of low cost and less pollution, but it has high environmental requirements and low metal leaching rate, and it is still in the laboratory stage[8]. Compared with mechanical and pyrometallurgy technologies, hydrometallurgy technology produces less toxic and harmful gases, showing a high metal leaching rate, strong applicability to raw materials and fewer impurities in the product. It is inevitable that traditional hydrometallurgy technology uses inorganic cyanide, strong acid and alkali reagents to recycle metals in waste printed circuit boards, which will cause a relatively low selectivity, and a large amount of toxic waste liquid, adding difficulty to the recycling process[9].

Traditional metal leaching agents include aqua regia[10,11], cyanide[12], and halide[13]. Although aqua regia can leaching all the metals, the subsequent metal separation is difficult. The cyanide process is widely for more than a hundred years, as the gold leaching rate is high, but cyanide is a highly toxic and dangerous substance, which is very harmful to people and causes environmental pollution[14]. At this stage, researchers have found that thiosulfate[15] and thiourea[16] can also leach gold from waste printed circuit boards. Thiosulfate is safer, non-toxic leaching agent. However, the cost of thiosulfate is high and the consumption of thiosulfate is huge, which is not suitable for industrial applications. Thiourea has extremely high requirements for the acidic environment. When pH> 2, thiourea will hydrolyze, increasing the consumption of thiourea used in the process, and resulting in more waste leaching solution, which is not suitable for industrial applications[16]. In recent years, Lin[17] and others have found that organic leaching agents composed of sulfoxide chloride and pyridine can effectively dissolve precious metals and have the advantage of selective leaching of precious metals. Compared with inorganic reagents, the amount of organic leaching agent is small, resulting in less liquid waste. The leaching agent selected in this article is trichloroisocyanuric acid, which is a common disinfectant used for industrial water, swimming pool water, and hospital water disinfection. It is a strong oxidant and chlorinating agent. Because of its strong oxidation and coordination ability, it was selected for the leaching of gold, nickel and copper in waste printed circuit boards.

2. Materials and methods

2.1 Materials

The dismantled waste printed circuit boards were purchased from the laboratory in Shanghai. The golden finger part of the printed circuit board was firstly cut into thin strips (0.5 × 1 cm) with a guillotine, then grinded into powder with grinder (IKA A11). The sample powder is less than 1 mm which can pass through 18 mesh screen. Studies have shown that the metal particles in the powder with such size have a large degree of dispersion and no adhesion[18].

2.2 Metal content quantification

1 g of golden finger powder was put into 40 mL of fresh aqua regia ($HCl: HNO_3 = 3: 1$), to carry out the leaching experiment in a wild-mouth bottle in the water bath with constant temperature. The leaching was proceeded at 30℃ with a rotating speed of 200 r / min for 24 h. After the reaction, the solution was filtered with a filter membrane of 0.45μm, and then fixed to a constant volume of 500mL. Then the Inductively Coupled Plasma Spectrometer (ICP-OES) was used to measure the concentration of gold, nickel and copper ions. In order to ensure the accuracy and reliability of the experimental results, three parallel experiments were performed.

2.3 Leaching reagent

The leaching agent used in this experiment was trichloroisocyanuric acid dissolved in aqueous solution. Trichloroisocyanuric acid is a very strong oxidant and chlorinating agent, and it is also an important bleaching agent, chlorinating agent and disinfectant. Generally, it is used for the disinfection of swimming pool water, industrial water, hospitals, restaurants, etc. It has the advantages of long effective chlorine release time in water, safety and non-toxicity, which has a strong application prospect. Because of its strong oxidation and coordination ability, it was selected for the leaching of gold, nickel and copper metals in waste printed circuit boards.

2.4 Leaching experiment

All leaching experiments were performed in a 250 mL erlenmeyer flask. Distilled water was added into the leaching agent after reaction to form a fixed 150 mL solution. Influencing factors for the metal leaching rate, include: (i) pH (0.5, 1, 2, 3, 4, 5, 6, 7, 8, 9, 10), (ii) leaching time (2, 5, 10, 15, 20, 25, 30 h), (iii) lixiviant concentration (5, 10, 20, 25 mM), (iv) leaching temperature (20, 25, 30 ℃). Typically, 0.5 g of golden finger powder was employed to react with 150 mL of leaching solutions. A water bath oscillator was employed to carry out leaching experiments. After the reaction, the solution was filtered with a filter membrane of 0.45 μ m and then fixed to a constant volume of 250mL for the concentration test of the three metals using ICP-OES. The leaching rates of the three metals were calculated, with an average figure of three parallel samples as the final leaching rate.

By changing the influencing conditions like pH, leaching time, leaching temperature and the concentration of trichloroisocyanuric acid, the optimal leaching rate of three metals was obtained. The sulfuric acid (60%) and solid sodium hydroxide were used for pH adjustment. To ensure the accuracy and reliability of the experimental results, three parallel experiments were performed.

The metal leaching rate was calculated by equ (1):

$$c(\%) = \frac{a}{b} \times 100\% \qquad (1)$$

a: The mass of metal in the leaching solution; mg

b: The mass of metal in aqua regia; mg

c: Leaching rate of metal; %

2.5 Experimental apparatus

All the apparatus used in this study was shown in Table 1.

Table 1 Experimental apparatus

Equipment name	Model	Production unit
Grinding machine	IKA ®A11 basic	Aika (Guangzhou) Instrument Equipment Co., Ltd.
Pipette	M45110F	Abend China Co., Ltd.
Ultrapure water equipment	Smart-S15	Shanghai Hetai Instrument Co., Ltd.
Analytical Balances	FA2204B	Shanghai Precision Scientific Instrument Co., Ltd.
Electric constant temperature blast drying oven	DGG-9053A	Shanghai Senxin Experimental Instrument Co., Ltd.
pH meter	FE-20	Swiss METTLER TOLEDO Group
Water bath oscillator	SHA-C	Changzhou Guohua Electric Co., Ltd.
Circulating water multi-purpose vacuum pump	SHB-III	Zhengzhou Great Wall Technology Co., Ltd.
Electric mixer	JJ-1	Changzhou Guoyu Instrument Manufacturing Co., Ltd.
Inductively coupled plasma spectrometer（ICP-OES）	Optima 8000	PerkinElmer Instruments Co., Ltd.

3. Results and discussion

After leaching the metal with aqua regia, the concentration of three metals was measured by ICP-OES, as shown in Table 2:

Table 2 Metal content in aqua regia leachate

Metal element	Au	Ni	Cu
Mass（mg/g Golden finger）	2.414	17.522	297.267

7.1. Effect of pH on the leaching

The leaching conditions were set as followed: the concentration of trichloroisocyanuric acid solution was 20 mM, the temperature was 25℃, the leaching time was 10 hours, the rotating speed was 200 r/min, the solid to liquid ratio was 1: 300. The effect of pH on leaching rates of three metals was carried out between the pH value from 0.5 to 10. The results were exhibited in Figure 1.

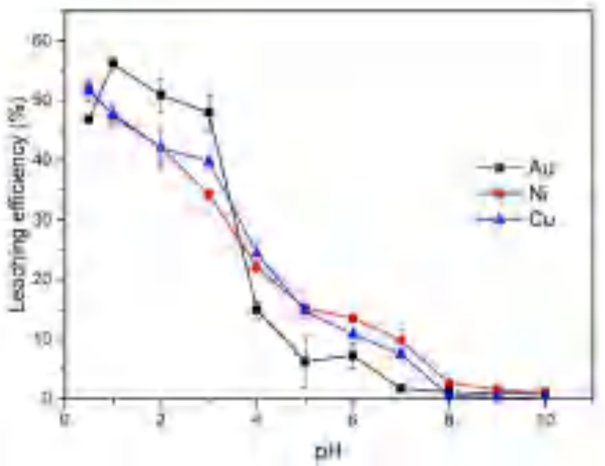


Figure 1 Effect of pH on the leaching rate of three metals

It can be seen from the figure that the leaching rate of Cu and Ni shows a decreasing trend as the pH value increases, the leaching rate is high in an acidic condition and relatively low in an alkaline condition. Consistent with traditional leaching agents like HCl, H_2SO_4 and HNO_3, the base metals were more easily leached in the acidic conditions[19,20]. The leaching rate of Au showed an upward trend initially, reaching a maximum value of 56.13% when pH was 1. But the figure decreased subsequently. When the pH value was adjusted from 3 to 4, the Au leaching rate plunged rapidly from 47.94% to 14.96%, and the leaching efficiency continued to decrease with the increase of pH. When the pH was above 8, the leaching rate of Au tended to balance around 1%. The leaching efficiency trend of Ni was close to Cu, decreasing as the pH increases. Overall, pH has a great influence on the metal leaching rate. At a low pH level, the leaching rates of the three metals were higher.

7.2. Effect of leaching time on leaching

The leaching conditions were set as followed: the concentration of trichloroisocyanuric acid solution was 20 mM, pH value was 1, the temperature was 25℃, the rotating speed 200 r/min, the solid to liquid ratio was 1: 300. The effect of the leaching time on leaching rates of three metals was carried out from 2 h to 30 h. The results are exhibited in Figure 2.

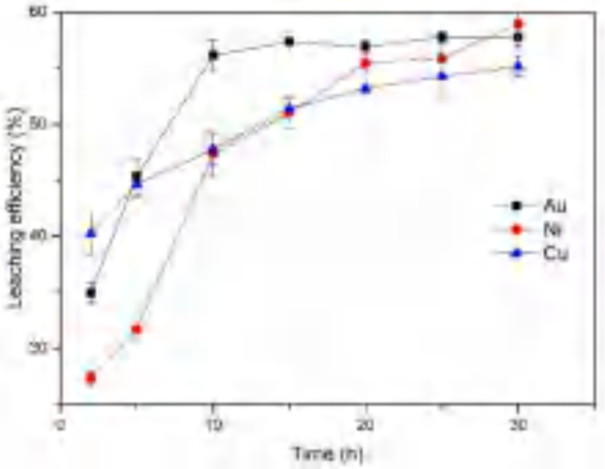


Figure 2 Effect of reaction time on metal leaching rate

It is revealed from Fig.2 that the leaching rate of all the three metals grew with the increase of the leaching time. The leaching rate of Au almost reached the equilibrium at 15 h, achieving 57.7%. The leaching rate of Cu increased with the leaching time, which showed a steady rising trend from 40.25% to 55.13%. Ni had a large leaching rate variation from 27.39 to 58.92%. After 5 h of leaching time, the leaching rate of Cu was the highest and the figure of Ni was the lowest. After 5 h, the leaching rate of Au started to exceed Cu to reach the highest leaching rate among the three metals. It was found that the leaching rate of Au was obviously different from the other two metals at the leaching time of 10 h. Furthermore, as the leaching time increased, the leaching rate of Au did not increase significantly. Therefore, the leaching time of the subsequent experiments was fixed at 10 h.

7.3. Effect of trichloroisocyanuric acid concentration on leaching

The leaching conditions were set as followed: the pH value was 1, the temperature was 25℃, the rotating speed was 200 r/min, the solid to liquid ratio was 1: 300. The effect of the concentrations of trichloroisocyanuric acid on leaching rates of three metals was carried out from 5 mM to 30 mM.

3.3.1. Effect of 5 mM trichloroisocyanuric acid on leaching

When the concentration of trichloroisocyanuric acid solution was 5mM, the leaching rate of the three metals increased with leaching time, as shown in Figure 3. As seen from the figure, the leaching rate of Au was very low, almost 0.07-0.75%, and the leaching rate trend of Ni and Cu was similar, while more Cu was dissolved than Ni. The leaching rates of the three metals were clearly distinguished. On same leaching conditions, the leaching rate of Cu was the highest overall, ranging from 30.14 to 41.15%, and the leaching rate of Ni ranged from 26.61-36.84%. Unlike the leaching process when trichloroisocyanuric acid concentration was 20mM, the leaching priority of Cu and Ni was higher than that of Au.

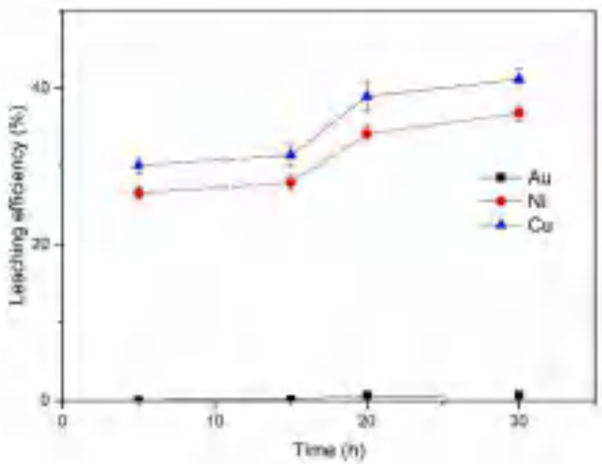


Figure 3 5mM trichloroisocyanuric acid metal leaching rate

3.3.2. Effect of 10 mM f trichloroisocyanuric acid on leaching

When the concentration of trichloroisocyanuric acid solution was 10 mM, the leaching rate results were shown in Figure 4. As seen from the figure, the leaching rates of Cu and Ni were in the same trend, both of them showed an upward trend firstly and then tended to be flat, different from them, the leaching rate of Au showed a continuously increasing trend with time. At 5 h, the leaching rate of Au was 5.01%, after 30 h, the leaching rate reached 48.55%. Obviously, the leaching rate of Cu was the highest among the three metals within the researched time, which rose from 40.81% to 51.27% in the first 15 h. However, the growth rate of Cu was slow after that, achieving 53.29% at 30 h. The leaching rate of Ni was lower than Cu and showed a similar trend with Cu. At 5 h, the leaching rate of Ni was 28.79%. After 10 hours, the leaching rate of Ni rose to 40.88%. With the extension of the leaching time, however, the leaching rate of Ni did not change much and tended to be balanced. Compared with the leaching when the trichloroisocyanuric acid was 5mM, the leaching rates of the three metals had been improved, and the leaching rate of Au has increased the most, probably because the leaching priority of Cu and Ni is higher than Au. As a result, when the concentration of the leaching agent increased, Au began to be leached in large quantities.

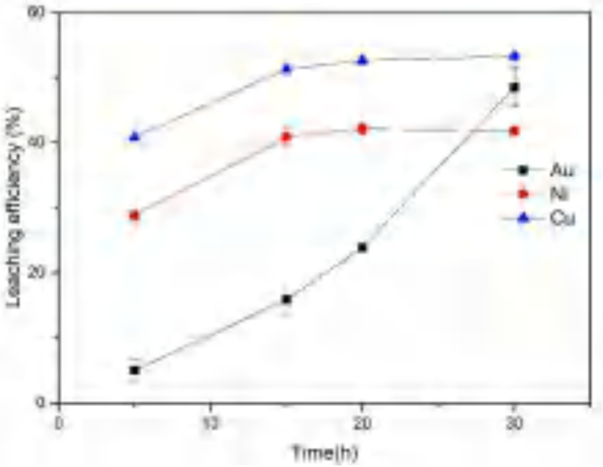


Figure 4 10mM trichloroisocyanuric acid metal leaching rate

3.3.3. *Effect of 20 mM trichloroisocyanuric acid on leaching*

When the concentration of trichloroisocyanuric acid solution was 20 mM, the leaching results were shown in Figure 5. Compared with lower lixiviant concentration conditions, the leaching rates of the three metals were improved. The leaching rate of Au reached 45.31% at 5 h and 56.36% of Au was dissolved after 15 h, with the extension of leaching time, the leaching rate of Au rose to 57.76% at 30 h, almost balanced at 15 h. And between 5-25 h leaching time studied, the leaching rate of Au was always higher than the other two metals. Under the conditions, the leaching rate of Ni was greatly affected by the concentration of the leaching agent, varying from 31.70% to 58.92% during the leaching period. In contrast, the leaching rate of Cu was not growth obviously, which ranged from 44.61% to 55.13%.

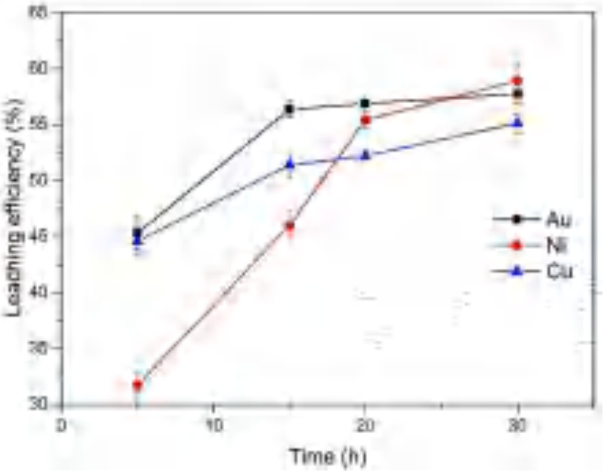


Figure 5 20mM trichloroisocyanuric acid metal leaching rate

3.3.4. *Effect of 25 mM trichloroisocyanuric acid on leaching*

When the concentration of trichloroisocyanuric acid solution was 25 mM, the leaching rate results were shown in Figure 6. The leaching rate of the three metals increased further than before. Au showed a clear leaching over the whole period. After 5 h, the leaching rate of Au reached 62.12% , but the figure increased slowly afterward, only 66.51% of Au was leached after 30 h. At the same time, the leaching rates of Ni and Cu both grew with the increased of leaching time. The leaching rate of Ni ranged from 39.36% to 61.62% and from 43.31% to 58.22% respectively.

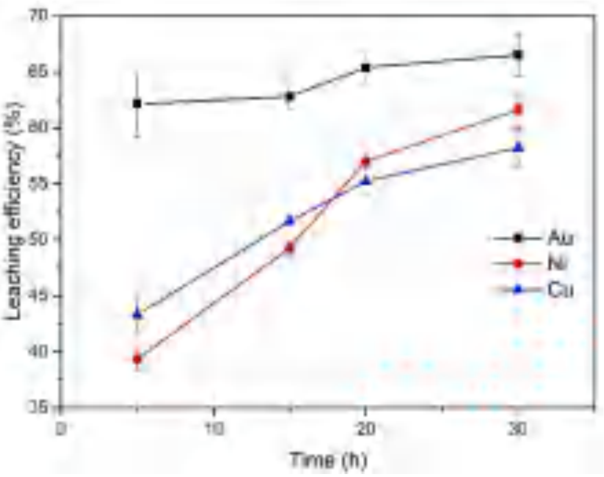


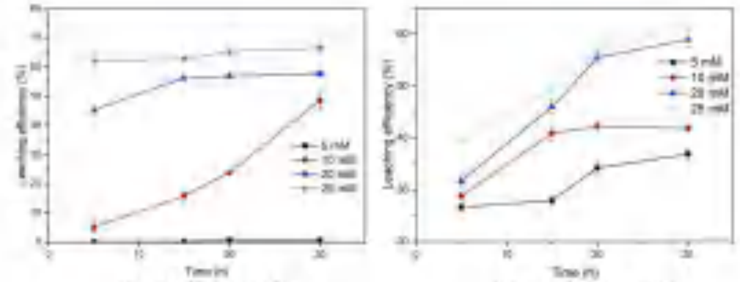
Figure 6 25mM trichloroisocyanuric acid metal leaching rate

3.3.5. Leaching rate of three metals under different leaching agent concentrations

The leaching rates of the three metals at different leaching agent concentrations with time were plotted separately, as shown in Figure 7. Overall, the leaching rates of the three metals increased with the concentration of the leaching agent. Among them, the concentration of the leaching agent has a great influence on the leaching rate of Au. When the concentration of trichloroisocyanuric acid was low, the leaching rate of Au was at a low level. This is because when the concentration of the leaching agent was low, the effective chlorine component was contained by Cu and Ni. As the concentration of the lixiviant increased to 10 mM, the leaching rate of Au increased significantly, from 5% to 48%. Until the concentration of the leaching agent increased to 25 mM, the leaching rate of Au reached 62% at 5 hours, but with the increasing of the leaching time, the increase trend was not obvious.

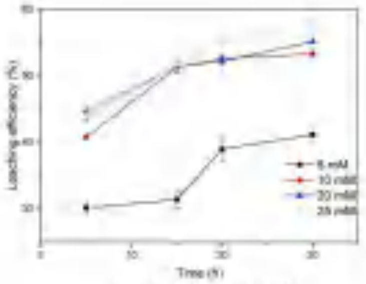
With the same leaching conditions, the leaching rate of Ni gradually rose as the concentration of the leaching agent increased. When the concentration of trichloroisocyanuric acid was low, the leaching rate of Ni increased little during the leaching time. However, when the concentration of the leaching agent increased to 10 mM, the leaching rate of Ni increased rapidly within 15 h. While in the case of 20 mM and 25 mM of the concentration of trichloroisocyanuric acid, the leaching rate was relatively insignificant.

Different from the above cases, the leaching rate of Cu increased from 30% to 40%, when the concentration of the leaching agent was 5mM. As the concentration of the leaching agent increased to 10mM, the leaching rate of Cu reached 40% at 5 h, and then increased with the increase of leaching time. However, when the concentration of the leaching agent increased to 20 mM and 25 mM, the leaching rate of Cu was not much different from that 10 mM.



Leach efficiency of Au

Leach efficiency of Ni



Leach efficiency of Cu

Figure 7 Effect of different leaching rate concentrations on the leaching rates of Au, Ni and Cu

7.4. Effect of temperature on leaching

The leaching conditions were set as followed: the concentration of trichloroisocyanuric acid solution was 25 mM, the pH value was 1, the leaching time was 10 hours, the rotating speed was 200 r/min, the solid to liquid ratio was 1: 300. The effect of temperature on leaching rates of three metals was carried out from 20℃ to 30℃. The results were exhibited in Figure 8.

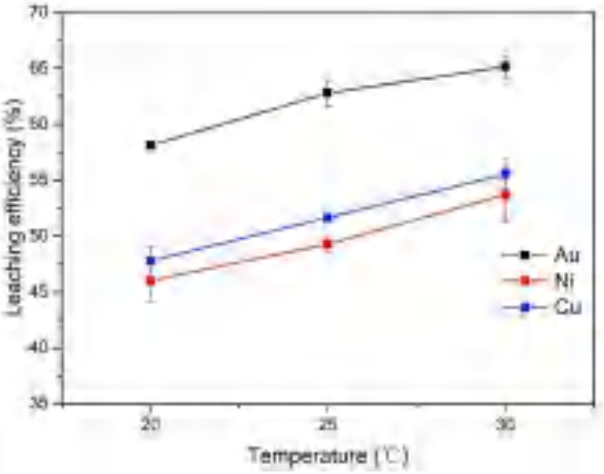


Figure 8 The effect of temperature on the metal leaching rate

It was revealed from Figure 8 that the leaching rates of the three metals grew with the increase of the temperature, and showed a clear distinction. At a temperature of 20°C, the leaching rate of Au was 58.12%. As the temperature increased, the leaching rate of Au increased to 65.15% at a temperature of 30°C. In the same conditions, the leaching rate of Cu was lower than Au, and the leaching rate ranged from 47.77% to 55.53%. Obviously, the leaching rate of Ni was the lowest, achieving 46.02% at the temperature of 20°C. As the temperature increased to 30℃, the leaching yield of Ni reached 53.69%.

4. Conclusion

In this study, it was found that trichloroisocyanuric acid could effectively leach gold, nickel and copper metals in the waste printed circuit boards. The highest leaching efficiency for the three metals under the experimental conditions was gold 65.15%, nickel 53.69%, and copper 55.53%. Compared with the traditional leaching agent, it could leach a large amount of Au, Ni, Cu at a relatively low cost (7.8-14 yuan/kg) and less dosage. Furthermore, this lixiviant is safe, non-toxic, and less environmentally polluted. As a result, the leaching technology studied in this paper could be combined with the subsequent solvent extraction technology to efficiently, quickly and selectively separate the three metals, which could provide technical benefits for the organic hydrometallurgy of metals in waste printed circuit boards.

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Selected Proceedings of the Fourteenth International Conference on Waste Management and Technology

Thought on Establishing the Joint Prevention, Control and Disposal Mechanism of Medical Waste under the COVID-19 Epidemic

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Abstract A range of shortcomings was exposed in China's medical waste disposal capabilities in responding to public health emergencies under outbreak of the novel coronavirus pneumonia (COVID-19) epidemic. Especially, the traditional medical waste disposal capacity allocation and the prevention and control mechanism oriented to "a single city" have been far from meeting the needs of medical waste disposal and management during the emergency period. Therefore, suggestions on establishing the regional joint prevention, control and disposal mechanism of medical waste were put forward in this paper with reference to the ideas of China's existing regional joint prevention and control mechanism for air and water pollution, which covered the aspects of establishment of coordinating agencies, cross-regional collaborative disposal, cross-regional joint response to emergencies, cross-regional collaborative management and effectiveness evaluation.

Keywords: COVID-19; medical waste; joint prevention, control and disposal; mechanism

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Separate collection, safe temporary storage, timely transportation and harmless disposal of medical waste play an important role in fighting against the COVID-19 epidemic [1]. The sharp increase in the amount of medical waste posed a severe test to the disposal capacity of medical waste [2] during the epidemic, especially at the beginning of the epidemic. A range of shortcomings were exposed in China's medical waste disposal capabilities in responding to public health emergencies, such as insufficient centralized disposal capacity in some regions, obviously insufficient emergency handling equipment reserves, and lack of cross-regional dispatching mechanisms. It was clearly required at the meeting of the Political Bureau of the CPC Central Committee held on February 21 that more efforts should be made to speed up fixing the shortcomings in the collection and disposal of medical waste and hazardous wastes. In accordance with the *Guidelines for Medical Waste Emergency Disposal Management and Technology under the COVID-19 Epidemic* (Trial) released by the Ministry of Ecology and Environment of the People’s Republic of China, cities and towns with insufficient medical waste disposal capacity may coordinate with other cities in the province or those with surplus medical waste disposal capacity in neighboring provinces to establish a cross-regional coordination mechanism for emergency disposal of medical waste. The *Work Plan about Comprehensive Treatment of Waste from Medical Institutions* jointly released by 10 departments including the National Health Commission also put forward the guiding opinions on "the establishment of a collaborative mechanism and an interest compensation mechanism for the cross-regional centralized disposal of medical waste". Thus, establishing a regional joint prevention, control and disposal mechanism of medical waste and enhancing of cross-regional medical waste disposal are important measures to promote the construction of the national medical waste disposal system after the outbreak, and as well as inevitable requirements for pushing forward the construction of the national ecological environment governance system and the modernization of governance capabilities.

1 Necessities to establish a regional joint prevention, control and disposal mechanism of medical waste

1.1 Inevitable requirements for enhancing the capacities to prevent and control environmental risks in health emergencies

A great number of transport vehicles and mobile emergency disposal facilities across the country have been mobilized to Hubei to assist in medical waste disposal after the outbreak. For instance, the medical waste disposal capacity of Wuhan increased from 50 tons/day before the epidemic to 262.8 tons/day during the epidemic after support from other cities and resource allocation, which basically met the medical waste disposal requirements for epidemic prevention and control in the city. However, the regional cooperation, with hurried response and inadequate preparation, had many shortcomings, especially in terms of information sharing, resource allocation, and supervision of disposal process. It can be seen that the traditional medical waste disposal capacity allocation and the prevention and control mechanism oriented to "a single city" have been far from meeting the needs of medical waste disposal and management during the emergency period. Therefore, the regional joint prevention, control and disposal mechanism of medical waste should be established, cross-regional cooperation and emergency drills should be carried out in terms of construction of long-acting collaboration mechanisms, joint prevention and control warnings, resource allocation and information sharing, and collaborative emergency disposal, and the schemes and preparations should be made to in advance to improve the national capacities to prevent and control environmental risks in health emergencies.

1.2 Urgent need to jointly cope with the transboundary pollution incident of medical waste

In recent years, the medical waste has frequently polluted the environment due to cross-regional illegal transfer, disposal and dumping[3]. The investigation and prosecution of transboundary pollution cases of medical waste become more difficult because the original linkage mechanism of the municipal-level ecological environment departments has been difficult to fit with this new situation, the new cross-regional (cities or provinces) cooperation mechanism has not been established, and supervision authorities failed to make the concerted efforts. The establishment of a regional joint prevention, control and disposal mechanism is conducive to enhancing the capacity to cope with the cross-regional emergent environmental incidents and effectively curbing the occurrence of illegal transfer, disposal and dumping of medical waste.

1.3 Establish a sound environment supervision system of hazardous wastes and enhance the basic requirements of the "three capabilities" of hazardous wastes

With regard to medical waste, a category of hazardous wastes, its environment supervision capability, utilization and disposal capability and environmental risk prevention capability (referred to as "three capabilities") should also be included in the hazardous waste environment supervision system. It was required in the *Guiding Opinions on Improving the Capacities of Environment Supervision, Utilization and Disposal and Environmental Risk Prevention of Hazardous Wastes* (HGT [2019] No. 92), "Regional and departmental joint prevention, control and disposal mechanism should be established. Local eco-environmental departments at all levels should strengthen the environment supervision and management of hazardous wastes in accordance with relevant environmental protection laws and regulations, and establish cooperation mechanisms with relevant administrative departments in charge of development and reform, health, transportation, public security and emergency, and enhance information sharing and collaboration ... ". It can be seen that the establishing a regional joint prevention, control and disposal mechanism of medical waste and strengthening the regional joint management and control of related departments are inevitable requirements to enhance the construction of "three capabilities" for hazardous wastes.

1.4 Important measures to create an ecological security pattern of super urban agglomerations and a good regional ecological environment

The production of medical waste is closely related to geographical and population distribution. The regions that are more economically developed and densely populated may enjoy higher medical and produce more medical waste. Especially at the outbreak of any infectious disease, these regions bear higher pressure on medical waste disposal and risk prevention and control and are exposed a range of problems in the construction of disposal capacity and the prevention and control mechanism carried out based on administrative divisions. For this purpose, the establishment of a cross-regional trans-department joint prevention, control and disposal mechanism of medical waste and integration of regional resources, information and supervision in key densely populated regions such as Beijing-Tianjin-Hebei Region, Guangdong-Hong Kong-Macao Greater Bay Area, the Yangtze River Delta, Changsha-Zhuzhou-Xiangtan Region, and Chengdu-Chongqing Region cannot only reduce the environmental risks of daily disposal and management and improve the efficiency of collection, transportation and disposal of medical waste during epidemic prevention and control, but also act critical role in guaranteeing the ecological safety of super urban agglomerations and building the good regional ecological environment in China.

2 Current situation of cross-regional joint prevention, control and disposal of medical waste in China

2.1 Lack of corresponding policy and legal support at the national level

All provinces and cities have been making gradual efforts to push forward the joint prevention and control of hazardous wastes in their respective areas after the management idea of "establishing a joint prevention and control mechanism for departments and regions" was put forward for the first time in the *Notice on Resolutely Curbing the Illegal Transfer and Dumping of Solid Wastes and Further Strengthening the Supervision of the Whole Process of Hazardous Wastes* issued by the Ministry of Ecology and Environment, but the research on the corresponding laws, regulations, policies and standards has been very lagging, especially in existing environment-related laws such as the *Law of the People's Republic of China on the Prevention and Control of Environmental Pollution by Solid Waste* and *Regulations on Administration of Medical Waste*, no requirements for joint prevention and control of hazardous waste or medical waste have been specified. The lack of upper-level policies and laws will lead to a lack of subjective thinking in the implementation of regional joint prevention and control policies for medical waste, and no corresponding binding force has been formed[4], and it is also difficult to form any concerted efforts in collaboration among various regions and departments.

2.2 Insufficient basic research and lack of scientific research support

Cities and provinces have made efforts to establish the medical waste disposal capacity allocation and the prevention and control mechanism oriented to "a single city" before the outbreak of COVID-19, and neither the state nor local has carried out any research on the cross-regional joint prevention and control mechanism for medical waste. Therefore, the emergency management and treatment equipment (such as transfer vehicles, transfer cases, and emergency treatment facilities) for medical waste disposal in Wuhan and even the entire Hubei province were in obvious shortage after the outbreak of COVID-19. During the peak outbreak period, the "crammed" approaches that depend on large-scale administrative means got stuck in a passive state due to such problems as untimely scheduling, uncoordinated resource allocation, and disordered management in the process of transferring emergency treatment facilities from other cities and provinces to Hubei[5]. This outbreak revealed the fact that the basic research on joint prevention and control of medical waste in China is in shortage, and the guidance documents issued by the Ministry of Ecology and

Environment, the National Health Commission and other departments are insufficient to fully support the needs of regional joint prevention and control for medical waste.

2.3 The joint prevention and control mechanism has not yet been established, and it is difficult to achieve cross-regional collaborative disposal

China has accelerated to push forward the construction of medical waste disposal capacity and regulate the treatment and disposal behavior during the "12th Five-year Plan" period[6]. However, a cross-regional collaborative disposal mechanism has not been established across the country up to now, especially in densely populated regions, the cross-regional collaborative disposal, joint law enforcement, information sharing and unified monitoring and supervision mechanisms still cannot meet demand, and a cross-regional emergency prevention and control system has not been established. In addition, the problem of medical waste "Not In My Back Yard" is extremely prominent, and a good cross-regional cooperative disposal and benefit compensation mechanism has not been established, leading to the cross-regional collaborative disposal difficult to develop.

3 Suggestions for establishing a regional joint prevention, control and disposal mechanism of medical waste

Practice has proved that regional joint prevention and control acts as a "trenchant edge" in coping with regional air and water pollution, in order to achieve the objective mechanism of "unified planning, unified monitoring, unified supervision, unified assessment, and unified coordination"[4, 7]. Therefore, the suggestions on establishing the regional joint prevention, control and disposal mechanism of medical waste were put forward in this paper with reference to the ideas of China's existing regional joint prevention and control mechanism for air and water pollution, which covered the aspects of establishment of coordinating agencies, cross-regional collaborative disposal, cross-regional joint response to emergencies, cross-regional collaborative management and effectiveness evaluation.

3.1 Establish a coordination mechanism and a cross-regional long-acting joint prevention, control and disposal mechanism

Centered on key densely populated regions such as Beijing-Tianjin-Hebei Region, Guangdong-Hong Kong-Macao Greater Bay Area, the Yangtze River Delta, Changsha-Zhuzhou-Xiangtan Region, and Chengdu-Chongqing Region, a regional coordination organization for joint prevention, control and disposal should be established, Composed of main administrative leaders in different regions, and relevant administrative departments at all levels in charge of medical treatment and public health, ecological environment, and road transportation, the organization should be responsible for developing the regional joint prevention, control and disposal working mechanism for medical waste, directly mobilizing the relevant departments and enterprises in the region, and taking unified action to guarantee the achievement of the medical waste disposal objectives in the region in daily and public health emergencies. At the same time, joint conferences should be held regularly to discuss and pragmatically push forward the specific work in regional joint prevention, control and disposal of medical waste.

3.2 Coordinate regional planning and establish a cross-regional collaborative disposal mechanism

It is necessary to set up regional collection, transfer or disposal of medical waste facilities following the principle of "prepared all the time rather than not prepared due to not always used" after comprehensively considering the geographical location distribution, serving population and occurrence of epidemic situation, so as to realize the "full coverage" of the regional collection, transfer and disposal system of medical waste. Proper measures should be taken such as introducing new technologies, and updating equipment and facilities, disposal methods should be optimized, and shortcomings should be resolved to greatly enhance the disposal capacity and emergency disposal capacity of existing medical waste centralized disposal facilities, and standardize the disposal of various types of medical waste. Great efforts should be made to explore the establishment of a collaborative mechanism for the cross-regional centralized disposal of medical waste and improve the efficiency of cross-regional disposal in emergency situations.

3.3 Improve an emergency management system and establish a cross-regional joint response mechanism for emergencies

The reserves of emergency disposal facilities system, emergency operation disposal team and expert guidance team should be incorporated into the national ecological environment risk prevention and control system. A good job should be done on a daily basis in reserves at the regional level of emergency disposal facilities and equipment (including suppliers) and the suppliers of on-site emergency operation companies, to ensure that the emergency equipment may be directly put into use once an emergency occurs. Great efforts should be made to establish a coordination mechanism of expert teams and emergency drill systems at the national and regional levels, and regularly carry out relevant emergency drills, including unified decision-making and command, information exchange and mutual reporting, joint monitoring and disposal, and unified deployment of personnel and resources.

3.4 Break administrative restrictions and establish a cross-regional collaborative management mechanism

A regional supervision big data platform for production, storage, collection, transshipment and disposal of regional medical waste with comprehensive information, complete elements, efficient disposal and scientific decision-making should be established by virtue of the big data technology. A coordinated and normalized, high-quality regional information disclosure system should be established to improve the regional medical waste management-related information sharing mechanism. A cross-regional law enforcement linkage working mechanism should be established to carry out cross-regional medical waste disposal special supervision and law enforcement inspection. A compensation mechanism for cross-regional centralized disposal of benefits should be established. According to the principle of "whoever benefits is responsible for the compensation", the ecological compensation should be made for areas receiving the medical waste in the forms of investment in infrastructure construction, direct financial subsidies and disposal surcharges.

3.5 Implement examination and evaluation, and establish an effectiveness evaluation mechanism for cross-regional joint prevention, control and disposal of medical waste

Great efforts should be made to develop standards and methods for evaluating the effectiveness of cross-regional medical waste supervision measures, and establish a mechanism for evaluating the effectiveness of cross-region medical waste supervision measures. The disposal and management capacities of enterprises that centrally dispose of medical waste should be evaluated, if they fail to meet the requirements of the corresponding standards and the proper rectification results are not achieved, the entrusted disposal contract should be terminated and a new disposal company should be introduced. The cost assessment of the medical waste disposal industry should be carried out, and the current disposal cost levels under different disposal technology routes should be fully considered to speed up the rationalization of medical waste disposal charges across the country. The management authority and responsibilities of the relevant regions and departments, the examination and evaluation criteria for joint prevention, control and disposal responsibilities, as well as the relevant system regulations for accountability, rewards, and punishment should be clearly defined. It is necessary to strengthen the effectiveness examination and evaluation, strictly claim responsibility and accountability, and take forced actions on joint prevention, control and disposal.

4. Conclusion

The Central Committee of the CPC and the State Council have attached great importance to the disposal of medical waste and quickly issued a range of important policies since the outbreak of COVID-19. In particular, General Secretary Xi Jinping put forward in *Comprehensively Improving the Ability To Prevent and Control According to Law, and Improving the National Public Health Emergency Management System* released in *Qiushi* Journal on February 29, 2020 that "completing the working mechanism of integrated prevention and treatment, joint prevention and control, and mass prevention and control" should act as specific measures to improve the national public health emergency management system, which further clarified the status of the joint prevention, control and disposal mechanism of medical waste in the national governance capacity construction work, and provided a new starting point and opportunity for China to accelerate the establishment and implementation of the regional joint prevention, control and disposal mechanism of medical waste at this stage. In this paper, the suggestions on establishing the regional joint prevention, control and disposal mechanism of medical waste were put forward from perspectives of establishment of coordinating agencies, cross-regional collaborative disposal, cross-regional joint response to emergencies, cross-regional collaborative management and effectiveness evaluation based on the ideas of China's existing regional joint prevention and control mechanism for air and water pollution, providing a reference for improving the prevention and control capacity against medical waste disposal risks and improving China's medical waste emergency management system.

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Optimum process of walnut peel-activated carbon preparing by phosphoric acid activation and its adsorption of hexavalent chromium

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Abstract

Walnut peel as precursors, phosphoric acid was used as activator for preparing activated carbon (CAPA) in a muffle furnace by orthogonal design. Yield, the specific surface area and iodine number of CAPA samples were measured in all designed experimental groups and the optimum experimental parameters of preparation were obtained after analysis of variance. The sample of WPAC prepared at the optimal condition was systematically characterized by scanning electron microscope (SEM), Brunauer-Emmett-Teller (BET) porosity analyzer, FT-IR spectroscopy (FT-IR). The obtained results of the optimum conditions included the activation temperature of 400℃, activation time of 2h, the concentration of phosphoric acid of 40%, and particle size of 20-mesh. The specific surface area of CAPA which was obtained at optimum conditions was found to be 1359.54 $m^2 \cdot g^{-1}$. CAZC (walnut peel-activated carbon, zinc chloride as activator, proposed in the former relevant report by the same research group), together with the sample CAPA were selected as target adsorbent to measure the adsorption performance of hexavalent chromium. For two samples, the optimum adsorption appears at 2.5 h. The acidic condition is favorable for adsorption of Cr (VI). The adsorption capacity also increases with the increase of temperature, indicating that the adsorption is endothermic process. Adsorption dynamics of the two kinds of activated carbon are more likely to be adjusted to the pseudo-second-order-kinetics equation. Therefore, walnut peel has a promising prospect in production of high-quality activated carbon with large specific surface area, and it is expected to a new resource for activated carbon to achieving recycling and reuse.

Keywords: Walnut peel; activated carbon; recycling; absorption; hexavalent chromium

1. Introduction

Adsorption has become highly effective and economical method to remove heavy metal ions in recent years[1,2]. And as an adsorbent, activated carbon has been widely used for the treatment of hazardous substances or waste water[3,4]. But in most cases, the applications of activated carbon are limited by its high cost in China. Then there is a requirement to select a cheaper and easily available precursor for preparing activated carbon.

Shaanxi currently ranks second in the production of walnut in China, producing 183.2 thousand metric tons walnut by the end of 2015[5]. It is evident that there is a great potential of walnut peels to be disposed each year.

Walnut peel has been considered to be an agriculture wastes that has little value. At the season when walnuts mature, these peeled biomass are always piled up so arbitrarily that has been an annoying environment concern due to the erosion from its strong alkaline. So there is an urgent need to convert these walnut peels, an agricultural residue to an useful, added value products, such as activated carbons.

Studies were carried out in the preparation of activated carbon with walnut peel by phosphoric acid activation. As a new precursor, walnut peel has the advantage of low-cost, renewability and abundance. It has been reported that heavy metal Cr (VI) can be adsorbed by activated carbon derived from biomass materials, such as straw, rice husk, etc[6,7,8,9]. However, there is no literature on the treatment of Cr (VI) by activated carbon prepared from walnut peel.

The present paper is concerned with the synthesis of activated carbons with phosphoric acid derived from walnut peel and the product was used in the adsorption of hexavalent chromium from aqueous solution. Four factors, such as agitation time, pH, adsorption dose, and temperature on the adsorption capacity, were investigated, as well as the kinetics model about the sorption of Cr(VI).

1.1 Materials

Walnut peel

1.2 Methods

CAPA was synthetized as the following procedures. The raw materials (walnut peel) were washed with distilled water several times and dried at 105℃. The obtained materials were milled and sieved at a particle size of 20~60 meshes, then soaked in H_3PO_4 solution of 40%-60%. Thereafter, the materials were activated at a temperature of 350-450℃in a furnace during 1-2 hours. Finally, the samples were rinsed with deionized water to neutral, dried and weighed to obtain activated carbon.

1.3 Characterization of walnut peel-activated carbon

(1) Calculation of yield: Yield (%) = (Mass of product/Mass of raw material) ×100%.

(2) Determination of iodine adsorption performance: Iodine number was tested according to National Standard of “GB/T12496.8-1999” on the determination of iodine adsorption properties[14].

(3) Determination of infrared absorption spectrum: The superficial chemical groups of the activated carbon samples were analyzed with BRUKER TENSOR 27 Fourier transform infrared spectrometer. Test conditions included scanning cumulative number of 20 times and the scanning range of 400-4000cm.

(4) Determination of the specific surface area (BET): The specific surface area (S_{BET}) was evaluated using the Brunauer-Emmett-Teller (BET) method.

1.4 Orthogonal design

Due to the factors such as concentration of activator, activation temperature, activation time and particle size, play important roles in the course of the preparation of activated carbon[10,11,12,13]. Those were selected each at three levels in $L_9(3^4)$ orthogonal design and 9 activated carbon samples were made. Afterwards, the yield, iodine number, as well as specific surface area of these samples were measured, which was referred to relevant methods. The optimal process of preparation was ranked through the analysis on ranges of the four factors. The best activated carbon sample (that was prepared through the optimal process) was selected and characterized by infrared spectroscopy and measurement of the aperture.

1.5 Hexavalent chromium adsorption performance

1.5.1 The preparation of Cr(VI) solution at desired concentration

A stock solution of Cr(VI) was prepared (50 $mg \cdot L^{-1}$) by dissolving required amount of K_2CrO_4(0.1878 g) in lL distilled water. The stock solution was diluted with distilled water to obtain desired concentration ranging from 10 to 50 $mg \cdot L^{-1}$. All the chemicals used to prepare reagent solutions were analytic reagent grade.

1.5.2 Batch equilibrium studies

Batch adsorption experiments were carried out in a series of stoppered reagent bottles. A weighed amount of adsorbent(CAPA and CAZC, the latter also is a walnut peel-activated carbon with zinc chloride as activating agent, proposed in the former relevant report[15] by the same research group) was introduced into reagent bottles (250 ml) containing 100 ml aqueous solutions of Cr(VI). The solution pH was adjusted to the desired value by adding HCl or NaOH. Then, the bottles were shaken at room temperature (30±2℃) using a mechanical shaker for a prescribed time. The solutions were filtered and the concentration of Cr(VI) was analyzed spectrophotometrically at a wavelength of 540 nm, with the method of diphenylcarbazide colorimetry. Adsorption experiments as a function of agitation time, pH, adsorption dose, and temperature were conducted. The effects of agitation time (0.5–3 h), adsorption dose (0.05–0.30 g), solution pH (0.90–6.87) and different temperatures (20–70℃) were studied.

2 Results and discussion

2.1 SEM image

Fig1 SEM of optimal walnut peel-activated carbon sample (200μm)

A porous structure was formed at the surface or in the interior of raw material, which was attributed to the phosphoric acid etching raw material continuously. By dehydration and washing away the phosphate in the pores of the materials, the SEM image of CAPA clearly exhibited that it was mainly composed of irregular and porous particles (Fig.1).

2.2 FTIR measurements

It can be seen from Fig.2 that there is carboxyl group in the stretching vibration at 1380-1400cm^{-1}, lactone group in the stretching vibration at 1558-1629 cm^{-1} and phenol hydroxyl stretching was found at 3000-3650 cm^{-1}[16].

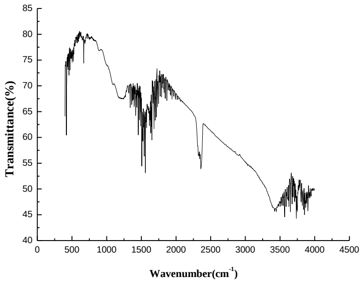

Fig2 Infrared spectrum of optimal walnut peel-activated carbon sample

2.3 pore size measurements

The adsorption-desorption isotherms of the best activated carbon by phosphoric acid activation with pore diameter analyzer were shown in Fig.3, which have been adjusted to the BET model. Determination of pore size distribution was presented in Table 1.

Table 1. The specific surface area, pore volume and average aperture distributions of the optimal charcoal sample.

BET surface area ($m^2\cdot g^{-1}$)	T-Plot micropore area($m^2\cdot g^{-1}$)	T-plot external surface area($m^2\cdot g^{-1}$)	Single point adsorption total pore volume ($cm^3\cdot g^{-1}$)	T-plot micropore volume($cm^3\cdot g^{-1}$)	Total adsorption average pore width (nm)
1359.54	622.94	736.60	1.1117	0.2722	3.27

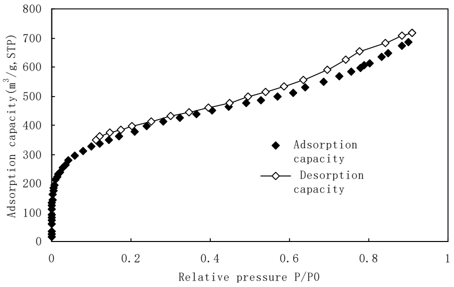

Fig3 Desorption-adsorption isotherms of optimal walnut peel-activated carbon sample

2.4 Analysis of orthogonal design

The range value was important for validation of the optimum process variables developed, which were listed in Table 2-3. For the range of yield, activation time (t)>activator concentration(c)>particle size (d)> activation temperature (T), it indicated that activation time seemed to has the most effect among the four factors on the yield of activated carbon, followed respectively by the activator concentration, particle size and the activation temperature.

A comparison of each factor on average indicated that the reasonable process conditions for the yield of activated carbon included activation temperature (450℃), activation time(2 h), phosphoric acid concentration(40%) and particle size (20 meshes).

Table 2. Analysis of orthogonal design.

Group		Activation temperature T(℃)	Activation time t(h)	Activator concentration c($\%$)	Particle size d($mesh$)	Yield ($\%$)	Iodine number($mg\cdot g^{-1}$)	Specific surface area($m^2\cdot g^{-1}$)
1		350	1	40	60	41.91	693.62	1064.38
2		350	1.5	50	40	40.46	450.44	833.68
3		350	2	60	20	47.97	693.67	1230.08
4		400	1	50	20	38.06	710.41	1325.17
5		400	1.5	60	60	38.78	492.32	813.70
6		400	2	40	40	49.38	671.40	1027.86
7		450	1	60	40	35.81	626.81	972.46
8		450	1.5	40	20	50.90	555.05	913.58
9		450	2	50	60	45.01	430.54	631.03
yield	K1	43.447	38.593	47.397	41.900			
	K2	42.073	43.380	41.177	41.883			
	K3	43.907	47.453	40.853	45.643			
	Range	1.834	8.860	6.544	3.760			
iodine number	K1	612.577	676.947	640.023	538.827			
	K2	624.710	499.270	530.463	582.883			
	K3	537.467	598.537	604.267	653.043			
	Range	87.243	177.677	109.560	114.216			
specific surface	K1	1042.713	1120.670	1001.940	836.370			
	K2	1055.577	853.653	929.960	944.667			

	K3	839.023	962.990	1005.413	1156.277
	Range	216.554	267.017	75.453	319.907

Table 3. Analysis of variance for yield, iodine number and specific surface area.

	Factor	The sum of squared deviations	Freedom	F ratio	Significance
Yield	T	5.459	2	1.000	
	t	118.004	2	21.616	*
	c	81.608	2	14.949	
	d	28.150	2	5.157	
	Error	5.460	2		
Iodine number	T	13400.129	2	1.000	
	t	47570.997	2	3.550	
	c	18728.865	2	1.398	
	d	19908.862	2	1.486	
	Error	13400.130	2		
Specific surface area	T	88550.428	2	8.134	
	t	108115.389	2	9.931	
	c	10886.390	2	1.000	
	d	158847.235	2	14.591	
	Error	10886.390	2		

Note：F0.01（2,2）=99.00; F0.05（2,2）=19.00; F0.10（2,2）=9.00

As listed in table 2 and table 3, the order of ranges for yield were activation time(t)>activator concentration(c)>particle size(d)>activation temperature(T). Owing to the factor of activation temperature with the least range for yield, it was designated as the error in analysis of variance. Thus the results indicated that activation time (t) was the most significant factor for yield at 95% confidence level. Activator concentration had such an impact on the yield as its levels might cause the alteration of yield. Whereas the effect of the particle size on the yield was not principal and its level could be chosen within the experimental scope. Therefore, it was concluded that the reasonable process for yield consisted of activation temperature(450℃), activation time(2h), phosphoric acid concentration(40%)and the particle size (20 meshes).

Table 2-3 also illustrated the relationship for the range of iodine number, activation time (t)>particle size(d)>activator concentration(c)>activation temperature (T). It was indicated that the greatest impact among four factors for iodine number was activation time, followed by particle size, activator concentration and activation temperature, respectively.

Through examining the mean value of each factor, a conclusion was arrived at that the reasonable combination for iodine number of activated carbon included activation temperature(400℃), activation time (1 h), phosphoric acid concentration (40%) and the particle size(20 meshes).

On account of activation temperature had the least range and was taken as the error for analysis of variance. Thus the results yielded that activation time, activator concentration and particle size had not significant impacts on the iodine number.

Table 2-3 exhibited the quantitative relationship of ranges for the specific surface area, which was: particle size(d)>activation time(t)>activation temperature(T)>activator concentration(c). It was proved that the particle size had the greatest effect on the specific surface area of activated carbon, followed by activation time, activation temperature and activator concentration, respectively. Then the mean values of all factors were evaluated, which was ascertained that the reasonable process conditions for the specific surface area of activated carbon consisted of activation temperature(400℃), activation time (1 h), phosphoric acid concentration(60%) and particle size (20 meshes).

The variance of four factors illustrated that activation time (t) and particle size (d) were the most significant factors for the specific surface area at 90% confidence level. Therefore, these two factors were considered to affect the specific surface area.

Based on above cases, the optimal process variables in preparation of activated carbon derived from walnut peel by phosphoric acid activation included activation temperature at 400℃, activation time of 2 h, phosphoric acid concentration of 40% and particle size of 20 meshes. The characterizations of the activated carbon sample prepared under these conditions were shown in Figs.1 to 3 and Table 1.

2.5 The effect of agitation time on the adsorption of Cr(VI)

The amount of Cr(VI) adsorbed on carbons actived by phosphoric acid(CAPA) and by zinc chloride(CAZC) was studied as a function of agitation time(0.5–3 h) at initial concentrations (50 mg·L^{-1}) of Cr(VI) at 30℃, 0.05 g of adsorbent and desired pH(2.0). The results are shown in Fig.4. It is evident from Fig.4 that the adsorption of Cr(VI) increased sharply with increase in agitation time within 0.5-1.5 h onto CAPA or CAZC, and the saturation is almost reached in 2.5 h in case of both samples. The increase of the amount of Cr(VI) adsorbed on CAPA and CAZC becames slow up from 1.5 to 2.5 h. So 2.5 h is the equilibrium point for two adsorbents and the adsorption became almost constant after the equilibrium point. That is probably due to the larger adsorption sites of two carbons at the beginning for the adsorption of Cr(VI). The uptake rate is controlled by the rate at which the adsorbate is transported from the exterior to the interior sites of the adsorbent particles as these surface adsorption sites almost become occupied[17]. Equilibrium time of 2.5 h was selected for all further studies.

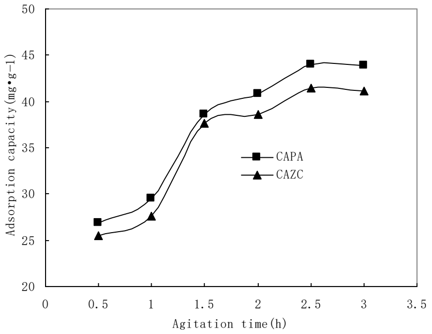

Fig.4 The effect of agitation time on the adsorption capacity of two activated carbons

2.6 The effect of pH on the adsorption of Cr(VI)

The solution pH may alter the solubility of adsorbates, concentration of the counter ions on the functional groups of the adsorbent and the degree of ionization of the adsorbate during reaction[18].So it is important to study the effect of solution pH on Cr(VI) adsorption on two carbons. The effect of pH on Cr(VI) removal was explored by using 100 mL solutions of Cr(VI), adjusted to initial pH 0.90 to 6.87 and agitated with 0.05 g of adsorbent for 2.5 h. From figure 5, it is clear that little adsorption takes place at all from pH 0.9 to 2.0 and the values of qe decreases greatly with increase in pH within the pH range 2.0-6.87 for two carbons. It is supposed that the increased H^+ ions neutralized the negative charge on adsorbent surface and thereby increased the diffusion of chromate ions into the bulk of the adsorbent[18].

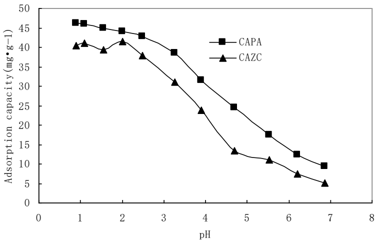

Fig.5 The effect of pH on the adsorption capacity of two activated carbons

2.7 The effect of temperature on the adsorption of Cr(VI)

The relationship between the amounts of Cr(VI) adsorbed(q_e) and different temperature (T) in solution was showed in Fig.6.The degree of adsorption of Cr(VI)increases with increased temperature, indicating that the adsorption is endothermic process. It may be due to the chemical interaction between adsorbate and adsorbent, which increased some new adsorption sites and rate of intra particle diffusion of Cr(VI) ions at higher temperature[19].

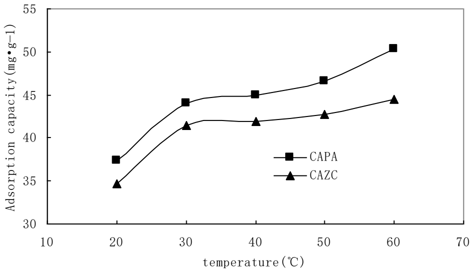

Fig.6 The effect of temperature on the adsorption capacity of two activated carbons

2.8 The adsorption kinetics of two carbons

pseudo-first-order and pseudo-second-order kinetics models proposed by Lagergren were checked in order to determine the adsorption kinetics of two samples, two kinetics models are generally expressed as follows[19].

$$\lg(q_e - q_t) = \lg q_e - \frac{k_1 t}{2.303} \qquad (1)$$

where q_t and q_e are the amounts of Cr(VI) adsorbed ($mg \cdot g^{-1}$) at time t (h) and at equilibrium, respectively, and k_1 is the rate constant of pseudo-first-order kinetics model (h^{-1}).

$$\frac{t}{q_t} = \frac{t}{q_e} + \frac{1}{k_2 q_e^2} \qquad (2)$$

where k_2 is the pseudo-second-order rate constant of adsorption ($g \cdot mg^{-1} \cdot h^{-1}$). By each linear plot of $\log(q_e - q_t)$ versus t, and (t/q_t) versus t, respectively, the values of the rate constant k_1, k_2 and q_e were obtained from the slopes and intercepts of the plots, respectively (Table 4). The linearity of these plots indicates the applicability of the two models.

The adsorption kinetics may also be described by an intraparticle diffusion model. The form of the model is as follows[18].

$$q_t = k_{id} t^{1/2} + C \qquad (3)$$

where q_t is the amount adsorbed at time t. The values of k_{id} were calculated from the slopes of respective plot (q versus $t^{1/2}$ of Fig.9).For the correlation coefficients, R^2 of pseudo-second-order model (R^2 =0.986, 0.9821) is higher than the pseudo-first-order model (R^2=0.9301, 0.9585) and intraparticle diffusion model(R^2=0.9336, 0.8976). It is evident from the Table 4 that among these three models, pseudo-second order kinetic equation was taken as the best fit model and the sorption of Cr(VI) ions from aqueous solution onto two carbons might be controlled by chemisorption. The value of q_e showed that the pseudo-second-order model fits better the experimental data. It was also indicated that the rate-limiting step may be a chemical sorption involving valance forces through sharing or exchange of electrons between adsorbent and adsorbate[17].

Table 4. Comparison of dynamic model parameters

	pseudo-first-order-kinetics			pseudo-second-order-kinetics			Intraparticle diffusion model		
	R^2	$k_1(h^{-1})$	$q_e(mg\cdot g^{-1})$	R^2	$k_2(g\cdot mg^{-1}\cdot h^{-1})$	$q_e(mg\cdot g^{-1})$	R^2	$k_{id}\ (mg\cdot g^{-1}\cdot h^{-1})$	$C(mg\cdot g^{-1})$
CAPA	0.9301	1.8947	76.23	0.986	0.0304	53.48	0.9336	18.742	13.356
CAZC	0.9585	1.6084	49.28	0.9821	0.0345	49.75	0.8976	17.401	13.09

Note: q_t is the adsorbed amount of p-nitrophenol at time t ($mg\cdot g^{-1}$); q_e is the amount adsorbed at equilibrium ($mg\cdot g^{-1}$); k_1 is the first-order rate constant (h^{-1}) of adsorption; k_2 is the equilibrium rate constant of pseudo-second-order adsorption ($g\cdot mg^{-1}\cdot h^{-1}$)

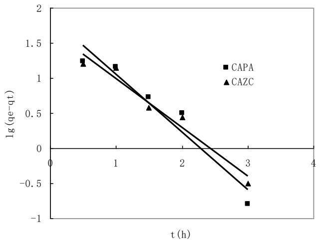

Fig.7 The fitting plot for pseudo-first-order kinetics.

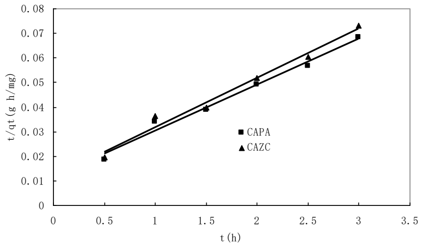

Fig.8 The fitting plot for pseudo-second-order kinetics.

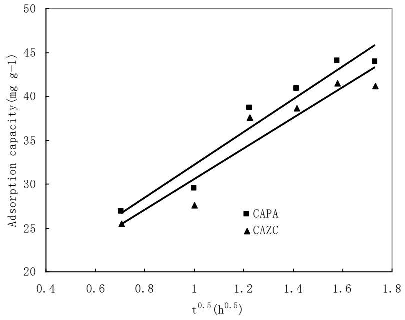

Fig.9 The fitting plot for intraparticle diffusion model.

3 Conclusions

These experimental studies have indicated that the optimal process conditions in preparation of activated carbon with walnut peel by phosphoric acid activation included activation temperature (400℃), activation time (2 h), phosphoric acid concentration(40%) and particle size(20 meshes).

The specific surface area of the optimal activated carbon sample(CAPA) reached 1359.54 $m^2 \cdot g^{-1}$, exhibiting that walnut peel could be used to process good quality activated carbon with high specific surface area for the purpose of re-use of this peculiar agricultural waste.

The adsorption capacity of Cr (VI) increase with the increase of agitation time, and the optimum adsorption appears at 2.5 h. The acidic condition is favorable for adsorption of Cr (VI). The adsorption capacity also increases with the increase of temperature, indicating that the adsorption is endothermic process.

The experimental values about adsorption dynamics of the two kinds of activated carbon(CAPA and CAZC) are more likely to be adjusted to the pseudo-second-order-kinetics equation. The sorption of Cr(VI) ions from aqueous solution onto two carbons might be controlled by chemisorption. There is a good prospect for walnut peel-activated carbon in the treatment of wastewater polluted by heavy metal Cr (VI).

Acknowledgements

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Biological exposure to PBDEs in e-waste areas: A review

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Abstract

This study conducts a systematic review to understand the plant, animal and egg exposure to PBDEs, from e-waste recycling, discovering PBDE levels and bioaccumulation potential in plant and animal samples. The results showed that the plant tissues in the e-waste recycling areas had higher PBDEs levels than control areas, while the PBDEs levels in terrestrial animals is often higher than that in aquatic animals. In addition, bioaccumulation potential of PBDEs can be found in animals in e-waste areas, and that the food chain accumulation effects of aquatic organisms and land animals differ, and are related to some specific congeners. Existing data indicate that PBDE exposure levels do not present any apparent downward trend, and will possibly cause serious environmental problems.

Keywords: Polybrominated diphenyl ethers (PBDEs); E-waste; Plant and animals; Exposure pathway

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1. Introduction

Polybrominated biphenyl ethers (PBDEs), one of the widely used brominated flame retardants (BFRS), are a family of 209 homologues, depending on the number of bromine atoms. There are three commercial mixtures of PBDEs: Penta-BDEs, Octa-BDEs, and Deca-BDE. Commercial PBDEs are widely used as flame retardants for electronic products, furniture, building materials, foam, textiles or automobile parts [1].

The lipid solubility, bioaccumulation and long distance migration of PBDEs lead to their persistence in the environment[2]. Worryingly, because PBDEs have biological enrichment and biological amplification, they may be transferred through the food web and eventually enter the organism[3]. In addition to the enrichment of food web, PBDEs may also exist in air, dust, soil and other environmental media and be exposed to plant and animal through different ways [4, 5]. Worryingly, PBDE has potential toxicity. However, a large number of studies have shown that PBDEs have accumulated in the liver, brain and muscles of animals[6,7], and may cause diseases such as hepatotoxicity, neurotoxicity, and reproductive problems in animals [8]. Therefore, since 2017, PBDEs have been listed as a controlled substance under the Stockholm Convention and are prohibited from being added to electronic products [9]. It is believed that with the control of PBDEs, the release of PBDEs from e-waste will be greatly reduced. However, the half-life of PBDEs in organisms is several weeks or even several months [10]. Therefore, it is still necessary to further explore the change trend of PBDEs in organisms.

The main objective of this study was to provide comprehensive information on the status of PBDE levels from e-waste, in plants, animals and eggs ; to determine the bioaccumulation and bioaugmentation potential of e-waste PBDEs at various nutrient levels of the food web, and finally determine the trend of PBDEs in plants, animals and eggs.

2. Review method

We conducted a systematic search of published literature focusing on the exposure pathways and human burden effects of e-waste PBDEs. Up to September 2019, we conducted the extensive literature review through the primary research databases such as Web of Science, Elsevier, ACS Publications, Springer, Google Scholar, and CNKI (database of Chinese journal). By looking for (electronic waste or

WEEE), (PBDEs or Polybrominated diphenyl ethers or Flame retardant), (plants, animals and eggs) and (bioaccumulation, biomagnification potential, BMF and BAF), the research areas refers to all the countries in the world, such as China, Vietnam and Nigeria. In addition, we have evaluated all the reference lists, and after the initial screening, excluded duplicate articles in the same region or in different languages. Finally, 30 articles were determined as the research content.

3. PBDE concentrations in plants, animals and eggs

3.1 Edible plants

As the beginning of the food web, edible plants are an important link to human exposure, especially through dietary intake. As shown in Fig. 1, high-bromine PBDEs may accumulate in plants through direct deposition, and low-bromine PBDEs may enter plant leaves through atmospheric transport [11]. Jin et al., (2008)[12] points out that PBDE concentration in leaves can be caused by atmospheric or dust deposition, and is related to plant species, structure and PBDE congeners. When PBDEs enter plants, they accumulate in plant organs such as roots, leaves and stems. Yang et al., (2008)[13] reports that PBDEs in plant leaves have a good linear relationship with PBDEs in the surrounding soil. Low-bromine PBDEs in soil can be more easily absorbed by plant roots than can high-bromine PBDEs [14]. It can be determined that PBDEs in the various organs (roots and leaves) in plants have good linear relationships [15], and PBDEs can be transferred into other organs within the plants [16].

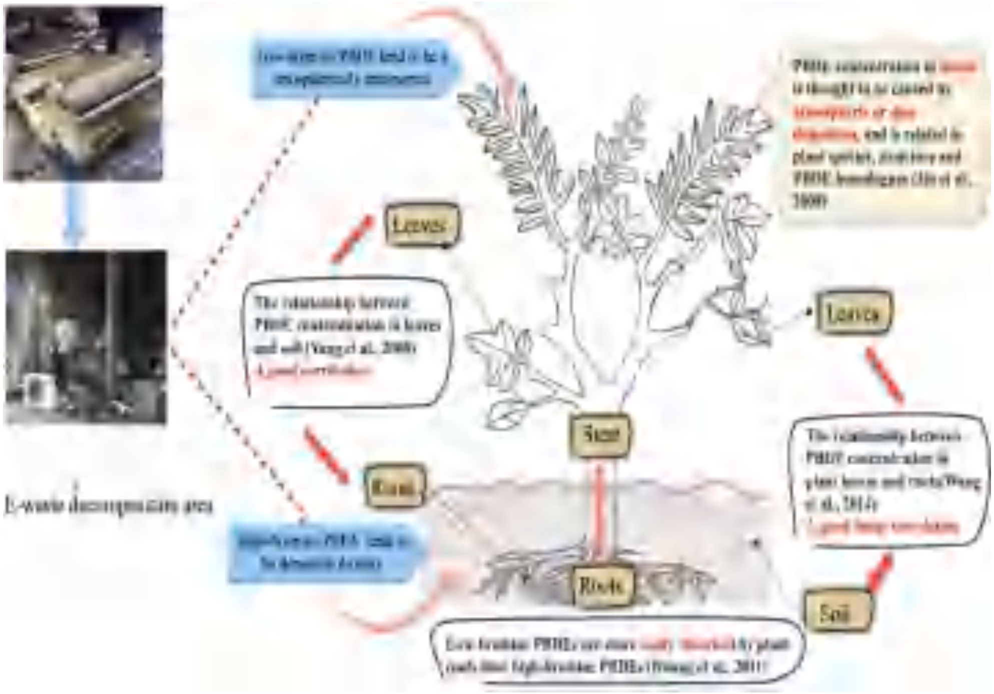

Fig.1 PBDE distribution in plants

For edible plants, the research areas mainly included Taizhou city, Qingyuan city, and Changzhou city in China during 2005-2014; only one study was conducted in Nigeria (see Table 1) [17, 18, 3, 19, 20, 21, 22]. According to Table 1, the average PBDE concentration in vegetables varies greatly, from only 0.8 ng/g [23] to 2239 ng/g ww [20]. Nie et al. (2015)[3] reports that PBDE content (119-291 ng/g dw) in vegetables in Qingyuan is an order of magnitude higher than that in Taizhou (0.8-15 ng/g dw) [23, 18]. Zhao et al. (2009) [23] points out that PBDE concentration (90.9 ng/g dw) in rice is much higher than that in vegetables (0.8-15 ng/g dw). The concentration of POPs in plants is related to the sampling location and plant species. Alabi et al., (2012)[22] reports that the concentration of PBDEs (Amaranthus spp:31.07 ng/g dw) in vegetables from Nigeria (Alaba plant) is 30 times higher than that of vegetables from Guiyu (Sorghum bicolor (L.) Moench and Rice stalk: 1.39 ng/g dw). These comparisons show that the PBDE pollution level in Guiyu soil is more serious than that in Nigeria, probably because of the different accumulation potentials of different plants. In addition to several typical e-waste recycling sites, PBDEs have also been detected in rice plant roots (65.3 ng/g dw) and leaves (30.9 ng/g dw) near the town of Niutang (Changzhou, Jiangsu, China). It has been shown that PBDEs from e-waste can enter the food web through vegetables or rice; this may explain the higher PBDE levels in vegetables in e-waste recycling areas, compared to those in other areas [3, 19]. However, Wu et al., (2019)[24] shows that rice plants have limited ability to pick up PBDEs from soil, and it is difficult to transfer PBDEs to leaves; furthermore, PBDEs in rice have a low impact on human health risks.

Table 1 PBDE concentrations in plant samples from the e-waste area

Sample type (N)	**Location (Sampling sites)**	**Sampling time**	**Concentrations (ng/g dw)**	**Congener**	**References**
Edible plants					
Vegetables (5) and Cereals (1)	Guiyu, Shantou, China	2005	1.1 and 2.8 ng/g ww	22	17
Vegetables (14) and Cereals (1)	Taizhou, China	2005–2007	0.2 and N.D. ng/g lw		
Vegetables, Pulses and Rice	Taizhou, China	2007.4	15, 0.8 and 90.9	12	23
Paddy (3)	Taizhou, China	2008.6-2009.6	4.1	8	18
Amaranthus spp	Nigeria (Alaba International market dumpsite soil)	2009.8-2010.10	31.07	8	22
Sorghum bicolor (L.) Moench and rice stalks	Guiyu, Shantou, China		1.39		
Sweet potato, Kudzu, Banana, Radish and Cabbage	Longtang, Qingyuan, China	2011.6-7	119, 189, 286, 291 and 288	21	3
Aquatic weed	Longtang, Qingyuan, China (Pond near incineration area)	2011.11	17.9	21	19
Cereals, Beans and Vegetables	China, southeast	2011.11	2239, 1216 and 1012 ng/g ww	11	20
10 Edible plant	Longtang, Qingyuan, China	2012.6-7	Shoot: 0.88-5.69; Roots: 0.97-13.0	7	15
Rice plants (5)	Guiyu, Shantou, China	2014.4	Root: 105; Stem: 15.1; Leaf: 51.4 and Grain: 8.31	15	24
Rice plants	Niutang, Changzhou, China	2014.8	roots :65.3; leaves: 30.9	9	21
Pumpkin roots (4)	Guiyu, Shantou, China (site1-3)	_	132.2, 245.7 and 347.7	21	14
Maize roots (4)			110.2, 194.5 and 305.4		
Ryegrass roots (4)			104, 200.6 and 316.2		

"N" is the sample size; "N.D." means data below the limit of detection;

3.2 Animals

The PBDE accumulation in aquatic animals (fish, molluscs and shrimp) comes from absorption and accumulation through the food web (water and sediment), while in land animals (birds, mice, frogs, insects and poultry) it is primarily from food uptake (plants or other animals) [8]. As shown in Fig. 2, PBDEs will accumulate in animal organs (or tissues), such as the brain, liver and muscles.

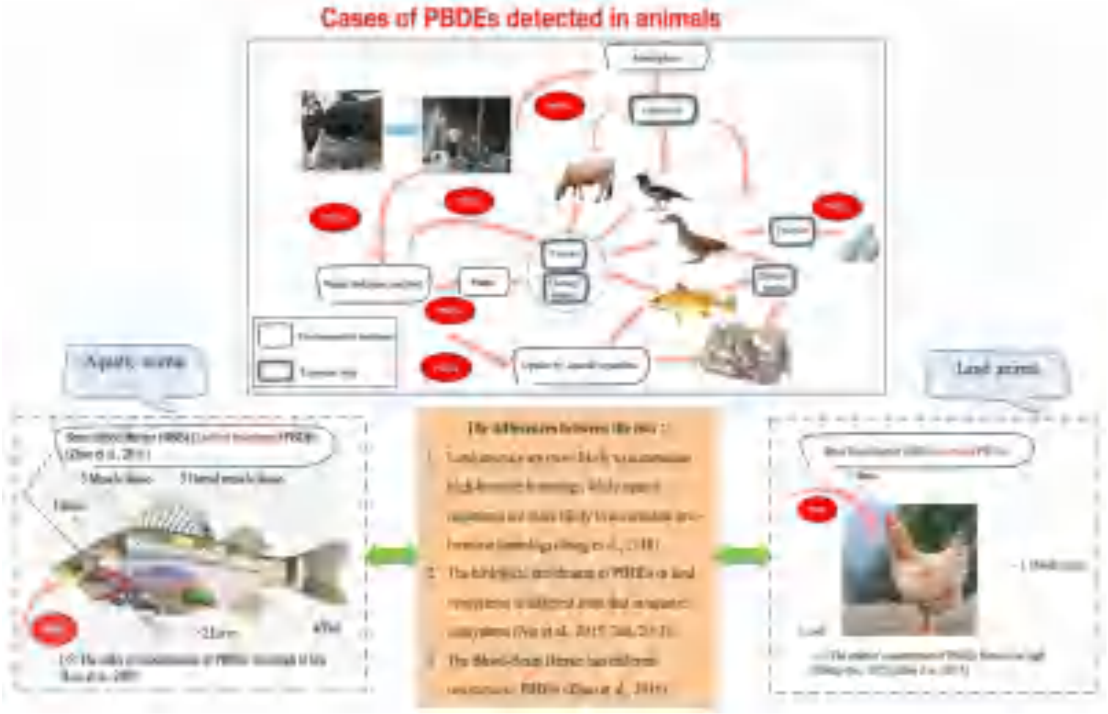

Fig. 2 PBDEs exposure pathway and burden in animals

3.2.1 Aquatic animals

Table 2 lists PBDE levels of aquatic animals from several e-waste dismantling zones, mainly referring to China and Vietnam. It is clear that the concentrations of PBDEs in fish samples from Guiyu and Qingyuan Longtang are high. Luo et al., (2007)[6] also indicated that PBDEs in fish samples in the Guiyu area are higher (by 2-4 orders of magnitude) than those in other areas (non-electronic dismantling areas). The highest concentration of PBDEs (2687 ng/g ww) have been found in the livers of bighead carp in the Nanyang River, followed by muscle tissue (1088 ng/g ww), tail (41.8 ng/g ww) and dorsal muscle tissue (35.1 ng/g ww). It is reported that the PBDEs in aquatic animals near e-waste recycling plants are 1-3 orders of magnitude higher than those in aquatic animals in other parts of China [25, 17]. Moreover, PBDEs levels vary among different types of fish, due to specific biological habits and their position in the food web. In Qingyuan's e-waste area, tilapia have the highest PBDE concentrations (50300 ng / g lw), followed by crucian carp (20600 ng / g lw), mud carp (12000 ng / g lw), and northern snakehead (11600 ng / g lw). The lowest is Chinese bitterling (1120 ng / g lw)[26]. The PBDEs in mud carp have shown a significant downward trend, compared with the value reported by Sun et al., (2016)[27] (18000ng / g lw). Compared with other organs, the brains of fish may retain more PBDEs because the brain-blood barrier (BBB) of fish is not resistant to PBDEs [7.] The distribution of PBDEs in fish appears to be: "brain > liver > muscle" [6, 7]. One study from Vietnam [28] showed that PBDE concentration in fish near an informal e-waste recycling station was significantly lower than that in Guiyu, but similar to that in Taizhou [6,18].

In addition to fish, amphibians and other reptiles are also important biological indicators for PBDE exposure in animals [29]. High PBDE concentrations in prawn (253 ng/g ww) and Chinese mystery snail (67.5 ng/g ww) were observed in a pond near the Qingyuan e-waste recycling plant [30]. It is noteworthy that the PBDE content in shrimp is on the rise (2011:843.2 ng/g lw; 2016:9200 ng/g lw [19, 26]. In addition, PBDE concentrations in field snails (4968.1ng / g lw), mussels (10298.7ng / g lw), dragonfly larvae (147000ng / g lw) and water beetles (1520ng / g lw) are still at very high levels [19, 26]. These studies imply that these mollusks easily adsorb PBDEs in sediments, leading to high PBDEs levels.

Table 2 PBDE concentrations in aquatic animal samples from the e-waste recycling area

Sample type (N)	Location (Sampling sites)	Sampling time	Concentrations (ng/g ww)	Congener	References
Fishes					

Bighead carps (6) (Abdomen muscle, Back muscles, Tail muscles and Liver)	Guiyu, Shantou, China	2004	1088, 35.1, 41.8, 2687	11	6
Freshwater fish (8) and Marine fish (1)	Guiyu, Shantou, China	2005	2180 and 2.2	22	17
Freshwater fish (7) and Marine fish (3)	Taizhou, China	2005-2007	60.4 and 2.8		
Mud carp (12), Crucian carp (17) and Northern snakehead (6) *	Longtang, Qingyuan, China	2006	830, 316 and 490	18	30
Fish	Taizhou, China	2007.4	43.3	12	7
Fish (10)	Taizhou, China	2008.6-2009.6	158.4	8	18
Sciaenops ocellatus, Sparus macrocephalus and Lateo- labrax japonicus	Jiang-xia, Taizhou, China (20-30 km downstream)	2008.8	1, 1.7 and 1.4	24	31
Fish (20) (Brain, Liver and Muscle)	Nanwan, Taizhou, China	2008 and 2014	9.8, 9 and 0.6	8	7
Fish and Shellfish	China, south-east	2011.11	2755	11	20
Crucian (6), Carp (6), Eel (3) and Snakehead (5)	Longtang, Qingyuan, China	2011	874.4, 1273.1, 1224.8 and 1774.2 ng/g lw	21	19
Fish (8)	Taizhou, China	2012.11-2013.2	44.2	14	4
Crucian carp (1), Climbing perch (3) and Mud carp (6)	Bui Dau, Vietnam	2014	1380, 160 and 520 ng/g lw	8	28
Mud carp	South China	2014.7-9	18000 lw	9	27
Northern snakehead (15), Mud carp (18), Chinese bitterling (6), Crucian carp (7), Tilapia (9)	Qingyuan, China	2016	11600, 12000, 1120, 20600 and 50300 ng/g lw	18	26
Molluscs and shrimps					
Shellfish (1)	Guiyu, Shantou, China	2005	0.2	22	17
Shellfish (9)	Taizhou, China	2005-2007	33.9		
Prawn and Chinese mysterysnail *	Longtang, Qingyuan, China	2006	253 and 67.5	18	30
Tegillarca granosa, Cyclina sinensis, Sinonovacula constricta and Ostrea cucullata	Jiang-xia, Taizhou, China (20-30 km downstream)	2008.8	0.7, 0.8, 1.4 and 0.6	24	31
Shrimp (5), Field snail (4) and Mussel (4)	Longtang, Qingyuan, China (Pond near incineration area)	2011	843.2, 4968.1 and 10298.7 ng/g lw	21	19
Shrimp (3)	Taizhou, China	2012.11-2013.2	0.3	14	4
Shrimp (7), Dragonfly larvae (3) and Water beetle (3)	Qingyuan, China	2016	9200, 147000 and 1520 ng/g lw	18	26

“N” is the sample size; “*” represents the median value;

3.2.2 Land animals

Birds are an important part of the ecosystem and have the ability to manifest the effects of environmental pollution. They are often used to monitor regional pollution and assess the indicators of adverse effects [32]. In Table 3 are shown several studies focusing on PBDE exposures of birds in Qingyuan and Taizhou, China. Under normal conditions, PBDE levels in birds near e-waste dismantling areas are 1-2 orders of magnitude higher than those in other background areas with no e-waste recycling [33, 34, 35]. In Qingyuan, the concentrations in the muscles of five waterfowl species reached 37-2200 ng/g lw [36]. Another study in Qingyuan city showed that the concentrations of serum PBDEs in eight species of birds were 0.6-580 ng/g lw [33]. By contrast, Tang. (2016)[37] indicates that the PBDE concentration in sparrows could be as high as 735.6 ng/g lw in Wenling, far higher than that in birds in Qingyuan. Meanwhile, the PBDE concentrations in sparrow tissues are ranked as follows: "feathers > intestines > muscles > lungs > heart > skin > stomach." For oriental magpie-robins, the distribution of PBDE concentration based on geographical location is in the following order: e-waste recycling sites> urban areas> rural areas (5740> 843> 244, ng / g, respectively). Furthermore, Wu et al., (2019)[38] indicated that the average PBDE levels in kingfishers located about 120km away Qingyuan e-waste recycling site (at the SNNR: Simentai

National Nature Reserve) was (84.8 ng/g lw), implying that illegal dismantling of e-waste has already had a serious impact on the surrounding area.

Currently, except for birds, studies have mainly focused on apple snails, mice, frogs, ants and snakes. A study by Fu et al., (2011)[39] shows that the PBDE levels in apple snails were negatively correlated with the distance from the e-waste dismantling zone (fengjiang), suggesting that this distance might be the most important influencing factor. In e-waste recycling areas, the average PBDE concentration in striped keelback snakes is 1410ng / g lw, and is higher in males than in females [40].

In addition to concentrations in individual species, biological accumulation and amplification provide important evidence for the accumulation of PBDEs in the food web, and more research is needed on this aspect.

3.2.3 Poultry

In recent years, a series of studies on poultry near e-waste recycling sites (Taizhou, Guiyu and Longtang) were conducted in China, and mainly focused on chickens, ducks and geese, whose PBDE levels ranged from 0.7 ng/g ww to 349 ng/g ww. As shown in Table 3, PBDE concentrations in poultry were still on the rise during 2005-2013. Zheng et al., (2015b)[41] reports that the PBDE levels (157-1660 ng/g lw) of chicken tissue from Southern China are equivalent to the average levels in Taizhou (5.3-2972 ng/g lw) [42]. It has been shown that PBDE levels (128 ng/g lw) in geese are significantly lower than those in chickens at the same site (4350 ng/g lw), due to their eating habits and living environment [3]. However, Zhao et al., (2016)[7]indicates that the PBDE concentrations in different types of chicken tissue (Brain: 1.5 ng/g ww, Liver: 14.9 ng/g ww, Muscle: 4.4 ng/g ww) are lower than those in ducks (Brain: 3 ng/g ww, Liver: 45.9 ng/g ww, Muscle: 25.1 ng/g ww), results contrary to those of Labunska et al., (2014)[4]. But it is certain (as shown in Fig. 3) that, unlike in fish, PBDEs are preferentially distributed in the liver and muscles of poultry rather than in the brain [41, 7, 4], since the blood-brain barrier in poultry is resistant to PBDEs [7]. It has also been shown that PBDE levels in ducks' livers, muscles and brains depend on exposure levels, while the levels in duck fat depend largely on exposure time [4].

Table 3 PBDE concentrations in land animal samples from the e-waste area

Sample type (N)	Location (Sampling sites)	Sampling time	Concentrations (ng/g lw)	Congener	References
Land animals -Birds					
5 Bird groups (29) *[a]	Qingyuan, China	2005-2007	600, 820, 37, 2200 and 340	13	36
8 Bird groups (29)[b]	Qingyuan, China	2008.3-7	0.6-54, 1.2-7.4, 6.2, 300- 580, 9.5, 1.3, 1.3-1.8 and 2.8	10	33
Turtledove (5）	Longtang, Qingyuan, China	2011.6-7	1704	21	3
Oriental magpie-robins (32)	Qingyuan, China (area of 330 km^2)	2011. 3 and 2011. 11	6221	17	35
Kingfisher (11)	SNNR, Qingyuan China	2013	84.9	14	38
Sparrow（90）	Wenling, Taizhou, China	2014.11-2015.12	735.6	16	37
Land animals -Mice, Frogs, Insects and Snakes					
Apple snail (40)	Taizhou, China (0-5, 5-10, 10-20, 20-30 and above 30 km)	2008.6	0.09 - 27.7 (excluding BDE 209)	13	39
Mice (Brain, Liver and Muscle) (13) and Frogs (Brain and Liver) (25)	Nanwan, Taizhou, China	2008 and 2014	Mice (9.3, 50.6 and 15.5 ng/g ww) and Frogs (11.1 and 22.8 ng/g ww)	8	7
Grasshopper (15), Dragonfly (9), Butterfly (9) and Ant (dozens)	Longtang, Qingyuan, China	2011.6-7	1024, 764, 1096 and 474	21	3

Striped keelback snake (14)	South China	2013.9	1410	18	40
Poultry					
Chickens (4)	Wenling, Taizhou, China	-	5.3-2972	7	42
Chickens	Guiyu, Shantou, China	2005	8.6 ng/g ww	22	17
	Taizhou, China	2005-2007	0.7 ng/g ww		
Chickens	Taizhou, China	2007.4	13	12	23
Chickens (9) and Ducks (6) (Brain, Liver and Muscle)	Nanwan, Taizhou, China	2008 and 2014	Chickens (1.5, 14.9 and 4.4 ng/g ww) and Ducks (3, 45.9 and 25.1 ng/g ww)	8	7
Chicken (2) and Goose (2)	Longtang, Qingyuan, China	2011.6-7	4350 and 128	21	3
Chicks* (Liver, Muscle, Heart, Lung, Fat, Brain, Stomach, Intestine, Ovary/Testis, Serum and Kidney)	Southern China	2011.10-2012.5	1660, 1450, 1240,796, 157, 242, 790, 1154, 1060, 579 and 536	12	41
Chicken (10), Chicken Liver (10) and Duck (7), Duck Liver (7)	Taizhou, China (1-300 m)	2012.11-2013.2	1160, 459, 150 and 256	14	4

“N” is the sample size; “-” means non-detectable or data not available;

3.3 Eggs

Many studies have reported on PBDE levels in eggs [43]. Eggs with high levels of fat may accumulate high levels of lipophilic contaminants such as PBDEs, a biological indicator for identifying levels of persistent organic pollutants [44]. As the chickens in the e-waste areas have close contact with the contaminated environment, local eggs often have higher PBDE levels than commercial eggs in other areas. The eggs from e-waste areas may be an important pathway for residents’ food PBDE intake. Meanwhile the consumers in other regions are also faced with PBDE exposure risks [45]. Currently, most studies have focused on chicken eggs, duck eggs and goose eggs, as shown in Table 4. Zheng et al., (2012)[46] reports that the PBDE concentration in eggs is 14100ng /g lw. Based on this study, Huang et al., (2018)[47] indicates that the PBDE concentrations in eggs were 4736 ng / g lw (2013) and 4741 ng / g lw (2016); their data show a significant decrease ($p<0.05$) from 2010 to 2013/2016, but indicate that the level remains high [47]. Moreover, regionally, the concentration of PBDEs in eggs around Qingyuan is much higher than that in the Taizhou region, by 1-2 orders of magnitude [46, 42]. The PBDE concentration (982 ng/g lw) of duck eggs in Taizhou is higher than that in other egg samples (656 ng/g lw), but still lower than that in Qingyuan eggs [48]. Zeng et al., (2016)[49] believes that PBDE levels in chicken eggs (3500-14000 ng/g lw) are higher than those in goose eggs (1200-2100 ng/g lw) in Guiyu.

Table 4 PBDE concentrations in egg samples from the e-waste area

Sample type (N)	**Location (Sampling sites)**	**Sampling time**	**Concentrations (ng/g lw)**	**Congener**	**References**
Special animals- Eggs					
Eggs (15)	Wenling, Taizhou, China	-	564	7	42
Egg (1)	Guiyu, Shantou, China	2005	8.2 ng/g ww	22	17
Egg (1)	Taizhou, China	2005-2007	2 ng/g ww		
Eggs	Taizhou, China	2007.4	4.8	12	23
Eggs (41)	Qingyuan, China	2010.7	14100	19	46
Duck Eggs (70)	PCB recycling sites vs Former PCB recycling sites vs Metal scrapping sites, Taizhou, China(10-500 m)	2011	982 vs 53 vs 939	14	48
Eggs	China, southeast	2011.11	2423 ng/g ww	11	20

Eggs (22)	Taizhou, China (1-300 m)	2012.11-2013.2	656	14	4
Chicken eggs (17) and Goose eggs (23)	Guiyu, Shantou, China	2013.12	3500-14000 and 1200-2100	17	49
Eggs	Baihe, Qingyuan, China	2013.7; 2016.9	4736; 4741	18	47

“N” is the sample size;

3.4. Bioaccumulation and biomagnification potential

It is reported that the most important exposure route of PBDEs to biological is uptake by food [50, 45]. The lipophilicity of PBDEs will cause them to accumulate in organisms and expand with the accumulation of trophic levels in food webs [3, 34, 35]. Bioaccumulation and biomagnification potential is one of the criteria for assessing the ecological risks of PBDEs to the environment [26 ,34,53].

For aquatic organisms, Wu et al., (2008)[30] reports that the bioaccumulation factors (Log BAF) of PBDEs in several aquatic animals (Chinese mysterysnake, prawn, fish, and water snake) are 2.9-5.3 in e-waste recycling areas, and depend on metabolic ability and environmental conditions among species. He et al., (2012)[34] indicates that, except for BDE47 and BDE100, the biota-sediment accumulation factors (BSAF) of all PBDE congeners in three species of fish are less than 1, indicating that the bioavailability of PBDEs in sediments is relatively low. Tao et al., (2019)[26] believes that the BAFs of BDE-28, 47, 66, 100, 138, 154 and 206 in aquatic biota are significantly higher than those of BDE-99, 153, 183, 207, 208 and 209 (t-test, $p<0.05$), and that the biomagnification factor (BMF) of PBDEs is negatively correlated with log-transformed octanol–water partition coefficients (log KOW). Some studies have shown that there are different bioaccumulation rates between aquatic and land ecosystems [3, 34, 51]. The BMF value of BDE-153 in the grasshopper-turtledove food chain is highest (3.4), while other high-bromine congeners (BDE-202, 203, 153, 183 and 209) are also amplified in the land food chain (BMF1.7-3.3). BDE-47, 99 and 100, however, are not biomagnified ($BMF<1$) [3, 19]. The BMFs in snake-frogs, though, indicate that BDE-28, 47, 66, 100, 153, and 154 have mild and moderate amplification, while there was no magnification for the other PBDE congeners [40]. The infuence factors of BAFs and BMFs could depend on predator/prey relationships, different trophic levels, biomagnification potential, pollutant concentration, etc. [26, 19]. It is reported that a stable nitrogen isotope ratio can independently measure the nutritional level of wild animals [52]. The low-bromine PBDEs in Oriental magpie-robins in e-waste areas are positively correlated with $\delta15N$ ($p<0.05$), while the levels in Oriental magpie-robins in other areas (both urban and rural) are not correlated, indicating serious PBDE pollution in e-waste areas [35].

4. Discussion

4.1 Trends of PBDEs pollution

With the establishment and implementation of laws and policies on PBDE control and mangement, PBDE concentrations in e-waste, and the release of PBDEs from e-waste recycling, have decreased significantly throughout the world, especially in China [47]. However, because of PBDEs’ long lifetimes and historical pollution problems, PBDE exposure in informal e-waste recovery areas is still at a high level, and there is no apparent decreasing trend, partly because of differences in research objects and methods. For example, for mud carp, the trend of PBDE levels is decreasing year by year in China [27, 26], but is still much higher than in Vietnam [28]. The PBDE level in eggs has shown a downward trend and is beginning to stabilize in the Qingyuan area, but it is still at a very high level [46, 47]. Thus, it can be seen that PBDE levels have had a tendency to first rise and then fall, over the past fifteen years. In the future, the declining process can be expected to continue, but very slowly.

4.2 Congener profiles of PBDEs

Currently, most studies focus on 9 kinds of PBDE congeners: BDE-28, BDE-47, BDE-66, BDE-99, BDE-100, BDE-153, BDE-154, BDE -183 and BDE-209. Wen et al., (2008)[30] indicates that the congeners with higher bromination are observed in highly polluted areas, while the congeners with lower bromination contributed relatively more in the reference cities. In e-waste dismantling areas, BDE-209 is the most common PBDE homologue in plants, but BDE-153, BDE-183 and BDE-47 are also major PBDEs in plant samples [54], while for aquatic organisms, BDE-47, BDE-99, and BDE-153 are the dominant PBDE congeners [8]. Several studies have shown that the low bromination degree and high relative concentration of PBDEs in fish could be caused by the debromination of high-bromine congeners [31]. Metabolism and dietary habits are the important causes of differences in PBDE congeners [34]. Land species often preferentially accumulate BDE-153 over BDEs 99 and 47 [55]. Existing data indicate that land animals are more likely to accumulate high-bromine congeners, while aquatic organisms tend to accumulate low-bromine congeners and to excrete or digest high-bromine congeners [55]. In addition, it has also been pointed out that snake size (snout-vent length and body mass) is positively correlated with BDE-28, -47 and -66 concentrations, but negatively correlated with high-bromine congeners [40].

5. Conclusions

Through literature research, we can conclude that PBDEs levels in plants around e-waste recycling plants were significantly higher than those in other areas. Due to the biological enlargement and bioaccumulation of PBDEs, terrestrial animals are more exposed to PBDEs than aquatic animals. Limited data show that the bioaccumulation and biomagnification of PBDEs are related to some PBDE congeners, and that there are differences among the various food chains (aquatic animals versus land animals) in e-waste areas. On the whole, PBDE exposure risks are higher in e-waste recycling areas.

E-waste is not just an environmental issue in one country; it is a global problem. With the restrictions on PBDEs enumerated in the Stockholm Convention, many countries have introduced laws and regulations to strictly control PBDEs. It has been shown that the exposure trend of PBDEs is decreasing, but at a very slow rate, especially in China. Due to weak bioaccumulation, the persistence of PBDEs and the weak link between PBDE exposure and the biological burden in e-waste recycling areas, this process can be difficult to observe. Further studies on the exposure characteristics of PBDEs, as well as the relationship between biological burden, are needed for further confirmation.

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Immobilization technology and ecological risk assessment of heavy metals

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Abstract

Heavy metal pollution has attracted more and more widespread attention due to its high toxicity, and could lead to unwanted environmental impacts, such as animal and human health hazards through the food chain and water contamination. With the development of social economy and improvement of living standards all over the world, large amounts of heavy metals are discharged. Heavy metals can have a serious impact on the environment if they are not handled properly. However, direct landfills, which have many disadvantages, such as high cost and may produce secondary environmental pollution problems when the physical and chemical conditions change. It cannot be denied that the disposal of contaminated heavy metals are feasible options which are currently practiced in many parts of the world. Therefore, the governments all over the world have been urged to consider alternative heavy metal remediation technology. Among the many remediation methods, stabilization/solidification (s/s) technology is a practical and effective heavy metal remediation technology. The immobilization technique is based on reducing the leaching and availability of heavy metals, so as to reduce the toxicity and harmfulness of heavy metals. It should be noted that the key point of this technique is to convert the unstable form of heavy metals into a stable form. Thus, concentrations and chemical speciation of heavy metals will be the research focus. In order to evaluate the immobilization effect of heavy metals, the European Community Bureau of Reference (BCR) three-step sequential extraction procedure is used, which can reveal the speciation of heavy metals. Sequential extraction can provide information about the differentiation of the relative bonding strength of metal on various solid phases and their potential reactivity under different physicochemical environmental conditions. After stabilization/solidification (s/s), the risk of heavy metals was significantly reduced. In addition, this work gives a new perspective for remediation of heavy metals and ecological risk assessment with multiple indices (including enrichment factor, geo-accumulation index, contamination factor and potential ecological risk index).

Keywords: heavy metals, stabilization/solidification (s/s), sequential extraction (BCR), chemical speciation, indices;

Introduction

Studies of heavy metal pollution in sediments and soils have increased in recent years. The contamination by heavy metals is a prevalent issue today, due highly to industrial growth and the expansion of human activities. Marine sediments, both coastal and open-ocean, are polluted by heavy metals originating from ships, dock-yards, rivers, and harbor facilities, mainly concentrated around ports, harbors, and estuaries. Furthermore, such pollution can negatively impact human health and ecosystems through a range of accumulation processes within the food chain[1,2]. With rapid economic growth, industrialization and urbanization, heavy metal pollution has become serious in China. Cadmium polluted farmland over 12,000 ha and high concentrations were detected in 11 irrigation regions in China[3]. The major rivers and lakes had been generally polluted by heavy metals at different levels, with the pollution rates of sediments being up to 80.1%[4]. Typical sewage sludge disposal methods, such as landfill, incineration, and agricultural applications, have become subject to increasing public opposition and stricter regulatory pressure because of groundwater pollution, odor emissions, soil contamination and heavy metal pollution[5-12]. Anthropogenic activities such as metal smelting, battery manufacture and municipal solid waste disposal give rise to very large quantities of heavy metal emissions each year. Heavy metals may cause contamination of water, soil or other receiving streams and then threaten the health of human beings, animals and plants[13]. Metal contamination in aquatic environments has received huge concern due to its toxicity, abundance and persistence in the environment, and subsequent accumulation in aquatic habitats. Heavy metal residues in contaminated habitats may accumulate in microorganisms, aquatic flora and fauna, which, in turn, may enter into the human food chain and result in health problems[14,15]. Heavy metals discharged into a river system by natural or anthropogenic sources during their transport are distributed between the aqueous phase and bed sediments[16]. Heavy metals are serious pollutants because of their toxicity, persistence, and non-degradability in the environment[17-19]. Industrial activities give rise to large quantities of wastewater containing toxic heavy metals. In contrast to organic pollutants in wastewater, heavy metals can only be removed by separation or converted to a chemically inert state[20-22].

To fully evaluate the environmental impact of heavy metal pollution, both chemical and biological analysis should be carried out[23]. The mobility, transport and fractionation of heavy metals are a function of the chemical form of the element, which, in turn, is controlled by the physicochemical and biological characteristics of the system. Landfills are known to be the more expedient, inexpensive method to dispose of MSW. However, this simple method has caused various problems such as groundwater pollution from landfill leachate, odor emission and soil contamination[24]. Moreover, spaces for landfills have becoming increasingly limited, especially in countries with a large population.

In recent years, various protocols for removing or stabilizing heavy metals in sewage sludge have been studied to minimize potential risks to human health and the environment. Heavy metal concentrations in sewage sludge can be reduced by chemical extraction, bioleaching, electrokinetic processes and supercritical fluid extraction[25]. An effective method for decreasing heavy metals leaching from sludge is stabilization, which can be achieved using physicochemical reactions at high temperatures or pressures. Re-use and environmental "neutralization" of waste are among the current energy-efficient and environmental-friendly methods for waste treatment[26]. If heavy metal contents in river sediment exceed environmental acceptable limits, cleanup action is warranted. Among remediation strategies for contaminated sediments, phyto-remediation, washing and cement-based solidification/stabilization (s/s) are most commonly used over the world at present[27,28]. Cement-based solidification/stabilization (s/s) reduces the mobility of pollutants and subsequent hazards for the environment by a combination of solidification and stabilization. It has been used for the disposal of various types of industrial wastes, but is particularly suited for lands contaminated with heavy metal compounds for re-development[27,28]. It is also considered to be one of the most effective options for treating severely contaminated sediments in terms of time and cost at present. The common binders used in cement-based solidification/stabilization (s/s) are Portland cement and various blended cements. With an optimized binder formulation and suitable operation conditions, cement-based solidification/stabilization (s/s) cannot only achieve and retain the desired physical properties for improving the handing characteristics, but also chemically stabilize or bind contaminants to lower the leaching rates[29]. The mechanical strength and the leaching resistance are two basic parameters of evaluating the effectiveness of the solidification/stabilization (s/s) process and allow direct comparisons of disposal options to be made. Cement based stabilization/solidification is a widely accepted treatment process for immobilizing hazardous substances that contain heavy metals[30]. Treatment by solidification/stabilization (s/s) combines two interrelated processes that occur simultaneously to yield a product that will have less environmental impact when disposed or reused. Solidification is the process of producing a solid product with improved physical properties (mainly strength), and stabilization is the process of converting the contaminant of concern to a less mobile and less toxic one[31,32]. In the past few decades, the most widely used solidification/stabilization (s/s) systems are the cement-based materials[33]. A major factor is that cement is easy to form a durable, monolithic material that will not easily leach hazardous components under the disposal conditions[34,35]. American State Bureau of Environmental Protection refers to cement immobilization as the best technology to dispose the poisonous and harmful wastes[36]. Surface treatment industries generate exhausted baths with a high content of heavy metals. Magnesium potassium phosphate cements are used for stabilization/solidification (s/s) of different wastes, mainly mixed wastes and low-level nuclear wastes[37–39].

Methods

The samples collected from each site consisted of 4-5 composite samples. Composite sediments (top 20 cm of surface) were taken by using a self-made sediment core sampler. After sampling, the sediment samples were sealed in clean polyethylene bags, placed in a cooler at 4 ℃, and transported to the laboratory immediately for further analysis. The dried samples for metal analysis were passed through a 100-mesh nylon sieve. The total concentrations of heavy metals were measured by inductively coupled plasma mass spectrometry (ICP-MS). The sequential extraction procedure applied in the present investigation to determine metal fractionation in the sediments[40-42]. In all of these sequential extraction methods, the four steps method mainly established by Tessier et al. won the most popular application[43]. The flow charts for speciation scheme of samples are present in Fig. 1. For each sequential extraction operation, the achieved mass recovery was computed, and the extraction was repeated as often as possible to achieve satisfying mass recovery (> 90%).

Normally, the summation of the mobile and the exchangeable fractions can be used to assess the environmentally available components. The fractions bound to Mn oxides and organic material are supposed to represent the potentially mobile component under changing conditions, which are reviewed as the most important components in sediments for metals binding. While the residual fraction represents the more stable metal forms associated with anthropogenic or geogenic components, the influence of which to ecological system is much less than the others in major conditions.

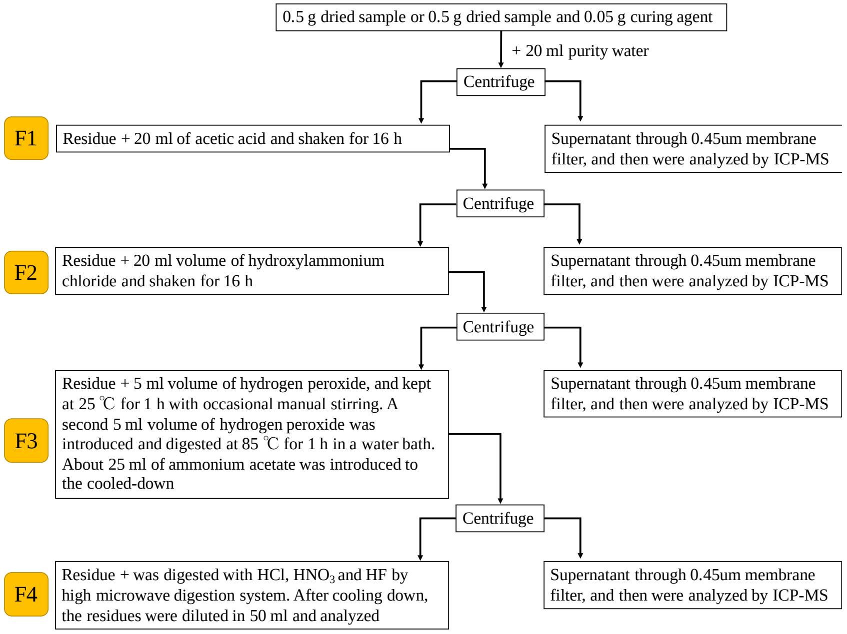

Fig. 1. Flow charts for speciation scheme of samples (F1, exchangeable metal and carbonate-associated fractions; F2, fraction associated with Fe and Mn oxides; F3, fraction bound to organic matter; F4, residual fraction).

Remediation technology and ecological risk assessment for the heavy metals

Remediation technology

The remediation technologies of heavy metals were listed in the Table 1, including methods, metals, results, and references.

Table 1. The remediation technologies for heavy metals.

Methods	Metals	Results	References
Stabilization	Cd, Cr, Cu and Pb	The results reveal that high temperatures accelerate the formation of CuO, Cd_2SiO_4, Cr_2O_3, $PbCrO_4$ and $PbSi_2O_3$, and heavy metal solidification rates remain above 95% in acidic solutions and above 98% in strong oxidative H_2O_2 solutions	44
Cement-based s/s	Hg, Pb, Cu, Ni and Zn	The cement-based solidification/stabilization (s/s) was capable of successfully remediating heavy metal-bearing sediment	45

Different useful tools, methods, guidelines	Fe, Mn, Cu, Pb, Zn, Ni, Cr, Co, As, and Cd	The results have indicated that the concentrations of Cr, Cu, Ni and Pb are likely to result in harmful effects on sediment-dwelling organisms which are expected to occur frequently	46
Sequential extraction, geochemical normalization	Fe, Mn, Cr, Ni, Cu, Zn and Pb	It is concluded that the Tisza River is slightly to moderately severely pollute with Cu, Zn and Pb, and minor pollute with Cr	47
Fixation technologies of heavy metals, long-term leaching test, NEN 7341 test and BCR sequential extraction method	As, Zn, Pb, Cr, Cd, and Ni	Both cement solidification/stabilization and co-processing by a cement rotary kiln could effectively fix heavy metals. Cement stabilization/solidification is more fitful for treating the wastes containing Cr	48
The concentrations, speciation, and assessment	As, Cd, Cr, Cu, Hg, Ni, Pb, and Zn	The discharge of urban sewage and industrial wastewater has been identified as a major pollutant source, thus these sources should address first in remediation efforts	49
MSWI fly ash-cement	Zn, Pb, Cu, Cd and Cr	Immobilization effect of cement on MSWI fly ash is good. Even if MSWI fly ash-cement hardened pastes were damaged, the leaching toxicity is still in a safety range	50
Fly ash–lime-carbonation	Zn, Pb, Cu and Cr	The precipitation of heavy metals with calcium oxide in the presence of fly ash has been shown to be successful in reducing the level of soluble heavy metals in solution	51
Magnesium potassium phosphate cements	Ni, Pb, Cu and Zn	The short term heavy metal retention by magnesium potassium phosphate cements is very effective	52
Washing experiments and fractionation analysis using five different extracting agents (EDTA, sodium citrate, HCl, HNO_3 and NaCl)	Cd, Cu, Ni, Pb, and Zn	EDTA was the most effective extracting agent for Cu, Pb, and Zn from sediments	53
Concentration, risk and toxicity assessment	As, Cd, Cr, Hg, Pb, and Zn	People would experience health risks from the intake of heavy metals through fish consumption in the studied area (the Yangtze River and Taihu Lake)	54

Intensity of the heavy metal pollution

In order to evaluate the extent of the heavy metal pollution affecting the river sediments, an enrichment factor (EF) is calculated as follows[55]:

$$EF = \frac{(Me/Sc)_{sed}}{(Me/Sc)_{Marcenac}} \qquad (1)$$

Where $(Me/Sc)_{sed}$ is the concentration ratio of a given metal to Sc in the river sediment and $(Me/Sc)_{Marcenac}$ is the average ratio of the same metal to Sc in the reference (non-polluted) site.

Zhang and Liu, 2002[56] recommend using EF = 1.5 as an assessment criterion, i.e., EF values between 0.5 and 1.5 (i.e., $0.5 \leqslant EF \leqslant 1.5$) suggest that the trace metals may be entirely from crustal materials or natural weathering processes while EF values greater than 1.5 (i.e., $EF > 1.5$) suggests that a significant portion of trace metal is delivered from non-crustal materials. Han et al., 2006[57] divided the contamination into different categories based on EF values. If $EF \leqslant 2$, it suggests deficiency to minimal metal enrichment. However, if a value of EF is greater than 2 (i.e., $EF > 2$), it suggests various degrees of metal enrichment[57].

Next criterion to evaluate the intensity of the heavy metal pollution in the river sediments is the geoaccumulation index (I_{geo}) introduced by Muller, 1979[58]:

$$I_{geo} = \log_2 \frac{Me_{sed}}{1.5 Me_{Marcenac}} \qquad (2)$$

Where Me_{sed} is the concentration of a given heavy metal and $Me_{Marcenac}$ is the average concentration of the same metal in the sediments of the reference site.

Table 2. Geoaccumulation index (I_{geo}) in relation to pollution intensity after Muller, 1979[58].

Igeo	Pollution intensity
>5	very strongly polluted
4-5	strongly to very strongly polluted
3-4	strongly polluted

2-3	moderately to strongly polluted
1-2	moderately polluted
0-1	unpolluted to moderately polluted
<0	unpolluted

Contamination factor (CF). The CF is the ratio obtained by dividing the concentration of each metal in the sediment by baseline or background value (concentration in uncontaminated sediment):

$$\mathrm{CF} = \frac{C_{heavy\ metal}}{C_{background}} \qquad (3)$$

CF values were interpreted as suggested by Hakanson[59], where: CF < 1 indicates low contamination; 1 < CF < 3 is moderate contamination; 3 < CF < 6 is considerable contamination; and CF > 6 is very high contamination.

Pollution load index (PLI). For the entire sampling site, PLI has been determined as the nth root of the product of the n CF:

$$\mathrm{PLI} = (\mathrm{CF}_1 \times \mathrm{CF}_2 \times \mathrm{CF}_3 \times \cdots \times \mathrm{CF}_n)^{1/n} \qquad (4)$$

This empirical index provides a simple, comparative means for assessing the level of heavy metal pollution. When PLI > 1, it means that a pollution exists; otherwise, if PLI < 1, there is no metal pollution[60].

Potential ecological risk index (PER)

To further screen sediment contamination degree caused by heavy metals, potential ecological risk index (PER), which was developed based on sedimentary theory, was introduced to assess the ecological risk degree of heavy metals in present sediments. Potential ecological risk index was originally proposed by Hakanson[59] and widely used[61,62]. The value of RI can be calculated by the following formulas:

$$C_f^i = C_D^i / C_B^i \qquad (5)$$
$$E_r^i = T_r^i \times C_f^i \qquad (6)$$
$$RI = \sum_{i=1}^{m} E_r^i \qquad (7)$$

Where RI is the sum of the potential risk of individual heavy metal, E_r is the potential risk of individual heavy metal, T_r is the toxic-response factor for a given heavy metal, C_f is the contamination factor, C_D is the present concentration of heavy metals in sediments, and C_B is the pre-industrial record of heavy metal concentration in sediments.

Table 3. Indices and corresponding degrees of potential ecological risk[59].

E_r value	Grades of ecological risk of single metal	RI value	Grades of potential ecological risk of the environmental
$E_r < 40$	Low risk	RI < 150	Low risk
$40 \leqslant E_r < 80$	Moderate risk	$150 \leqslant RI < 300$	Moderate risk
$80 \leqslant E_r < 160$	Considerable risk	$300 \leqslant RI < 600$	Considerable risk
$160 \leqslant E_r < 320$	High risk	$RI \geqslant 600$	Very high risk
$E_r \geqslant 320$	Very high risk		

Conclusions

The immobilization mechanism of heavy metals requires further investigation and long-term monitoring is an absolute necessity. The speciation of metals and their interactions with precipitant ions in solution is an important area for further study, as it will provide key information for optimization of the treatment-step described here. The management of contaminated sediment and dredged materials is an environmental problem of major concern. A wide number of studies have addressed such problem, with various approaches (physical, chemical, biological) and application (in situ, ex situ/on site). As a whole, the present work reviews the most recent approaches based on chemical and biotechnological processes targeted at the treatment of sediments contaminated with metals. Chemical and biological processes should focus on understanding how the characteristics of the sediment and the metal contamination affect the efficiency of remediation strategies. In the future, full scale applications for sediment decontamination are expected to be found; nevertheless, a new thinking is necessary for a really sustainable management of dredged sediments. Additionally, when metals in sediment are mainly composed of the mobile and the exchange fraction, such methods as amendment, ultrasound, electrochemical remediation, immobilization and washing can effectively lower the release of metal adsorbed; when the Mn-oxides fraction and the OM fraction take up a large proportion of sediment, such methods (e.g. ultrasound, electrochemical remediation, amendment, sand cap and chelating reagents washing) often present better remediation effects. In all environmental factors, the pH, ORP and OM are the most important factors affecting heavy metal distributions. The pH and OM can directly change metals distributions in sediment[63].

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Study on extraction of titanium from iron tailings by flotation

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Abstract: In order to improve the secondary utilization of valuable resources in tailings, this paper explores the possibility of extracting titanium from iron tailings by flotation. The floatability of ilmenite and quartz was explored by flotation test of pure minerals. The flotation rules and dosage conditions of ilmenite and quartz with pH, water glass and Pb $(NO_3)_2$ under sodium oleate reagent system were obtained. The separation conditions of the two minerals were explored by artificial mixing of pure minerals. Finally, the actual ore flotation was explored with sulfuric acid and water glass as the regulator, Pb $(NO_3)_2$ as the activator and sodium oleate as the collector. Under the conditions of 900g / t sulfuric acid, 400g / t water glass, 30g / t Pb $(NO_3)_2$ and 450g /t sodium oleate in the reagent system, titanium concentrate with grade of TiO_2 of 39.55% and recovery of 54.61% could be obtained after one roughing and two cleaning. It is proved that it is possible to extract titanium from iron tailings by flotation separation.

Key words: ilmenite; iron tailings; flotation; Flotation reagents

Mineral resources are the very important material basis for human development and survival. They are nonrenewable and irreplaceable raw materials in the short term. With the rapid development of China's industrialization, the demand for mineral resources is increasing day by day, but in the process of using mineral resources, the loss and waste of resources are quite serious. With the continuous development and utilization of mineral resources, ore is increasingly scarce, tailings as a secondary resource for reuse has become a necessary link. Tailings recovery technology mainly includes low-energy monomer dissociation control technology, high-efficiency recovery technology of magnetic materials, deep reduction and control technology, high-efficiency flotation agent synthesis and application technology, comprehensive recovery and utilization technology of various associated components, flash roasting and re separation technology, etc. The main development direction of iron tailings resource recovery and utilization is reasonable recovery of valuable resources, improvement of metal recovery rate and optimization of beneficiation process to achieve the purpose of reasonable development[1-3]. At present, a lot of research work has been done on the recovery of iron, copper, gold and non-metal from iron tailings, but the recovery of titanium from tailings is rarely studied.

In this paper, the possibility of recovering titanium metal from iron tailings is explored and studied. The experimental conditions of flotation separation are obtained through the study of flotation characteristics of single mineral and artificial mixed ore, and verified by the actual ore.

1 Experiment

1.1 Materials

Pure minerals of ilmenite and quartz are from Beihai ilmenite placer concentrator. The particle size range (0.025-0.038mm) prepared by manual selection, crushing, grinding and screening. Table 1 and table 2 are multi-element analysis of ilmenite and quartz respectively. Through calculation, the purity of ilmenite is above 90% and that of quartz is above 99%. The actual ore sample is taken from tailings of ilmenite placer concentrator. Table 3 shows the multi-element analysis structure of the ore sample

Table 1 Chemical multi-elements analysis of the pure ilmenite

Element	TiO_2	TFe	S	Al_2O_3	MgO	CaO	P
Content%	51.05	31.51	0.033	0.64	0.14	0.11	0.20

Table 2 Chemical multi-elements analysis of the pure quartz

Element	SiO_2	TFe	Al_2O_3	MgO	CaO	P	S
Content%	99.6	0.012	0.3	0.01	0.011	<0.005	-

Table 3 Chemical multi-element analysis of iron tailings

Element	TFe	TiO2	SiO2	Al_2O_3	MgO	CaO	S
Content%	15.65	7.33	75.43	6.3	1.61	3.211	0.13

1.2 Method

Flotation test of pure mineral:XFG flotation machine was selected in the flotation test of pure minerals, with a rotating speed of 1800r / min. Weigh 2.0g each time, add 30ml distilled water to prepare pulp and adjust the pulp for 2min, adjust the pulp pH value in the flotation machine with H_2SO_4 or NaOH, and stir for 2min after reaching stability, and then float for 3min through the appropriate reagent system in the flotation process. The recovery rate is calculated by the dry mineral weight of foam products and tank products.

Actual ore flotation test:XFD-63 single cell flotation machine is selected for the flotation of actual ore samples, with 200.0g ore samples tested each time and 35 ℃ pulp temperature adjusted. The recovery rate of the product is calculated by the weight of dry mineral and the grade of test.

2 Results and discussion

2.1 Single mineral flotation test

The influence of the amount of collector, pulp pH value and regulator on the floatability of ilmenite and quartz in sodium oleate (NaOl) flotation system was studied by single mineral flotation test. The test results are shown from Fig.1~Fig.4. The floatability of ilmenite is greatly affected by the amount of NaOl, pH value, water glass (main component: Na_2SiO_3) and Pb $(NO_3)_2$. It can be seen from Fig.1 and fig.2, with the increase of sodium oleate, the recovery of ilmenite increases gradually. When the amount of NaOl is 144mg/L, a higher recovery rate is obtained, and the suitable pH range of ilmenite is 5-9; The dosage of Na_2SiO_3 is in the range of 0-15mg/L, it has little effect on ilmenite, when the dosage is more than 15mg/L, it has obvious inhibition on the recovery of ilmenite; Pb $(NO_3)_2$ has obvious activation effect on ilmenite. When the dosage is increased to 80mg / L, the recovery effect of ilmenite is better. The results show that the floatability of quartz in sodium oleate system is poor, almost no floatation, and a small amount of Na_2SiO_3 has obvious inhibition on quartz.

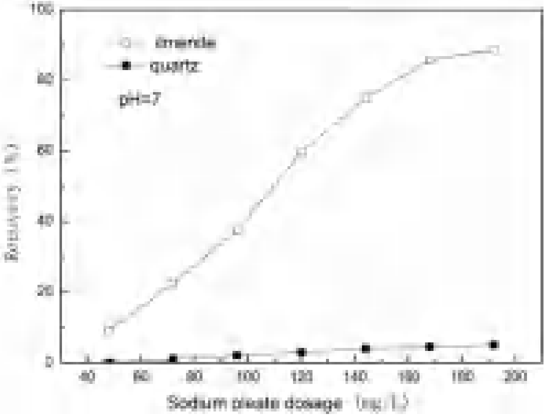

Fig.1 Relationship between recovery and the dosage of sodium oleate(pH=7)

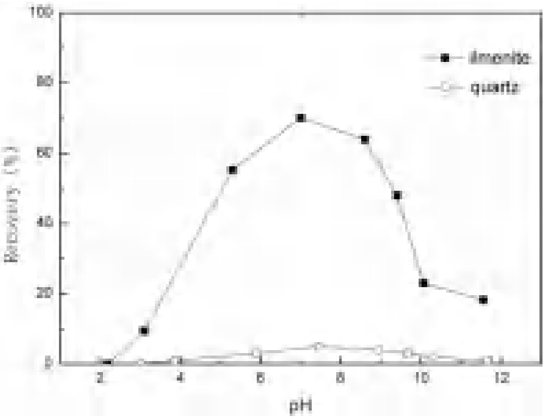

Fig 2 Relationship between recovery of minerals and pH value (NaOL,144mg/L)

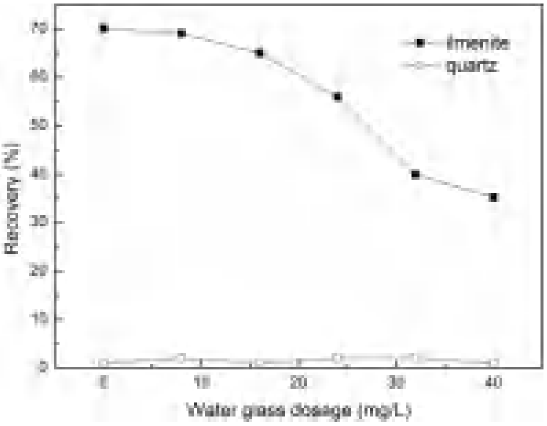

Fig.3 Relationships between recovery of minerals and the dosage of water glass (NaOL,144mg/L; pH=7)

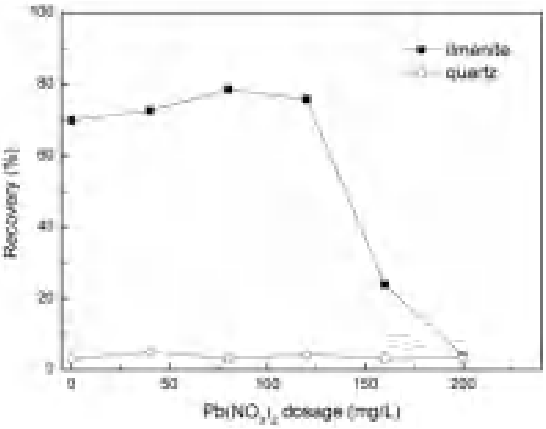

Fig4 Relationships between recovery of minerals and the dosage of $Pb(NO_3)_2$(NaOL,144mg/L; pH=7)

2.2 Flotation test of artificial mixed ore

The mixture of ilmenite and quartz was prepared according to the mass ratio of 1:1, and 3g was weighed each time for the flotation test. The effects of Pb $(NO_3)_2$, Na_2SiO_3 and NaOl on the flotation separation of the artificial mixture were studied.It can be seen from Fig. 5 ~Fig. 7 that the amount of Pb $(NO_3)_2$ and Na_2SiO_3 has little impact on the recovery rate of the artificial mixed minerals, but has a greater impact on the grade; when the amount of Pb $(NO_3)_2$ is 120mg/L, the grade and recovery rate reach the maximum value. With the increase of Na_2SiO_3 dosage, the concentrate grade increases gradually. The amount of sodium oleate has a great influence on the recovery and grade. Na_2SiO_3 has a strong inhibitory effect on quartz in the artificial mixed minerals, and with the increase of its dosage, the concentrate increases significantly. Na_2SiO_3 has a strong inhibitory effect on quartz in the artificial mixed ore. When the amount of Na_2SiO_3 increases, the grade of concentrate increases significantly, because water glass has a strong inhibition on quartz, there are a large number of H_2SiO_3 and $HSiO_3^-$ in the slurry. On the other hand, they can be adsorbed on the surface of quartz, they have strong water absorption performance. A large number of quartz surfaces are attached to make quartz hydrophilic and inhibited [4-5].

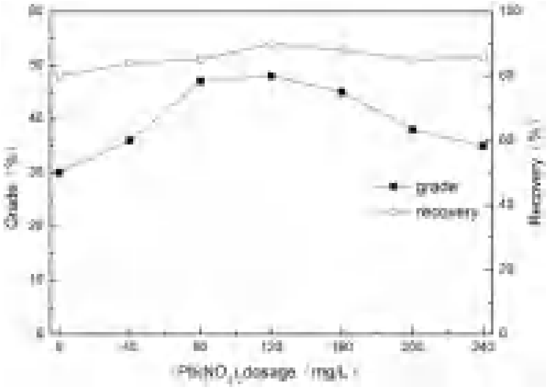

Fig.5 Effect of $Pb(NO_3)_2$ dosage on flotation of mixed ore (NaOL,144 mg/l; pH=9)

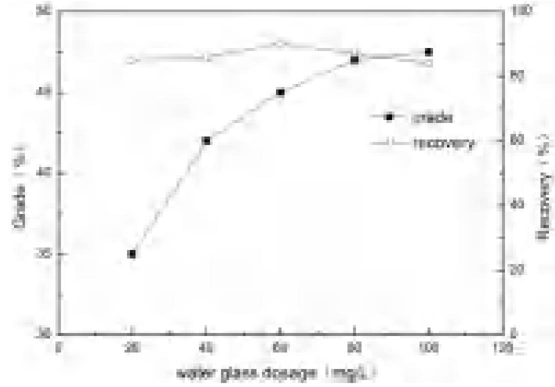

Fig.6 Effect of water glass dosage on flotation of mixed ore (NaOL,144 mg/l; pH=9)

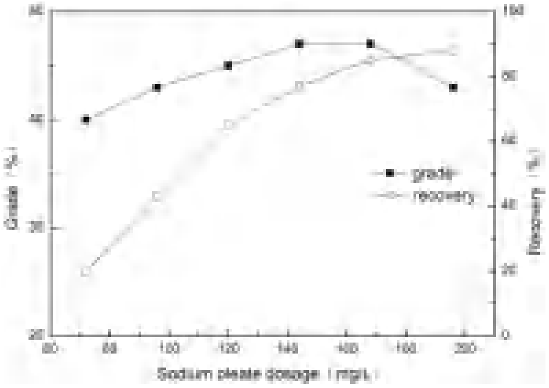

Fig.7 Effect of NaOL dosage on flotation of mixed ore (pH=9; $Pb(NO_3)_2$, 80mg/l; Water glass, 90mg/l)

2.3 Actual ore flotation test

According to the results of single mineral flotation test and mixed mineral flotation test, the flotation agent is properly enlarged and adjusted according to the characteristics of flotation agent system. The amount of flotation agent is selected as H_2SO_4 900g /t, Na_2SiO_3 800g / t, Pb (NO_3) 30g / t, NaOL 160g / t, and the flotation process is determined as primary roughing, and the test process of two cleaning is shown in Figure 8. The test results are shown in Table 4, the final tailings closed-circuit test results in a concentrate with a grade of 39.55% and a recovery rate of 54.61%. It is proved that the effective recovery of titanium in the tailings of seaside placer is realized through one-time roughing and two-time cleaning.

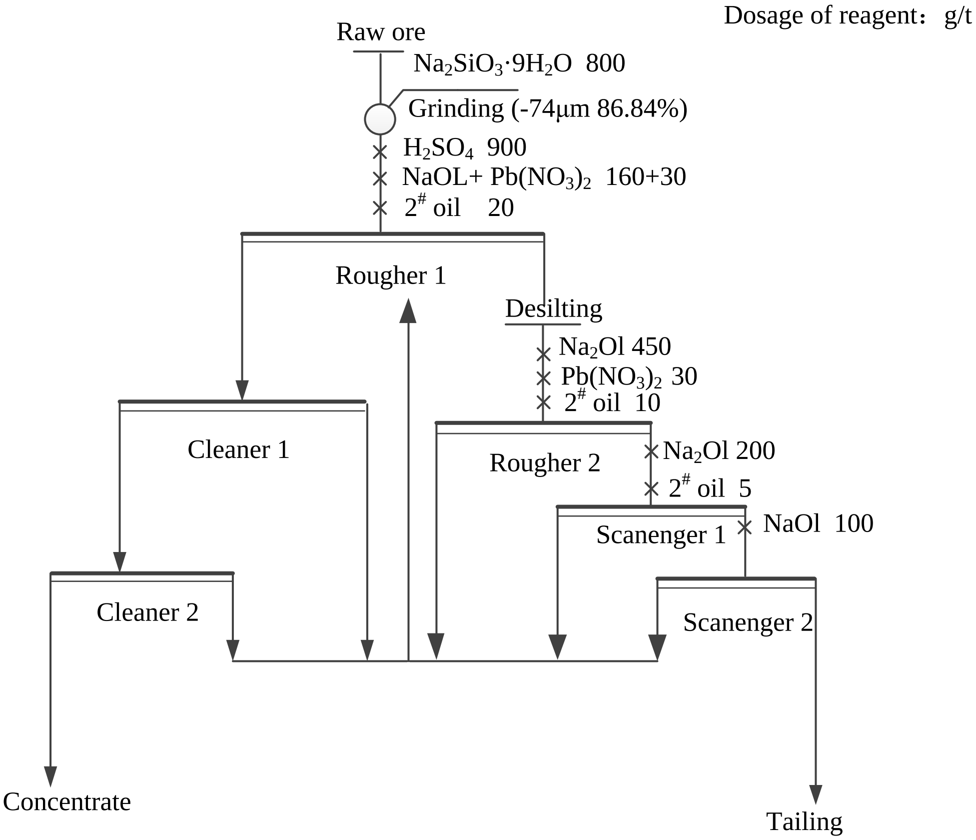

Fig. 8 The closed-circuit flowsheet of ilmenite beach sands tailings flotation

Table 4 The result of ilmenite beach sands tailings flotation closed circuit

Product	Yield（%）	TiO_2 grade（%）	TiO_2 recovery（%）
concentrate	10.12	39.55	54.61
tailing	89.88	3.70	45.39
total	100.00	7.33	100.00

3 Conclusion

1) Single mineral test shows that the floatability of quartz and ilmenite is quite different in the flotation system of sodium oleate, quartz is almost not floating, and ilmenite is relatively good.

2) The results show that quartz and ilmenite can be separated effectively in the flotation system of sodium oleate, and the amount of Pb $(NO_3)_2$ and Na_2SiO_3 has a great influence on the recovery and grade.

3) Under the suitable medicament system, the titanium concentrate with TiO_2 grade of 39.55% and recovery of 54.61% can be obtained by one roughing and two cleaning.

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The Trend of Centralized Disposal of Medical Waste and Countermeasures for the 14th Five-Year Plan Period

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Abstract

In order to promote environmental management in the field of medical waste in an orderly way and help to fight the upgraded battle of pollution prevention and control, based on the current situation of medical waste generation and disposal in the whole country, this paper analyzes the trend and demand of centralized medical waste disposal during the "14th Five-Year Plan" period by adopting qualitative and quantitative analysis. It is estimated that the amount of medical waste generated by the end of the "14th Five-Year Plan" period will reach about 1.5 million t/a, and safe disposal of medical waste will face greater pressure. This paper identifies the shortcomings of the current centralized medical waste disposal system, namely, the inability of centralized disposal capacity to meet disposal needs, improper disposal of medical waste in some rural and remote areas, insufficient emergency disposal capacity reserve of medical waste, and the needs of technical route of centralized medical waste disposal to be optimized. It is suggested to promote the environmental management of medical waste during the "14th Five-Year Plan" period by improving the centralized disposal capacity of urban medical waste, promoting the safe disposal of medical waste in rural and remote areas, speeding up the allocation of emergency disposal capacity of medical waste, and improving the technical route of medical waste disposal.

- *Keywords:* Medical Waste; Centralized Disposal; Disposal Facilities; Emergency Treatment; Technical Route

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1. Introduction

Medical wastes refer to wastes generated by medical and health institutions during medical treatment, prevention, health care and other related activities that are directly or indirectly infectious, toxic and hazardous, mainly including five categories, namely infectious wastes, traumatic wastes, pathological wastes, drug-induced wastes and chemical wastes[1]. Infectious wastes account for 80~90% of medical wastes, and eliminating their infectious hazards is the main purpose of medical waste disposal. After the SARS epidemic in 2003, the former State Environmental Protection Administration issued the *National Plan for the Construction of Hazardous Waste and Medical Waste Disposal Facilities* (hereinafter referred to as the *Plan for the Construction of Facilities*), which established a centralized medical waste disposal system covering the whole country with prefecture-level cities as units, thus effectively ensuring the safe disposal of medical waste[2]. However, after the outbreak of novel coronavirus (COVID-19), China's centralized medical waste disposal system still exposes many shortcomings [3-5]. In order to fight for an upgraded version of pollution prevention and control and promote environmental management in the field of medical waste in an orderly manner, it is urgent to scientifically study and judge the trend of centralized disposal of medical waste during the 14th Five-Year Plan period and take corresponding measures to optimize and upgrade the disposal system.

2. Current Situation of Medical Waste Generation and Disposal

2.1 Current situation of medical waste generation

The amount of medical waste generated is closely related to the population and the number of beds[6]. According to the *Notice on Adjusting the Classification Standard of City Size* (Guo Fa 2014 Document No.51), cities are divided into five categories and seven grades according to the number of permanent residents in urban areas (see Table 1). In 2018, a total of 477,000 t of medical wastes were generated in 28 supercities, megacities and type I megacities, accounting for 48.7% of the total medical wastes generated in the country (see Fig. 1).

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Table 1 China's Classification Criteria of City Size

No.	City Type	Number of permanent residents in urban areas	City name
1	Supercity	Over 10 million	Shanghai, Beijing, Chongqing, Guangzhou, Shenzhen, Tianjin
2	Megacity	5 to 10 million	Wuhan, Chengdu, Dongguan, Nanjing, Hangzhou, Zhengzhou, Xi'an, Shenyang, Qingdao
3	Big city	Type I big city: 3 to 5 million	Harbin, Changchun, Hefei, Jinan, Kunming, Dalian, Changsha, Taiyuan, Ningbo, Nanning, Suzhou, Xiamen, Fuzhou
		Type II big city: 1-3 Million	
4	Medium city	500,000 to 1 million	
5	Small city	Type I small city: 200,000 to 500,000	
		Type II small city: less than 200,000	

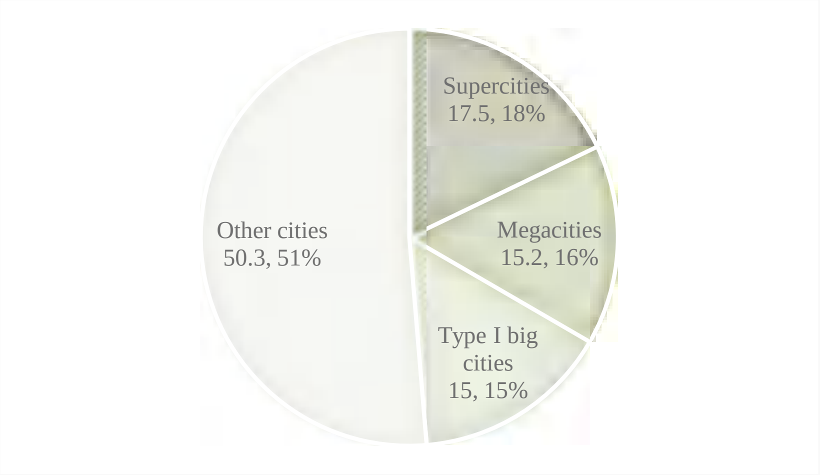

Fig. 1 Medical Wastes Generation in Different Types of Cities in China in 2018

Based on the population data of supercities, megacities and type I big cities in 2018 and the output of medical wastes in that year, this paper compares the intensity of medical wastes generated per million population (see Table 2). The results show that the intensity range of medical wastes per million population in supercities, megacities and type I big cities is 3~9, 4~10 and 5~10 t/d respectively.

Table 2 Intensity Range of Medical Wastes Generated in Different Types of Cities in 2018

City Type	Intensity range of medical waste generated per million population (t/d)
Supercities	3~9
Megacities	4~10
Type I big cities	5~10

2.2 Current status of medical waste disposal facilities

In recent years, the number of medical waste disposal facilities has continuously increased, especially since the 13th Five-Year Plan period (see Fig. 2). In 2018, there were 407 medical waste disposal facilities nationwide, with an approved operation scale of 1.29 million t/a. Among the 407 disposal facilities, 152 are incineration facilities, 255 are non-incineration facilities using high-temperature steam, microwave disinfection, chemical disinfection and high-temperature dry heat measures, and 24 are hazardous waste disposal facilities for collaborative disposal of medical waste. Incineration and high-temperature steam are main medical waste treatment and disposal technologies. In 2018, incineration facilities disposed 588,000 t of medical waste, accounting for 60% of the total disposal, while high-temperature steam disposed 332,000 t of medical waste, accounting for 33.9% of the total. The scale of disposal facilities is generally small, with the disposal capacity of 61% incineration facilities smaller than 10 t/d (see Fig. 3).

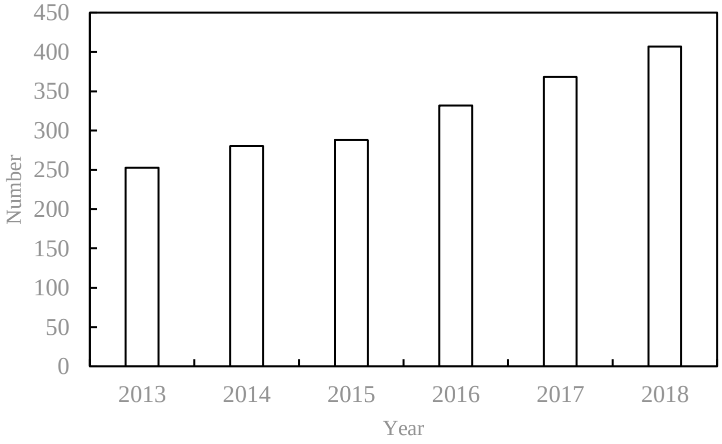

Fig. 2 Number of Medical Waste Disposal Facilities from 2013 to 2018

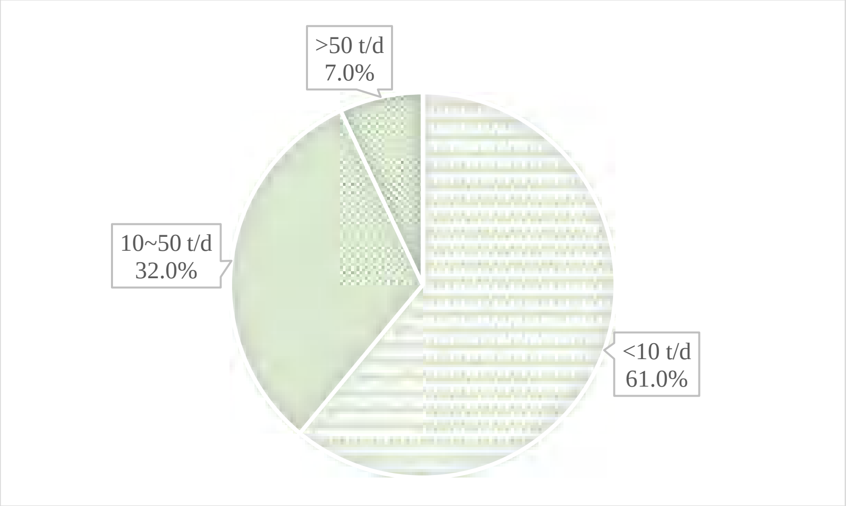

Fig. 3 Proportion of Facilities of Different Sizes for Medical Waste Incineration and Disposal

3. Demand Analysis for Medical Waste Centralized Disposal During the 14th Five-Year Plan Period

3.1 Forecast of medical waste generation

(1) Forecast based on medical waste generation over the years

According to the statistics of the Ministry of Ecology and Environment, medical waste generation from 2014 to 2018 showed a linear growth trend (see Fig. 4), with an annual average growth rate of 9.3%. Based on this, it is predicted that the medical waste generated in 2020 will be 1.128 x 10^6 t under normal conditions, 1.15 times of that in 2018, and the medical waste generated in 2025 will be 1.495 x 10^6 t , about 1.53 times of that in 2018.

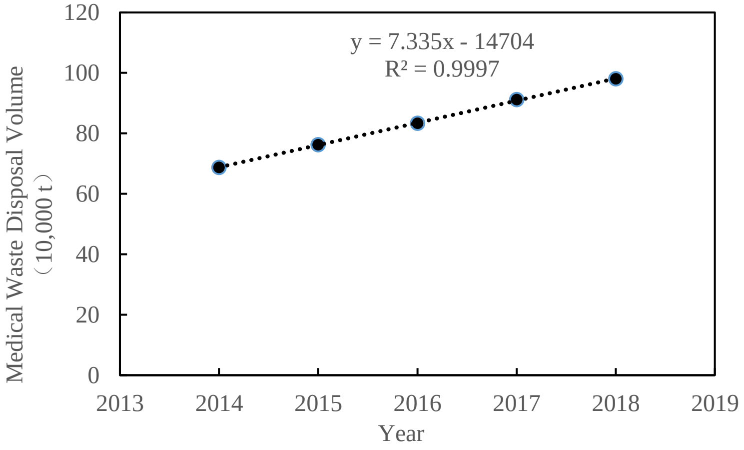

Fig. 4 Changes in Medical Waste Disposal (Generation) from 2014 to 2018

(2) Forecast based on the number of beds in medical and health institutions

Both the amount of medical waste generated and the number of beds have increased year by year from 2014 to 2018, showing a linear relationship between the two (see Fig. 5).

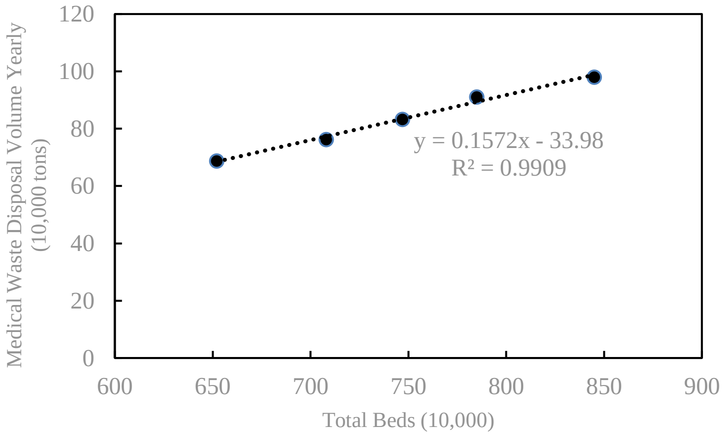

Fig. 5 Relationship Between Medical Waste Production and Total Number of Beds From 2014 to 2018

The amount of medical waste generated is closely related to the number of beds in medical and health institutions, the number of people diagnosed and treated, the number of people hospitalized, etc. During the 13th Five-Year Plan period, the number of beds in China's medical and health institutions increased from 7.08 million in 2015 to 8.92 million in 2019 (see Fig. 6), with an average annual growth rate of about 6%, of which the number of beds in hospitals increased from 5.34 million to 6.97 million and that in township health clinics increased from 1.21 million to 1.38 million. The total number of medical visits and discharges yearly increased from 7.8 billion and 220 million in 2016 to 8.52 billion and 270 million in 2019 respectively. According to this forecast, the number of beds in medical and health institutions will reach 9.364 million and 11.72 million in 2020 and 2025.

According to a study by Fan Yugai[7], in OECD countries, the number of beds per thousand population in China in 2014 (3.62) was much lower than that in Japan (13.20), South Korea (11.66), Germany (8.23), France (6.20) and other countries. Even if the 2020 target (6.0) of the *National Health Service System Planning Outline (2015-2020)* is met, there is still some room for improvement. Meanwhile, the COVID-19 has exposed the shortcomings of public health service facilities in China. During the 14th Five-Year Plan period, all localities will continue to increase public health investment, and the growth rate of beds is expected to be basically the same as that during the 13th Five-Year Plan period.

According to this calculation, the medical waste generated in 2020 and 2025 will be 1.132 x 10^6 t and 1.503 x 10^6 t respectively, which is very close to the predicted result of medical waste generation.

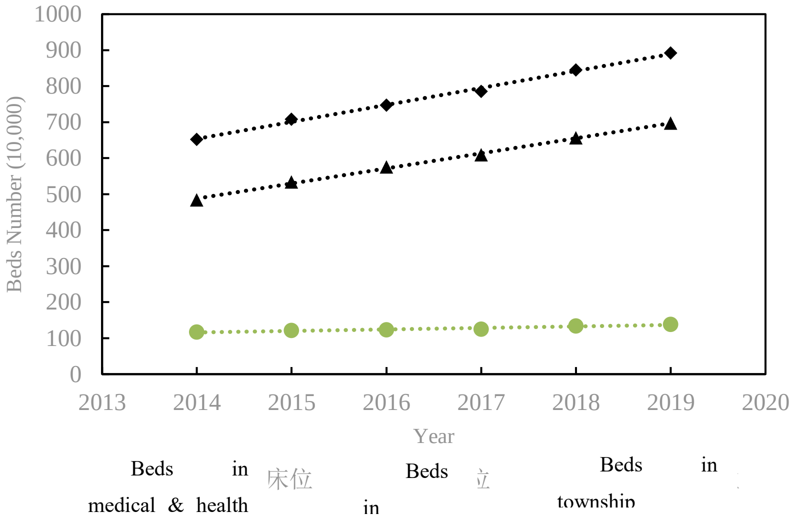

Fig. 6 Trend of Beds Number in China from 2014 to 2019

3.2 Research and judgment on the trend of centralized disposal of medical waste

According to the *Guidance on Improving the Environmental Supervision Capacity, Utilization and Disposal Capacity and Environmental Risk Prevention Capacity of Hazardous Wastes* (Huan Gu Ti [2019] No.92) issued in October 2019, it is proposed that medical waste disposal capacity of cities with districts shall meet the actual needs of the region before the end of 2020, and each county (city) shall have a relatively perfect medical waste collection, transportation and disposal system before the end of June 2022. After the outbreak of COVID-19, the centralized disposal of medical waste has been vigorously promoted. Documents issued during the epidemic period, such as the *Comprehensive Treatment Plan for Waste in Medical Institutions* (Guo Wei Yi Fa [2020] No.3) and the *Implementation Plan for Capacity Building of Centralized Disposal Facilities for Medical Waste* (Fa Gai Huan Zi [2020] No.696), further strengthened the capacity building of medical waste disposal during the 14th Five-Year Plan period: large cities and megacities should have sufficient emergency treatment capacity as soon as possible to strive for standardized disposal of medical waste in rural areas.

In addition, the *Standard for Pollution Control on Medical Waste Treatment and Disposal* will soon be released. The *Technical Specifications for Construction of Centralized Incineration and Disposal Engineering on Medical Waste* (HJ/T 177-2005), *Technical Specifications for Centralized Steam Treatment Engineering on Medical Waste (Trial)* (HJ/T 276-2006), *Technical Specifications for Chemical Disinfection Centralized Treatment Engineering on Medical Waste* (HJ/T 228-2006) and *Technical Specifications for Microwave Disinfection Centralized Treatment Engineering on Medical Waste* (HJ/T 229-2006) are currently being revised. The medical waste management system will be further improved and higher requirements will be put forward for the standardized operation of centralized disposal facilities. According to the requirements of relevant documents and the trend of prevention and control of medical waste pollution, the centralized disposal capacity of medical waste should be further improved during the 14th Five-Year Plan period. At the same time, the collection capacity of medical waste in rural areas should be further strengthened.

Based on the current load of centralized medical waste disposal facilities in the country and the forecast of future medical waste generation, as well as the load rate target of centralized medical waste disposal facilities completed and put into operation no more than 75% by the end of the 14th Five-Year Plan period, prefecture-level cities with centralized medical waste disposal facilities having over 50% load rate need to enhance centralized medical waste disposal capacity, which shall reach twice the medical waste generation volume in 2018 in order to meet the demand for centralized medical waste disposal during the 14th Five-Year Plan period.

4. Main Shortcomings of Centralized Medical Waste Disposal System

4.1 Insufficient centralized disposal capacity in some cities

Since the 12th Five-Year Plan period, China's medical waste generation has increased rapidly, from 336,000 t in 2010 to 980,000 t in 2018. The improvement of medical waste disposal capacity is relatively lagging behind. China's active medical waste disposal facilities are mainly projects under the Plan for the Construction of Facilities, most of which were completed and put into operation before 2010. Most cities have and only have one medical waste disposal facility, and 6 prefecture-level cities have not yet completed centralized medical waste disposal facilities. In 2018, the average load rate of centralized medical waste disposal facilities nationwide reached 76.0%. Specifically, over 1/3 cities had a load rate of more than 90%, 1/5 medical waste disposal facilities were in full or overloaded operation, and the load rate of medical waste disposal facilities in supercities and megacities was generally high. In addition, some centralized disposal facilities are in poor operation and need to be upgraded urgently. The actual disposal capacity may not reach the approved operation scale.

4.2 Improper medical waste disposal in some rural and remote areas

At present, the base figures of generation and disposal of medical waste in rural and remote areas is still unclear. Some medical wastes in rural and remote areas are difficult to be covered by centralized disposal due to scattered sources, small amount of generation and long transportation distance[8]. Simple incineration and other on-site disposal methods are usually adopted, thus posing great environmental risks. The centralized disposal facilities built in some remote areas have not played a good role due to the lack of reasonable layout. For example, the load rate of facilities in Qinghai, Tibet and other provinces is extremely low, at 17.2% and 27.7% respectively. The load rate of facilities in Guoluo, Haixi and Yushu prefectures in Qinghai Province is even lower than 10%, and many facilities in Tibet have not been put into operation for a long time after completion.

4.3 Insufficient capacity reserve for emergent disposal of medical waste

During the COVID-19, the amount of medical waste generated in some cities in China rose rapidly. The daily amount of medical waste generated during the peak period in Wuhan, the city hit by the epidemic most severely, reached 247.3 t, which was 5-6 times that of the normal amount. The amount of medical waste generated in Xiaogan, Huanggang and other surrounding cities also increased 4-5 times compared with that before the outbreak. Due to the overall high load rate of centralized medical waste disposal facilities, the capacity reserve for emergent disposal of centralized disposal facilities is not sufficient. At the same time, the emergency disposal capacity of directly deployable mobile disposal facilities, hazardous waste incineration cooperative disposal facilities, domestic waste incineration cooperative disposal facilities and other medical waste emergency disposal facilities is extremely limited[9-10], resulting in a shortage in emergency disposal of medical waste in some cities. Most of the medical waste disposal capacity increased during the COVID-19 is temporary and contingent, which is far from standard disposal.

4.4 Technical route for centralized medical waste disposal needs to be optimized

The *Plan for the Construction of Facilities* issued in 2004 identified pyrolysis and incineration as the main technical methods for medical waste treatment. The *Technical Specifications for Construction of Centralized Incineration and Disposal Engineering on Medical Waste* (HJ/T 177-2005), *Technical Specifications for Centralized Steam Treatment Engineering on Medical Waste (Trial)* (HJ/T 276-2006), *Technical Specifications for Chemical Disinfection Centralized Treatment Engineering on Medical Waste* (HJ/T 228-2006) and *Technical Specifications for Microwave Disinfection Centralized Treatment Engineering on Medical Waste* (HJ/T 229-2006) and other technical specifications have been issued for more than ten years, which have weakened their guiding role in the selection of centralized disposal technology routes. Some clauses, such as "the scale of high-temperature steam centralized treatment facilities for medical wastes should not be greater than 10 t/d", have even misled local governments in the selection of technologies. Recently, a northern province issued a document requiring each prefecture-level city to build at least one medical waste incineration facility and planning to add more incineration facilities with a scale of less than 10 t/d, which may not meet the dioxin limit requirements. Since the 12th Five-Year Plan period, the environmental protection situation has changed greatly. It is urgent to issue relevant documents to guide the application of technology.

5. Countermeasures and Suggestions for Medical Waste Centralized Disposal During the 14th Five-Year Plan Period

5.1 Improve centralized disposal capacity of medical waste

It is suggested to comprehensively evaluate the disposal capacity of medical waste in existing facilities based the impact of economic, population, transportation, medical and health conditions on the collection and disposal of medical waste. Centralized medical waste disposal capacity shall be built and improved in cities, especially for those with operating load rate of centralized medical waste disposal facilities over 50% in the past three years. Focusing on incineration facilities with a processing capacity of less than 10 t/d and an operation time of more than 10 years, the operation evaluation of centralized medical waste disposal facilities shall be carried out. For incineration facilities that are difficult to stably meet the discharge standards, technical upgrading and transformation shall be conducted or mature and reliable non-incineration alternative technologies shall be adopted.

According to regional distribution and capacity of centralized medical waste disposal facilities, cities shall plan and construct centralized medical waste disposal facilities in the counties (cities) as a whole. During the 14th Five-Year Plan period, the focus shall be on strengthening the construction of county (city) medical waste collection, transportation and disposal systems, further expanding the coverage of the existing systems, and promoting the completion of relatively complete systems at the county (city) level. For counties (cities) with a medical waste collection and disposal capacity of over 5 t/d or with a distance of over 200 kilometers from centralized disposal facilities, centralized disposal facilities for medical waste can be separately constructed. Neighboring counties (cities) can adopt the mode of co-construction and sharing when building centralized medical waste disposal facilities.

5.2 Promote safe disposal of medical waste in rural and remote areas

Medical waste in rural areas will be collected level by level through "small boxes into large boxes" and then disposed of in a centralized way so as to gradually realize full coverage of the collection, transportation and disposal system in rural areas. Temporary storage facilities for medical wastes can be established in remote areas, and measures such as spraying disinfection, refrigeration and sealing can be taken to appropriately extend the storage time. After medical wastes are concentrated step by step, they are uniformly sent to centralized disposal facilities for processing. For remote areas that are difficult to be covered by the collection, transportation and disposal system, small non-incineration treatment facilities can be built or mobile treatment facilities can be equipped for decentralized disposal.

5.3 Accelerate the equipment of medical waste emergency disposal capacity

Cities shall be equipped with adequate emergency disposal capacity for medical waste in line with their size, which shall be at least twice the intensity of medical waste generated per million population during non-epidemic period. Specifically, it is recommended that no less than 10 t/d shall be established per million population. It is also suggested that hazardous waste incineration facilities, domestic waste incineration facilities, cement kiln coordinated disposal facilities and other facilities in the region should be fully utilized for synergy disposal. The provincial government shall establish an overall resource list of emergency medical waste disposal facilities. The cooperative emergency disposal facilities included in the list shall be provided with special unloading areas, special loading equipment, cleaning and disinfection equipment, etc.

5.4 Improve the technical route of medical waste disposal

It is suggested to issue technical standards for mobile and small medical waste disposal facilities. Relevant technical guidelines shall be formulated and issued on the premise of technical applicability, cost-effectiveness, international compliance and other requirements, which shall propose technical selection principles for facilities with different disposal scales, and standardize and define the calculation method for the scale of centralized medical waste disposal facilities. For Beijing-Tianjin-Hebei, Fenwei Plain and other key air pollution prevention and control areas, it is recommended that newly built facilities to adopt non-incineration treatment technology, and centralized disposal facilities and domestic waste incineration facilities should be planned and constructed in a coordinated way.

6. Conclusion

a) It is estimated that by the end of the 14th Five-Year Plan period, nationwide medical waste generation will reach about 1.5 million t/a. With the release of medical waste management policy documents, higher requirements will be put forward for the safe disposal of medical waste.

b) Current centralized medical waste disposal system still face many shortcomings, and the existing centralized medical waste disposal capacity cannot meet the disposal needs during the 14th Five-Year Plan period. Therefore, it is urgent to overcome the shortcomings.

c) It is suggested to focus on key areas, specifically, constructing centralized medical waste disposal facilities in cities with no disposal capacity, enhancing the capacity of disposal facilities with an operating load rate of over 50%, strengthening the collection, transportation and disposal systems in rural and remote areas, and equipping the emergency disposal capacity of medical waste at a standard of not less than 10 t/d per million people as suggested and improving the disposal technology route, so as to comprehensively promote centralized medical waste disposal system during the 14th Five-Year Plan period.

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Management of waste containing persistent organic pollutants in China: current practices and findings

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Abstract

This study presents an overall analysis of current practices of the management of waste containing persistent organic pollutants in China. Data were collected from China's National Implementation Plan for the Stockholm Convention on Persistent Organic Pollutants, national report, information submitted to the Stockholm Convention Secretariat, and evaluation reports from some GEF-funded projects. The findings indicated that great progress has been made in the disposal of waste containing the initial 12 POPs. The study also found challenges in terms of waste containing new POPs and a need to address regulatory and information gaps for the management of POPs waste.

Keywords: Persistent organic pollutants, hazardous waste, Stockholm Convention

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Introduction

The Stockholm Convention on Persistent Organic Pollutants (hereinafter referred to as the Stockholm Convention) entered into force for China on November 11, 2004[1]. Besides the initial 12 POPs listed in the Stockholm Convention, there are 11 new POPs also entered into force for China[2,3]. China is one of the largest chemical producers in the world as well as one of the largest waste generators. Waste containing persistent organic pollutants (POPs) is of special concern since POPs persist in the environment, bioaccumulate through food chain, have the potential for long-range environmental transport, and pose risks to human health and the environment. As a party to the Stockholm Convention, China is obliged to take measures to reduce or eliminate release from waste containing POPs. An analysis of current practices and gaps in terms of the management of waste containing POPs in China was conducted. Data were collected from China's National Implementation Plan for the Stockholm Convention, national report, information submitted to the Stockholm Convention Secretariat, and evaluation reports from some GEF-funded projects. This study aims to facilitate the effective implementation of China's obligation under the Stockholm Convention.

Status of waste containing POPs in China

The initial 12 POPs

2.1.1. Pesticide POPs waste

Among the initial 12 POPs, there are 7 pesticide POPs, i.e. aldrin, chlordane, dieldrin, endrin, heptachlor, hexachlorobenzene (HCB), mirex, toxaphene, and DDT. According to China's National Implementation Plan (NIP) for the Stockholm Convention on Persistent Organic Pollutants, the production and use of toxaphene and heptachlor were completely stopped in the 1970's, and large-scale production of dieldrin, endrin and aldrin has never been started, so identified pesticide POPs waste was mainly waste containing DDT, chlordane, mirex and HCB, and the investigation conducted showed that the total quantity of pesticide POPs waste in China was

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estimated to be 4,000 to 6,000 tons, with 2,600-4,500 tons of DDT and 1,500 tons of HCB, chlordane and mirex in total[4].

2.1.2. Waste containing polychlorinated biphenyls (PCBs)

The production of PCBs oils started in 1965 in China and was gradually stopped from 1974 to the 1980's, and the total production was about 7,000 to 10,000 tons; the total amount of high-density (>500 ppm) PCBs waste in china was estimated to be approximately 50,000 tons (including crushed waste capacitors), and the total amount of low-density (50-500 ppm) waste estimated to be 500,000 tons[4].

2.1.3. Waste containing dioxins

Waste containing dioxins in China include ash, residue and slurry produced in the process of production, which mainly come from processes of waste incineration, metal smelting, chemical production, outdoor incineration, etc. In 2004, the amount of dioxins released in China to the environment through waste was 4,978.7g TEQ[4].

The new POPs

Out of the 11 new POPs entered into force for China, according to the national report[5], China has no history of manufacture of chlordecone, hexabromobiphenyl, hexabromodiphenyl ether and heptabromodiphenyl ether, pentachlorobenzene; the production of alpha hexachlorocyclohexane, beta hexachlorocyclohexane, lindane, tetrabromodiphenyl ether and pentabromodiphenyl ether, endosulfan have already ended in China; perfluorooctane sulfonic acid, its salts and perfluorooctane sulfonyl fluoride (PFOS/PFOSF) and hexabromocyclododecane (HBCD) are currently still being produced. The estimated total production of lindane, endosulfan, tetrabromodiphenyl ether and pentabromodiphenyl ether is shown in table 1. China began large-scale production of PFOS in 2003, before 2004, total production was less than 50 tons, from 2005 on while production in developed countries was restricted, China's annual output has grown rapidly; and the statistics showed that more than 200 tons of PFOSF was produced in 2006, about 100 tons of which was for export[6]. The production of HBCD in 2011 was more than18,000 tons, with 5,500 to 6,000 tons for export[7]. In order to fulfill the obligation in terms of waste containing new POPs, the National Implementation Plan (Enlarged Edition) requires to carry out research on environmental management of new POPs waste[8].

Table 1. The estimated total production of lindane, endosulfan, tetrabromodiphenyl ether and pentabromodiphenyl ether

10. Chemicals	11. Estimated total production (*kg*)
12. Lindane	13. 20,000,000
14. Technical endosulfan and its related isomers	15. 9,000,000
16. Tetrabromodiphenyl ether and pentabromodiphenyl ether	17. 800,000

* Data source: China's National Report[4].

Regulatory framework of waste containing POPs

POPs waste is managed as hazardous waste in China. The concentration limits for waste containing the initial 12 POPs, lindane, chlordecone and endosulfan were set up in the Identification Standards for Hazardous Waste—Identification for Toxic Substance Content (GB5085.6—2007)[9], the detailed limits are shown in Table 2. Waste exceeding such concentration limits should be identified as hazardous waste.

Table 2: Concentration limits referred to in GB 5085.6—2007

The initial 12 POPs	**Concentration limits referred to in GB5085.6—2007**
aldrin	50mg/kg
chlordane	50mg/kg
DDT	50mg/kg
dieldrin	50mg/kg

The initial 12 POPs	Concentration limits referred to in GB5085.6—2007
endrin	50mg/kg
heptachlor	50mg/kg
hexachlorobenzene	50mg/kg
mirex	50mg/kg
toxaphene	50mg/kg
PCBs	50mg/kg
polychlorinated dibenzo-p-dioxins (PCDD)	PCDD/PCDF 15ug TEQ/kg
polychlorinated dibenzofurans (PCDF)	
The new POPs	**Concentration limits referred to in GB5085.6—2007**
Alpha hexachlorocyclohexane	/
Beta hexachlorocyclohexane	/
Lindane	≥ 3%
Chlordecone	≥ 3%
Hexabromobiphenyl	/
Hexabromodiphenyl ether and heptabromodiphenyl ether	/
Tetrabromodiphenyl ether and pentabromodiphenyl ether	/
Pentachlorobenzene	/
PFOS/PFOSF	/
Technical endosulfan and its related isomers	≥ 3%
HBCD	/

There are no special laws on POPs waste management in China. So the management requirements of POPs waste are usually integrated into laws and regulations on hazardous waste management. A summary of laws, regulations and technical standards of hazardous waste management is as follows.

Table 3: Laws, regulations and technical standards of hazardous waste

Name	Latest edition	Contents related to POPs waste
Law on the Prevention and Control of Environmental Pollution Caused by Solid Waste	2020	/
Interpretation of the Supreme People's Court and the Supreme People's Procuratorate on Several Issues concerning the Application of Law in the Handling of Criminal Cases of Environmental Pollution	2016	/
National Catalogue of Hazardous Waste	2016	Pesticide waste including pesticide POPs waste is listed in Category 4, waste containing PCBs and polybrominated biphenyl (PBB) in Category 10.
Regulation on the Prevention of Environmental Pollution from Electrical Equipment Containing PCBs and their Waste	1991	Management requirements of electrical equipment containing PCBs and PCBs waste are stipulated.
Measures on the Management of Duplicated Form for Transfer of Hazardous Waste	1999	/
Principles for the Environmental Impact Assessment Technology on Hazardous Waste and Medical Waste Treatment Facility Construction Project (On Trial)	2004	/
The National Program of Disposal Facilities Construction for Hazardous Waste and Medical Waste Treatment	2004	/
Measures for the Prevention and Control of Environmental Pollution Of Electrical and Electronic Waste	2007	/
Identification Standards for Hazardous Waste General Rules (GB5085.7—2019)	2019	/

Name	Latest edition	Contents related to POPs waste
Identification Standards for Hazardous Waste ● Identification for Corrosivity (GB 5085.1—2007) ● Screening Test for Acute Toxicity (GB 5085.2—2007) ● Identification for Extraction Toxicity (GB 5085.3—2007) ● Identification for Ignitability (GB 5085.4— 2007) ● Identification for Reactivity (GB 5085.5— 2007) ● Identification for Toxic Substance Content (GB5085.6—2007)	2007	GB5085.3—2007 sets up concentration limits for some pesticide POPs and PCBs in leachate. GB5085.6—2007 sets up concentration limits for waste containing the 12 initial POPs.
Technical Specifications on Identification for Hazardous Waste (HJ298—2019)	2019	/
Technical Policy on the Pollution Prevention and Control Technologies of Hazardous Waste	2001	Special requirements for the disposal of waste containing PCBs and fly ash from combustion of municipal waste are highlighted.
Technical Policy on the Pollution Prevention and Control of Waste Household Appliances and Electronic Products	2006	Cables and plastic cases with PBB and polybrominated diphenyl ether (PBDE) should be separately dismantled.
Standard for Pollution Control on Hazardous Waste Storage (GB18597—2001)	2013	/
Standard for Pollution Control on the Hazardous Waste Landfill (GB18598—2019)	2019	/
Pollution control standard for hazardous wastes incineration (GB18484-2001)	2001	Pollution control requirements for incineration of POPs waste and waste containing PCBs are specified.
Standard for Pollution Control on Co-Processing of Solid Waste in Cement Kiln (GB30485-2013)	2013	/
Standard for Pollution Control on PCBs-Contaminated Waste (GB13015—2017)	2017	Technical requirements for environmentally sound management and disposal of waste containing PCBs, monitoring, etc. are stipulated.
Technical Specifications for the Supervision and Management to the Operation of Centralized Incineration Disposal Facilities for Hazardous Waste (On Trial) (HJ515—2009)	2009	Ash from combustion containing PCDD/PCDF is required to be safely landfilled.
Technical Specification of Performance Testing for Facilities of Hazardous Waste (Including Medical Waste) Incineration (HJ561-2010)	2010	/
Technical Specifications of Pollution Control for Processing Waste Electrical and Electronic Equipment (HJ 527—2010)	2010	Plastics and cables containing PBB and PBDE should be disposed separately, and when they can’t be reused or recycled, they should be disposed of as hazardous waste. Capacitors containing PCBs should be treated as hazardous waste.
Technical Specifications for Collection, Storage, Transportation of Hazardous Waste (HJ2025-2012)	2012	/
Environmental Protection Technical Specification for Co-Processing of Solid Wastes in Cement Kiln (HJ 662-2013)	2013	Special requirements for POPs waste are included.
Technical Specification for Co-Processing of Solid Waste in Cement Kiln (GB30760—2014)	2014	/

Hazardous waste is defined as solid waste listed in the National Catalogue of Hazardous Waste, or solid waste with hazardous characteristics identified in accordance with the state-stipulated hazardous waste identification standards and methods[10]. The Law of the PRC on Prevention and Control of Environmental Pollution Caused by Solid Waste established rules for the state’s hazardous waste management system. Pursuant to this law, the National

Catalogue of Hazardous Waste should be established and periodically updated; generators of hazardous waste should make hazardous waste management plans, and report to local competent authorities; distinguishing labels on hazardous waste containers, packagings as well as facilities and sites related to hazardous waste collection, storage, transport and treatment are required; the units engaged in collection, storage and treatment of hazardous waste should obtain a permit for such undertakings; transportation of hazardous waste is implemented with the use of hazardous waste manifest; preventive measures for accidents and emergency plans are required; transfer of hazardous waste via the territory of the PRC is prohibited. Those also apply to the management of waste containing POPs. Collection, storage, packaging, labelling, transportation, disposal of waste containing POPs should also comply with the requirements of other laws, regulations and technical standards listed in Table 3.

Progress in the disposal of the waste containing POPs

Pesticide POPs waste

Activities in terms of pesticide waste disposal were carried out in several Global Environment Facility (GEF) funded projects to help China fulfill its commitment under the Stockholm Convention. The GEF project "Demonstration of Alternatives to Chlordane and Mirex in Termite Control" selected two sites for contaminated site cleanup and 6,946m^3 contaminated soil, 550m^2 contaminated buildings inner surface, 398m^2 contaminated buildings and 6.4 tons of hazardous waste were cleaned up and/or disposed[11]. Under the GEF project "Improvement of DDT-Based Production of Dicofol and Introduction of Alternative Technologies Including IPM for Leaf Mites Control in China", 54 truckloads containing 1,600 tons of high risk DDT waste were soundly disposed, and the project achieved the elimination of the consumption of 2,800 MT/a of DDT use as intermediate in dicofol production, 1,000 MT/a DDT discharge with waste and 170 MT/a DDT residues in dicofol consumption[12]. The GEF project "Environmentally Sound Management and Disposal of Obsolete POPs Pesticides and other POPs Wastes" disposed 6,352 tons of pesticide POPs, mainly DDT and hexachlorocyclohexane (HCH), which covered all the POPs pesticide identified in China during the project implementation (2009-2018); meanwhile, 42,000 tons of soils contaminated by DDT/HCH were also soundly disposed under the project[13].

Waste containing PCBs

The GEF project "PCB Management and Disposal Demonstration" implemented from 2006 to 2012 helped to dispose 11,428 tons of low- and 1,040.5 tons of high-concentration PCB waste in 13 provinces in China using thermal desorption and incineration technologies[14]. Besides this project, China is continuously working on the environmentally sound disposal of waste containing PCBs, the data in the national report showed that a total of 5611.034 tons were disposed[5].

Table 4: Numbers of quantity of waste containing PCBs from the National Report[5]

Year	Total quantity of disposal (t)
Before 2001	835.589
2001	156.406
2002	52.527
2009	754.87
2010	215.6
2011	485.8
2012	699.58
2013	1159.55
2014	250.82
2015	222.34
2016	148.152
2017	629.8
Total	5611.034

Waste containing dioxins

There are few data of the quantity of waste containing dioxins disposed in China. The GEF project "Environmentally Sound Management and Disposal of Obsolete POPs Pesticides and Other POPs in China" conducted disposal of fly ash, and the independent terminal evaluation report of the project showed that a total of 80,000 tons of fly ash were disposed of by cement co-processing technology and high temperature sintering technology with 106.9 g TEQ PCDD/PCDF was destructed [13].

E-waste

Recycling, dismantling, treatment and disposal process of waste electrical and electronic equipment might involve the release of POPs like PBB, PBDE and heavy metals classed as persistent toxic substances (PTS), notably mercury, lead and cadmium. The GEF project "Reduction of POPs and PTS Release by Environmentally Sound Management throughout the Life Cycle of Electrical and Electronic Equipment and Associated Wastes in China" (hereinafter referred to as the "e-waste project") still under implementation will help China to address e-waste issues. Mid-term review shows that more than 173,000 tons of plastics containing brominated flame retardant were processed, avoiding the emission of a total of 277 kg of PBDE[15]. This number will be definitely increased by the completion of this project.

Findings

Great progress achieved in the disposal of waste containing the initial 12 POPs

By 2018, all the identified waste containing pesticide POPs was disposed of[13]. Great progress has also been made in the disposal of waste containing PCBs and dioxins. And efforts to reduce POPs and PTS from e-waste are expected to yield good result. The NIP (Enlarged Edition) indicated that over 50,000 tons of legacy waste containing POPs has been disposed of in China[8]. It can be affirmed that this number is underestimated based on this study. Excluding the achievement from the e-waste project that is still being implemented, the total quantity of waste containing POPs disposed of by other GEF projects mentioned above plus the quantity from the national report have already exceeded 100,000 tons.

Challenges encountered in terms of waste containing new POPs

Despite of the great progress made in the disposal of waste containing the initial POPs, there is still a lot of work to be done with the waste containing new POPs. The production and use of lindane, endosulfan and PFOS/PFOSF (except for the acceptable purposes) have been banned very recently from March 26, 2019[16]. And China aims to phase out the production and use of HBCD from December 26, 2021[8]. All of those chemicals will end up in the waste flow. Industrial chemicals like PFOS/PFOSF and HBCD were or are still commonly used as additives in many fields. Products and articles containing these new POPs are very hard to be tracked. Stockpiles of pesticide containing new POPs also need to be identified, managed and disposed of as waste since they are no longer allowed to be used. So it is necessary to develop, in a timely manner, appropriate strategies for identifying stockpiles, products, articles in use and waste containing the new POPs, and take measures to prevent and control risks posed by waste containing the new POPs. It is also needed to carry out evaluation on the feasibility and efficiency of disposal technologies for waste containing new POPs.

Regulatory gaps

The management of the waste containing POPs is integrated into the system of hazardous waste management in China. However, only a few types of POPs waste were listed in the National Catalogue of Hazardous Waste. The concentration limits for the new POPs are still needed to be set up or updated. And there is a lack of detection standards for some new POPs, for example, HBCD, PBDE, and PFOS/PFOSF. It might be better to take and list waste containing POPs as a special category in the National Catalogue of Hazardous Waste. And when China ratify new POPs amendments to the Stockholm Convention, regulations and technical standards in terms of hazardous waste should also be updated or developed to incorporate relevant management requirements for waste containing new POPs. Meanwhile, requirements of the *General Technical Guidelines on the Environmentally Sound Management of Wastes Consisting of, Containing or Contaminated with POPs* and other specific POPs waste technical guidelines under the Basel Convention on the Control of Transboundary Movements of Hazardous Wastes and their Disposal should also be taken into account in domestic regulations and national standards.

Information gaps

The information on new POPs is incomplete. The total production and use of some industrial chemicals and how much of them ending up in waste are not known yet. The NIP also highlighted the information gap on electrical equipment containing PCBs and their waste. In the 1980s, China began to seal or temporarily seal electrical equipment containing PCBs and their waste, however, due to improper management most information on such sealing has been lost[4]. And it is also not very clear that how much waste containing dioxins generated and were safely disposed or landfilled, because the sources of such waste are various and complicated. In order to address the information gaps, it is necessary to establish proper inventories for waste containing POPs.

Conclusion

Although great progress has been made in the disposal of waste containing some POPs, China, as one of the largest chemical producers and waste generators, are still facing great challenges posed by waste containing new POPs. Regulatory and information gaps have been found in terms of the management of waste containing POPs. Regulations and technical standards should be improved; the concentration limits for waste containing new POPs should be updated or developed. There is also an acute need to carry out assessment of the production, use of the new POPs, to identify stockpiles, products, article in use, and to develop inventories for waste containing these chemicals. Environmentally sound treatment and disposal technologies should also be encouraged and developed. In addition, public awareness activities for governments, chemical producers, the downstream enterprises using these chemicals, waste disposal entities, and workers engaging in the production, sale, and consumption of POPs are also needed to increase awareness on these waste issues.

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Sustainable metal recovery from waste streams in municipal solid waste incineration (MSWI) fly ash in different seasons in Beijing

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Abstract: In this paper, the fly ash from the annual municipal solid waste incineration (MSWI) in Beijing is taken as the research object. The metal content, toxic leaching concentration, bioavailability and chemical morphology of MSWI fly ash were investigated. The results showed that MSWI fly ash is a kind of hazardous waste with high solubility, strong alkalinity and high pollution. A large number of elements in MSWI fly ash are Ca, Cl, Si, S, Na and K, accounting for more than 80.00wt%. The average content of heavy metals in MSWI fly ash is Zn>Pb>Ba>Cu>Cr>Cd>Ni. In the TCLP system, all heavy metals were within the leaching toxicity range. In the GB50853-2007 system, only the leaching concentration of Pb exceeded the threshold. The bioavailability concentration of heavy metals in MSWI fly ash is Pb>Ba>Zn>Cd>Cu>Cr>As>Ni. Under acidic conditions, the metal leaching increased significantly, and the leaching concentration reached its maximum at pH=2. The improved BCR stepwise extraction method showed that Cr, Ni and As were the most stable, Pb, Cu and Ba were relatively stable, and Cd and Zn were relatively unstable and the leaching environment was the easiest. This study effectively and accurately evaluates the risk of heavy metals in MSWI fly ash, which provides an important basis for the harmless and resource-based of MSWI fly ash.

Keywords: MSWI fly ash; Heavy metals; Pollution characteristics; Bioavailability; BCR

1.Introduction

Fly ash is the by-product of municipal solid waste incineration（MSWI）, which accounts for about 3-5% of the total waste residue(Lu et al. 2017, Quina et al. 2018, Silva et al. 2017, Zhang et al. 2020b, Zhu et al. 2019). More than 100 years ago, European countries began to use incineration technology to treat municipal solid waste(MSW)(Zhao et al. 2002). According to statistics, the world burns 130 million tons of MSW every year (Liu et al. 2019). Calculations show that the world produces 40 million tons of MSWI fly ash every year. China produces about 4 million tons of fly ash from MWSI each year, accounting for one tenth of the global production of MSWI fly ash(Zhang et al. 2020a). The MSWI fly ash contains a large amount of toxic heavy metals(Pb, Zn, Cd, Ni, etc.) and dioxins, and is recognized as hazardous waste by China's environmental protection agency(Huang et al. 2011, Huawei et al. 2018, Xie et al. 2020, Xiong et al. 2014). Some toxic heavy metals in MSWI fly ash, such as Pb, Cd, and Zn, are easily deposited to the surface and, if not handled properly, they can seep into groundwater, which can pose major hazards to the environment and human health(Wang et al. 2015a). If MSWI fly ash is directly discharged into the air, it will adhere to the surface of atmospheric aerosol, or enrich in the soil cause more serious pollution(Yao et al. 2020). Therefore, it is very necessary to evaluate the pollution characteristics of heavy metals in MSWI fly ash.

At present, the treatment methods of MSWI fly ash mainly include washing(Chiang and Hu 2010), heat treatment(Islam and Park 2017), acid extraction, vitrification, sintering and solidification/stabilization (S/S)(Kan et al. 2020). S/S is one of the internationally recognized methods to treat MSWI fly ash(Yakubu et al. 2018). Cement is the most commonly used stabilizer in developed countries such as Europe and America (Bie et al. 2015). In China, the most commonly used method for treating MSWI fly ash is also chemical stabilization/fixation (Vavva et al. 2017). A variety of chemicals, including phosphates, silicates and chelators, have been successfully used to stabilize MSWI fly ash(Huawei et al. 2018). Heavy metals are a key indicator in the disposal of household waste(Zhang et al. 2018). The type, quantity and leaching amount of heavy metals in MSWI fly ash will affect its S/S process(Zhou et al. 2015). Hence, it is essential to study the pollution characteristics of heavy metals in MSWI fly ash, which can not only enable us to better understand the physical and chemical properties of MSWI fly ash, but also provide a theoretical basis for the selection of subsequent MSWI fly ash treatment methods.

So far, many scholars have analyzed the characteristics of heavy metals in MSWI fly ash. However, only one or several aspects have been studied, and no scholars have carried out a comprehensive and systematic study on the characteristics of heavy metals in MSWI fly ash. Long(Long et al. 2011) pointed out that the main sources of heavy metals in MSW are kitchen waste, ash, plastic, paper. Zhou(Zhou et al. 2015) studied the morphological characteristics, mineral characteristics, heavy metal content and types of MSWI fly ash with different particle sizes and pointed out that Zn, Pb, Cu and Cr are easy to gather in small particles. Zhao(Zhao et al. 2002) showed that the content of heavy metals is related to the composition of the incinerated waste and the melting and boiling point of the heavy metals themselves. Liu(Liu et al. 2019) showed that the increase of soluble chlorine in MSWI fly ash solution and the decrease of pH value could stimulate the leaching potential of heavy metals. Yahaya(Yakubu et al. 2018) also reached the same conclusion that compared with the extremely alkaline condition, the extremely acidic condition is more conducive to the leaching of heavy metals. Jiao(Jiao et al. 2016a) pointed out that the type of heavy metals in MSWI fly ash and pH influence the leaching behavior, and the leaching mechanism of heavy metals was further studied. Zhang's experiment proved that after the heavy metals in fly ash were stabilized with a certain concentration of additives, the leaching risk in acid and alkali environment could be reduced and the stabilization time increased(Zhang et al. 2020b) . Generally speaking, t there are many studies on the effect of pH on leaching behavior, few on the chemical morphology of heavy metals, and almost no analysis on the bioavailability of heavy metals. The pollution characteristics of heavy metals in fly ash from MSWI in different seasons have not been studied. By studying the characteristics of heavy metal pollution in MSWI fly ash in different seasons in Beijing, this paper provides experimental and data support for the environmental risk assessment of MSWI fly ash in the future, and provides help for the subsequent harmless or resource-based MSWI fly ash.

The main research contents are as follows: (1)the total amount, toxic leaching and chemical forms of heavy metals in the external environment; (2)the reaction of different chemical forms of heavy metals with biofilm to form corresponding toxicity. Different experimental schemes at home and abroad were adopted, such as total amount of heavy metals (microwave digestion ICP-OES Method), leaching toxicity {sulfuric acid nitric acid method (HJ/T 299-2007), TCLP method}, chemical form (improved BCR step-by-step extraction method), pH correlation (sulfuric acid nitric acid method) and bioavailability experiment.

2.Materials and Methods

2.1.Materials

Representative MSWI fly ash samples from a waste incineration power plant in Beijing were used in the experiment. The waste incineration power plant usually adopts the domestic mainstream incineration technology and flue gas purification process. And these treatment objects are mainly from the main urban area of Beijing and the nearby districts and counties. MSWI fly ash samples were collected in spring (March to May), summer (June to August), autumn (September to November) and winter (December to February) at a rate of 5kg once a month. And 12 groups of samples were collected throughout the year. 12 groups of MSWI fly ash samples were evenly mixed and dried at 80°C to constant weight. Then, the obtained samples were stored in a self-sealing bag and keep in a dry and cool place for use. The obtained MSWI fly ash samples are light gray, with small particle size and uniform texture. In this study, all the chemical reagents (HNO_3, HCI, HF, H_2SO_4, CH_3COOH, NaOH, NH_4SCN, $NH_4Fe(SO_4)_2 \cdot 12H_2O$, $AgNO_3$, $C_{15}H_{15}N_3O_2$, $NH_3 \cdot H_2O$, CH_3COONH_4, $HONH_2HCl$, H_2O_2, EDTA-Na_2) were analytical grade expect special requirements. Deionized water was provided by the Water Purification System (Advantage A10, Millipore, Burlington, MA, USA), and all experiments were carried out at room temperature.

2.2 Element content analysis

Refer to "The Technical Specification for soil Environmental monitoring" (HJ/T 166-2004)(Tian et al. 2020). First, 0.2000g of dried MSWI fly ash was weighed and put into the digestive tube. 6mL HNO_3 (69%), 2mL HCI (72%), and 2mL HF(48%) were added to the digestive tube. After mixed, the digester was placed in a Multiwave PRO for digestion(Anton Paar, Graz, Austria) . Next, these samples were cooled and filtered. In the filtrate, the heavy metals such as Pb, Cu, Zn, Cd, Cr, Ni, As, and Ba were determined by ICP-OES (Optima 8300, PerkinElmer, USA).

2.3 Leaching toxicity of MSWI fly ash

(1) Toxic leaching of solid waste sulfuric acid nitric acid method

Refer to "Solid Waste—Extraction procedure for leaching toxicity —Sulfuric acid＆nitric acid method" (HJ/T299-2007)(Wang et al. 2015a). 100.00g MSWI fly ash sample was weighed and put into 2L extraction bottle. Then the extraction agent was prepared according to the water content, acidity and alkalinity of MSWI fly ash sample. Meanwhile, 1L ultrapure water was weighed and put into 2L beaker. In order to make the pH 3.20±0.05, the mixed acid was added into the beaker (mixed acids are mixtures of concentrated H_2SO_4 and concentrated HNO_4 with a mass ratio of 2:1). The extractant agent was poured into the extractor bottle according to the solid-liquid ratio of 10:1 (kg/L), and the extractor bottle was fixed to a tilting oscillating device, which was oscillated at room temperature for 18±2h, with the tilting speed of 30±2r/min. And the obtained samples were filtered by 0.45μm microporous membrane. Finally, the contents of Pb, Cu, Zn, Cd, Cr, Ni, As and Ba were measured by ICP-OES.

(2)Toxic leaching of solid waste-TCLP

Referring to the standard "Toxicity Characteristic Leaching Procedure"(TCLP) recommended by the US environmental protection agency(Tian et al. 2020). 75.00g MSWI fly ash sample was weighed and put into 2L extraction bottle. The extraction agent was prepared according to the water content, the acidity and alkalinity of MSWI fly ash sample. 1.5L ultrapure water and 5.7mL acetic acid was added to 2L beaker. In order to make the pH 2.88±0.05, the HNO_3 or NaOH was added into the beaker. The extractant agent was poured into the extractor bottle according to the solid-liquid ratio of 20:1 (kg/L), and the extractor bottle was fixed to a tilting oscillating device, which was oscillated at room temperature for 18±2h, with the tilting speed of 30±2r/min. And the obtained samples were filtered by 0.45μm microporous membrane. Finally, the contents of Pb, Cu, Zn, Cd, Cr, Ni, As and Ba were measured by ICP-OES.

2.4 Effect of pH value on the toxic concentration of heavy metal leaching

Refer to "Solid waste—Extraction procedure for leaching toxicity —Sulfuric acid & nitric acid method" (HJ/T299-2007)(Wang et al. 2015a). HNO_3 or NaOH was used to adjust the initial pH value of the extractant to keep the pH value at 2, 4, 6, 8, 10 and 12, respectively. 4.0000g MSWI fly ash sample was added to the 50mL centrifugal tube. 40mL of the prepared extract agent was also added to the centrifuge tube. After the lid was tightened, the centrifugal tube was fixed on the tilting oscillating device, and oscillating at a speed of 30±2r/min for 18±2h at room temperature. And the obtained samples were filtered by 0.45μm microporous membrane. Finally, the contents of Pb, Cu, Zn, Cd, Cr, Ni, As and Ba were measured by ICP-OES.

2.5 Sequential Extraction Procedure

The improved BCR stepwise extraction method was used to extract heavy metals in MSWI fly ash with different chemical forms (acid soluble state, reducible state, oxidizable state and residue state) in order to minimize their interaction(Tian et al. 2020). (1)Acid-Soluble: 1.0000 g of fly ash sample was weighed and placed in a 50ml centrifuge tube, and the 40ml of 0.11mol/L CH_3COOH was added to it. Then the centrifuge tube was shaken for 16h, and centrifuged for 20min (4000r/min). The supernatant was filtered with 0.45μm microporous membrane and stored for testing. Added 25ml ultrapure water to the centrifuge tube to wash the residual residue, shaken for 20min, centrifuged for 20min, and the liquid supernatant was abandoned. (2)Reducible: 40mL 0.5mol/L $HONH_2HCl$ was added to the remaining residue of the previous step, which was oscillated at room temperature for 16h, and the remaining operation was the same as the previous step. (3)Oxidizable: 10ml of 30% H_2O_2 was added to the remaining residue of the previous step, which was digested at room temperature for 1h and occasionally shaken. Then put the centrifuge tube into a water bath at 80°C for digestion for 1h, take off the bottle cap, and digested until the liquid in the centrifuge tube was less than 3ml. Add 10ml of 30% H_2O_2 to continue digestion until the liquid in the centrifuge tube was nearly dry. Added 50ml of ammonium carbonate solution into the residue centrifuge tube filled with wet cooling, shaken at room temperature for 16h, centrifuged and filtered. (4)Residual: After the residue in the previous step was dried, weighed 0.1000 g and put it into the digestion tube for digestion and constant volume. Each solution was filtered with a 0.45μm membrane, the contents of Pb, Cu, Zn, Cd, Cr, Ni, As and Ba were measured by ICP-OES.

2.6 Analytic methods

The main chemical components of MSWI fly ash were quantitatively analyzed by the X-ray fluorescence spectrometer (XRF, UltimaIV, Rigaku, Tokyo, Japan). X-ray diffraction spectrometer was used to analyze the phase of the sample (XRD, Axios MAX, PANalytical B.V., Almelo, Netherlands). Scanning electron microscopy was used to observe the microstructure of the samples (FESEM, S-3400N, HITACHI, Tokyo, Japan). The samples were also analyzed by thermogravimetry (TGA, Q500, America). The ion concentration of MSWI fly ash was quantitatively analyzed by inductively coupled plasma mass spectrometer (ICP-OES, Optima 8300, PerkinElmer, USA). The solution pH was measured using ultra-trace sample volume-type pH electrode (FiveEasy Plus, Shanghai, China).

3 Results and discussions

3.1 Characteristics of MSWI Fly Ash

Table 1 shows the chemical composition of metal oxides or their element states in MSWI fly ash. The content of Cl and S is 27.35wt%, and the content of perchloride and sulfate makes the MSWI fly ash unsuitable for use in cement and concrete industry, which must be pretreated before resource recovery(Yakubu et al. 2018). In order to reduce the emission of acid gas (SO_2, HCl.), the excessive lime slurry was injected into the flue gas, resulting in high CaO content (39.18wt.%) in MSWI fly ash(Jiao et al. 2016a). The high content of Cl (18.38wt.%) in MSWI fly ash comes from the incineration of plastics and kitchen garbage(Zhao et al. 2020).

Table 1. Chemical composition of MSWI fly ash by XRF (wt.%)

Compound	CaO	Cl	SiO_2	SO_3	Na_2O	K_2O	Al_2O_3	MgO	Fe_2O_3	other
Original Sample	39.18	18.38	10.02	8.97	5.99	4.47	3.81	3.75	2.11	3.32

As seen from the XRD spectrum of the MSWI fly ash in Figure 1a, the main crystalline phases are $CaSO_4$, $CaCO_3$, SiO_2, NaCl, KCl, CaClOH. It is the same as other literature(Wongsa et al. 2017, Zhou et al. 2015). CaCl could not be found in the MSWI fly ash sample, which may have reacted with SiO_2 (Assi et al. 2020). CaSO4, NaCl, and KCl mainly come from the burning of fabric filter bags(Ma et al. 2017). The high content of KCl and NaCl is due to their low boiling point, which is easy to volatilize into MSWI fly ash during incineration(PÖYKIÖ et al. 2016). CaClOH is a by-product of the desulfurization process(Ma et al. 2017). The crystalline phase of heavy metals is not detected, which may be due to the low content of heavy metals in MSWI fly ash, the presence of most complex compounds or amorphous phases embedded in aluminosilicates or silicates. The crystal phase structure is too small to be detected by XRD(Xiong et al. 2014).

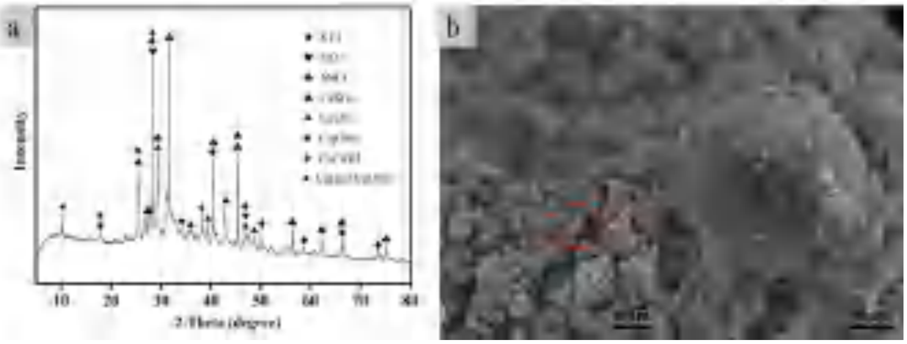

Fig 1. a) XRD patterns of MSWI fly ash and b) SEM images of MSWI fly ash

The particles that make up MSWI fly ash are very small, and the smallest particle size and quantity will cause great harm to the environment. Thus, it is necessary to observe the microstructure of MSWI fly ash. As can be seen from Figure 1b, the surface of MSWI fly ash particles is rough and the whole is relatively loose. The particle size and shape distribution of MSWI fly ash particles are uneven, with large spacing between particles and high porosity, which makes volatile heavy metals easy to accumulate on the MSWI fly ash specific surface and easy to leach, causing environmental pollution (Gong et al. 2017). The irregular spherical magnification shows that the surface is not smooth, and more and smaller particles are attached to the surface, indicating the complex structure of MSWI fly ash.

As shown in Fig 2, the thermogravimetric experiment on the raw MSWI fly ash was carried out to obtain its thermal stability characteristics. It could be seen that the TG curve of fly ash mainly has four weight-loss intervals (1-2, 2-3, 3-4 and 4-5). The first weight loss (1-2) of 3.75% in the temperature range from 35°C to 250°C was ascribed to the loss of free water and organic matter in fly ash. The weight loss (2-3) of 2.35% in the range of 250-

600°C was caused by caused by the removal of crystal water from fly ash and the decomposition of $Ca(OH)_2$. Compared whit the previous (1-2), the decline speed (2-3) is significantly slower. With the quality decreasing sharply, the weight loss (3-4) of 4.27% intherangeof 600-700°C was attributed to the SO_2 emission caused by $CaSO_4$ decomposition, the decomposition of $CaCO_3$ and some chlorides . The fourth weight loss (4-5) of 8.5% in the range of 700-900°C was mainly caused by the chloride in MSWI fly ash continued to decompose.

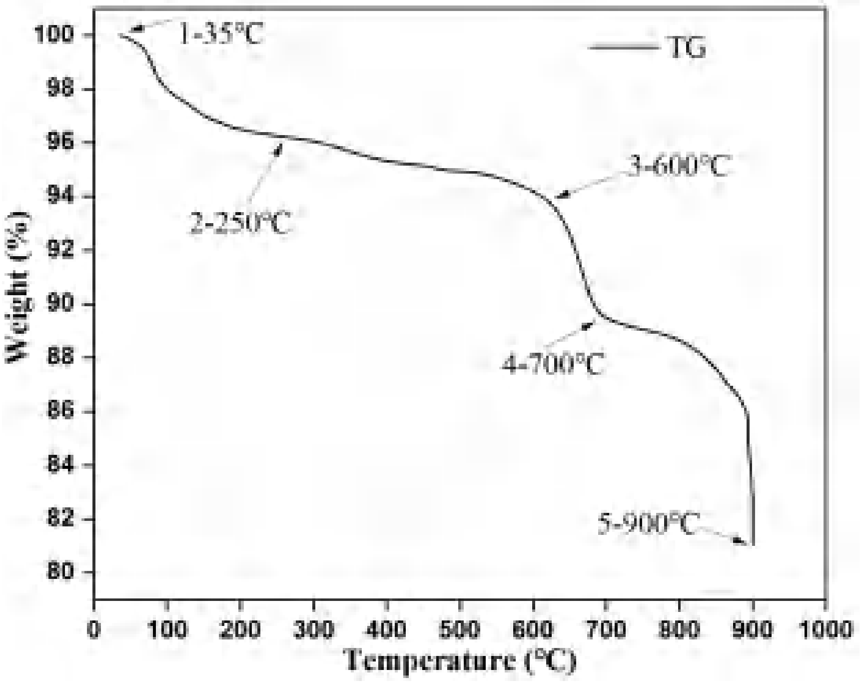

Fig 2. Thermogravimetric analysis of MSWI fly ash

3.2 Analysis of soluble salts in MSWI fly ash

The annual content of soluble salts in MSWI fly ash from waste incineration in Beijing is shown in table 2. It can be seen from the table that the content of soluble salts in MSWI fly ash is very high. The soluble salts mainly exists in the form of chlorine salts of Na, K and Ca. The content of soluble salts in MSWI fly ash is as follows: $Cl^{-}>Na^{+}>Ca^{2+}>K^{+}>SO_4^{2-}$, their annual average content is 22.96wt.%, 9.74wt.%, 7.73wt.%, 7.32wt.% and 0.46wt.%. The content of Cl^{-}, Na^{+} and K^{+} in MSWI fly ash in spring is higher than that in other three seasons corresponding to 31.40wt.%, 39.32wt.% and 19.40wt.%, respectively. Therefore, the soluble salt content in fly ash has seasonal variations, as shown in Fig 3. The soluble salt content is the highest in spring, followed by winter and the lowest in summer. The high content of chloride volatilized and condensed during incineration, resulting in the high level of soluble salts in MSWI fly ash, the annual average content of chlorine element can account for 22.96 wt.%**.** The high concentration of soluble salts not only has the risk of water pollution but also increases the leaching risk of heavy metals and other pollutants in MSWI fly ash.

Table 2. The content of salts in MSWI fly ash at different time periods（wt.%）

	Cl-	K^{+}	Na^{+}	Ca^{2+}	SO_4^{2-}
Spring	82.93	32.07	52.36	21.83	1.32
Summer	51.53	14.06	13.76	30.87	1.14

Autumn	75.06	13.67	13.04	19.60	2.27
Winter	66.04	28.08	37.68	20.47	0.82
Average	22.96	7.32	9.74	7.73	0.46

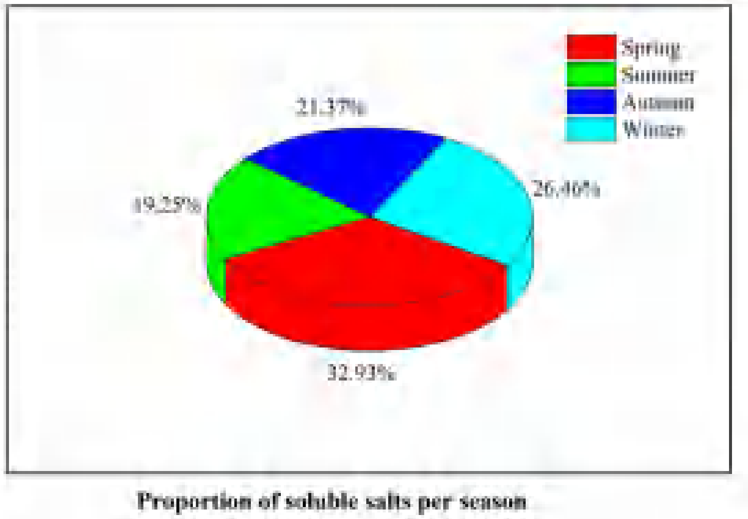

Fig 3. Proportion of soluble salts in different seasons

3.3 The content of heavy metals

The concentration of different metals in different seasons is shown in Fig 4. It is found that Zn content is the highest, followed by Pb, Ba, Cu, Cr, Cd, As and Ni. Zn, Pb, Cu mainly come from dust, plastics, wrapping paper and batteries(Zhang et al. 2018). The concentration of heavy metals is not only related to the composition of waste incineration, but also closely related to its own melting and boiling point(Zhao et al. 2002). The boiling point of salts (especially chlorides) of Zn, Pb, Cd and Cu is below 1000℃, so these metals tend to be volatilized and enriched in MSWI fly ash. The melting point and boiling point of the metal Ni are respectively 1555℃ and 2837℃, so most of the non-volatile Ni remained in the MSWI fly ash. In terms of seasonality, the Zn content in the four seasons was 2829.76mg/kg, 3576.54mg/kg, 4328.79mg/kg and 3110.76mg/kg, with an annual average concentration of 3488.55mg/kg. The content of Zn was unstable in the four seasons and fluctuated greatly. The content in autumn was 1607.4mg/kg higher than that in spring. The contents of Cd, As and Ni was relatively stable in the four seasons and fluctuated within 100mg/kg. The average content of Cr was higher in spring and winter than in summer and autumn, and the content of other elements is higher in summer and autumn than in spring and winter. The seasonal variation of heavy metal content is closely related to the composition of kitchen waste. In summer and autumn, a large number of various summer food and fruit on the market, in the process of consumption produced a large number of perishable components such as fruit skin and plastic packaging and wrapping paper. This kind of MSW has a high content of heavy metal, such as Cu, Zn(Long et al. 2011).

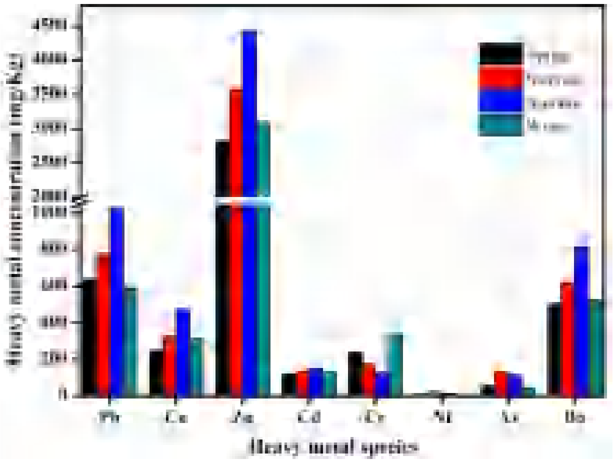

Fig 4. Contents of heavy metals in different seasons

In order to better characterize the pollution degree of heavy metals in MSW in Beijing, soil background value and soil environmental quality standard of Beijing is used as references(Zhang et al. 2018). As can be seen from Table 3 that the pollution of Pb, Cd, and Zn is relatively serious. The highest value is about 42, 1260, and 77 times of background value of soil in Beijing. Only Ni is lower than the soil background value in Beijing. The concentration of Pb, Cd, As, and Zn exceeds the third level standard of soil environmental quality in China.

Table 3. Heavy metal concentrations of MSW in Beijing (mg/kg)

Season	Pb	Cr	Cd	As	Zn	Cu	Ni
Spring	639.56	240.56	120.57	55.65	2829.76	248.79	11.47
Summer	779.48	174.35	130.81	134.16	3576.54	326.02	22.74
Autumn	1031.41	130.75	149.99	114.25	4437.16	475.11	14.56
Winter	590.17	337.60	132.87	45.67	3110.76	313.42	7.74
Average	760.15	220.82	133.56	87.4	3488.55	340.83	14.13
Soil background value in Beijing	24.60	29.80	0.119	7.09	57.50	18.70	26.80
GB15618-1995	≤500	≤400	≤1	≤30	≤500	≤400	≤200

Note: GB15618-1995 is the third level standard of soil environmental background value

3.4 Toxicity leaching experiment

Heavy metal leaching toxicity is an important index to evaluate the environmental impact of MSWI fly ash(Xiong et al. 2014). Table 4 shows the leaching toxicity of heavy metals under two different leaching procedures, and the rule is as follows: Pb>Ba>Zn>Cu>Cr. These may be related to the high content of Pb, Ba, Zn in MSWI fly ash. It shows that the heavy metals in MSWI fly ash are not inert substances and have serious leaching toxicity(Gong et al. 2017). Compared with the two leaching procedures, the leaching concentration of Cr, Cu and Pb in sulfuric acid nitric acid method was higher than that in TCLP method, which was 0.1641mg/L>0.1051mg/L, 0.2557mg/L>0.1005mg/L and 6.4408mg/L>4.6278mg/L. Under the leaching procedure of GB5085.3-2007, only heavy metal Pb exceeds the national standard value. Under the TCLP leaching procedure, all heavy metals have not been removed. Different heavy metals are leached differently under different leaching procedures, which shows that leaching methods have a great influence on the leaching ability of heavy metals.

Table 4. Heavy metals leaching characteristic from MSWI fly ash in Beijing (mg/L)

	Cr^{3+}	Cu^{2+}	Zn^{2+}	Ba^{2+}	Ni^{2+}	As^{3+}	Pb^{2+}
GB5085.3-2007 Standard	15	100	100	100	5	5	5
GB5085.3-2007	0.1641	0.2557	0.7899	1.7484	ND	ND	6.4408
TCLPStandard	5	-	-	-	-	-	5
TCLP	0.1051	0.1005	0.9865	2.4900	ND	ND	4.6278

Annotation: "ND" Not detected.

Fig 5 shows the relationship between the content of heavy metals in MSWI fly ash and their leaching concentration. We can see that the Zn leaching concentration is not positively correlated with the Zn content in MSWI fly ash, while the Pb leaching concentration is positively correlated with the Pb content in MSWI fly ash. As can be seen from Fig 5, the content of Zn in MSWI fly ash is significantly higher than that of Pb, but the leaching concentration of Zn is lower than that of Pb, indicating that most of the Zn in MSWI fly ash exists in a stable form. The results showed that the leaching concentration is not only related to the composition of waste, melting and boiling point of heavy metals, but also related to other factors. There is a certain correlation between the leaching of Ba, Cu and Cr and the content in MSWI fly ash.

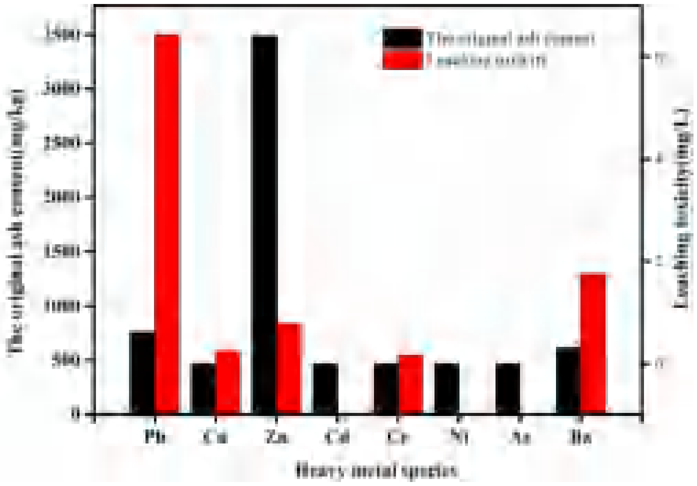

Fig 5. The content of different metals in fly ash and its leaching toxicity

3.5 Bioavailability analysis of heavy metals in MSWI fly ash

The bioavailability concentration of heavy metals in MSWI fly ash throughout the year is shown in Table 5. It can be seen that the bioavailability concentration ranking of heavy metals in MSWI fly ash is as follows: Pb>Ba>Zn>Cd>Cu>Cr>As>Ni. The highest bioavailability concentration of Pb is 34.35mg/kg-71.47mg/kg, with an average value of 49.32mg/kg. The second is Ba, with a concentration of 13.26mg/kg-52.08mg/kg, with an average value of 30.49mg/kg. The average bioavailability concentration of Cr and As is lower than 1mg/kg, and the bioavailability of Ni is not detected in all periods. From the period of four seasons, the bioavailability concentration of Pb, Zn and Cd in spring and autumn is higher than that in summer and winter. The bioavailability concentrations of the other two metals Cr and As are relatively low in four seasons.

Table 5. The desorption concentration of MSWI fly ash at different time periods (mg/kg)

	Pb	Cu	Zn	Cd	Cr	Ni	As	Ba
Spring	52.61	2.67	34.12	14.29	0.80	ND	ND	52.08
Summer	38.84	5.86	19.92	9.76	0.37	ND	0.53	13.26
Autumn	71.47	16.18	34.92	13.11	0.43	ND	0.67	28.26
Winter	34.35	1.10	10.72	9.49	1.00	ND	ND	28.39
Average	49.32	6.45	24.92	11.66	0.65	ND	0.30	30.49

Annotation: “ND” Not detected.

Table 6 shows the bioavailability and sequencing of heavy metals in MSWI fly ash. It can be seen from Table 6 that the bioavailability concentration of Pb and Ba are ranked in the first two places, respectively. Compared with the ranking of the total average metal content in MSWI fly ash, the bioavailability ranking of As and Ni has not changed, and they are still in the 7th and 8th positions. It may be due to the correlation between bioavailability and mean content, and the ranking only changes in a small range. In particular, the average content of Zn is the first, as high as 3488.55mg/kg, while the bioavailability decreased to the third. Although the average content of Cd is only 133.56mg/kg, the bioavailability concentration of Cd is still 11.66mg/kg, which indicates that Cd is easy to be adsorbed and enriched in plants after into the environment. In general, the heavy metals in the untreated MSWI fly ash are easy to leach into the surrounding environment and be absorbed by plants. It is not only the total content to measure the environmental harm of heavy metals in MSWI fly ash, but also the average content of metals, leaching behaviour, toxic effect. It needs to be considered comprehensively, in order to screen out the heavy metal pollution categories that pose the greatest threat to the environment and human health, and give priority to their control.

Table 6. Bioavailability and ranking of metals in MSWI fly ash

Element	Average		Bioavailability	
	mg/kg	sort	mg/kg	sort
Zn	3488.55	1	24.92	3
Pb	760.15	2	49.32	1
Ba	616.09	3	30.49	2
Cu	340.83	4	6.45	5
Cr	220.82	5	0.65	6
Cd	133.56	6	11.66	4
As	87.43	7	0.30	7
Ni	14.13	8	ND	8

Annotation: “ND” Not detected.

3.6 Effect of pH value on the toxic concentration of heavy metal leaching

The leaching concentration of heavy metals at different initial pH values is shown in the Table 7. We can see that the initial pH is changed and the leaching concentration of heavy metals is changed. When pH=2, the leaching concentration of heavy metals in MSWI fly ash reached the highest level (5.49mg/L for Pb, 0.34mg/L for Cu, 12.84mg/L for Zn, 0.17mg/L for Cr and 2.25mg/L for Ba) could indicate that the leaching behaviour of heavy metals in MSWI fly ash is more active in low pH environment. When the range pH value is 2-8, with the increase of pH value, the leaching concentration of various metals in MSWI fly ash shows a downward trend. However, the leaching concentration of Pb and Zn increased from 3.15mg/L to 4.38mg/L and from 0.59mg/L to 2.76mg/L, when pH value is higher than 8. Because Pb and Zn belong to amphoteric metal, which will be redissolved in strong alkaline solution, part of $Pb(OH)_2$ will be complexed with OH to generate $Pb(OH)_3^-$, $Pb(OH)_4^{2-}$, and Zn will also be complexed with OH to generate $Zn(OH)_3^-$, $Zn(OH)_4^{2-}$, but the solubility of Zn is not as strong as Pb(Jiao et al. 2016b). When pH increases, the concentration of Cr also slightly rises, which is due to its ability to form oxyacid anion, and its solubility will increase under the condition of extremely alkali(Zhang et al. 2016). The leaching rules of Cu, Cr and Ba are very similar, when pH=2, the leaching concentration drops rapidly. When pH is greater than 4, the leaching concentration fluctuates in waves. When pH is 4-12, the leaching concentration of Cu is relatively low, and the leaching concentration of Ba changes little. Under all pH conditions, the three metals Cd, Ni and As are not detected.

Table 7. Concentration of heavy metals in MSWI fly ash under different pH (mg/L)

Metals	pH =2	pH =4	pH =6	pH =8	pH =10	pH=12
Pb	5.49	5.11	3.52	3.15	4.49	4.38
Cu	0.34	0.09	0.04	0.08	0.10	0.05
Zn	12.84	8.97	3.64	0.59	2.44	2.76
Cd	ND	ND	ND	ND	ND	ND
Cr	0.17	0.16	0.09	0.07	0.14	0.09
Ni	ND	ND	ND	ND	ND	ND
As	ND	ND	ND	ND	ND	ND
Ba	2.25	1.59	0.99	1.11	1.29	1.23

Annotation: “ND” Not detected.

3.7 Speciation of heavy metals in MSWI fly ash

Different forms of heavy metals can affect the biological toxicity and migration rate of heavy metals in nature(Lin et al. 2018). The environmental effects of heavy metals (migration, bioavailability and leachate toxicity) are mainly determined by their chemical morphology or occurrence morphology in environmental media(Quevauviller 2002). The improved BCR stepwise extraction method is used to study the different chemical forms of heavy metals in MSWI fly ash. The results are shown in Fig 6. We can see that the acid solubility of the metal:

Cd(30.47%)>Zn(28.97%)>Cu(18.64%)>Ba(15.02%)>Pb(8.30%)>Cr(5.81%)>Ni(2.33%)>As(0.48%). As the acidity of the environment increases, acid-soluble metals easily migrate out and are absorbed and enriched by plants, thus affecting the surrounding environment. The fluidity and bioavailability of acid solubility are the strongest, the reducibility is the second, the oxidizability is the second, and the residue state is the weakest, indicating that reducible and oxidizable metals are more stable than acid-soluble metals, if external conditions change, these reducible and oxidizable fractions may be still released into the environment, which means that these fractions are potentially bioavailable(Wang et al. 2015a). The ratio of reducible state and oxidizable state of heavy metals in MSWI fly ash is from large to small: Pb>As>Cu>Zn>Ba>Cd>Ni>Cr. In the natural environment, heavy metals with the residual state as the main form are very stable in nature. In the natural environment, heavy metals with residual state as the main form are very stable in nature. They can be stable for a long time, not easy to release, poor migration and transformation ability, not easy to be absorbed and enriched by organisms, and do little harm to the natural environment(Wang et al. 2015b). The proportion of residue in MSWI fly ash is Cr > Ni>As>Ba>Pb>Cd>Cu>Zn. Cr, Ni and As the residue of state accounted for 77.52%, 58.24% and 30.99% respectively. Thus, the bioavailability of Cr, Ni and As in fly ash is low, with little harm to the environment, which is the same as the bioavailability ranking in Table 5. Studies(Tian et al. 2020) have shown that when the MSWI fly ash is washed by the electric field, all the other three forms of metal except the residual state can be reduced, and the harm of heavy metals to the environment can be reduced.

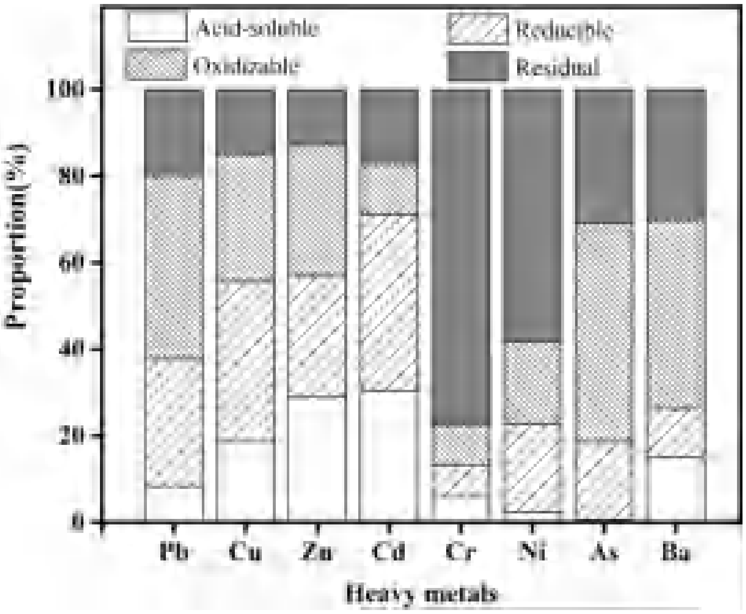

Fig 6. The proportion of targeted metal species in the MSWI fly ash sample determined by BCR.

4 Conclusions

In this paper, The annual MSWI ash in Beijing was taken as the research object. Microwave digestion ICP-OES Method, solid waste leaching toxic leaching method sulfuric acid nitric acid method, TCLP method, bioavailability method and improved BCR step-by-step extraction method are used to test the average content, toxic leaching concentration, bioavailability concentration and chemical form of various metals in the MSWI fly ash.

1. The contents of heavy metals in MSWI fly ash are Zn>Pb>Ba>Cu>Cr>Cd>As>Ni, and the annual average concentrations of the first three metals Zn, Pb and Ba are 3488.55mg/kg, 760.15mg/kg and 616.09mg/kg respectively. The contents of Pb, Cu, Zn, As and Ba in MSWI fly ash showed seasonal same, the average contents in summer and autumn are higher than those in spring and winter.

2. According to the TCLP leaching procedure, all heavy metals in MSWI fly ash did not exceed the leaching threshold. According to the leaching procedure of sulfuric acid and nitric acid (GB5085.3-2007), only the metal Pb in MSWI fly ash exceeds the leaching threshold.

3. The bioavailability concentration of heavy metals in MSWI fly ash is as follows: Pb>Ba>Zn>Cd>Cu>Cr>As>Ni. The average concentrations of Pb, Ba and Zn are 49.32mg/kg, 30.49mg/kg and 24.92mg/kg , respectively. The bioavailability concentrations of Pb, Zn and Cd in spring and autumn are higher than that in summer and winter.

4. The metals in MSWI fly ash are easier to leach in an acid environment, and the leaching amount reaches the maximum when pH=2, 5.49mg/L for Pb, 0.34mg/L for Cu, 12.84mg/L for Zn, 0.17mg/L for Cr and 2.25mg/L for Ba. Except for the amphoteric metals Pb and Zn, the leaching concentration of other metals decreases rapidly when the pH＞2.

5. The metals Cr, Ni and As in MSWI fly ash are stable, and the residual states are 77.52%, 58.24% and 30.99% respectively. Pb and Cu are relatively stable, and the sum of reducible state and oxidizable state both exceeds 65%. Cd and Zn are easy to leach from the external environment, and the weak acid extraction states are 30.47% and 28.97%, respectively.

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The Characteristic Value of Wood in the Building of Zero Waste City – Vancouver as an Example

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Abstract

Vancouver, Canada is one of the first cities in the world to issue a Zero Waste City strategic plan and outline clear measures. By summarizing and analyzing Vancouver's management model, legal regulations and institutional measures for wood in the construction and demolition sector, as well as demonstrating its typical practices and successful experience, this article provides reference for the building of Zero Waste City in other part of the world.

Keywords: wood, construction, demolition, waste, WFC, Vancouver

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1. Introduction

Located on the southwest corner of Canada, Vancouver is one of Canada's most important port cities with great industrial and economic importance. The city of Vancouver is part of the Greater Vancouver area of the Province of British Columbia (B.C. hereafter) with a total area of 115 square kilometers. The 2016 Census population for the City of Vancouver is 631,486, making it the eighth most populous city in Canada. While the Greater Vancouver area had a population of 2.55 million in 2016.

Vancouver's urban waste mainly includes household waste, commercial waste, construction waste (including land clearing), etc. Construction waste refers to the waste generated during the construction and demolition of buildings. Overall, waste treatment in the City of Vancouver include recycling, composting, incineration and landfilling. The latter two methods are considered final treatments, which Vancouver strives to reduce.

In 2011, Vancouver sets its goal of becoming the world's greenest city by 2020. The Greenest City Action Plan (GCAP hereafter) is a strategy for staying on the leading edge of urban sustainability. The Plan is divided into 10 goal areas addressing three overarching areas of focus, namely Zero Carbon, Zero Waste and Healthy Ecosystems. For Zero Waste, the target is to reduce solid waste going to the landfill or incinerator by 50% from 2008 levels. The total amount of waste generated in Vancouver was 976,000 tonnes in 2016, of which 605,000 tonnes were recycled or composted, accounting for 62% of the total amount; the remaining 371,000 tonnes were used for incineration or landfill, accounting for 38% of the total amount. 40% of the waste disposed (incineration and landfilling) were from the construction and demolition sector. Vancouver continued to improve the recycling and composting of waste in 2008-2016, with a large year-on-year decline in waste disposed volumes. The rate of waste disposed had declined from 480,000 tonnes in 2008 to 371,000 tonnes in 2016, a decrease of 23%[1] (Fig.1).

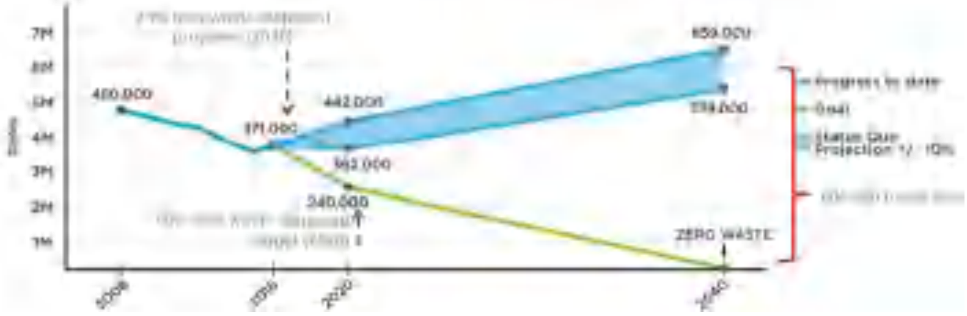

Fig. 1. Vancouver waste disposal status quo projection to 2040[1]

The GCAP had catalyzed a significant shift in solid waste management approaches in the city of Vancouver

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that have greatly increased recycling rates and innovative approaches to material recovery. However, the GCAP and associated targets only project to 2020. On May 31, 2016, Vancouver Council approved creation of a Zero Waste Strategy that creates a framework to achieve the Greenest City long term goal of zero waste, or 100% material recovery.

By consulting with industry experts, other levels of government, residents and businesses, the city government drafted the strategy framework which included the vision, the strategic approach and the objectives in 2016. By multi-stakeholder engagement, the city government identified opportunities and evaluated directions and roles. The Final Consultation Summary Report and Zero Waste 2040 Strategic Plan were approved by the Vancouver Council on May 16, 2018. The Plan helps guiding future decisions and investments relating to solid waste and provides a framework to continue the work and success of current zero waste policies and programs. The plan includes forward looking policies and actions to help stimulate, support, and allow Vancouver to become a zero-waste community. Part of these actions can be implemented right away, while the remaining part will lay the groundwork to progress over time[2].

Based on materials disposed and the source of those materials, four areas of strategic focus are defined for further action in the Zero Waste 2040 Strategic Plan: Built Environment, Food & Packaging, Products & Packaging and Residuals. All the four areas support moving to a close-loop, cradle-to-cradle economy where resources are put to the highest and best use.

2. Characteristic value of wood in Vancouver's built environment

Home to one of the world's most sustainable and globally competitive forest sectors, B.C. is actively taking steps to advance the use of wood. Through its Wood First Program launched in 2009[3], the province encourages wood use and innovative wood construction technologies in B.C. and aims to establishing the province as a global showcase for forest products in construction, interior design and daily living. B.C. was also the first province to adopt building code changes in both 2009 and 2019, permitting respectively six-story and twelve-story wood frame residential buildings. Following 13 municipalities already opted-in to this change, the City of Vancouver Council also approved by-law amendments in May 2020, allowing mass timber construction up to twelve stories for residential and commercial use as of July 1, 2020.

The report 2018 Construction & Demolition (C&D hereafter) Waste Composition Study[4], prepared by TRI Environmental Consulting and submitted to Metro Vancouver, indicates a clear growing portion of wood in regional C&D waste composition (Table 1). This result is positively correlated with the ongoing Wood First Program.

Material Category	2011 % by Weight	2015 % by Weight	2018 % by Weight	2011 Estimated Annual Weight (tonnes)	2015 Estimated Annual Weight (tonnes)	2018 Estimated Annual Weight (tonnes)
Wood	54.00%	56.00%	60.80%	198,263	217,739	243,179

Table. 1. Wood in regional C&D Waste Composition

The regional C&D composition in 2018 was largely composed of wood (60.8%), plastic (11.5%) and rubble/soil (6.4%). Under the Primary Material Category of Wood in the report, there were several Secondary Categories, namely clean wood, treated wood, pallets-clean, pallets-treated, wood flooring, wood shakes and shingles, etc. As the wood disposed of in this study by TRI Environmental Consulting was a mix of the all secondary categories, the estimated breakdown of types of wood could not accurately be determined. Therefore, all secondary categories of wood were assigned a Density Conversion Factor of 297 kg/m^3.

Material from C&D (incl. renovation) of buildings makes up one-third of Vancouver's waste and Vancouver aims to increase the recycling rate of C&D industry to 80% by 2020, by diverting recyclable materials such as wood from disposal. Construction waste is clean at every construction stage and easy to sort. For example, cardboard packaging is generated when interior finishes and appliance are installed; while most wood waste is produced during framing.

2.1. Prefabrication

Prefabricated wood frame construction (Prefab WFC) can contribute to less waste produced on the construction sites. Prefabrication can cover off-site prefabrication of materials, parts, components and subassemblies as well as volumetric units or modules. Prefab WFC has gained widely consideration in Vancouver in the past decade when designing and building both multi-family and commercial buildings, such as multi-family housing, education, retail, healthcare and institutional buildings as prefabrication is an efficient and sustainable building practice. Wood prefabrication has a multitude of benefits, including process efficiency, a controlled environment, a greater return on investment, material efficiency, reduced waste both on- and off-site and sustainability[5]. The other benefit is that it is less hassle. The construction time is shorter and there is less guesswork and mid-construction changing involved.

Prefab WFC buildings have the structural simplicity needed for cost-effective projects and design versatility and they can be rapidly installed. Reduced waste both on- and off-site minimizes the environmental impact of project, as specific sizes and dimensions of components are determined in advance and components are made or cut to tight specifications.

Panelization means framing of dimension lumber or mass timber walls produced with a high degree of accuracy in a factory. Computer numerical control (CNC) machining technology is used at the plant to profile wood panels for installation, and sophisticated connection systems with a high degree of accuracy and efficiency are incorporated during prefabrication. Since wood panels are manufactured specifically for each project, there is almost no job site waste and manufacturers can re-use any fabrication scraps for stairs and other architectural elements or as biofuel. Panelization speeds up the delivery of walls and floors to a site where framing crews install quickly, compared with on-site framing. As a result, project budgets are easier to meet as redundancies and waste in both materials and time are streamlined[5].

2.2. Clean wood disposal ban

Metro Vancouver, the regional district with its major urban center being the City of Vancouver, introduced a Clean Wood Disposal Ban at regional facilities on January 1, 2015. From July 1, 2015, a 50% surcharge were applied to all loads of garbage containing clean wood delivered to regional facilities, if the quantity of wood exceeds 10% of the garbage load. The threshold in the Ban was further decreased from 10% to 5% January 1, 2017 and has officially remained at 5% to date.

Clean wood is solid wood, lumber and pallets that are unpainted, unstained, untreated and free of glue. Wood must be separated from other construction materials such as drywall, plastics and concrete prior to recycling. Clean wood pierced with nails, screws or staples is accepted for recycling[6]. Based on the Metro Vancouver Waste Composition Study Report published in 2014, clean wood waste makes up approximately 9% of all waste from the Metro Vancouver region going to disposal. There has been positive result from the ban. In the 2018 Metro Vancouver Waste Composition Study Report published in June 2019, this figure decreased to 7.5%[7].

Clean wood can be used for landscaping mulch, composting or alternative industrial fuels. Some clean wood can also be reused in construction[8]. Metro Vancouver had engaged the Centre for Advanced Wood Processing at University of British Columbia (UBC) to research for market alternatives for clean wood. UBC determined the most practical use for clean wood is particle board manufacturing at this time for Metro Vancouver. Despite this alternative being a common practice in Europe, the appetite from local investors was not very strong. However, it may become viable if current market conditions change[9].

It worth mentioning that treated or painted wood accounts for 14.3% of all waste from the Metro Vancouver region going to disposal in the 2018 study, compared with 7.5% for clean wood. The recycle and reuse of pressure-treated or painted wood have been a tough issue worldwide. For example, Pressure-treated wood often contain of a variety of toxic substances such as arsenic, making it unsuitable for compost. Painted furniture and glue-laminated timber (Glulam) are facing the same issue. In conjunction with a local cement plant, Metro Vancouver conducted a study of air quality implications of sending hard-to-recycle wood to district energy or cement kilns. The study results did conclude that creosote loads are not appropriate for cement kilns and that pressure-treated wood is likely to pass cement kiln requirements based on preliminary findings. Further testing is needed to confirm[9].

3. Beyond Zero Waste City – the value of wood from a life cycle perspective

A recent Life Cycle Assessment (LCA) research shows that wood frame construction (WFC) projects can greatly reduce carbon emissions during the building's full life cycle compared with steel and concrete structure[10]. The result provided strong support to the positive environmental benefits of WFC. The research was funded by FII Consulting (Shanghai) Co., Ltd. and represents a collaborative effort by Canada Wood Group (Shanghai), China Academy of Building Research (CABR) – one of the most recognized Chinese governmental-sponsored building research institute and think tank, as well as the Athena Institute – a leading Canadian LCA research firm.

The project conducted LCA of carbon emissions on 7 WFC projects around China based on newly published Chinese National Standard GB/T51366-2019 - Standard for Building Carbon Emission Calculation. The result showed WFC projects can reduce the use of steel and concrete. Compared with benchmark buildings using only steel and concrete, carbon emissions during the production phase of building materials can be reduced by 48.9% to 94.7%; carbon emissions for the full life cycle of a building can be reduced by 8.6% to 13.7%[11].

The 7 WFC projects included in the research were all mid-rise or low-rise light wood structure. Similar researches on LCA of carbon emissions by scholars in other countries, were also focused on light wood structure buildings mostly. In British Columbia, where tall-wood buildings are more common, researchers from UBC conducted a comparison between two different construction technologies - wood and concrete, to understand the environmental benefits and drawbacks of each technology in terms of 9 LCA impact categories. Two 18-story residential buildings in Vancouver, one traditional cast-in-place concrete frame building called Ponderosa Commons and one mass-timber hybrid building using Glulam and Cross-laminated Timber (CLT) called Brock Commons, were considered for this study. The result showed that in 8 of the 9 impact categories, the wood buildings had lower environmental impacts[12].

Wood is a renewable resource with neutral carbon balance. Even if all wood waste after the demolition of a WFC building is sent for incineration, the carbon released into the atmosphere will eventually be absorbed by the growth of new trees, thereby reducing the total carbon footprint of the entire lifecycle of a WFC building. Moreover, the wood incineration process can recover energy. In both the delivery of materials to the construction site and the removal from the demolition site, wood bears lower weight, around 80% lower than concrete. Glulam beams and CLT floors can all be prefabricated in the plant resulting in much less on-site installation time, water and electricity consumption, compared with cast-in-place concrete. A group of researchers from Poland conducted LCA study of four functionally equivalent buildings with different materials structure, building technology and energy standards. Their study had considered a full life cycle of the buildings including the following stages: production of building materials, prefabrication, transport to the building site, building, use, demolition, transport of waste and final disposal of waste. Wood and wood-based materials are the only ones from among the analyzed building materials showing an environmental benefit from the full life cycle perspective[13].

4. Conclusion and recommendation

Zero Waste City is an advanced urban management concept, led by the promotion of sustainable development and green lifestyles, with focus on the source reduction of solid waste, maximized resources utilization and minimized incineration and landfilling. Using Vancouver as an example, this study exhibits the characteristic value of wood in the built environment that contribute to the building of Zero Waste City.

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Harmful components migration and transformation in the chemical looping gasification of phosphogypsum as oxygen carrier

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Abstract:

The phosphogypsum (PG) in Kunming, China, is one of the largest integrated phosphogypsum (PG) basin newly found. The present work concentrates on the application of chemical looping gasification (CLG) with a Kunming phosphogypsum (PG), which is characterized by many types of harmful impurities content, such as fluorine, phosphorus, potassium and sodium. In order to study the pollution behavior in the preparation of syngas by melting method using Kunming phosphogypsum (PG) as oxygen carrier, the thermodynamic equilibrium states of fluorine, phosphorus, potassium and sodium elements were calculated by Factsage7.1 software package combined with the chemical composition analyses of the Kunming phosphogypsum (PG). The transport and transformation of fluorine, phosphorus, potassium and sodium elements were explored at different temperatures. The results show that the fluorine element gradually reach up to thermodynamic equilibrium state while the phosphorus, potassium and sodium elements a higher temperature are required during the heating process using Kunming phosphogypsum (PG) as oxygen carrier. At 900°C, fluorine mainly exists as HF(46.53%) gases and $Ca_4Si_2F_2O_7$(53.47%) solids; phosphorus exists as $Ca_5HO_{13}P_3$ solids; potassium exists as $KAlSiO_4$ solids; sodium exists as $NaAlSiO_4$ solids. After 900℃, with the temperature gradually increasing, fluorine has the transformation trend from solids $Ca_4Si_2F_2O_7$ into HF, KF, NaF gases; phosphorus has the transformation trend from solids $Ca_5HO_{13}P_3$ into solids $Ca_{10}(PO_4)_6F_2$; potassium has the transformation trend from solids $KAlSiO_4$ into KOH, KF, K gases; sodium has the transformation trend from solids $NaAlSiO_4$ into NaF, NaOH, Na gases. In addition, the experiments at 900°C are conducted to verify the prediction on the transformation of fluorine and phosphorus, the results from which are well in agreement with the theorectical calculations. The information obtained in this study could be used to evaluate the feasibility of phosphogypsum(PG) as an oxygen carrier chemical looping gasification (CLG), mitigating the pollution to the environment.

Keywords: Phosphogypsum(PG), Chemical looping gasification (CLG), Harmful components, Migration and transformation

1. Introduction

Phosphogypsum(PG) is a common large-tonnage waste of phosphoric fertilizers industry[1]. The waste is often disposed as slurry to storage or settling pond or waste heap. Chemically, the content of

$CaSO_4.2H_2O$ in PG is above 90% and impurities such as H_3PO_4, phosphates, fluorides, and organic matter that adhere to the surface of gypsum crystals[2]. For many years, it had been explored the effective utilization of PG from various aspects because calcium sulfate has the characteristics of low solubility and difficulty in separation. In India, a large number of PG is being used in agricultural soil as sulfur and calcium supplement for enhanced crop production[2, 3]. Yang et al.[4] utilized the original PG to prepare filling material. Li et al.[5] investigated the recycling PG as backfill (CPB) for filling underground mine openings. Some researchers studied the PG as the material prepared by the cemented paste backfill, and has suggested that this is technically feasible[6, 7]. Li et al.[8] investigated the performance of PG and calcium magnesium phosphate fertilizer for nitrogen conservation in pig manure composting. Hao et al.[9] reported that PG can reduce methane emissions during cow manure composting, but has no significant effect on total carbon and total nitrogen content.

However, the presence of complicated impurities make it hard to be utilised effectively[10] and also severely restrict its resource utilization field[11]. Although PG can solve some problems through pretreatment in the application process, it may increase costs or cause secondary pollution. In recent years, with the development of agriculture and fertilizer industry, the global emission of PG has reached 280 million tons, and only 15% of them have been used, and the rest have been largely abandoned[12]. At present, the cumulative stock of PG in China exceeds 120 million tons, and its resource utilization rate is less than 20%[13]. The disposal of a large amount of PG not only occupies a large amount of land, but also causes serious environmental pollution problems[14]. In order to achieve this goal, people have been looking for ways to use PG efficiently.

Chemical Looping Gasification (CLG) is a novel gasification technology[15, 16], which introduces oxygen for gasification, instead of from ambient air, but from the lattice oxygen of oxygen carrier (OC)[15, 17]. One of a crucial factor of CLG is the choice of oxygen carriers[18]. The most important criteria for selecting oxygen carriers are oxygen carrying capacity, reactivity, high mechanical strength, high impedance, low cost and harmless[19]. Up to now, there are many researchers investigating the use of oxygen carrier in solid fuel CLG and the investigated oxygen carriers mainly are metal oxides(such as Fe, Co, Ni, Cu, Cd, Mn, et al.), which have high reactivity and stability[20-25]. In addition, in recent years, non-metallic oxygen carriers represented by $CaSO_4$[26-28] have been attracting more and more attention due to the abundant storage of raw materials, low price, strong oxygen carrying capacity and no secondary pollution. In recent years, our group have paying attention to the application of CLG with PG as oxygen carrier to replace $CaSO_4$ and has suggested that this is technically feasible[28-31]. Although some basic experimental studies about the reaction characteristics had been performed of PG and there is no consideration the impact of impurities in PG in CLG gasification process. In the high temperature process for synthesis gas, complex phase transformation and thermochemical reaction processes are often accompanied. FactSage7.1 chemical thermodynamics software has been widely used in materials, chemicals and other fields[32, 33]. Yoshiie et al.[34] conducted a coal gasification experiment in a tube furnace to analyze the particle size and elements of coal gasification gas, focusing on the distribution of Pb and Se elements, and using thermodynamic equilibrium calculations to derive the presence in the discharge process. Jie yang et al.[29] used the Factsage7.1 to calculate the thermodynamic parameters with PG as oxygen carrier in chemical looping gasification process, and paid attention to the migration and transformation of the main elements. However, the migration and transformation of harmful elements in the CLG process of PG as oxygen carrier by thermodynamic software has not been reported so far.

In this work, equilib module of FactSage7.1 was used to simulate the distribution and existence of four elements F, P, K ,Na in the CLG process of PG as oxygen carrier, and selected F and P as the representative for relevant experimental verification, which was based on the comprehensive determination of the chemical composition of Kunming PG and lignite and combined with the formulation and process of the previous reaction mechanism[28-31].

2 Experimental

2.1 Experimental Materials

The PG was gathered from Yunnan YunTian Hua CO. LTD, China. In this paper, the PG was named Kunming PG. The powder of the Kunming PG was prepared by pulverizing (GJ100-1) with a sample pulverizer and passing through a sieve of 120 mesh. The chemical composition was analyzed using a ZSX100e single-channel scanning X-ray fluorescence spectrometer (XRF). Test conditions included Rh target, filament current of 40KV and 40mA, respectively. The time of qualitative analysis is 0.2-0.8s, and the time of quantitative analysis is 20-40s. Among this, the content of F and Al_2O_3 were determined by XRF empirical coefficient method, and the content of MgO and Fe_2O_3 were determined by XRF basic parameter method. The content of P_2O_5, CaO , SiO_2 and SO_3 in Kunming PG were determined by extraction-phosphomolybdate blue spectrophotometry, EDTA titration method, burning method and sodium carbonate-zinc oxide semi-melting method, respectively. The composition is shown in Table 1. The proximate analysis and ultimate analysis of Yunnan lignite are shown in Table 2.

Table 1 Chemical components of Kunming phosphogypsum(wt%)

Chemical components								
	SO_3	CaO	SiO_2	Al_2O_3	Fe_2O_3	MgO	Total P_2O_5	HydrotropicP_2O_5
Content(%)	40.86	29.82	9.43	0.236	0.132	0.005	1.17	0.87
Chemical components								
	Total F	Hydrotropic F	Na_2O	K_2O	MnO	Free water	Crystal water	Acid-insoluble
Content(%)	0.52	0.12	0.043	0.086	0.002	5.38	4.27	8.42

Table 2 Proximate and ultimate analysis of yunnan lignite

Coal	Proximate analysis/%(wt)					Ultimate analysis/%(wt)				LHV/
	M_{ar}	M_{ad}	A_d	V_{daf}	F_{cd}	$S_{t,ad}$	H_{ad}	N_{ad}	C_{ad}	$MJ.Kg^{-1}$
Lignite	25.7	3.85	6.54	50.45	46.31	1.09	4.36	1.35	62.47	17.82

X-ray Diffractometer (XRD, D/max-2200) were used to analysis Kunming PG of solid phase. Scans were performed at 0-90 degrees at a rate of 0.02 degree per minute with an accelerating voltage and filament current of 36KV and 30mA, respectively. All the XRD spectra were analyzed using PDXL software and identified with the JCPDS database. The result was shown in Figure 1. The results showed that the crystallization peak in Kunming PG were mainly about calcium sulfate hydrate ($CaSO_4.2H_2O$) and silicon dioxide (SiO_2).

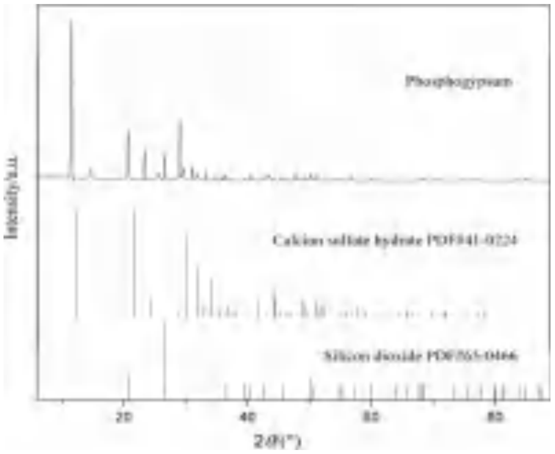

Fig.1 XRD pattern of the Kunming PG powder

2.2 Apparatus and methods

Before the start of the experiment, the PG powders and lignite powders were dried in a drying box in air at 105℃ for 24 hours. Then crushing and screening the PG powders and lignite powders ensured that both PG powders and lignite powders size were through 120 mesh sieves. Mixed PG powders and lignite powders with mole rate 0.2. The mixed powders in the fixed bed reactor were heated treated in a 100mL/min flow of gas containing H_2O balanced with N_2 and sintered at 1173K for 2 hours using a 5℃/min heating rate and 5℃/min cooling rate, respectively. The experimental flow chart is shown in Fig.2.

The gas components were analyzed by SP-2100A gas analyzer (Beijing Beifen-Ruili Analytical Instrument (Group) Co. Ltd). X-ray Diffractometer (XRD, D/max-2200) were used to analysis the product of solid phase. Scans were performed at 0-90 degrees at a rate of 0.1 degree per minute with an accelerating voltage and filament current of 40KV and 40mA, respectively. All the XRD spectra were analyzed using PDXL software and identified with the JCPDS database. X-ray Photoelectron Spectrometer (XPS, PHI5500) were used to analysis and characterize the product of solid phase. The spectra were collected at room temperature. Binding energy (B.E) values were referenced to the standard C is binding energy of 284.8eV. The Casa XPS program was used for data analysis. For the morphological changes and chemical evaluation of the ilmenite particles a Scanning Electron Microscopy coupled with Energy Dispersive X-ray Spectroscopy (SEM-EDS), Quanta 200FEG with an Oxford EDS system have been used.

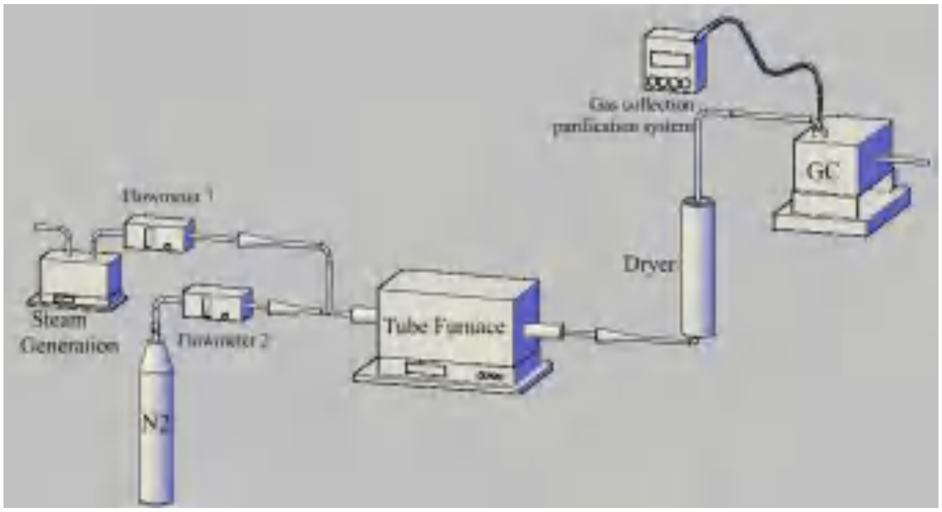

Fig.2 The experimental flow chart

2.3 Data evaluation

Instantaneous components of different Gases (S_i;(%)): The instantaneous components refers to the components of difference gases at different times during the reaction process, which is given by Eq(1).

$$S_i = \frac{Ni}{N(CO)+N(CO2)+N(CH4)+N(H2)+N(H2S)} \times 100\% \qquad (i=CO, CO_2, CH_4, H_2, H_2S) \qquad (1)$$

Conversion of C(χ_C;(%)): The carbon is converted by CO,CO_2 and CH_4 in the fuel reactor, the composition rate of carbon is defined by the Eq.(2).

$$\chi_C = \frac{\sum_0^T N_{CO}+\sum_0^T N_{CO_2}+\sum_0^T N_{CH_4}}{N_{C,Lignite}} \times 100\% \qquad (2)$$

Where $N_{C,Lignite}$ refers to the total molar mass of carbon in lignite required for the experiment, and N_{CO},N_{CO_2},N_{CH_4}mean that the total cumulative molar mass of each of them according to some stated condition from the beginning to the end , respectively.

Sulfur recovery(f_S;(%)):it can be represented using Eq(3).

$$f_S = \frac{M_{S,CaS}}{M_{S,Lignite}+M_{S,PG}-M_{S,H2S}} \times 100\% \qquad (3)$$

The $M_{S,Lignite}$ is the molar quantity of sulfur of lignite; the $M_{S,PG}$is the molar quantity of sulfur of PG ;the $M_{S,H2S}$ is the molar quantity of H_2S; the $M_{S,CaS}$ is the molar quantity of sulfur of CaS.

3 Results and discussion

2.1 Theoretical simulation

The temperature of Kunming PG as the oxygen carrier in chemical looping gasification process can reach 900°C. The powder mixed with PG and lignite is heated to 900 °C, in which each phase is also in a stable state. From room temperature to high temperature, toxic and harmful substances in PG are also released in different chemical forms. The simulation prediction of the migration and transformation process of harmful substances in the heating process of the system is based on the following conditions. ① It is considered to be a normal pressure and high temperature reaction process; ②The gas phase product participating in the reaction at equilibrium at a certain temperature is treated as an ideal gas; ③ At high temperatures, the molten phase above the liquid phase is considered as a solution. Using the the oxide data (FToxid) and the pure substance database (Fact53) of FactSage7.1 thermodynamics database and the phase equilibrium Equilib module calculate the composition and distribution of the phase products of the PG as the oxygen carrier in chemical looping gasification heating process. The changes of F, P, K and Na in the chemical looping gasification process of PG as oxygen carrier were investigated.

Conditions before the simulation are set as follows.

(1)Determine the composition of PG:

1mol PG$\rightarrow$0.52mol$CaSO_4$+0.157molSiO_2+0.0023molAl_2O_3+0.000825molFe_2O_3+ 0.00824molP_2O_5+0.02737molF+0.0019molNa_2O+0.0009molK_2O (Converted by mass fraction in Table 1);

1. Determine the composition of lignite:

5 mol lignite$\rightarrow$2.6molC+2.2molH+0.0096molO+0.048molN+0.017molS.(Converted by mass fraction in Table 2 and the PG and lignite molar ratio should be about 0.2)[28];

2. Pressure: set to normal pressure 101325Pa.

- **Pollution Prediction of Kunming PG as Carrier Oxygen in CLG**

The formation of gaseous products of F, P, K, Na elements are shown in Fig.3 in the process of CLG using PG as the oxygen carrier. As is clear from Fig. 3, the amount of gas phase product of the four elements increased with a rising of temperature. The gas phase product of F begins to form at about 100 °C. When the temperature reaches about 980 °C, the results show that the fluorine element gradually reach up to thermodynamic equilibrium state. The potassium element begins to appear as a gas phase material at 550 °C, the sodium element exhibits a gas phase product at 670 °C and the phosphorus element begins to appear as a gas phase product at 1150 °C.

When the temperature reaches 900 °C, the existence form of four elements of F, P, K, Na are shown in Fig. 4 in CLG process of Kunming PG as oxygen carrier. The results of simulation calculations by FactSage7.1 software package show that fluorine mainly exists as HF (46.53%) gases and $Ca_4Si_2F_2O_7$(53.47%) solids; phosphorus exists as $Ca_5HO_{13}P_3$ solids; potassium exists as $KAlSiO_4$ solids; sodium exists as $NaAlSiO_4$ solids.

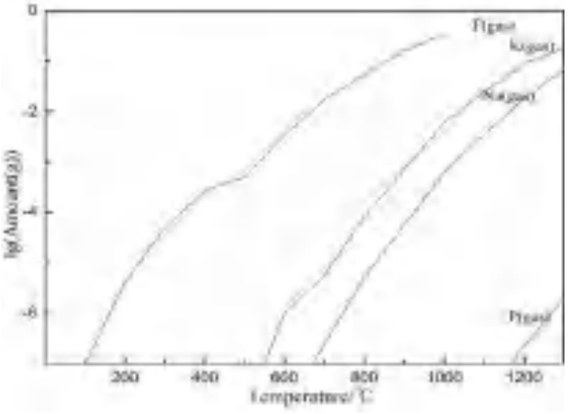

Fig.3 Gas formation amount as a function of temperature in the process

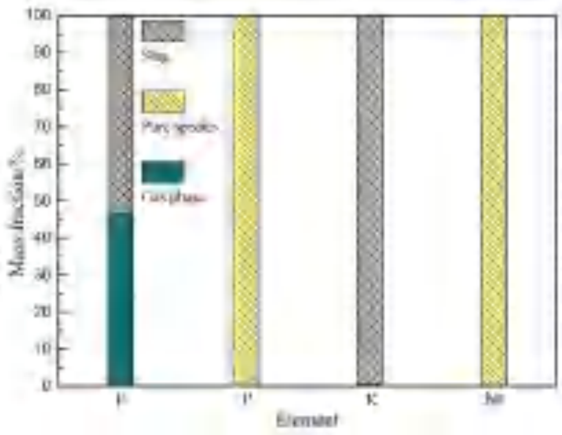

Fig.4 Distribution of F，P，K，Na in different phases at 900℃

- **Fluorine migration and transformation in CLG using Kunming PG as oxygen carrier**

The phase transformation of fluorine under different temperatures during the CLG process using Kunming PG as oxygen carrier is showed in Fig.5. When the temperature rising from 300℃ to 400℃, the fluorine element exists as solid phase CaF_2 (80.02%) and $Ca_{10}(PO_4)_6F_2$ (19.98%). It was confirmed that fluorine existd as CaF_2 solid and $Ca_{10}(PO_4)_6F_2$ solid in PG[35], which indicates that the form of fluorine element does not change in CLG process with the temperature lower than 500°C. When the temperature is gradually increased from 400°C to 500°C, the fluorine in the solid CaF_2 is changed into solid $Ca_4Si_2F_2O_7$. At 500℃, fluorine element exists as solid $Ca_4Si_2F_2O_7$(80.02%) and solid

$Ca_{10}(PO_4)_6F_2$(19.98%) with a small amount in HF gas at 600℃. When temperature rises to 1000℃, the fluorine in the solid $Ca_4Si_2F_2O_7$ and $Ca_{10}(PO_4)_6F_2$ are changed into gases HF and KF. However, with the high temperature from 1200℃ to 1300℃, the fluorine in the gas HF and KF are changed into gas KF and NaF. It is particularly noted that fluorine element exists as solid phase $Ca_4Si_2F_2O_7$ (53.47%) and gas phase HF (46.53%) at 900℃.

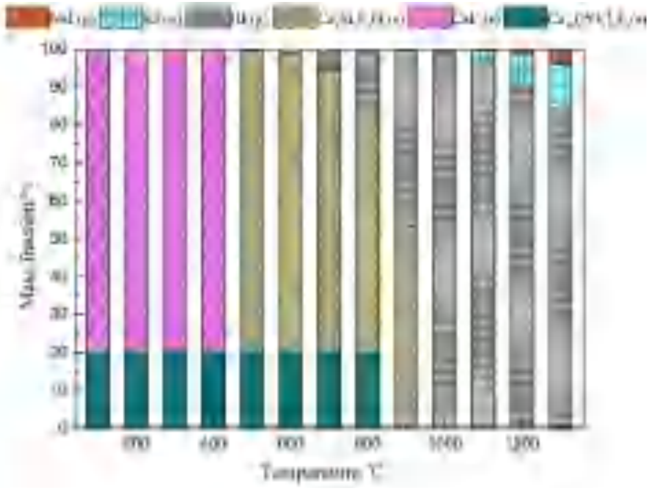

Fig.5 The phase transformation of fluorine under different temperatures during the CLG process.

- **Phosphorus migration and transformation in CLG using Kunming PG as oxygen carrier**

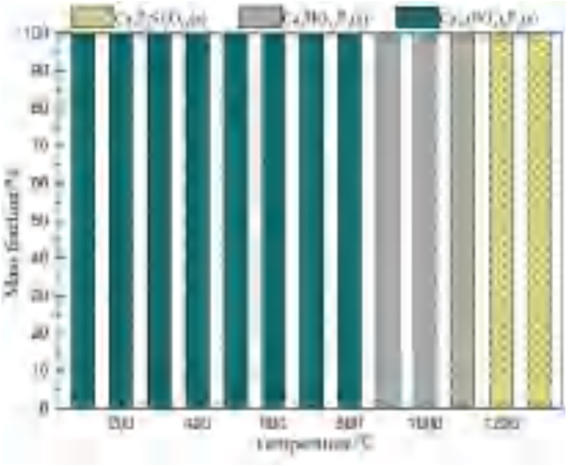

Fig.6 The phase transformation of phosphorus under different temperatures during the CLG process.

The phase transformation of phosphorus under different temperatures during the CLG process using Kunming PG as oxygen carrier is showed in Fig.6. From Fig.6, it is seen that the phosphorus element exists as solid phase fluor apatite($Ca_{10}(PO_4)_6F_2$) and solid phase $Ca_5HO_{13}P_3$ during the CLG process. To be more more specific, the phosphorus element exists as solid phase fluor apatite ($Ca_{10}(PO_4)_6F_2$) with the temperature lower than 800℃ and the phosphorus element is transformed from solid phase fluor apatite($Ca_{10}(PO_4)_6F_2$) into solid phase calcium phosphate tribasic ($Ca_5HO_{13}P_3$) with the temperature higher than 800℃. After 1100 °C, with the temperature rising, the phosphorus element is transformed from solid phase calcium phosphate tribasic ($Ca_5HO_{13}P_3$) into solid phase $Ca_7P_2Si_2O_{16}$. At 900 ℃, the phosphorus element exists as solid phase calcium phosphate tribasic ($Ca_5HO_{13}P_3$).

- **Potassium migration and transformation in CLG using Kunming PG as oxygen carrier**

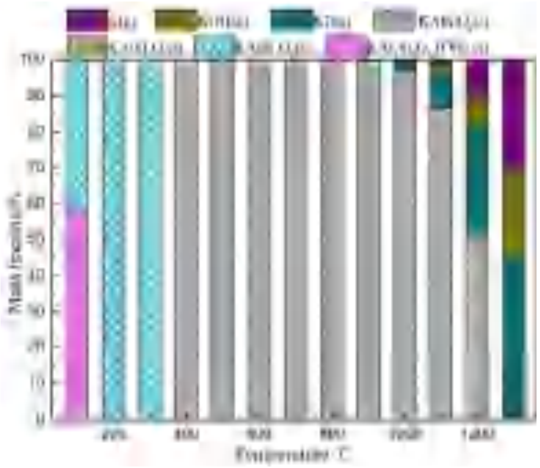

Fig.7 The phase transformation of potassium under different temperatures during the CLG process.

The phase transformation of potassium under different temperatures during the CLG process using Kunming PG as oxygen carrier is showed in Fig.7. From Fig.7, it is seen that the potassium element exists as solid phase $KAl_3Si_3O_{10}(OH)_2$ and solid phase $KAlSi_3O_8$ with the temperature lower than 200℃during the CLG process. When the temperature is gradually increased from 200°C to 300°C, the potassium element exists as pure solid phase $KAlSi_3O_8$; when the temperature is raised from 400°C to 900°C, the potassium element exists as pure solid phase $KAlSiO_4$. After 1000°C, the potassium element is transformed from pure solid phase $KAlSiO_4$ into solid phase $KAlSiO_4$ and gas phase KF. However, the potassium element exists as solid phase $KAlSiO_4$ and gas phase KF, K, KOH with the temperature higher than 1100 ℃ and the potassium element exists as gas phase KF(43%), K(32.3%), KOH(24.7%) at 1300℃.

- **Sodium migration and transformation in CLG using Kunming PG as oxygen carrier**

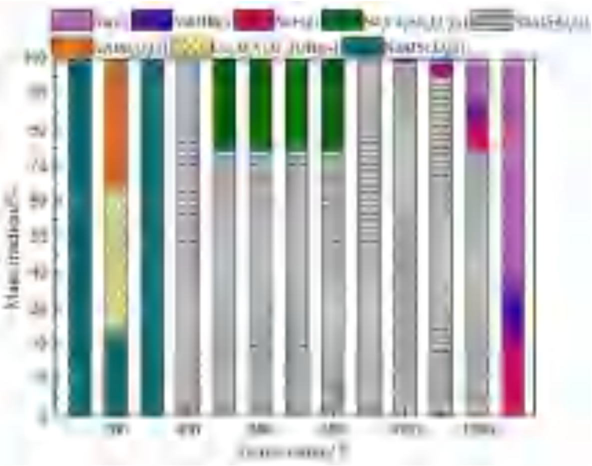

Fig. 8 The phase transformation of sodium under different temperatures during the CLG process.

The phase transformation of sodium under different temperatures during the CLG process using Kunming PG as oxygen carrier is showed in Fig.8. From Fig.8, it is seen that the sodium element exists as solid phase $KAlSi_3O_8$ or solid phase $Ca_2Al_3Si_3O_{12}(OH)$ with the temperature lower than 400℃. When the temperature is gradually increased from 400°C to 800°C, the sodium element exists as solid phase $NaAlSiO_4$ and solid phase $Na_2Ca_3Al_{16}O_{28}$. At 900℃, the sodium element exists as solid phase $NaAlSiO_4$. After 900°C, with the temperature increasing, the sodium element is transformed from solid phase into gas phase and the sodium element exists as gas phase Na, gas phase NaOH and gas phase NaF at 1300 ℃.

2.2 Experimental results

- **Combustion performances**

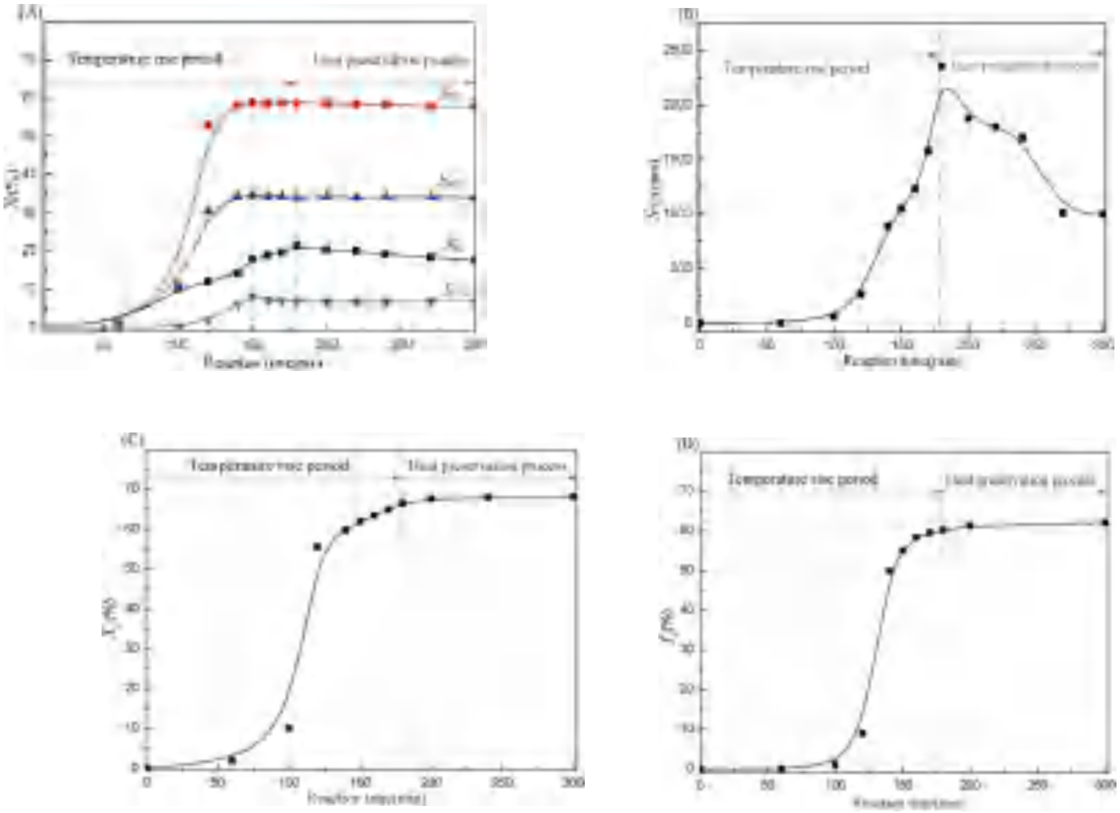

Fig.9 Experimental results at different reaction time

The production of the reaction process of the synthesis gas and side product H_2S were quantified and compared in tube furnace reactor tests at 900℃. Mixed PG powders and lignite powders with mole rate about 0.2. The mixed powders 50g in the tube furnace reactor were heated treated in a 100mL/min flow of gas containing H_2O balanced with N_2 and sintered at 900℃for 2 hours using a 5℃/min heating rate and 5 ℃/min cooling rate, respectively. The quantitative data of each component yield produced from PG oxygen carrier reactions were shown in Fig.9. There were two periods (temperature rise period and heat preservation process) for syngas production process with the changes of reaction time. The synthesis gas production was quantified and compared in Fig.9(A). As a whole, gas yield of each synthesis gas component at each condition increased as the reaction temperature rises in temperature rise period. When the temperature reached 900℃, it entered the heat preservation process. At this stage, there were some differences trend in the synthesis gas composition, which the CO_2 and CH_4 compositions increased slowly but the CO and H_2 decreased. This difference was mainly caused by the decomposition of lignite and the low content of lignite in tube furnace reactor experiments. Fig.9(C) showed that the conversion of carbon from lignite was increasing with the increase of temperature from 650℃(110min) to 900℃(180min) and the high conversion rate of carbon was related to the reaction temperature. When the reaction temperature was about 750℃(150min), the high conversion trend of carbon was gradually maintained, which was more obvious after 700℃ (140min). Finally, the carbon conversion rate was up to 68.9% in the heat preservation process.

When selecting an oxygen carrier for CLG using PG as oxygen carrier, sulfur and environmental aspects should be always taken into account. So, the gaseous substance sulfur conversion was one of the conditions which we need to pay attention to. Fig.9(B) showed the trend of H_2S concentration at different reaction time in the tubular furnace reactor experiments. From Fig. 9(B), it was found that H_2S component increased as the reaction temperature rises in temperature rise period and H_2S component slowly decreased as the reaction time rises in the heat preservation process. In order to deeply analyze the ability of S capture of the PG as oxygen carrier in CLG process, the experimental results of CaS were carried out. Fig. 9(D) stated clearly the ability of PG as oxygen carrier to capture

S. From temperature rise period to the heat preservation process (Fig. 9(D)), the conversion rate of CaS increased, reached 63.8%, finally.

- **Fluorine and phosphorus transfer**

Fig.10 SEM-EDS of ash after reaction

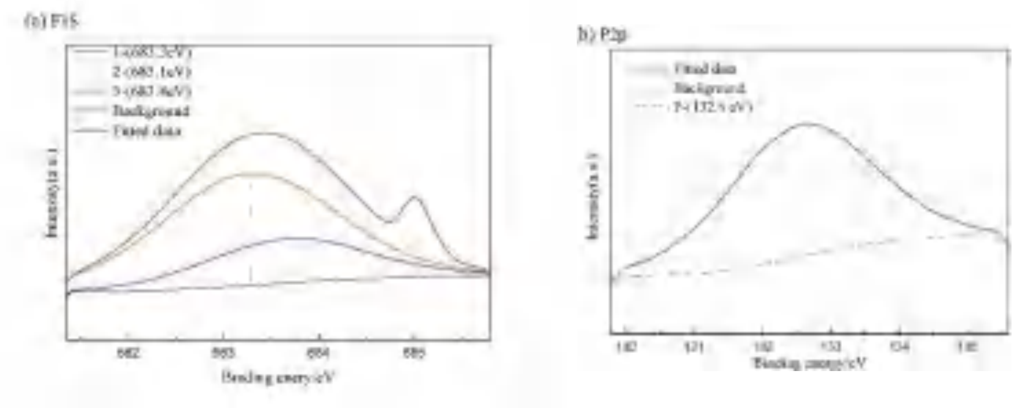

Fig.11 XPS patterns of ash after reaction

Figure 10. Showed the distribution of the F and P elements of the ash after the reaction under the tubular furnace experimental conditions. It was shown in Fig. 10 that the distribution of F and P elements in the ash after the reaction was uniformly distributed and the content of the P element was more than F element. This indicated that the solid phase ash after the reaction contained the F element and the P element and the P element content was more than the F element. This conclusion was consistent with the theoretical calculation results (Fig. 5 and Fig. 6), which were F element in the form of 53.2% solid phase and 46.8% gas phase and P element in the form of pure solid phase at 900℃.

Figure 11 were the XPS spectrum of the F and P elements in the ash after the reaction under the tube furnace experimental conditions. As seen from Fig. 11(a), there were three characteristic peaks of 683.3, 683.8, and 685.1 around F(1s). The X-ray photoelectron spectroscopy database of the National Institute of Standards and Technology (NIST) of the United States was found that the Na_2SbF_5 corresponded to the vicinity of the binding energy 683.3; KF and NaF corresponded to the vicinity of the binding energy 683.8; CaF and FeF_2 corresponded to the vicinity of the binding energy 685.1. There was a distinct peak of 132.6 around P(2p). After searching NIST, it was found that there was $Ca(H_2PO_4)_2$ or $Ca_5HO_{13}P_3$ corresponded to the vicinity of the binding energy 132.6.

In a word, the experiments results of F and P at 900°C are well in agreement with the theorectical calculations.

4 Conclusions

[1] Fluorine element gradually reach up to thermodynamic equilibrium state while the phosphorus, potassium and sodium elements a higher temperature are required during the heating process in $CaSO_4$-C-H_2O(g) system using Kunming phosphogypsum (PG) as oxygen carrier.

[2] At 900 °C, fluorine mainly exists as HF (46.53%) gases and $Ca_4Si_2F_2O_7$(53.47%) solids; phosphorus exists as $Ca_5HO_{13}P_3$ solids; potassium exists as $KAlSiO_4$ solids; sodium exists as $NaAlSiO_4$ solids. After 900℃, with the temperature gradually increasing, fluorine has the transformation trend from solids $Ca_4Si_2F_2O_7$ into HF, KF, NaF gases; phosphorus has the transformation trend from solids $Ca_5HO_{13}P_3$ into solids $Ca_{10}(PO_4)_6F_2$; potassium has the transformation trend from solids $KAlSiO_4$ into KOH、 KF、 K gases; sodium has the transformation trend from solids $NaAlSiO_4$ into NaF、NaOH、Na gases.

[3] The experiments at 900 °C are conducted to verify the prediction on the transformation of fluorine and phosphorus, the results from which are well in agreement with the theorectical calculations.

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Breaking inhibition impact of low concentration polyaluminum chloride on sludge anaerobic fermentation by the presence of sodium citrate

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Abstract

Polyaluminum chloride (PAC) are widely and increasingly used in wastewater treatment plant which would be accumulation in excess sludge. Our former research found that low concentration (especially lower than 0.15 gAl/gTS) PAC can inhibit the acid production efficiency during excess sludge anaerobic fermentation process. In this study, sodium citrate was firstly to be used to break the inhibition of low concentration PAC in sludge anaerobic fermentation. Results showed that the accumulation of SCFAs increased in the presence of sodium citrate, especially when the ratio of sodium citrate to PAC was 2:1, the maximum SCFAs accumulation reached 2890 mg/L, which is 2.5 times than that of the control group (only PAC and concentration is 0.07 mg/gTS). The mechanism study shows that sodium citrate facilitates the destruction of sludge floc, accelerating the destruction of extracellular polymers and release soluble substances in the sludge. At the same time, the key enzymes that are originally bound and hidden in the sludge base are also released, thereby promoting the further degradation of organic matter and shortening the anaerobic fermentation time. This research provides a new idea for the research and practical application of sludge anaerobic fermentation at high efficiency.

Keywords: sludge; anaerobic fermentation; polyaluminum chloride; sodium citrate; short-chain fatty acids.

1. Introduction

With the development of economic society and the improvement of residents' living standards, the output of sludge is also increasing rapidly[1]. In addition, sludge contains a large number of toxic and harmful substances, which will have a bad impact on the environment, so it has attracted wide attention from scholars[2]. Anaerobic fermentation technology has become the mainstream technology for the utilization of sludge resources, because the organic matter in the sludge can be effectively used [3]. And in the process of methane production, there will inevitably be an acid production process, so the study of the acid production process in turn can better serve the methane production process [4]. However, many sludge anaerobic fermentation operations are not good. The reasons are that in addition to the shortage of funds and low technical level, the characteristics of the sludge itself will also lead to a slow sludge anaerobic fermentation process[5].

Polyaluminum chloride (PAC), as an inorganic flocculant, inevitably accumulates at high concentrations in sludge. According to the literature report [6]and previous studies by the research group show that a certain concentration of PAC can inhibit anaerobic fermentation of sludge, mainly because the addition of PAC is beneficial to sludge reunion. The trivalent cation Al^{3+} can interact with the negative sites on EPS (such as polysaccharides and proteins), thereby increasing the size and strength of the flocs, making the flocculation of sludge flocs dense, and the organic substances cannot be fully

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dissolved for the use of microorganisms. So as to slow down the sludge solubilization process.

According to reports[6, 7], PAC has regional differences. The concentration of polyaluminum chloride in sludge in different regions is different, such as 2.6~17.4 mgAl/gTS in Taiwan, 81.6 mgAl/gTS in Hangzhou, 112.5 mgAl/gTS in India, and 104~320 mgAl/gTS in dehydrated sludge in the United States. Therefore, it is very necessary to study the strategy of breaking low concentration PAC to inhibit sludge anaerobic fermentation.

Sodium citrate was selected as the pretreatment reagent by consulting the literature[8, 9], because the cationic binder sodium citrate can remove the bridged ions (such as Al^{3+}) in the floc so that the sludge floc structure is deflocculated. Sodium citrate (Sodium Citrate, SC) is a hydroxy carboxylate compound. It is white crystalline particles or crystalline powder and is easily soluble in water but insoluble in ethanol. It can be slightly weathered in hot air and stable in normal temperature air. Sodium citrate, as the most important citrate at present, has the following excellent properties[10-12]: ① It has metal ion complexing ability; ②It has biodegradability; ③It has excellent dissolution performance; ④It is safe and non-toxic; ⑤ It has good pH adjustment and buffer performance; ⑥ Sodium citrate also has excellent retarding performance and stability performance. At present, there is no report mentioning that when a low concentration of PAC inhibits sludge anaerobic fermentation, the efficiency of anaerobic fermentation is improved by adding sodium citrate to destroy the sludge flocculation structure.

Therefore, the purpose of this study is to breaking the inhibition impact of low concentration PAC on sludge anaerobic fermentation by the presence of sodium citrate. First, the effect of adding sodium citrate on the production of short-chain fatty acids from sludge fermentation was studied. Then, its effects on material dissolution, sludge floc stability, key enzyme activities, and sludge dewatering performance were evaluated. This is the first study on the impact of sodium citrate on breaking low-level polyaluminum chloride to inhibit anaerobic fermentation of sludge, with a view to providing a reference for the research and practical application of sludge treatment technology.

2. Materials and methods

2.1 *Sludge and agent*

The sludge used in this study was taken from the secondary sedimentation tank of a sewage treatment plant in Tianjin, without being treated with polyaluminum chloride. The sludge was first precipitated by gravity in the laboratory for 24 h, and the supernatant was drained off. The concentrated sludge was stored in a refrigerator at 4℃. Main characteristics of sludge are as Table 1.

Table 1. Main characteristics of sludge.

Parameters	Sludge
pH	6.9 ± 0.1
Total solids (TS)	25100 ± 370 mg / L
Volatile solids (VS)	16800 ± 210 mg / L
Total chemical oxygen demand (TCOD)	19800 ± 450 mg / L
Soluble chemical oxygen demand (SCOD)	165 ± 10 mg / L
Total protein	9740 ±330 mg / L
Total polysaccharide	2200 ± 120 mg / L

Polyaluminum chloride in the test was of analytical grade and was produced from Tianjin Damao Chemical Reagent Factory. Sodium citrate in the test was analytically graded and was produced from Tianjin produced Recovery Institute of Fine Chemicals.

2.2 *Experimental design*

According to the ratio of raw materials, six 500 mL anaerobic bottles were set up in the experiment, which were recorded as: T1 (Control group), T2 (1:0), T3 (2:1), T4 (1:1), T5 (1:2) and T6 (0:1). Take 400 mL sludge and 50 mL inoculated sludge into each fermentation bottle, and then add the sodium citrate and polyaluminum chloride stock solution prepared in advance to five of the anaerobic bottles to reach the predetermined dose. The predetermined doses of sodium citrate and polyaluminum chloride are as follows： polyaluminum chloride is 70 mgAl/gTS (1:0), 70 mgAl/gTS polyaluminum chloride plus 35 mg/gTS sodium citrate (2:1), 70 mgAl/gTS polyaluminum chloride plus 70 mg/gTS sodium citrate (1:1), 70 mgAl/gTS polyaluminum chloride plus 140 mg/gTS sodium citrate (1:2), 70 mg/gTS sodium citrate (0:1). Then pass N_2 into the fermentation bottle for about 2 minutes to remove the excess air in the fermentation bottle, so that the fermentation bottle is an anaerobic environment, and then immediately seal it with a rubber stopper. The sealed fermentation bottle is placed in a 37℃ air bath constant temperature shock box for 7 days, and the shaking speed was 120 rpm/min.

2.3 Analysis method

TS and VS and soluble chemical oxygen demand (SCOD) were determined according to standard methods[13, 14]. The soluble protein was measured by the Lowry method (Lowry Protein Assay Kit, Solarbio PC0030) according to the manufacturer's instructions with BSA as a standard substance. And the polysaccharides were determined by the anthrone-sulfuric method with glucose as a standard substance[15]. SCFAs were determined by a high-performance liquid chromatography (HPLC, Waters, e2695) unit with ultraviolet (UV) detection (λ = 210 nm) equipped with a C_{18} chromatographic column. The injection volume was 10 μL, and the mobile phases used were phosphate-buffered saline (10 mmol/L, pH = 2.5) and methanol (78:22, v/v) circulated at 1.0 mL/min at 30℃. Total SCFAs were calculated as the sum of measured acetic, propionic, n-butyric and n-valeric acids[16]. The microscopic morphology of sludge was measured by scanning electron microscopy (SEM) [17]. The method for measuring the dewatering performance of sludge is the specific resistance method of sludge[18]. Key enzyme activities were evaluated using the Lowry-Folin kit, alpha-amylase kit, and acetate kinase kit according to the manufacturer's instructions.

3. Results and discussion

2.4 Effects of sodium citrate on SCFAs produced by sludge anaerobic fermentation

Acid production is an important parameter in the anaerobic digestion process, which can intuitively reflect the performance of the anaerobic digestion system, and it is an important basis for judging the quality of an anaerobic digestion process [19]. Fig. 1 reflects the variation of SCFAs accumulation with time under different dosages of sodium citrate. It can be seen in Fig. 1 that the maximum SCFAs accumulation amount in the inhibition group (0.07 gAl/gTS) was 1164.31 mg/L. While a certain proportion of sodium citrate was added, the SCFAs accumulation amount increased. When the ratio of sodium citrate to polyaluminum chloride is 2:1, the accumulation effect of SCFAs is the best, and the accumulation of SCFAs can reach 2891.6 mg/L. It is 2 times the cumulative amount of SCFAs in the control group and 2.5 times the cumulative amount of SCFAs in the inhibition group during the same period, and it also shortens the time of maximum acid production. As time increased, when the total organic acid reaches the maximum value, it gradually decreases. This is because the methanogens gradually adapted to the environment and metabolized, and the SCFAs were used to produce methane. The above experimental results show that the presence of sodium citrate can increase the cumulative amount of SCFAs, and can achieve the purpose of strengthening anaerobic fermentation to produce acid.

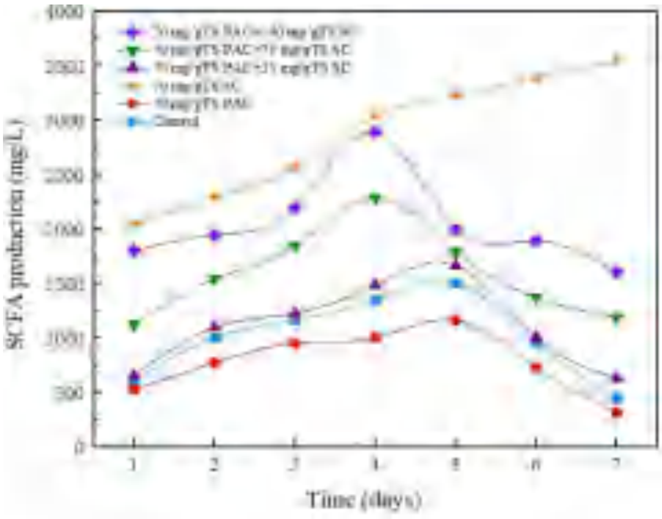


Fig. 1. Variation of SCFAs accumulation with different dosages of sodium citrate

2.5 Effects of sodium citrate on sludge dissolution during sludge anaerobic fermentation

As is known to all, the hydrolysis efficiency of substrates during fermentation greatly affects the subsequent SCFAs yield. Therefore, to explore the mechanism of increasing SCFAs yield, we must first analyze the level of substrate hydrolysis efficiency during fermentation[20]. The degree of sludge hydrolysis during anaerobic fermentation can be demonstrated by SCOD. SCOD shows the dissolution and output of organic substrates[21]. Soluble polysaccharides and proteins are the main components of SCOD, and the hydrolysis of soluble polysaccharides and proteins have been confirmed to be closely related to the composition of SCFAs[22]. Therefore, the hydrolysis effect of the fermentation substrate in this paper is expressed by SCOD, soluble polysaccharide, and soluble protein.

The concentration of SCOD in the fermentation with different proportions of sodium citrate depicts in Fig. 2. It can be seen that the concentration of SCOD in each group showed an increasing trend after the addition of sodium citrate. The increasing SCOD concentration indicates that the organic matter in the sludge is more and more converted into soluble matter, and the organic matter is decomposed. Especially when the concentration of sodium citrate and the concentration of polyaluminum chloride was 2:1, the maximum amount SCOD was 9251 mg/L. It can be judged that there were more soluble organic matters in the fermentation broth at this time. With the progress of fermentation, SCOD gradually decreased after reaching the maximum. Analysis of the reasons is that there are also different types of consumption processes, such as the hydrolysis of dissolved organic matter by acid-producing microorganisms for further use.

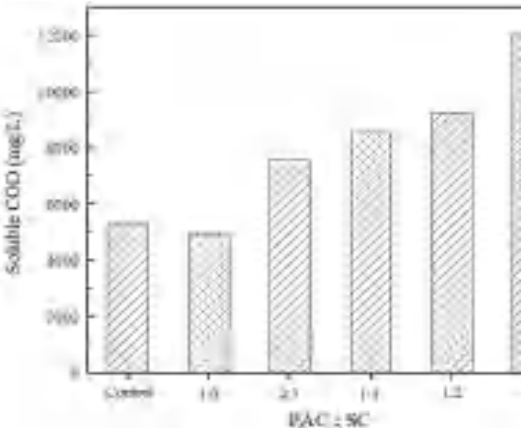
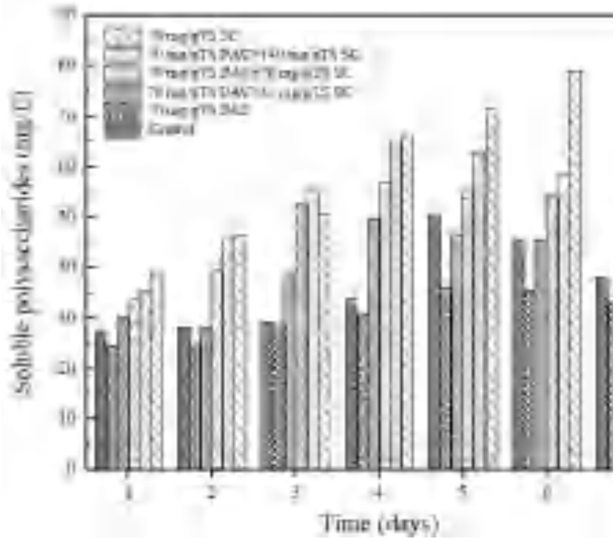


Fig. 2. SCOD production under different dosages of sodium citrate

Protein and polysaccharides are the main components in sludge. Therefore, in addition to SCOD can characterize the sludge dissolution effect, protein and polysaccharides can also show the dissolution effect of sludge. The changes of proteins and polysaccharides with the running time of anaerobic fermentation described in Fig. 3 and Fig. 4. It can be seen that the dissolution of soluble protein and soluble polysaccharides increased after sodium citrate addition by sludge anaerobic fermentation. The soluble polysaccharides and soluble protein were significantly higher than without sodium citrate. The maximum soluble protein concentration in the control group and the inhibitory group was 1420 mg/L and 1055 mg/L, respectively. And the maximum soluble polysaccharide concentration was 50.7 mg/L and 36.2 mg/L, respectively. After the addition of sodium citrate, the maximum soluble protein and polysaccharide concentrations increased, especially when the ratio of sodium citrate to polyaluminum chloride was 2: 1. The values of soluble protein and soluble polysaccharide were 1650 mg/L and 69.2 mg/L, respectively. The above data indicates that the insoluble particulate organic matter in the sludge has been hydrolyzed. It was further proved that the addition of sodium citrate broken the inhibitory effect of low-level polyaluminum chloride on sludge dissolution, and dissolving more soluble organic matter could provide more substrate for subsequent further fermentation.



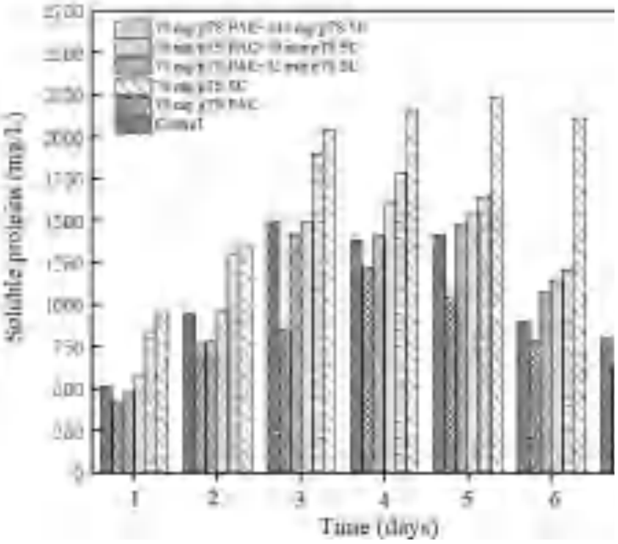


Fig. 3. Production of soluble polysaccharides under different dosages of sodium citrate

Fig. 4. Soluble protein production under different dosages of sodium citrate

2.6 *Effect of sodium citrate on the structure of sludge floc*

- *Effect of sodium citrate on microscopic morphology of sludge*

Scanning electron microscope (SEM) was used to observe the effect of sodium citrate on sludge morphology. The changes in the appearance of sludge floc at different dosages of sodium citrate showed in Fig. 5. It can be seen that compared with the control group when only the polyaluminum chloride with a concentration of 70 mgAl/gTS is present, the sludge structure becomes compact and dense, and the size of the sludge particles becomes larger, making it difficult for the organic matter in the sludge particles. However, after the addition of sodium citrate, the surface structure of the sludge changed greatly, the size of the sludge particles became smaller, the sludge floc became dispersed, and the specific surface area of the sludge particles was increased. Organic matter is easier to dissolve. This is because sodium citrate has to retard properties, and it can remove bridging ions (such as Al^{3+}) to deflocculate the sludge floc structure, thereby eliminating the inhibitory effect of low-level PAC on sludge and strengthening sludge anaerobic fermentation.

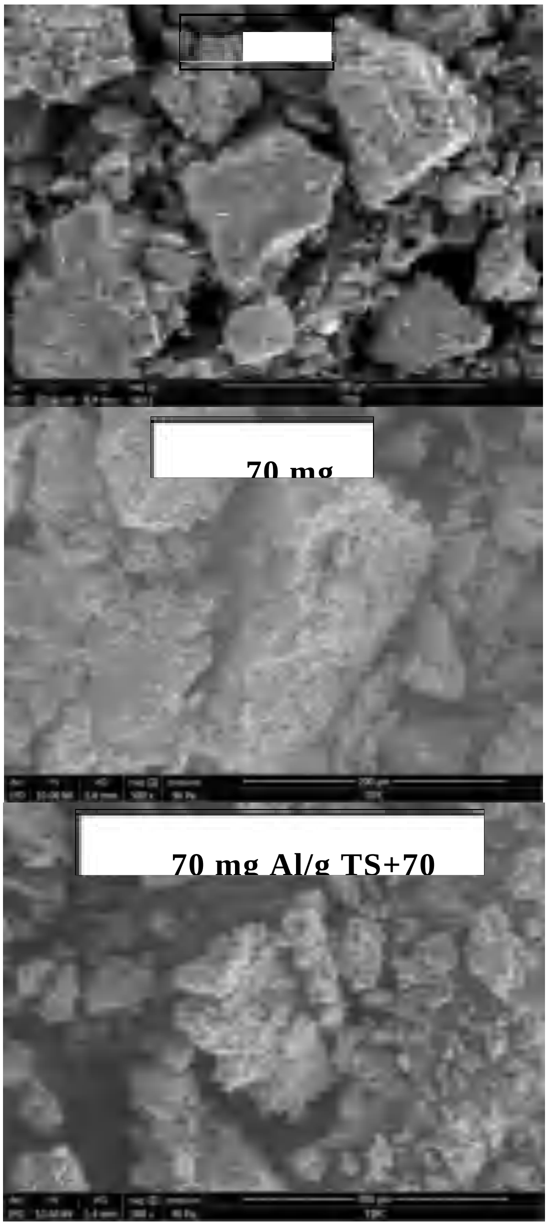


Fig. 5. Changes in the appearance of sludge floc under different dosages of sodium citrate

- *Effect of sodium citrate on extracellular polymer distribution*

EPS surrounds bacterial cells and forms a stable floc structure[23], so this work evaluated the effect of adding sodium citrate on sludge floc by studying the distribution and content of EPS. The distribution of EPS in sludge at different dosages of sodium citrate showed in Fig. 6. It can be seen that the T-EPS content decreases and the L-EPS increases, indicating that the stability of the sludge floc was greatly damaged, as the sodium citrate increases. The reason for the analysis may be that the addition of sodium citrate will replace the polyvalent cations in sludge, destroy the structure of the EPS, and release the macromolecular organic substances encapsulated in the EPS. And the organic matter in the sludge diffuses from the inner layer T-EPS to the outer layer L-EPS and S-EPS. L-EPS and S-EPS are more easily dispersed or hydrolyzed by extracellular enzymes, making it easier to be utilized by microorganisms, which further enhances the production of SCFAs and promotes the sludge anaerobic fermentation process.

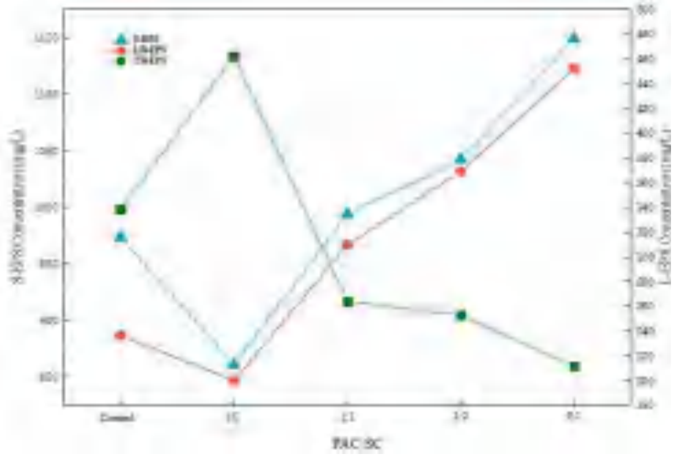


Fig. 6. Distribution of extracellular polymers in sludge under different dosages of sodium citrate

2.7 *Effect of sodium citrate on key enzyme activities*

The extracellular enzymes that play a major role in anaerobic fermentation are protease, a-amylase, and acetate kinase, respectively. Proteases can hydrolyze proteins into amino acids, α-amylase can catalyze the hydrolysis of carbohydrates into glucose and maltose, and acetate kinases are mainly responsible for converting monosaccharides and amino acids into acetate[24]. The relative activity of key enzymes after the addition of sodium citrate showed in Fig. 7. It can be seen that the key enzyme activities are significantly enhanced after the addition of sodium citrate. The relative activities of protease, α-amylase, and acetate kinase were 84%, 73%, and 82% in the inhibitor group (the concentration of PAC was 0.07 g/gTS), respectively. While the relative activities of the enzymes were significantly improved under the addition of sodium citrate, especially when the ratio of sodium citrate to polyaluminum chloride was 2: 1, the relative activities of the three key enzymes were the highest. At this time, the relative activities of protease, α-amylase and acetate kinase was 129%, 116%, and 121%, respectively. It can be seen that the addition of sodium citrate will increase the key enzyme activities of anaerobic fermentation, which may be due to the de-flocculation of sodium citrate, releasing the enzyme that was originally bound and hidden in the sludge matrix, and the hydrolysis activity is expressed, thereby promoting the further degradation of organic matter. The above results show that the addition of sodium citrate broken the inhibitory effect of low-level polyaluminum chloride on the key enzyme activities of anaerobic fermentation, and improves the efficiency of anaerobic fermentation.

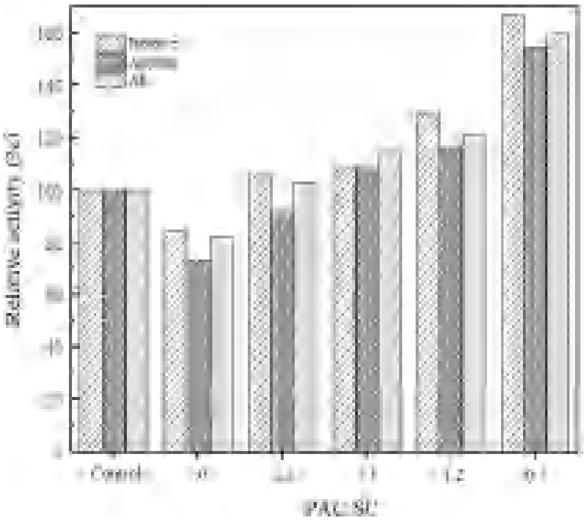


Fig. 7. Effect of different dosages of sodium citrate on key enzyme activities

2.8 Effect of sodium citrate on sludge dewatering performance

The sludge dewatering performance also determines the sludge anaerobic digestion performance[25]. Generally, the specific resistance of sludge is used as a key indicator for studying the dewatering performance of sludge[26]. The effect of different dosages of sodium citrate on the dewatering performance of sludge showed in Fig. 8. It can be seen that as the dosage of sodium citrate increases, the specific resistance of the sludge increases. When the percentage of sodium citrate to the polyaluminum chloride is 1:2, 1:1, 2:1, the specific resistance of the sludge is 1.6E+12, 2.2E+12, 4.1E+12, respectively, which shows that the addition of sodium citrate makes it more difficult for the sludge to dehydrate. It may be that sodium citrate causes the large particles of organic matter in the sludge to be broken, and the particles of the sludge are greatly reduced, resulting in an increase in the specific resistance of the sludge. Therefore, it can be considered that the dosage of sodium citrate and polyaluminum chloride is optimal when the ratio is 1: 1. At this time, the dehydration ability is not too bad, and it can break the inhibitory effect of low-level polyaluminum chloride on sludge anaerobic fermentation.

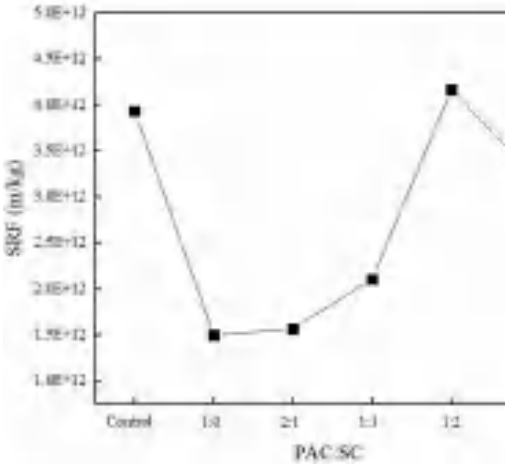


Fig. 8. Effect of different dosages of sodium citrate on the dewatering performance of sludge

5 Conclusion

This work investigated the effect of the low concentration PAC on sludge anaerobic fermentation in the presence of sodium citrate. Results revealed that the inhibition of PAC on anaerobic fermentation was broken by sodium citrate. The mechanism study shows that sodium citrate can deflocculate the sludge floc structure by removing the bridging ions Al^{3+} in the floc, and destroy the floc structure of the sludge, increasing the content of soluble and loosely bound extracellular polymers. And the activity of key enzymes was improved, thereby promoting the further degradation of organic matter and shortening the anaerobic fermentation time. However, the high dosage of sodium citrate is not conducive to sludge dehydration. Therefore, the optimal distribution ratio of sodium citrate to polyaluminum chloride should be 1: 1.

Acknowledgements

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Recovery of value-added products from the pyrolysis of end-of-life tires (ELTs)

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Abstract

The environmental concern associated with ELTs' disposal and the necessity of sustainable waste management policies have promoted the development of ELTs valorization processes in the last decades. Pyrolysis allows converting this solid wastes into three product fractions of potential interest, as are gases, pyrolysis oil (TPO), and pyrolytic carbon-blacks (CBp), with their yield and features being conditioned by pyrolysis conditions. Catalytic pyrolysis is an interesting alternative to improve the quality of the products and the selectivity of the process. Catalytic pyrolysis of ELTs with three selected cheap and readily available chemical materials of Calcium Oxide (CaO), Magnesium oxide (MgO), and Zinc oxide (ZnO) as the catalyst, have been conducted using a fixed bad pyrolysis reactor under atmospheric pressure. The effects of the different catalysts and their ratio (5, 10, 15, and 20% w/w) on product properties were investigated as well as the results were compared with non-catalyst experiments. The enhancement of cracking activity makes the TG and DTG curves shift to a lower temperature section, results in the reduction of maximum weight loss rate and temperature of nearly 30℃ from 400 to 373℃. Fewer energy requirements will benefit a lot from the economic and environmental points of view. It is to note that all three kinds of catalysts show good activity for sulfur removal, leading to a liquid fraction with low sulfur content. The adding of 15 wt% CaO caused the maximum reduction ratio of 55.3%. Obtained results were compared with fossil fuels and determined the possibility of being a potential source of renewable fuels. The CBps is a carbon-rich material, which contains the initial carbon black and inorganic compounds (such as Zn, Si and Ca) used in the tyre manufacture, and also other carbon based solids generated by repolymerization reactions involving BR and SBR. It shows significant potential in the direct re-utilization as carbon black in tires production.

Keywords: end-of-life tires; catalytic pyrolysis; CBp; TPO; Base catalysts

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1. Introduction

In recent years, automobile industry has developed rapidly, especially with the fast growth of the global economy. After 2010, China has replaced the USA and Europe as the world's biggest automobile market, with an increasing rate of 24% per year between 2005 and 2011.Moreover, it is predicted by McKinsey, a world-renowned management and consulting firm, that the amount of new vehicles in China will reach 22 million by 2020 [1]. However, booming of the automobile market has also induced a global issue of the ELTs recovery. According to the statistics released by European Tire and Rubber manufacturers' association, ELTs arisings have been reached up to 2.88 million tons in 31 countries (EU28 plus Norway, Switzerland and Turkey) in 2013 [2]. And it is also estimated that ELTs have been generated over 1 billion per year globally [3, 4] and discarded in landfills and stockpiles almost 4 billion [4], where more than 50% of them remain untreated before discarded [5]. Due to its incompressibility, ELTs have occupied ample space in landfills and became the breeding grounds for mosquitoes and rodents. Moreover, the variety of chemical leakage induced by ELTs after excessive rain washing and sun exposure lead to the pollution of soil and air, which will finally add risks to the environment and human health [6].

Tyres are made of three dimensional chemically cross-linked rubber (such as natural rubber, styrene-butadiene rubber, polybutadiene rubber, etc.) networks, steel, polymer fiber, CB and other organic (accelerator, antioxidant) / inorganic compounds (sulfur, zinc oxide). In the last 40 years, many research institutions and enterprises around the world have employed various methods to treat ELTs, including recycling, recovered fuel, energy recovery and pyrolysis.

In these kaleidoscope methods, pyrolysis has been addressed as an attractive thermochemical process to tackle the problem of ELTs while allowing energy recovery, exhibiting a decomposition and separation process under non-oxidative conditions (inert atmosphere or vacuum) usually between 400℃-700℃ to allow the breakage of chemical bonds in ELTs [7]. For example, recent research of a wider range of pyrolysis temperature of 400-1050℃ was conducted by Yazdani [8]. Besides some experiments also conducted in laboratory, recent researches put more attentions on the pyrolysis process in semi-industrial plants [9-12]. The catalytic pyrolysis of tire waste was also carried out by several researchers (Shah et al., 2009; Ilkılıc and Aydın, 2011; Islam et al., 2010; Frigo et al., 2014; Umeki et al., 2016; Boxiong et al., 2007; Zhang et al., 2008). For instance, Boxiong et al. (2007) carried out the catalytic pyrolysis of tire waste to examine the effect of zeolite catalysts and tempera- ture on pyrolysis yield. Zhang et al. (2008) reported that the use of basic additives and catalysts decreased the reaction tempera- ture.

CBp and volatile matter composed of condensable and non-condensable compounds mostly from rubber are two major products in this process (CBp refers to the solid fraction that have difficulty separating from each other). However, the surface activity of CBp is rather weak due to the high content of inorganic ash and carbonaceous deposits [13], limiting its practical application because of its low commercial value.

In this work, the in situ fixed-bed pyrolysis were conducted on the ELTs with and without a catalyst in order to produce value-add products of TPO, CBp and pyrolytic gases. The effects of different operation factors such as pyrolysis temperature, gas (N_2) flow rates as well as catalyst types on the pyrolysis yields and the characteristics of TPO and CBp were investigated. The optimum operation condition was determined to achieve maximum TPO yields. The effect of catalysts CaO, MgO and ZnO ratio on the yields and Sulphur retention was discussed. The morphological characteristics and physicochemical properties of CBp were analyzed using scanning electron microscope System

(FESEM), high-resolution transmission electron microscopy (HRTEM), Brunauer–Emmett–Teller (BET), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS) analytical methods.

2. Materials and methods

2.1 Materials

The ELTs was provided by Shanghai Tire Craftsman Technology Co., Ltd., and the sample was crushed into granules (40 mesh, particle size≤0.425 mm) to get a homogeneous mixture. The powder feedstock of ELTs was firstly dried in a vacuum oven at 65℃ overnight until constant weight before use in all pyrolysis experiments. Catalytic and non-catalytic pyrolysis of ELTs was carried out using a pyrolysis reactor with different catalysts such as Calcium Oxide (CaO), Magnesium oxide (MgO), and Zinc oxide (ZnO). The catalyst to feedstock ratio used in experiments were 5%, 10%, 15%, 20% on a weight basis. The catalysts, including CaO (chemically pure, CP), MgO (CP) and ZnO (CP) were purchased from Sinopharm Chemical Reagent Co., Ltd. and used as received without any further modification.

Table 1. Proximate and ultimate analysis of ELTs powder

Proximate analysis (wt.%, on air-dried basis)		Ultimate analysis (wt.%, on air-dried basis)	
Volatile	66.79	C	83.12
Fixed carbon	26.37	H	6.37
Ash	5.51	N	0.69
Moisture	1.33	S	1.57
		Others (O+ash)*	11.25

*Others: calculated by difference

2.2 Apparatus

The schematic diagram of the *in situ* fixed bed pyrolysis system is made up of gas carrier system, heating system, condensing system and collecting system, is shown in Fig. 1. The pyrolysis reactor made of quartz with the inner diameter of 40 mm and length of 800 mm equipped with electrically heating coil. Programmable temperature controller (PID controller) was used to control the temperature of the reactor to reach a specified temperature. Mass flow controller (MFC) was used to control the flow rate of the carrier gas N_2 with a purity of 99.99%. The thermal insulation tie was used between the pyrolysis reactor and the cooling system in order to avoid early condensation of pyrolysis vapor. The separation of liquid products and uncondensed gases was conducted when the pyrolysis vapor passing the helical condensing tube with the condensate temperature of 0.4℃ by a cooling water circulation machine.

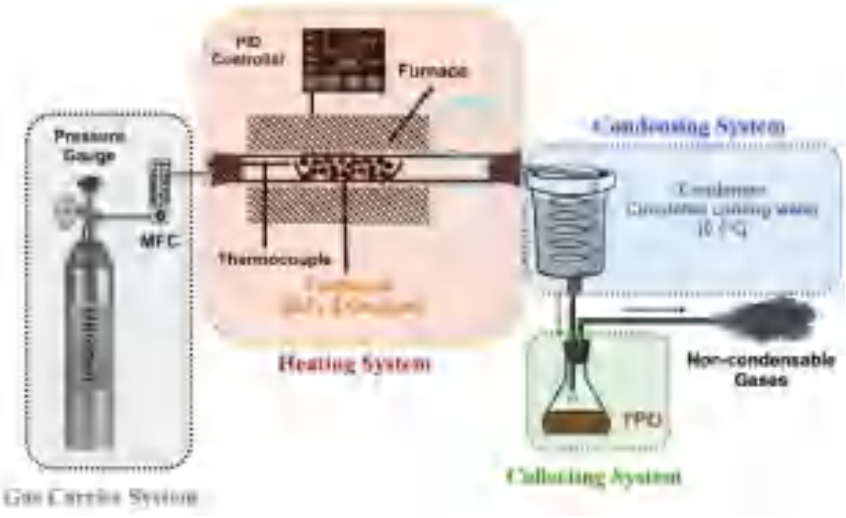

Fig.1 *In situ* fixed bed pyrolysis system

2.3 *Experimental procedure*

Experiments were carried out in two series of non-catalytic pyrolysis and catalytic pyrolysis. The aim of the non-catalytic pyrolysis was to determine the effect of the pyrolysis temperature and flow rate of carrier gas on pyrolysis yields. Firstly, the N_2 flow rate was controlled as 500 mL/min by MFC as well as a heating rate of 10 ℃/min from room temperature to the target temperature were kept constant in all temperature experiments. The 15g vacuum-dried sample placed in a quartz boat was put into the reactor from one side of the quartz tube to the center of heating zone when the final pyrolysis temperature of 400, 450, 500, 550 or 600℃ reached. The pyrolysis temperature kept unchanged for 60 min until the pyrolysis completed. The liquid phase was collected in a helical condensing tube with the condensate temperature of 0.4℃ by the circulation of cooling water. The CBp was taken out until the reactor cooling to room temperature. The aim of the catalytic pyrolysis was to study the effect of different catalysts and the optimum catalyst-ELTs ratio on pyrolysis products yields and their characteristics. The catalytic pyrolysis experiment was conducted by adding three different catalyst of CaO, MgO and ZnO at various catalyst ratio of 5, 10,15 and 20% wt of ELTs. The reactor temperature was increased at a heating rate of 20℃/min from room temperature to an optimum temperature of 550℃ with a continuous purge of inert nitrogen (N_2 purity of 99.99%). The optimum condition of 550℃ for 60 min was determined by Thermogravimetric analysis (TGA) of the ELTs (as displayed in Supplementary S1) under controlled conditions together with the consideration of energy efficiency and safety. The liquid products were collected by washing with ethanol. The TPO was finally obtained by an electric boiling plate at the temperature of 80 ℃overnight in which the solvent was evaporated and removed. The solid char was collected and weighed until the reactor cooling to room temperature. The gases' yield was calculated from deducting the weights of TPO and CBp from input material. All pyrolysis yields were expressed on dry-ash-free (daf) basis and each experiment was performed three times for each experimental condition. The average yields are given within the experimental error of ＜±1 wt.%.

2.4 *Characterization methods*

The morphologies of the CBp were characterized by field emission gun scanning electron microscope

System (FESEM, SIRION 200) and high-resolution transmission electron microscopy (HRTEM, JEM-2100F) operating at an acceleration voltage of 200 kV. The specific surface area and pore size distribution were determined from nitrogen adsorption–desorption measurement (ASAP2020 physisorption analyzer) based on the Brunauer–Emmett–Teller (BET) multipoint method and the Barrett–Joyner–Halenda (BJH) model, respectively. The particle size distribution of CBp were characterized by Zetasizer (Nano ZS 90). The crystal structures of solid materials were characterized by an X-ray diffraction (XRD, Bruker D8 Advance) with Cu Kα (λ = 1.5418 Å) radiation. X-ray photoelectron spectroscopy (XPS) spectra were acquired on a Kratos Axis ULTRA X-ray photoelectron spectrometer. The element analysis of the ELTs feedstock and CBp were obtained by a Vario EL III Element Analyzer (Elementar Analysensysteme GmbH, Germany) to determine the weight percentage of hydrogen, nitrogen and carbon, according to ASTM D5373-08.

3. Results and discussion

3.1 Pyrolysis yields

- *Effect of pyrolysis temperature on product yields*

The non-catalytic pyrolysis experiments were conducted at a constant N_2 flow rate of 500 mL/min and a constant heating rate of 10 ℃/min from room temperature to different pyrolysis temperatures. Various pyrolysis temperatures from 400 to 600 in every 50℃ were used to explore the effect of the temperature on the product yields and the optimum pyrolysis condition. The experimental results were shown in Fig. 2(a). The maximum CBp yield of 40.3 wt% and the minimum TPO yield of 37.35 wt% suggested the incomplete pyrolysis below 450℃. The increasing pyrolysis temperature enhanced the TPO yields while the CBp yield was decreased. The CBp yield decreased from 40.3 wt% to 38.02 wt% while the TPO increased from 37.35 wt% to 46.37 wt% at 500℃ to 550℃. Then, by further increasing the pyrolysis temperature to 600℃, an obvious decrease of the liquid yields to 41.03 wt% and the increase of gas yield to 20.45 wt% were observed.

In most cases, lower temperatures (＜450 ℃) favor char yields, while higher temperatures (>600 ℃) favor gas production. In the low pyrolysis temperature, since the ELTs could not be decomposed completely, the CBp yields were relatively higher. With the pyrolysis temperature increasing, both yields of liquid and gaseous products were increased because of either greater primary decomposition of the raw material or secondary decomposition of char residue. Decreasing of the liquid yields from 550 to 600 ℃may be interpreted by secondary reactions of the liquid fraction of volatiles while the little increasement of CBp yield maybe due to the desorption of hydrocarbons adsorbed during pyrolysis.

The non-catalytic pyrolysis experiments of different temperatures were also carried out to determine the optimum temperature for the maximum decomposition of the ELTs and TPO yield at 500 to 550℃.

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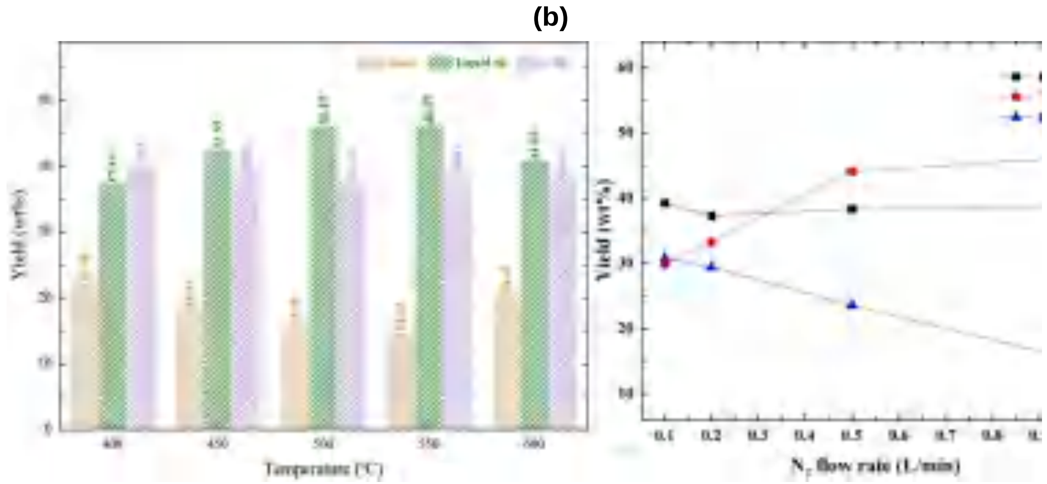

Fig.2 Effect of (a) pyrolysis temperature (b) nitrogen flow rate on product yields.

- *Effect of nitrogen flow rate on product yields*

The effect of nitrogen flow rate on ELTs' pyrolysis product yields was carried out by keeping the pyrolysis temperature at 550℃ for 60 min. The experiments were conducted while adjusting the nitrogen flow rate of 100, 200,500 and 1000 mL/min. The results could be seen in Fig 2(b). In short, an increasement in TPO yield and a decrease in gases yield were obvious with the increasing of nitrogen flow rate, while it seemed no clear effect on CBp yield. TPO yield elevated from 29.90 wt% to 46.37 wt% achieving an increase rate of nearly 55.1% with the raising nitrogen flow rate from 100 to 1000 mL/min. However, the yield of gases plummeted from 30.86 wt% to 14.82 wt% with the raising nitrogen flow rate from 100 to 1000 mL/min. Theses results could be explained by a review of the reactor structure. The residence time of pyrolysis gases as it passed through the hot region of reactor was strongly affected by the nitrogen flow rate. The higher the nitrogen flow rate, the less possibility of secondary reactions (such as, repolymerization, recondensation, thermal cracking and char formation) could occur. So that the yield of TPO increased due to the completed quenched liquid product as there were insufficient time for secondary reaction of pyrolysis vapor.

3.1.3 Effect of catalysts on pyrolysis products yield

The valorization process of converting ELTs into CBp, TPO and gases through catalytic and non-catalytic pyrolysis and the products yields and features being conditioned by pyrolysis conditions. The results of a series of experiments was shown in Fig. 4(a) by setting the pyrolysis temperature to 550℃ and nitrogen flow rate to 500mL/min in all experiments. In the non-pyrolysis experiment, a maximum TPO yield of 46.37 wt% was obtained with the CBp yield of 38.81wt% and gasses yield of 14.82 wt%. Whereas the use of three different catalysts, CaO, MgO and ZnO, overall decreased the TPO yields with increased yields of CBp and gasses. Earlier studies have found out that various characteristics of a catalyst controlled the formation and transformation of hydrocarbon molecules through selectivity or adsorption mechanisms, which resulted in the increase of gases yield and decrease of TPO yield [14]. Catalyst pyrolysis of ELTs was carried out with the various CaO-ELTs ratio of 5, 10, 15, and 20 wt%, respectively. The experiment was carried out at the pyrolysis temperature as 550 °C and the nitrogen flow rate as 500 mL/min. The results were indicated in Fig. 4(b). With the increasing CaO-ELTs ratio, the TPO yields decreased from 46.37 wt% to 29.28 wt% with the catalyst ratio of 15 wt%. In other words, approximately 36.9 % decrease was observed. The CBp yields almost kept almost constant at 38.8-41.9 wt%. With the increasing catalyst amount, the gas product yields increased in the range of 14.8-30.76 wt%, which corresponding to the decomposition of TPO.

All of these studies concluded that use of catalyst decreased the TPO yields due to the enhanced decomposition process of ELTs into lighter gases, which primarily lies on the catalysts characteristics. Moreover, catalytic pyrolysis of tire waste with 5 wt% CaO catalyst produced maximum char (41.99 wt%) with less amounts of TPO (31.97 wt%) and gasses (26.04 wt%).

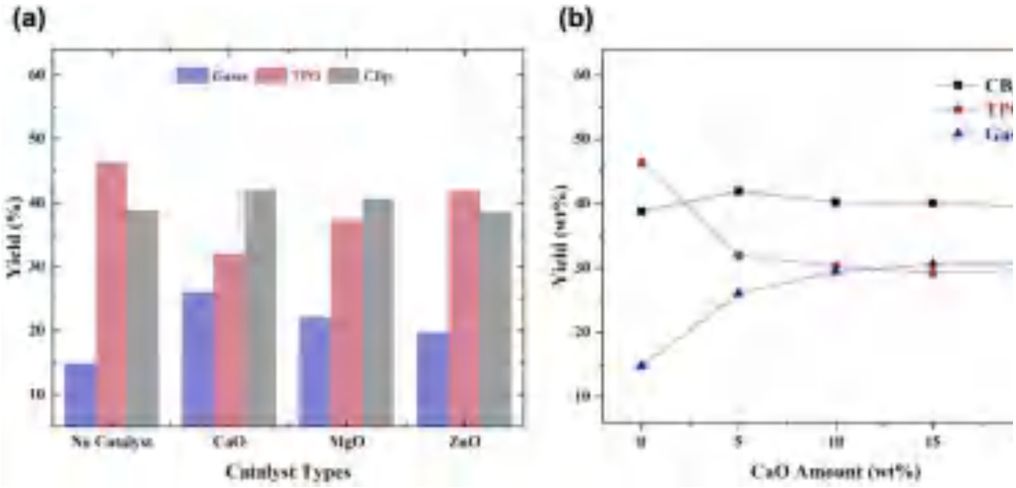

Fig.4 Effect of the (a)catalyst types and (b) catalyst amount on product yields.

3.2 Effect of catalysts on TPO sulphur retention

One of the main purpose of using basic catalyst in the pyrolysis of ELTs is to reduce the sulphur content in TPO products. The desulphurization effects of CaO, MgO, ZnO on the sulphur content of TPO were presented in Fig. 5. The sulphur amount of TPO rapidly decreased from 19.77 mg/mL to 10.90 mg/mL (CaO), 11.87 mg/mL (ZnO) and 15.39 mg/mL (MgO) with the addition of 5 wt% catalyst in ELTs. Lower Sulphur retention were obtained by increasing the content of Cao and MgO catalyst. The adding of 15% CaO caused the maximum reduction ratio of 55.3%. However, the sulphur reduction was not linear with the amount of the catalyst. Thus the increasing of catalyst proportion to 20 wt% have resulted in almost similar effects of 15 wt% on the reduction rate.

With catalyst addition the possible desulphurization reactions occurred in the pyrolysis of ELTs which are presented below. Eqs. (1) and (2) represent the desulphurization reactions with CaO, eqs. (3) and (4) represent MgO as well as eqs. (5) and (6) represent ZnO.

Same results have been reported by Cumali İlkılıç and Hüseyin Aydın [15] by using $Ca(OH)_2$ basic catalyst and observed a sharply decrease of Sulphur content from 1.4 to 0.9 wt% when adding 5 wt% $Ca(OH)_2$. Similarly, Jasmin Shah et al[16] have compared the Sulphur content between commercial diesel and TPO derived with MgO and $CaCO_3$. Results showed that the TPO have a Sulphur content of 0.6 % and 0.55 %, completely meets the demand of commercial diesel of ＜0.7 %.

$$CaO + H_2S = CaS + H_2O \quad (1)$$

$$CaO + COS = CaS + CO_2 \quad (2)$$

$$MgO + H_2S = MgS + H_2O \quad (3)$$

$$MgO + COS = MgS + CO_2 \quad (4)$$

$$ZnO + H_2S = ZnS + H_2O \quad (5)$$

$$ZnO + COS = ZnS + CO_2 \quad (6)$$

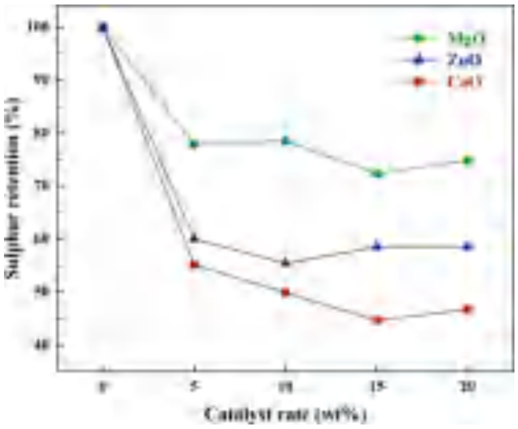

Fig.5 Effect of catalysts ratio on sulphur retention of TPO

3.3. Morphology of pyrolysis products CBp

As shown in Fig. 6, the microstructure of pyrolysis product CBp was clearly revealed by HRTEM. CBp nanoparticles, approximately 25-45 nm in diameter (shown in Fig. 6(a-c)), had a relatively homogeneous contrast as well as spherical morphology that easily fuse to clusters. What's more, TEM combined with Energy-dispersive X-ray spectroscopy (EDX) measurements to achieve the element mapping showing elemental distributions, has been applied widely for characterizing microstructures. Elemental mapping of CBp (shown in Fig.7) clearly showed the distribution of Carbon, Oxygen, Silicon, Sulphur, Zinc and Calcium. The sympathetic and homogeneous distribution of Oxygen and Silicon as well as Sulphur and Zinc implied the existence of silicon dioxide (SiO_2) nanoparticle and Zinc Sulfide (ZnS). Obviously, pyrolysis products CBp mostly ascribed to commercial carbon-blacks and SiO_2 nanoparticles added during the tire manufacturing as well as ZnS generated from the reaction of ZnO with S (from the decomposition of S-containing polymers) during the pyrolysis process. Other HRTEM further confirmed the formation of carbon-blacks in CBp by showing the onion-like lattice fringe characteristic of carbon black [17]. Different from the light-pyrolysis of ELTs[18-21], no observation of the rubber shell on the surface of CBp particles identified the completely destroy and remove of bound rubber structure in ELTs' particles.

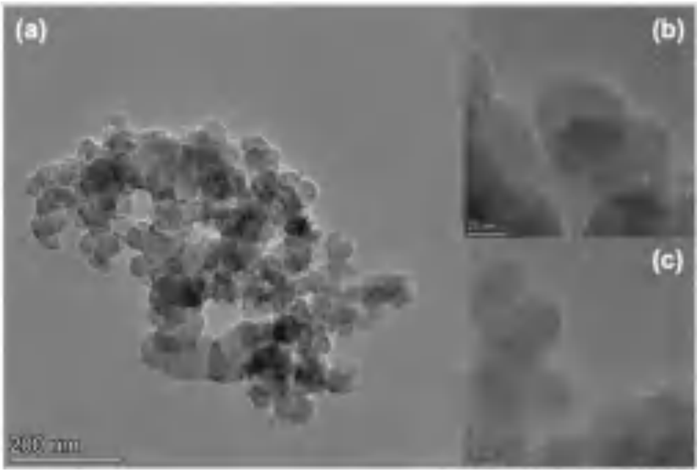

Fig. 6 HRTEM micrography of CBp

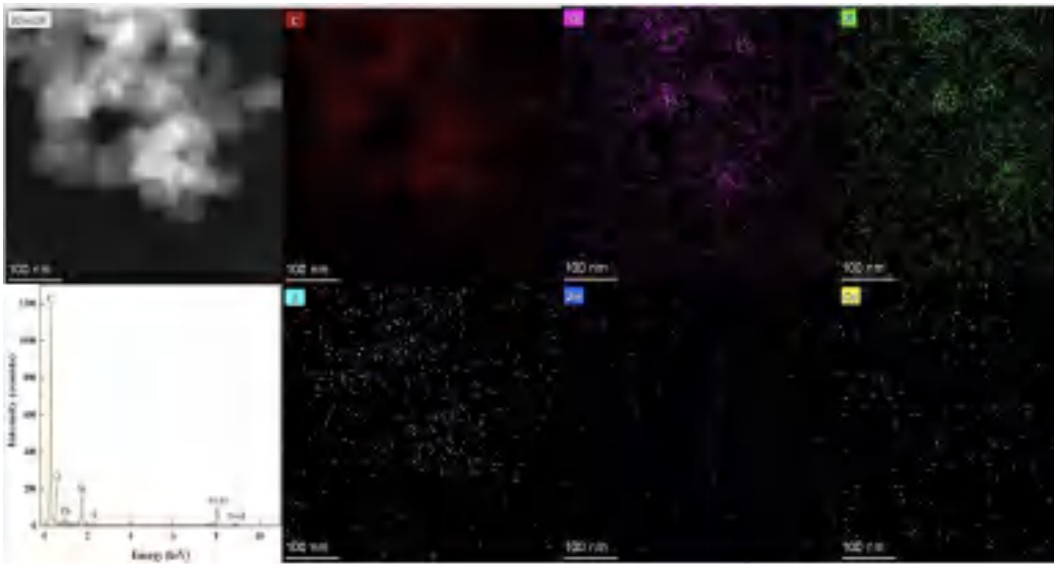

Fig. 7 Elemental mapping of CBp particles

3.4 Physicochemical properties of pyrolysis products CBp

27.ray diffraction analyses (XRD) is useful in identifying the chemical components of the solid sample. Comparing with N330, distinct peaks are observed at approximately 28.558, 47.515, and 56.289° (2θ), which can be indexed to the (101), (006), (108), and (116) planes of the hexagonal structure of ZnS with a P63mc space group (JCPDS No. 89-2156) (as shown in Fig.7). The XRD results implied existing of ZnS in CBp, corresponding to the analysis from elemental mapping. A low graphitization degree of both CBp and N330 was found out by showing of two broad diffraction peaks at 25°and 44°.

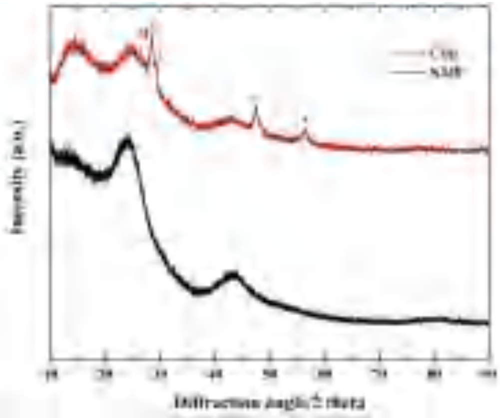

Fig. 7 X-ray diffraction patterns for CBps and N330 (S = Sphalerite (ZnS), M = Moganite (SiO_2), C = Calcite ($CaCO_3$)).

The distribution of particle sizes of CBp and N330 was shown in Fig. 8. CBp and N330 samples were dispersed in DI water by sonicating for 5 minutes. The Z-average particle size of CBp is 499.9 nm, which is higher than double the size of N330 (200.5nm).The polydispersity index (PDI) of the samples shows that the N330 has a more uniform distribution of 0.23, comparing to that of 0.56 for CBp. It could be concluded that CBp fused to clusters during pyrolysis process for the obvious bigger particle size of D(90),D(50) and D(10) as well as the size distribution than N330. The BET specific surface area of CBp is 64.19 $m^2 g^{-1}$, which is 20.3% smaller than that of N330. The conglomeration of CBp particles lead to a larger average particle size with lower specific surface area, which was in agreement with the results of particle size distribution.

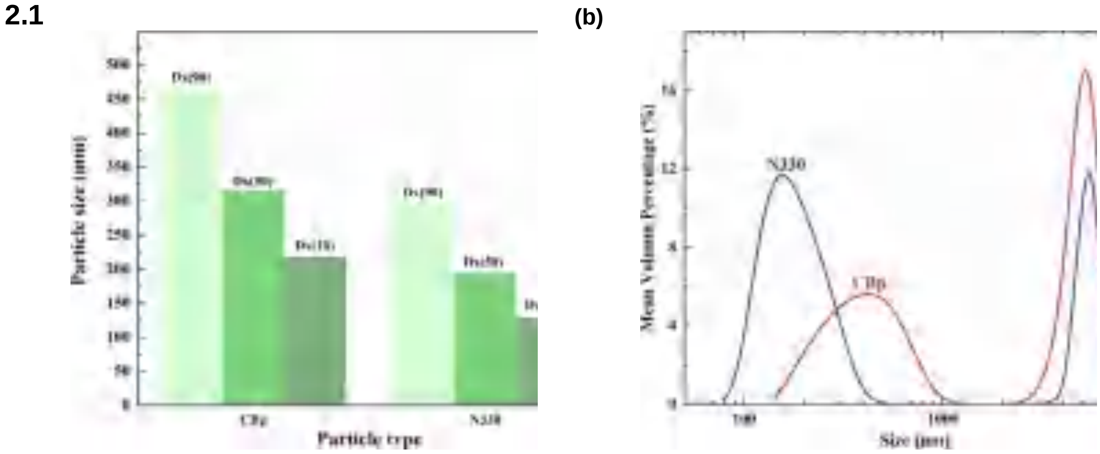

Fig.8 Particle size distribution of CBp and N330

XPS is applied to determine the composition as well as surface properties of the CBp. The curve fitting of the C1s peaks from the XPS spectrum are shown in Fig. 9. The XPS spectrum of C_{1s} for CBp was fitted to four peaks: C-C or C-H (C_1, BE = 284.8 eV), CeO (C_2, BE = 285.5 eV), C=O (C_3, BE = 286.7 eV), and COOH (C_4, BE = 289.0 eV)[22, 23]. The results of the curve-fitting of the C_{1s} spectrum are summarized in Table 3. As shown in Table 3 (left) and Fig 9(a), CBp has a higher content (55.91%) of C-C or C-H compared with 45.99% of N330, indicating the formation of carbonaceous deposits on the CBp surface through condensation and dealkylation of hydrocarbons process. The low content of C-O, C=O and COOH functional groups might result in the low reactivity in particle surface of CBp.

As shown in Fig. 9 (b) and Table 3 (right), the O1s spectra are fitted to three peaks: a peak with a binding energy of 532.5 eV(O_1), 533.5 eV(O_2) and 535.8 eV(O_3) are assigned to the C=O, C-O groups and a shake-up peak, respectively[24, 25]. The results of the curve-fitting of the O_{1s} spectra are shown in Table 3 (right). The oxidation of particle surface during pyrolysis might result in a higher ratio of C=O to C-O of CBp compared with N330. The shake-up peak observed in the spectrum of CBp, which was different from N330, showing the existence of free O_2 on or close to the surface of CBp.

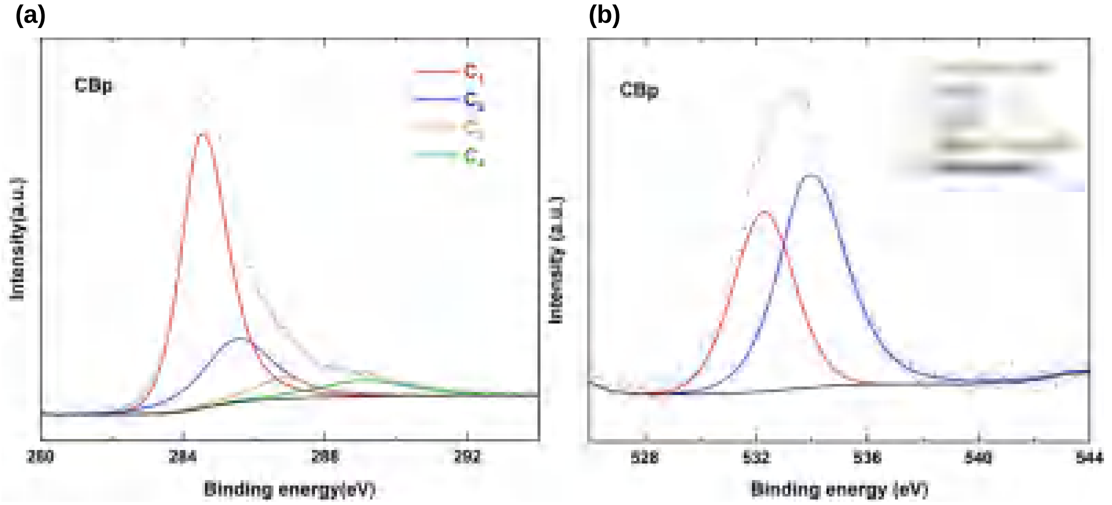

Fig. 9 XPS spectrum of (a) C_{1s} and (b) O_{1s} of CBp

Table 3 Area of the C_{1s} (left) and O_{1s} (right) peaks of CBp.

	Area of C_{1s} peaks/at%		Area of O_{1s} peaks/at%
C_1 (C-H or C-C)	55.91	O_1(C=O)	41.86
C_2 (C-O)	26.07	O_2 (C-O)	58.14
C_3 (C=O)	16.19	O_3	0
C_4 (COOH)	1.83		

3.5. Potential applications of CBp

As analyzed above, CBp is a complex mixture consisting of not only the original carbon-blacks but also carbonaceous deposits and oils as well as various organic and inorganic additives. CBp usually have two major applications: combusted as fuel and used as reinforcing filler directly or after further modification. Being used as fuel is uneconomic because the combustion suffers a lot for the ash in CBp will act as anti-flaming materials. As for being used as fillers, distinguishes can be made between functional fillers (such as carbon-blacks and modified CBp) that are to improve or generate new properties of the polymer composites as well as nonfunctional fillers (such as CBp) which are mainly used to reduce production costs. Usually, carbon-blacks and modified CBp are the predominant functional fillers used in commercial rubber manufacturing, including tyres and industrial rubber goods such as belts and mats. And due to its small particle size and large specific surface area make it difficult to disperse uniformly in the polymer matrix, CBp has a limited application [26, 27].

There are ongoing tests in tire factory to demonstrate the blending compatibility for using CBp as a functional filler or extender. This CBp product can be produced in several grades between a functional reinforcing filler or as a cost saving extender filler. The tyre or rubber manufacturer receives the CBp masterbatch using the same facilities as for receiving bales of rubber without carbon black. The advantages include, but not limited to:

[4] Mixing time saved because CBp is already pre-dispersed before using Banbury or roller mills.
[5] Saved electric power for mixing.
[6] Allows Banbury single stage mixing.
[7] Clean operations at customer's plant by eliminating or reducing the loss of airborne carbon black dusting.
[8] Easy stocking of raw materials and clean storing.
[9] Easy quality control on incoming CBp products at customer's plant.
[10] There are reasons to be optimistic about the economic feasibility of ELTs pyrolysis industries for the TPO and CBp could be upgraded into high-quality value-added products through the modification process in the near future.

4. Conclusions

In this study, non-catalytic and catalytic pyrolysis experiments using ELTs as feedstock were performed in a fixed-bed reactor under various conditions to obtain value-added products of CBp, TPO and gases. Various operation factors such as pyrolysis temperature, nitrogen flow rates and different catalyst (CaO, MgO and ZnO) were conducted to explore the yields of pyrolysis products as well as the characteristics of CBp and TPO. In the non-pyrolysis experiment, a maximum TPO yield of 46.37 wt% was obtained with the CBp yield of 38.81wt% and gasses yield of 14.82 wt%. Whereas the use of three different catalysts all decreased the TPO yields with increased yields of CBp and gasses due to the catalyst controlled formation and transformation of hydrocarbon molecules through selectivity or adsorption mechanisms. The adding of 15 wt% CaO caused the maximum Sulphur reduction ratio of 55.3%, which contributes a lot in deducting SO_2 emissions by the combustion of fossil fuel. The morphological characteristics and physicochemical properties of CBp were analyzed using FESEM, HRTEM, BET, XRD, XPS, EDX analytical methods and the results indicated that CBp was a complex mixture of carbon-blacks and SiO_2 used in tyre manufacture process together with ZnS generated during pyrolysis. Carbonaceous deposits and oils absorbed during pyrolysis process as well as various organic and inorganic additives resulted in the low reactivity of CBp comparing to commercial carbon-blacks. The catalytic pyrolysis of ELTs is proven to be an environmental-friendly and efficient method as well as a promising technique for producing high-value pyrolysis products.

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Sustainable metal recovery from waste streams via intensified electrochemical processes

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Abstract: Due to the wide spread development of chemical, electronic, metallurgy and energy, considerable hazardous heavy metals-bearing wastewater and solid waste are directly or indirectly discharged into the environmental. In order to overcome the drawbacks of long process-flow and large chemicals requirements in conventional treatment technologies, novel electrochemical metal extraction techniques are developed in this study including alkaline electrochemical oxidation processes (A-EAOPs) and cyclone electrowinning (emew® cell). Efficient and selective metal extraction is achieved from refractory spent SCR catalysts and vanadium slag via in-situ generated reactive oxygen species (ROS), while controllable Cu, Te, Se powdery products are obtained from dilute multi-component wastewater. Besides, the electrochemical recovery mechanism and behavior are revealed using in-situ dynamic X-ray synchrotron imaging and fluid flow calculation techniques, particularly in the complicated HCl effluents. Based upon the systematic investigations of reactors, mass transfer, phase transition and electrochemical reactions, the process-mechanism-products (PMP) rational design of electrochemical metal recovery is proposed rather than simply metal removal.

Keywords: Metal recovery, Reactive oxygen species, Mass transfer, in-situ dynamic X-ray imaging, Process-mechanism-products (PMP)

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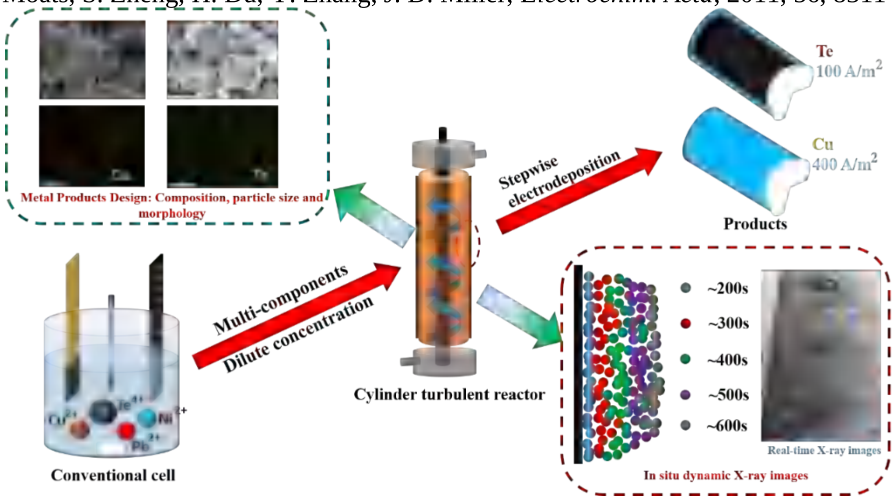

Fig. 1: The process-mechanism-products (PMP) during electrochemical metal recovery

A molten-salt electrolysis approach for the recycling of spent lithium-ion batteries

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Recycling spent lithium-ion batteries can close the strategic metal cycle while averting ecological and environmental footprints. High-temperature molten salts could act as both a promising electrolyte and a solvent to recover valuable Li and transition metals assisted by an electrochemical method that use electrons to break down the crystal structure and thereby sperate the Li and transition metal. In this paper, the molten salt paired electrolysis method employs electrons as both reducing and oxidizing agents and the molten salt as the solvent to separate the desired products without producing any hazardous secondary waste. Since the valence of Fe in $LiFePO_4$ is 2+, the valence can be moved at both directions if proper electrolytes are chosen and appropriate potentials are applied (Fig. 1). Moreover, molten salt electrolytes have a wide electrochemical potential range (e.g., electrochemical window) and considerable capability for dissolving lithium salt, which can be used as an electrolyzer to entail specific electrochemical reactions and solvent extraction processes. A molten salt electrolyzer with a solid $LiFePO_4$ cathode and three types of anodes. All the three electrolyzers work well to electrochemically split $LiFePO_4$ to Fe, Li^+, and PO_4^{3-}. Besides molten carbonates, other types of molten salts such as halides, hydroxide, sulfates can be used. The anodic products are CO_2, O_2 and Fe_3O_4 if graphite, Ni10Cu11Fe alloy and $LiFePO_4$ anodes are employed, respectively. To minimize the energy consumption and CO_2 emissions, the paired electrolysis cells with dual $LiFePO_4$ electrodes is preferable. In all types of eletrolyzers, the recovery rates of both Li and Fe are over 95.2%. Beside $LiFePO_4$, the molten-salt electrolysis approach can be used to treat a variety of cathode materials of LIBs.

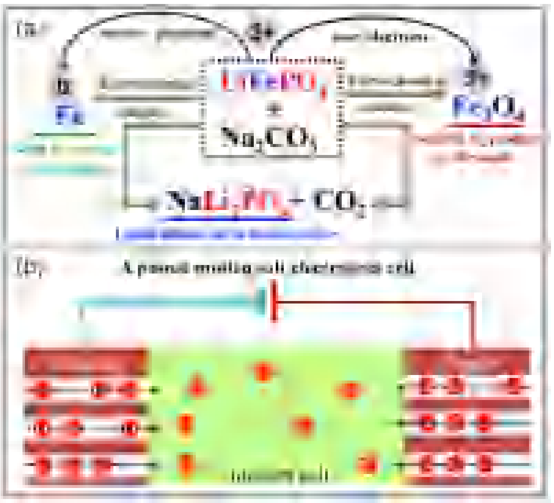

Fig. 1 (a) The schematic illustration of the reactions and element follow, (b) the paired electrolysis cell.

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Oxalic acid as an agent for electro-leaching and direct recovery of REE oxalates from spent NdFeB magnets

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Abstract

Economic, political, and geochemical problems connected to recovery of rare-earth elements (REEs) give new challenges for developing new affordable technologies. One of the most perspective secondary waste for REEs recovery is NdFeB magnets as they contain high amount of neodymium (25−30%). They are widely used in hybrid cars, turbines, hard drive disks, and headphones as nowadays they are the strongest magnets. In this study, a simple, cheap and eco-friendly hydrometallurgical route is offered for a process, in which the rare-earths metals are recovered in high purity by using only several steps: demagnetization, etching, and combined electro-leaching and recovery from solution based on sulfuric and oxalic acids. During electrolysis a compact layer of REE oxalates in a purity of up to 91−93% is obtained on the cathode, while iron remains in the solution and as solid residue for further recovery. The mechanisms of oxalate precipitation were subsequently investigated and proposed electrostatic attraction as the force of the REE-oxalate particles formation. For this purpose, number of analytical methods (SEM, EDX, XRD, XPS) were used to investigate the composition and structure of sediment. The most interesting finding of this study is deposition of the REEs on the cathode from aqueous solution. This study provides a new insight on electronic waste recycling by implementing principles of electrochemistry.

Keywords: Recycling; Electrolysis; Leaching; Oxalic Acid; NdFeB

Study on Separation Process and Mechanism of Electrode Metal and Non-metal Materials in Waste Lithium-ion Battery

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Abstract（200-400 words）

Lithium-ion batteries have excellent electrochemical performance and are widely used in various electronic products. With the popularity of lithium batteries, the amount of waste LIBs is also rising. Based on the potential environmental risks and resource value of LIBs, the recycling of waste LIBs has been a research hotspot. This article is based on the widely used lithium cobaltate/graphite battery in mobile phone products. Based on the structural composition and characteristics of waste LIB, separation of the electrode material of the waste LIB was carried out by ultrasonic process, because ultrasonic wave can produce mechanical effect, cavitation effect and local transient high temperature and high pressure in liquid medium. Based on the opposite surface wetting characteristics of lithium cobaltate and graphite, the flotation process is used to separate the active electrode material after ultrasonic separation. All of these provide support for the development of the recovery process of the waste LIB electrode materials. The mechanism of ultrasonic separation of electrode materials is mainly to destroy the contact interface between the active materials and the aluminum foil. The specific mechanism of this action is the impact pressure on the surface of the electrode material, which is caused by the liquid medium and the microjet generated by the cavitation effect, so that PVDF falls off from the electrode material. The so-called "hot spots" are formed in the solution because of ultrasonic cavitation, resulting in a large amount of free radicals which cause the degradation of PVDF.

Keywords: waste lithium-ion battery; electrode material; ultrasonic separation; flotation separation; cavitation effect

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Anaerobic digestion is a proper way to treating kitchen waste in China

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Abstract（200-400 words）

With the proposal of the concept of zero-waste city and the implementation of waste classification in China, a large amount of centralized kitchen waste leads to prominent problems about resource and environment, and there is an urgent requirement for technology research and development of large-scale treatment and disposal of kitchen waste. In recent years, the anaerobic digestion of methanogenic technology for urban organic waste such as kitchen waste has attracted more attention. This paper reviews the production and characteristics of kitchen waste in China and abroad, and summarizes the research progress of anaerobic digestion technology for kitchen waste. In addition, this paper analyzes the influence factors of the anaerobic digestion process and the technology to promote the anaerobic digestion process of kitchen waste, and discusses the secondary pollution control of the anaerobic digestion technology. It is considered that anaerobic digestion treatment is a suitable technical solution to realize the large-scale production of methane from kitchen waste. Future research should focus on pretreatment, co-digestion, improvement of anaerobic system stability, methane purity and biorefining model to achieve efficient conversion of kitchen waste into methane.

Keywords: kitchen waste; anaerobic digestion; biogas

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1. Introduction

Kitchen waste includes food waste, vegetable market waste, household kitchen waste, etc., which is an important part of municipal solid waste. With the rapid growth of the world's population and the improvement of living standards, the abundance of food and diet is getting higher and higher, the emissions of kitchen waste are also increasing[1]. According to the statistics, the output of food waste in Asia will increase to 4.16 billion tons in 2025[2]. According to the China Statistical Yearbook (2019), the total municipal solid waste of China in 2018 is about 228 million tons. The output of kitchen waste is about 127 million tons considering that kitchen waste accounts for 56.79% of China's municipal solid waste[3]. The disposal of kitchen waste is a complicated and difficult problem due to its complex composition, high moisture content and organic content. Whether in developed countries or in developing countries, the search for appropriate disposal methods is the hot spot of kitchen waste research. In the past, kitchen waste would be disposed by landfill and incineration together with municipal solid waste. In China, the proportion of household waste in landfill and incineration can reach 53.0% and 43.8% respectively[4]. However, neither of the two disposal methods has realized the resource utilization of kitchen waste, which is not an appropriate disposal method. Landfills occupy land resources and the landfill leachate may contaminate ground water and soil. The high moisture content of kitchen waste leads to high energy consumption and low efficiency for incineration, which will produce dioxins and other toxic substances that cause secondary pollution. Moreover, both landfill and incineration emit more greenhouse gases. Studies have shown that the global warming potential(GWP) of landfill or incineration is about twice that of composting and incineration[5]. The kitchen waste has a very high recycling value. The recycling of kitchen waste can not only solve the pollution problem, but also realize the recycling of resources. At present, the commonly used recycling technologies for kitchen waste include: anaerobic digestion, aerobic composting and feedstuffs. With the shortage of fossil energy in the world, people pay more attention to the development of renewable energy, and there are more and more researches on transforming kitchen waste into renewable energy. Kitchen waste is considered as an appropriate anaerobic digestible substrate because of its high concentration of organic matter, high moisture content and good biodegradability[6]. So the methane-producing technologies for anaerobic digestion of urban organic waste such as kitchen waste have received increasing attention in

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recent years.

Chinese kitchen waste production is very large at present, so the need to find appropriate resources, harmless, large-scale treatment technology is very urgent. In May 2019, China began the pilot construction of “waste-free cities” in 16 cities to continuously promote the source reduction and resource utilization of solid waste, minimize landfill capacity and reduce environmental impact[7]. Therefore, more and more attention has been paid to the recycling and harmlessness of kitchen waste. In July 2019, Shanghai officially implemented garbage classification, and kitchen waste was separated as wet waste, leading to a sharp increase in the amount of kitchen waste collection. So China's kitchen waste treatment field is in urgent need of appropriate resource-based, harmless and large-scale treatment technology[4].

Aiming at the resource utilization problems faced by Chinese kitchen waste, this paper reviews the production and characteristics of kitchen waste in China and abroad, and summarizes the research progress of anaerobic digestion technology for kitchen waste. In addition, this paper analyses the influence factors of the anaerobic digestion process and the technology to promote the anaerobic digestion process of kitchen waste, and discusses the secondary pollution control of the anaerobic digestion technology. It is considered that anaerobic digestion treatment is a suitable technical solution to realize the large-scale production of methane from kitchen waste in China. The future development of biogas from anaerobic digestion of kitchen waste is prospected.

2. Production and characteristics of kitchen waste

2.1. Production of kitchen waste

Food production, circulation and consumption process losses are the main source of kitchen waste. According to the statistics of the Food and Agriculture Organization of the United Nations (FAO), one-third of the global food is wasted in production, circulation and consumption process[8]. Most of these food wastes with an annual waste volume of 130 million tons are treated as kitchen waste[9]. The per capita kitchen waste of consumers in Europe and North America is about 95-115 kg/a. More than 40 percent of food production ends up in landfills without being on the dining table in the United States. In 2016, the global municipal solid waste output was 2.01 billion tons, and about 44% of MSW was kitchen waste and garden waste with an output of 880 million tons[10]. In 2010, Chinese kitchen waste production was the highest in the world[11]. In addition, kitchen waste is the main component of municipal solid waste, and the proportion of kitchen waste in municipal solid waste is shown in Fig. 1[3, 12, 13]. It can be seen that kitchen waste in most countries accounts for about 12%-30% of municipal solid waste, while China has the highest proportion of 56%. The effective treatment of kitchen waste can reduce the pressure on the management and treatment of municipal solid waste.

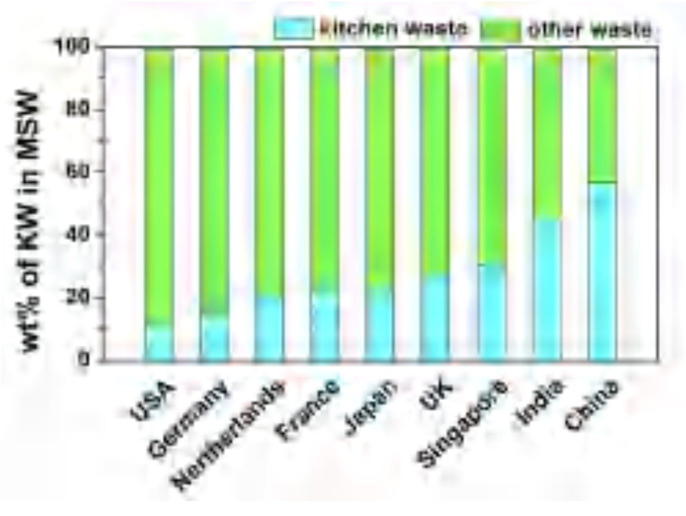

Fig. 1. Proportion of kitchen waste in municipal solid waste in some countries[3, 12, 13].

China produces large amounts of kitchen waste with complex ingredients due to the huge population and diverse eating habits. Chinese kitchen waste consists of food waste, vegetable market waste and household kitchen waste. The food waste and vegetable market waste have the characteristics of large quantity and concentrated distribution, while household kitchen waste in community has the characteristics of small single-household output , large total output and scattered distribution[14]. According to the data from the “China Statistical Yearbook” released by the China National Bureau of Statistics and the “Analysis Report on the Development Prospects and Investment Strategic Planning of Chinese Kitchen Waste Treatment Industry” released by the China Prospective Industry Research Institute, we obtained the “Municipal solid waste collection and transportation volume in China from 2011 to 2018” (Fig. 2) and “kitchen waste production in China from 2011 to 2018” (Fig. 3) [15]. The production of Chinese municipal solid waste and kitchen waste have increased every year. In 2018, the annual collection and transportation volume of Chinese municipal solid waste have reached 228 million tons, and the annual production of kitchen waste have reached 108 million tons. In addition, Chinese kitchen waste accounts for a high proportion of municipal solid waste, and some scholars analysed the proportion of Chinese kitchen waste in municipal solid waste from 1991 to 2016 (Fig. 4)[3]. The proportion of Chinese kitchen waste in municipal solid waste is North China (50.8%), Northeast (58.9%), East China (64.5%), Central China (49.4%), South China (51.2%), Southwest (52.2%) and Northwest (51.9%). In 2019, China began to implement waste sorting, and a large amount of household food waste (kitchen waste) was separated from municipal solid waste. The timely disposal of kitchen waste plays an important role in realizing the “reduction, recycling and harmlessness” of MSW.

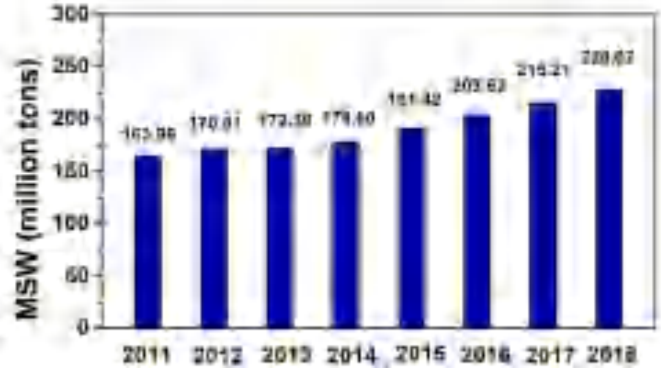

Fig.2. Municipal solid waste collection and transportation volume in China from 2011 to 2018.

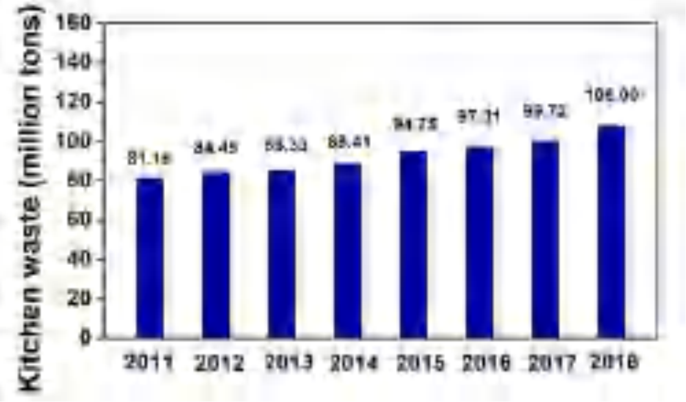

Fig.3. Kitchen waste production in China from 2011 to 2018[15].

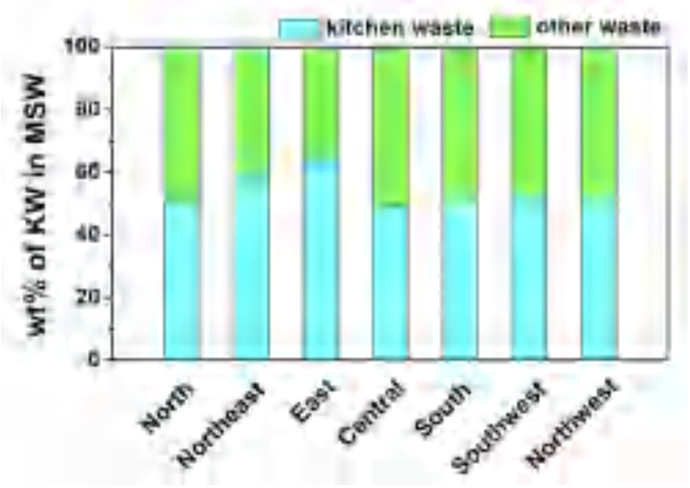

Fig.4. Proportion of Chinese kitchen waste in municipal solid waste from 1991 to 2016[3].

Through the analysis of domestic and foreign kitchen waste production, we know that the production of Chinese kitchen waste and the proportion of kitchen waste in MSW are higher than other countries. The treatment and disposal of Chinese kitchen waste is extremely important for environmental and ecological protection. The implementation of the waste sorting policy in China will greatly promote the development of the kitchen waste treatment market. The demand for kitchen waste treatment capacity has increased sharply, and the recycling of kitchen waste is imperative.

2.2. Characteristics of kitchen waste

Due to different dietary and cultural habits, the composition of kitchen waste in different regions has its own characteristics. However, kitchen waste has several common characteristics, such as high organic matter content, high water content, high fat content, high salt content, and perishable deterioration. Kitchen waste is rich in organic matter and nutrients, so it is a suitable substrate for anaerobic digestion and has a high potential for resource recovery. In the process of resource utilization, we should consider the unique component characteristics of kitchen waste in different regions. The content of oil and salt in Chinese kitchen waste is high, especially the oil content is much higher than other countries[16, 17]. Therefore, the effect of high salt and oil should be considered in the process of resource treatment of Chinese kitchen waste. Table 1[18], Table 2[19] and Table 3[20-22] list the composition, element analysis and nutrient content of Chinese kitchen waste. It can be seen that Chinese kitchen waste mainly consists of grains, vegetables, peels, vegetable oils, fats, meat, eggs, bones and debris, which contains a large amount of water, carbohydrates, proteins, lipids and other organic matter, and has a high Total solids (TS) content and volatile solids (VS) content. The C/N ratio of kitchen waste is lower than other organic wastes because of its higher N content. In addition, kitchen waste is rich in P, Na, K, Ca and other constant elements, but the content of trace elements such as Fe, Ce and Ni is relatively low. The efficient anaerobic digestion process of kitchen waste can be achieved by adjusting the C/N ratio of the anaerobic digestion substrate and adding some beneficial trace elements. In addition, perishable kitchen waste in storage and disposal will produce stench and landfill leachate, which will cause environmental pollution of the atmosphere, soil and water. Therefore, harmless and resourceful treatment of kitchen waste should be carried out in a timely and efficient manner.

Table 1. Main components of kitchen waste in China (Content %)[18].

General composition		**Main components**	
Moisture	77-95	Food	75-90
Salt	0.5-3	Grease	2-17
Crude Protein	13-27	Bone	5.2
Crude Lipid	17-42	Wood	1.0
Crude Cellulose	2.6-6.5	Paper	0.8
		Plastic	0.7

		Metal	0.1

Table 2. Elemental composition of 1000 g of Chinese kitchen waste[19].

Element	C	H	O	N	S
% M/M	47.60	7.04	33.30	3.44	0.15

Table 3. Composition of mixed kitchen waste in China (%)[20-22].

Moisture	Total solid	Volatile solid	Total sugar	Starch	Lipid	Protein	Reference
82.80	17.20	15.33	62.70	46.10	18.10	15.60	[20]
81.70	18.30	16.01	35.50	NR	24.10	14.40	[21]
85.7	14.3	14.04	42.3	28.3	NR	17.8	[22]

Total solid, total sugar, starch, lipid and protein contents were given in wt% on the basis of dry weight. NR: not reported.

3. Research progress of anaerobic digestion technology of kitchen waste

At present, the main ways to recycle kitchen waste in China are anaerobic digestion (74.3%), aerobic composting (13.5%) and feed (12.2%)[23]. The state does not advocate the use of kitchen waste to produce feed, which may contain microorganisms such as foot-and-mouth disease and swine fever bacteria, and there is a risk of protein homology pollution. In addition, the technology of converting kitchen waste into organic fertilizer by aerobic composting has been quite mature. Compared with anaerobic digestion technology, current aerobic composting technology of kitchen waste is more focused on shortening the composting cycle, reducing odor and greenhouse gas (GHG) emissions, which is suitable for treating the small-scale and dispersed kitchen waste of community households[24]. At present, China still lacks the national standard for organic fertilizer produced by aerobic composting of kitchen waste, and this organic fertilizer still lacks a broad market. Compared with the aerobic composting of kitchen waste, the anaerobic digestion process which is suitable for centralized large-scale treatment projects has the advantages of low carbon emissions, less secondary pollution, and low economic cost. Anaerobic digestion can also produce biogas which is a clean energy, and it efficiently completed the resource utilization and harmless treatment of kitchen waste. Biogas production by anaerobic digestion is currently the mainstream resource utilization method of kitchen waste.

3.1. Anaerobic digestion of kitchen waste

The principle of anaerobic digestion is the process that organic substances are decomposed into small molecular compounds by anaerobic bacteria or facultative anaerobic bacteria under anaerobic or hypoxic conditions to produce methane, water, carbon dioxide and other substances[25]. Anaerobic microorganisms use the energy released during the degradation of organic substances for metabolism and growth and reproduction. The total reaction of anaerobic digestion can be expressed as:

$$\text{Organic} + H_2O \rightarrow \text{New cellular material} + \text{Organic residue} + CH_4 + CO_2 + NH_3 + H_2S + \text{energy}$$

The anaerobic digestion theory has gone through three theoretical stages: two-stage theory, three-stage theory and four-stage theory [26]. At present, the four-stage theory points out that the anaerobic digestion process mainly includes the four-step reaction of hydrolysis, acidogenesis, acetogenesis and methanogenesis[27], as shown in Fig. 5. The first step (hydrolysis stage) is that insoluble polymer organics (lipids, carbonhydrate, protein, etc.) undergo hydrolysis reaction under the action of anaerobic bacteria to produce water-soluble small molecule organics (Fatty acids, Glucose, Amino acids, etc.). The second step (acidification stage) , the water-soluble small molecule organic matter is decomposed into volatile fatty acids and alcohol products (acetate, propionate, butyrate, etc.) by acid-producing fermentation bacteria. The third step (hydrogen and acetic acid production stage), volatile fatty acids are decomposed into acetic acid, water and carbon dioxide by obligate anaerobic acid-producing bacteria, and the same type of acetic acid bacteria synthesize carbon dioxide and water into acetic acid. The fourth step (methane production stage), methanogenic bacteria convert acetic acid, H_2, CO_2 into methane.

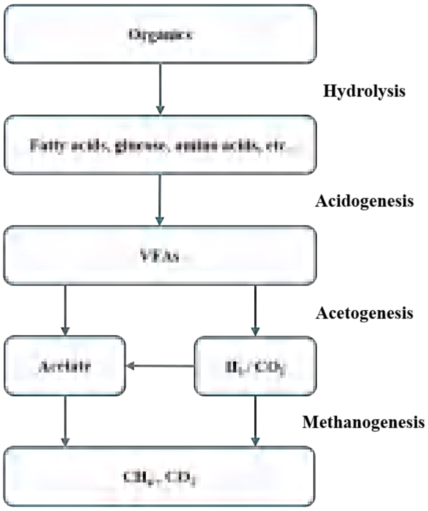

Fig. 5. Four steps in the AD of kitchen waste[27].

Kitchen waste is an easily degradable part of municipal solid waste, which is often treated by landfill and incineration. With the increasing hazards of landfill and incineration, more and more regions of the world prohibit the landfill and incineration of municipal solid waste. Therefore, Europe has promulgated the landfill directive which reduces the proportion of biochemical urban landfills to 35%, and Germany prohibits all landfilling of any biodegradable waste[28]. Prohibition of landfilling of biochemical waste has promoted the development of other disposal technologies such as anaerobic digestion. The currently applied anaerobic digestion process of kitchen waste is shown in Fig. 6. After oil and water separation and pre-treatment, kitchen waste enters the anaerobic digestion system for fermentation to obtain methane and digestive substrate. The methane can be used as a clean fuel or combined heat and power generation after purification. Solid digestate can be used as organic fertilizer in agricultural production and soil improvement, and liquid digestate can be used as liquid fertilizer. Anaerobic process does not need to supply oxygen, which is beneficial to save energy consumption, and also reduce greenhouse gas emissions, which meet the dual needs of environmental protection and sustainable development. Therefore, it is in line with the concept of green circular development. Compared with landfill, incineration and other technologies for kitchen waste, anaerobic digestion treatment has obvious advantages in environmental protection and economy, which has become one of the mainstream technologies of kitchen waste recycling.

At present, the anaerobic digestion and treatment technology of kitchen waste in the United Kingdom, Switzerland, Belgium, Germany, France and other countries is relatively advanced. As of 2014, there are 244 anaerobic digestion facilities in Europe that process municipal organic waste with a total annual processing capacity of 8 million tons[29]. The United States widely uses kitchen waste and other easily biodegradable organic wastes for co-digestion treatment to produce methane, which can be used as a source of combined heat and power (CHP) systems to generate electrical and thermal energy[30]. At present, the technology of anaerobic digestion of kitchen waste has been widely promoted in China, and many anaerobic digestion treatment plants have been established, such as the Chongqing Black stone kitchen waste Treatment Plant with a processing capacity of 365,000 tons/year and a biogas output of 28 million m^3/year[31]. Compared with developed countries, the anaerobic digestion treatment of kitchen waste in China started late and is currently in a rapid development stage.

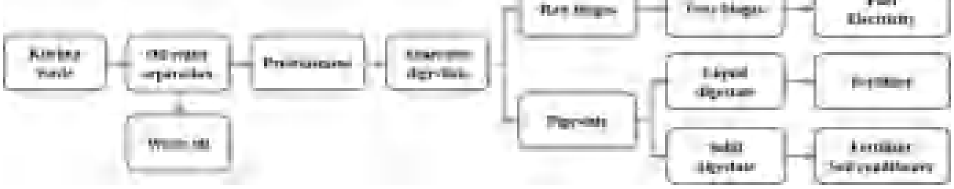

Fig. 6. Anaerobic digestion process of kitchen waste.

3.2. Factors affecting anaerobic digestion of kitchen waste

There are many factors that affect the anaerobic digestion process, mainly including temperature, C/N ratio, ammonia nitrogen, VFAs, pH and metal elements. Temperature will affect the activity of enzymes in anaerobic microorganisms, which will affect the production of methane and the quality of digested liquid[27]. According to different reaction temperatures, anaerobic digestion can be divided into three types: normal temperature (5℃-20℃), medium temperature (20℃-45℃) and high temperature (45℃-70℃) digestion. The anaerobic digestion treatment effect of kitchen waste is poor at normal temperature (5℃-20℃), but the digestion efficiency is higher at medium temperature (35℃-40℃) and high temperature (60℃-65℃)[32].

The growth of anaerobic bacteria and the stability of the system in anaerobic digestion require a digestion substrate with a suitable C/N ratio. When the C/N ratio is too high, the system buffer capacity and pH value will decrease. However, a low C/N ratio of kitchen waste will cause ammonia nitrogen inhibition. At present, the most appropriate C/N ratio for anaerobic digestion is 20-30[33], but Zhang[34] found that the appropriate C/N ratio was 15.8 when co-digesting kitchen waste with cattle dung, indicating that the optimal C/N ratio for anaerobic digestion depends on Raw materials and substrates. Regardless of the C/N ratio of anaerobic digestion, efficient digestion requires a proper balance between C and N.

During the degradation process, proteins and other nitrogen-containing substances in kitchen waste will generate ammonia nitrogen in the form of free ammonia (NH_3) and ammonium (NH_4^+)[35]. Appropriate concentration of ammonia nitrogen is beneficial to the growth of anaerobic microorganisms, but too high ammonia nitrogen concentration will inhibit the activity of anaerobic microorganisms (methane-producing bacteria), thereby inhibiting the anaerobic digestion process. Ammonia nitrogen will promote the anaerobic digestion process when the total ammonia nitrogen concentration is less than 200mg/L. In addition, some scholars have proved that anaerobic digestion will have an inhibitory effect when the total ammonia nitrogen concentration exceeds 1200 mg/L[36]. Yenigün[35] found that anaerobic digestion was inhibited under the conditions of ammonia nitrogen concentration of 1.7-1.8 g/L, and proved that it was mainly caused by the inhibition effect of free ammonia (NH_3). At present, the research on the inhibition of ammonia nitrogen in anaerobic digestion mainly focuses on reducing ammonia nitrogen concentration, removing ammonia nitrogen substances, and improving the ammonia nitrogen tolerance of the anaerobic system.

In addition, when the concentration of volatile fatty acid VFAs in the hydrolysate of the anaerobic system exceeds 6.7-9.0 mol/m^3 [37], it will inhibit the growth of anaerobic organisms and cause the system pH to decrease. High concentrations of organic acids and low pH can cause failure of anaerobic digestion. The ammonia nitrogen and VFAs in the anaerobic system can form a buffer system, which could make the anaerobic system have a certain buffer capacity and could ensure the stability of the system during high-load processing. The optimal pH value of the anaerobic digestion methanogenic system is 6.5-7.2[38]. The growth and metabolism of anaerobic organisms will be affected when the system pH value is too high or too low, so the appropriate alkalinity should also be maintained in the anaerobic digestion system to improve the buffering capacity of the digestion system and ensure the appropriate pH of the digestion system.

The growth and metabolism of anaerobic organisms also require a variety of metal elements, such as conventional elements of K, Ca, Na, Mg, Al, and trace elements of Fe, Mn, Zn, Cu, Co, Mo, Ni, etc. Zhang[6] found that trace elements can promote the co-digestion process of kitchen waste and swine wastewater. Studies have shown that trace elements could improve the stability of the anaerobic system[39]. However, excessive amounts of these metal elements will inhibit the anaerobic digestion process. Therefore, we could increase the anaerobic digestion efficiency of kitchen waste by adding metal elements reasonably.

3.3. Research on promoting anaerobic digestion of kitchen waste

At present, the efficiency of anaerobic digestion of kitchen waste is low, and problems such as nutritional imbalance, system acidification, ammonia nitrogen inhibition, and fatty acid inhibition are common in the process of anaerobic digestion. In order to obtain higher treatment efficiency, stable operation status and high gas production rate, some control methods could be adopted to ensure the kitchen Stable anaerobic digestion of kitchen waste, such as pretreatment, co-digestion, two-phase anaerobic digestion, mitigation of ammonia nitrogen and VFAs suppression and other methods.

3.3.1. Pretreatment

The hydrolysis of kitchen waste is a step to limit the rate of anaerobic digestion. Enhancing the hydrolysis process of kitchen waste can significantly improve the efficiency of anaerobic digestion. Pretreatment can reduce the particle size of kitchen waste and promote the dissolution of organic matter. Pretreatment can increase the specific surface area of kitchen waste, improve biodegradability and increase methane yield. Common pretreatment methods include chemical methods, physical methods (mechanical grinding, ultrasonic treatment, heat treatment, microwave treatment), physical chemical methods, biological and combined pretreatment methods, as shown in Table 4[40] . The physical pretreatment method mainly changes the particle size of the substrate. After the kitchen waste is pretreated by physical method (grinding), its particle size decreases and the specific surface area of the substance increases, which accelerates the hydrolysis rate of the organic substrate. Esposito[41] found that the production of chemical oxygen demand (COD) and methane will increase with the reduction of anaerobic substrate particles, indicating that physical pretreatment can promote the anaerobic digestion process of kitchen waste. However, if the particle size of the kitchen waste particles is too small after pretreatment, it will cause rapid accumulation of VFAs and inhibit the anaerobic digestion process[42]. In addition, the chemical method, physicochemical method, and biological combined pretreatment method of kitchen waste can promote its hydrolysis process. However, some pretreatment processes will produce some toxic and hazardous compound that will inhibit the anaerobic digestion reaction, such as acidification pretreatment that can produce carboxylic acids, furans, phenols and other compounds[43]. The cost and energy consumption of kitchen waste pretreatment process has become an obstacle to restrict its large-scale application[44]. For example, freeze-thaw treatment and heat treatment have the same effect on increasing the methane production of kitchen waste, but the energy cost of freeze-thaw treatment is 1/3 of that of heat treatment. Therefore, when selecting pretreatment, it is necessary to consider both the advanced nature of the technology and the economic type. A proper pretreatment process will greatly promote the anaerobic digestion of kitchen waste and increase methane production.

Table 4. Pretreatment approaches of organic substrates degradation[40].

Methods	Raw materials	Measures	Results	Reference
Mechanical grinding	Waste activated sludge	Pretreatment at 30 bar	Shorted the sludge retention time from 13 to 6 days.	45
Ultrasound	Municipal sludge	With frequency of 40 kHz power of 500 W	Resulted in VS reduction up to 47% and higher biogas yield	46
Microwave	Kitchen waste	145 °C	Increased biogas production	47
Thermal	Kitchen waste	120 °C + 30 min	Biogas production 106 increased by 11%	48
Freezing–thaw	Kitchen waste	-80-55 °C	Biogas production increased by 23%	48
Pressure- depressure	Kitchen waste	Pressure changed from 10 bar to 1 bar with CO_2 as pressurizing gas	Biogas production increased by 35%	48
Acid	Kitchen waste	With 10 mol/L HCl at 18 ±2°C until pH 2 for 24 h	Biogas production decreased by 66%	48
Biological solubilization	Kitchen waste	FW+ water	Decreased organic concentration in the effluent	49
Thermo-acid	Kitchen waste	With 10 mol/L HCl at 18 ±2 °C until pH 2 for 24 h, and 120 °C + 30 min	Biogas production increased by 18%	48
Biological–physicochemical	Oily wastewater	Bacillusat 9 wt%, ultrasonic for 10 min and 500 mg/L citric acid.	Biogas production increased by 280%	50

3.3.2. Co-digestion

Co-digestion is an important methods to adjust the anaerobic digestion performance of kitchen waste. The C/N ratio of kitchen waste is not in the optimal ratio range for anaerobic digestion[51], and there is still a lack of metal trace elements (Zn, Fe, Mn, Se) that promote anaerobic digestion[52]. However, kitchen waste contains a large amount of Na, K, fat and salt, which will inhibit the anaerobic digestion process and affect the production of methane. Co-digestion of kitchen waste and its organic waste can form complementary advantages and synergistic effects between different substrates, and eliminate the restrictive factors of anaerobic digestion of kitchen waste. Co-digestion has become an effective method for regulating anaerobic digestion of kitchen waste. At present, the co-digestion matrix of kitchen waste that has been studied to promote anaerobic digestion includes municipal solid waste, agricultural waste, human and animal feces, microalgae, sludge, domestic sewage, industrial sewage, etc, as shown in Table 5. The main reason of co-digestion technology improves anaerobic digestion performance is that the supplemented nitrogen element improves the buffer capacity of the system, improves the C/N ratio of the anaerobic system and supplements trace elements. The co-digestion process can realize co-processing and utilization of multiple substrates, sharing equipment, saving operating costs, and having economic advantages. In addition, the co-digestion treatment of kitchen waste and microalgae has become a new research field. Cogan and Antizar-Ladislao[53] co-digesting seaweed waste with kitchen waste can promote the gas production rate and system stability of the anaerobic digestion process, and the highest gas production (252 cm^3/g VS) was obtained at FW: SW ratio of 90:10. The anaerobic co-digestion of kitchen waste and other organic waste is an effective method to improve the yield of biogas and methane and has been widely used in industrial production.

Table 5. Co-digestion strategy for improving anaerobic digestion of kitchen waste.

Feedstock	Influencing factor	Action of co-digestion	Reference
KW+ cattle manure	Nutrient balance	Improve methane yield	34
KW+ sludge	Hight protein content High buffering capacity from ammonia	Improve methane yield and VS reduction	54
KW+ cattle manure +sludge	C/N ratio High buffering capacity from ammonia	Improve methane yield	55
KW+ animal slurry wastewater	High buffering capacity	Improve both methane yield and TOC utilization	56
KW+ yard waste	Less VFA accumulation	Improve methane yield	57
KW+ distiller grains	High buffering capacity from ammonia	Increase biogas production	58
KW+ sewage sludge	High buffering capacity from ammonia	Afford high organic loading rate	54
KW+ green waste	C/N ratio	Improve VS reduction	59

KW：kitchen waste

3.3.3. Two-phase anaerobic digestion

Although the single-phase anaerobic process is widely used in industrial production due to its simple process characteristics, the four stages of hydrolysis, acidification, acetic acid production and methane production in the single-phase anaerobic digestion process are all carried out in the same system. Any stage of inhibition will lead to the efficiency of anaerobic digestion. Kitchen waste is so easily biodegradable that the faster rate of hydrolysis and acid generation can easily cause acid accumulation and inhibit the activity of methanogens, which has the disadvantages of long anaerobic digestion time and low methane production efficiency. In order to solve the shortcomings of single-phase anaerobic digestion, we began to focus on the research of two-phase anaerobic digestion process to improve the efficiency of anaerobic digestion. Two-phase anaerobic digestion process was proposed in the 1970s[60]. In the two-phase anaerobic digestion system, the hydrolytic acidification stage and the methanogenic stage of anaerobic digestion of organic matter are in different treatment units, respectively, and the acidogenic bacteria and methanogenic bacteria grow under their respective optimal conditions. The two-phase anaerobic process is shown in Fig. 7. In the first stage, the kitchen waste is decomposed into small molecules such as acetic acid and propionic acid through the hydrolysis and acidification process. The second stage is the conversion of acidification products into CH_4 by methanogens. The two-phase process has stronger biological stability during the anaerobic digestion of kitchen waste, which can avoid the accumulation of volatile organic acid VFAs under high load, prevent VFAs from inhibiting the subsequent methane production stage, and increase the methane yield. Song[61] used the two-phase digestion process to obtain biogas yields of 236.5 mL (H_2) / g VS and 263.7 mL (CH_4) / g VS, which the energy conversion rate of the two-phase digestion process compared with the single-phase process increase by 10.85% . Kim[62] used a sequential batch reactor (SBR) and upflow anaerobic sludge bed reactor (UASB) reactor combination in a two-phase process, which could efficiently convert 44% of marine organics into a yield of 296 ml (CH_4) / g COD methane. Although the two-phase process has the advantages of high degradation capacity and high gas production rate, its complex system and high economic cost limit its industrial application. At present, the industrial application of anaerobic digestion of kitchen waste mostly adopts single-phase process, but the two-phase anaerobic process is the trend of industrial development in the future.

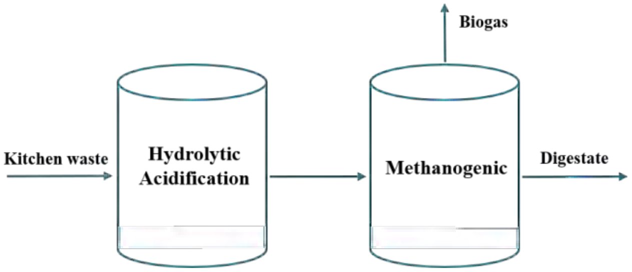

Fig.7. Two-stage anaerobic digestion process.

3.3.4. Relieves ammonia nitrogen and VFAs inhibition

The inhibitory factors that inhibit the anaerobic digestion of kitchen waste include ammonia nitrogen inhibition and VFAs inhibition. Excessive ammonia nitrogen concentration will inhibit the activity of anaerobic microorganisms (methane-producing bacteria), cause the pH to rise, and inhibit the anaerobic digestion process. In view of the ammonia nitrogen inhibition phenomenon, the current research mainly focuses on reducing the ammonia nitrogen concentration, removing ammonia nitrogen substances, and improving the ammonia nitrogen tolerance of the anaerobic system. The corresponding methods to alleviate the ammonia nitrogen inhibition are physical method (air stripping), chemical Method (chemical precipitation) and strain acclimation method (ammonia nitrogen tolerance of bacteria). Through these measures, the ammonia nitrogen inhibition phenomenon of anaerobic digestion of kitchen waste can be greatly alleviated or solved. Serna[63] uses a biogas stripping reactor to reduce the TAN concentration in the reactor by recovering ammonia for nitrogen fertilizer production. Banks[64] controls the TAN concentration in the anaerobic system to be stable at 5000mg/L by adding selenium (Se) and cobalt (Co) elements to the anaerobic system. In addition, if the concentration of VFAs is too high, it could penetrate into the cell membrane, causing anaerobic microorganisms to die due to the acid-base imbalance in the cell, and it will also cause the system pH to decrease. The current research is mainly to use ammonia nitrogen and VFAs to form a buffer solution, $NaHCO_3$ buffer solution and two-phase anaerobic digestion process to solve VFAs inhibition. Some scholars alleviated the problem of VFAs inhibition in the kitchen garbage anaerobic system by adding zero-valent iron. The principle is that zero-valent iron can accelerate the conversion rate of butyric acid to acetic acid, and increase the methane yield to 380 cm^3/g VS[65].

3.4. Secondary pollution during anaerobic digestion of kitchen waste

Although anaerobic digestion of kitchen waste is a clean resource utilization technology, but the odor, digestate that pollute the environment are generated during the anaerobic digestion process. The odors generated by the anaerobic digestion process include NH_3, SO_2, H_2S and VFAs volatile from the system. The discharge of these odors into the environment will cause air pollution problems and threaten human health. In addition, if these odors are not removed during the methane purification process, they will also burn with the biogas to generate sulfur dioxide, nitrogen oxides, carbon monoxide and other compounds, causing environmental problems such as photochemical smog, acid rain and water eutrophication. Therefore, the purification of biogas and the collection and treatment of waste gas are very important links, which can effectively solve the problem of odor pollution caused by anaerobic digestion.

The digestate contain a large amount of nitrogen, phosphorus and potassium nutrients, heavy metal ions, pathogenic bacteria and organic matter. If the digestate is not properly disposed, it will cause secondary pollution of soil and water. At present, the treatment of digestate is mainly returned to farmland as agricultural organic fertilizer, but this treatment method will also bring some environmental problems. For example, digestate will decompose again in farmland to produce CH_4, N_2O and NH_3. Ebner[66] found that the digestate would release 1.5 m^3 CH_4/t of biogas after centralized storage. Chantigny[67] found that after fertilizing digestate on farmland, 35% of the ammonia nitrogen will volatilize into the air in the form of ammonia gas. If solid-liquid separation of digestate is carried out, the odor of digestate will be greatly reduced. In addition, the use of digestate as fertilizer can cause problems such as salinization of the land, pollution of heavy metal ions, and accumulation of heavy metals in crops. In the future, it is necessary to strengthen the research on the harmless treatment and resource utilization of anaerobic digestion odor and digestate, so that eliminating the secondary pollution in the process of kitchen waste anaerobic digestion.

4. Anaerobic digestion status and prospect of Chinese kitchen waste

China has introduced a series of policies and laws in recent years to promote the resource utilization of kitchen waste. In 2010, China issued a notice on the "Pilot program for the utilization and safe disposal of kitchen waste" and set up 100 pilot cities for kitchen waste disposal from 2011 to 2015. With the support of the policies and funds of the Chinese government, the recycling of Kitchen waste in China mainly consists of three ways: anaerobic digestion (74.3%), aerobic composting (13.5%) and feed production (12.2%)[23]. It has also formed the "four modes" for the recycling of kitchen waste: the "Beijing mode" based on anaerobic digestion, the "Xining mode" based on feedstuffs, the "Shanghai mode" based on dynamic aerobic digestion, and the "Ningbo mode" for the production of bacterial proteins, feed additives and industrial fats[68]. In 2019, China started the construction of "zero-waste city" and the sorting of household garbage, the rapidly increasing amount of kitchen waste is in urgent need of treatment and disposal. Chinese kitchen waste resource market has bright prospects.

At present, anaerobic digestion is the main way to recycle kitchen waste in China. About 80% of China's 100 pilot cities will use a variety of anaerobic digestion processes[69]. Li[70] analysed the amount of kitchen waste disposal technology in China and the scale of anaerobic treatment. It can be seen that the quantity and processing capacity of anaerobic digestion treatment plants in the processing facilities of Chinese kitchen waste are ranked first, and the processing capacity of AD plants is mainly concentrated above 200 t/d, indicating that anaerobic digestion is suitable for large-scale operation. Due to the characteristics of high moisture content of Chinese kitchen waste, the anaerobic digestion process of Chinese kitchen waste mostly adopts the wet anaerobic digestion process of continuous stirred tank reactor (CSTR) systems. With the continuous development and popularization of dry anaerobic digestion with high impact load resistance and high gas yield abroad, the application of dry anaerobic digestion in China is also increasing gradually, such as the large dry anaerobic digestion reactor developed by Beijing Capital Environmental Investment Company. In addition, the co-digestion of kitchen waste and other organic waste has also applied more and more in practice. Djavan[69] summarized the situation of some Chinese kitchen waste anaerobic digestion plants (Table 6), it can be seen that China has established a variety of technology, scale of kitchen waste anaerobic digestion plants.

Table 6. Part of China's kitchen waste anaerobic digestion pilot project[69].

Technology	Capacity (t/d)	Methane production in 2017 (10,000 m^3 / year)	Location
Co-digestion	KW 500 + Sludge 100 + Bio-MSW 50	1429	Chongqing
High-temperature AD	KW 65 + Sludge 435	612-816	Changsha
High-solids AD	KW 300	551	Shenzhen
Co-digestion	KW 200 + Sludge 250 + Dead livestock 30	1163	Linyi
Anaerobic digestion + pyrolysis	Sludge 300 + FW 200	561	Zibo

The energy structure of China is dominated by coal, which has greatly damaged the ecological environment, causing environmental pollution such as smog, photochemical smog and acid rain. In recent years, China has made great efforts to develop clean and renewable energy to improve the ecological environment. Biogas from the anaerobic digestion of kitchen waste is a suitable clean energy source. It can be used as an alternative to coal as a fuel, or provide electricity through combined heat and power (CHP) generation. In addition, anaerobic digestion has lower greenhouse gas emissions and less secondary pollution to the environment. Therefore, the kitchen waste in China is suitable for the use of anaerobic digestion technology to achieve resources. However, there are some problems in anaerobic digestion, such as low production of biogas, large amount of digestate, which lead to low economic benefits and government subsidies to maintain the operation of the plant. Therefore, advanced anaerobic digestion technology should be developed for kitchen waste in China in the future. The anaerobic digestion process equipment should be adjusted according to the characteristics of kitchen waste in different regions, large-scale anaerobic digestion system should be developed to reduce operating costs, and combined process (anaerobic + aerobic) should be carried out to improve substrate utilization rate and methane production. In addition, it is necessary to improve the purity of methane, strengthen the treatment of odor, digestate, and control secondary pollution well.

5. Perspectives for the anaerobic digestion of kitchen waste

At present, the anaerobic digestion of kitchen waste is confronted with problems such as unbalanced nutrition, inhibition, poor system stability, low methane production and purity, resulting in low methane production and purity and unstable anaerobic system, which seriously hindering the development of kitchen waste anaerobic digestion. In the future, we should continue to strengthen the pre-treatment and co-digestion process to improve the anaerobic digestion efficiency of kitchen waste.

Secondly, the stability of kitchen waste anaerobic digestion system should be further improved, and the online monitoring and process control of the anaerobic digestion process can be strengthened. In addition to the monitoring of basic parameters (flow rate, temperature, pH, gas, etc.), key indicators (VFAs, ammonia nitrogen, enzyme activity, etc.) and microbial management should also be tested to ensure the stability of anaerobic digestion system[71, 72]. Moreover, the purity of methane and the heat value of methane should be improved, and other harmful gases should be avoided to produce pollutants during combustion. If the purified methane is incorporated into the natural gas pipe network, the application value of methane will be greatly improved.

Finally, the anaerobic digestion process of kitchen waste can increase the conversion value of kitchen waste through a biorefining model. Chen[73, 74] proposed a “waste biorefinery model” combining anaerobic digestion and microalgae cultivation, and this model have better development prospects in the future. Microalgae can use the C/N/P elements in liquid digestate to produce biofuels and biomass, and it can also absorb CO_2 in biogas through photosynthesis to purify biogas. Ren[72] proposes a biorefinery model based on the anaerobic digestion of kitchen waste, which covers the conversion of kitchen waste into fuel, electricity, chemical products, fertilizer and etc. At present, the biorefinery of kitchen waste is still in the theoretical research stage. In the future, biorefinery technology could greatly improve the conversion efficiency and commercial value of waste. Therefore, we propose a theoretical bio-refinery model of kitchen waste, which combined with anaerobic digestion, microalgae cultivation, and biological fermentation. This biorefinery model is shown in Fig. 8. Kitchen waste is processed in four stages of refining biodiesel, biofermentation, anaerobic digestion and microalgae cultivation to obtain clean biogas, biodiesel, ethanol, lactic acid, fertilizer, protein, fat, pigment, fatty acid, carbohydrate, water and other products. The biological refining model improves the conversion efficiency of kitchen waste into high-value-added products, not only enhances the commercial value of anaerobic digestion of kitchen waste, but also achieves zero emissions of kitchen waste in the process of resource recycling, which has better development prospects.

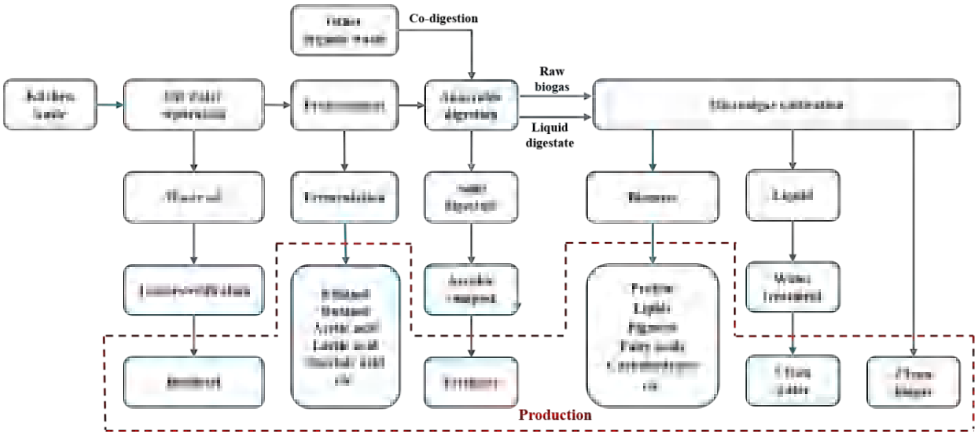

Fig. 8. A biorefinery model for biogas production from kitchen waste.

6. Conclusion

With the increasing production of kitchen waste in China and foreign countries, it is imperative to realize the utilization of kitchen waste. Food waste is the major source of kitchen waste. Domestic and foreign kitchen waste has some common characteristics. In general, anaerobic digestion is an appropriate technology to realize the recycling of kitchen waste. At present, the anaerobic process of kitchen waste is inefficient, which will be affected by many factors. Therefore, scholars from domestic and foreign take measures such as pre-treatment, co-digestion, two-phase anaerobic digestion, mitigation of ammonia nitrogen inhibition and VFAs inhibition to ensure the stable anaerobic digestion of kitchen waste. In addition, the odor, biogas and residue produced by anaerobic digestion of kitchen waste will cause secondary pollution. In China, anaerobic digestion technology has been widely used in the resource treatment of kitchen waste, which is a better technical solution to realize the large-scale production of kitchen waste methane. The future research directions of kitchen waste anaerobic digestion should focus on pre-treatment, co-digestion, anaerobic system stability improvement, methane purity and biorefining mode to achieve efficient conversion of kitchen waste into methane.

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Solid Waste Management based on Big Data Analysis

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Abstract（200-400 words）

With the development of economy and society, the solid waste generated by people in production, life and other activities has increased rapidly, posing a great threat to people's health and the stable development of the urban economy. From the perspective of environmental risk, the production, transportation, utilization and disposal of the solid waste as well as other links have always been the difficulties in environmental management. Traditional management can no longer meet the requirements of digital environmental protection. With the rapid development of the Internet and the explosion of data technology, big data has become one of the latest means of environmental governance. In view of the conditions and deficiencies of solid waste treatment in China, solid waste management based on big data analysis and some of its application achievements has been illustrated in this paper. Some suggestions are summarized according to the current practice. In the future, China should promote the sharing and disclosure of information in the construction of big data of solid waste disposal, to realize the parallelization of big data management and big data assisted decision-making, and finally provide services for daily decision-making, resource integration, and emergency response, which will promote the streamlined, refined and intelligent disposal and utilization of solid waste in China.

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Keywords: Big data; solid waste;

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Supervision of cross-regional transfer of hazardous waste in China under the background of zero-waste city

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Abstract

With the acceleration of industrialization, more and more kinds and quantities of hazardous waste (hereinafter referred to as hazardous waste) are produced. Most of the hazardous waste is produced in economically developed areas and a considerable part of the hazardous waste is transferred to other areas. Hazardous wastes are flammable, corrosive, toxic and unstable. Improper disposal will not only affect people's health, damage the ecological environment and restrict the development of social economy. On December 29, 2018, the General Office of the State Council issued the Work Plan for the Pilot Construction of waste-free Cities (hereinafter referred to as the Plan), putting forward Suggestions for the pilot construction of waste-free cities. In particular, the plan emphasizes the need to strengthen integrated safety control of hazardous wastes. Therefore, it is of great significance to strengthen the management of hazardous waste and improve relevant laws for the construction of "zero-waste city". By analyzing the current situation of legislation and law enforcement of trans-regional transfer of hazardous waste, it is found that there is a lack of perfect legal system for trans-regional transfer of hazardous waste in China. The subject of law enforcement is unknown, and the phenomenon of multiple management is prominent. The lack of a unified regional damage relief system and the establishment of a sound legal system; Improve law enforcement supervision institutions; A proposal on the establishment of a compensation system for inter-regional transfer of hazardous waste.

Keywords: Hazardous waste, Cross-regional transfer transfer, supervise；

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A wet compounding technology by using carbon black from waste tire pyrolysis

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Abstract（200-400 words）

Pyrolysis offers a more focused alternative to the waste tires treatment. Pyrolytic carbon black (CBp), as the main product of waste tire pyrolysis, and its modified one can be applied to tire manufacturing realizing its high-value utilization. Modified pyrolytic carbon black / natural rubber composites prepared by a wet compounding and latex mixing process has become an innovative technology route for waste tire remanufacturing. The main properties and applications of pyrolytic carbon black reported in recent years are reviewed, and the main difficulties affecting its participation in tire recycling are pointed out. We summarize the research progress of new tire manufacturing using wet compounding technology instead of dry mixing. Based on the literature data and through comparative study, this paper points out that if modified pyrolytic carbon black is applied to tire manufacturing, the characteristic of high ash content can be well utilized. This paper proposes a new method for high-value utilization of pyrolytic carbon black. The composite mixing of pyrolytic carbon black and carbon nano-materials under wet conditions is conducive to the realization of their good dispersion in the rubber matrix. It provides a new idea for the manufacture of green tires.

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Keywords: Waste tire; Pyrolytic carbon black; Wet compounding; Higher value application

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A novel method for screening deep eutectic solvent to recycle spent Lithium-ion batteries

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Abstract

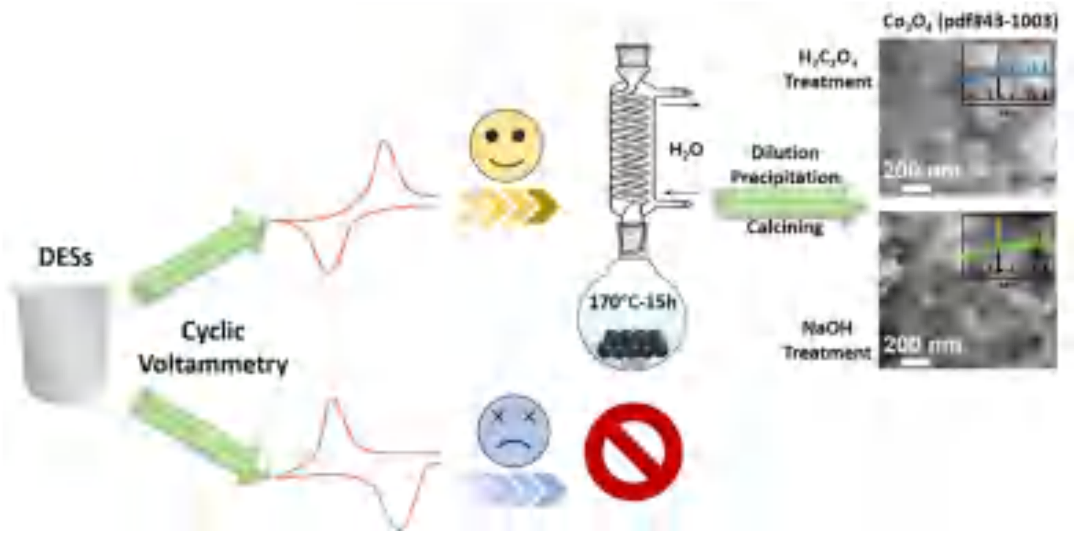

Figure 1 Cyclic voltammetry (CV) method and recycling of spent lithium-ion batteries (LIBs)

As a green alternative technology, deep eutectic solvents (DESs) have exhibited a huge potential to recycle spent lithium-ion batteries (LIBs) for the goal of valuable elements resue. The harsh production conditions of DESs, such as raising temperature and extending processing duration, limit the use area of DESs, due to their weak reduction power. Here, a novel, simple and robust experimental method was proposed to identify suitable DESs for recycling of spent LIBs on the basis of the classical electrochemical principle. This method can quickly determine the reducibility of DESs. As a result, a choline chloride : urea DES was found to extract Li and Co with leaching efficiency of 95% from spent LIBs at 180°C for 12 h. The results agreed with the results from Fukui functions calculations well. The Li and Co extraction was controlled by solution diffusion and electron diffusion in this process. Furthermore, a cubic cobalt oxide spinel (Co_3O_4) also can be obtained in a dilution-precipitation-calcining process from loaded DES by using precipitants, such as $H_2C_2O_4$ and NaOH. This novel method demonstrates huge potential to rapidly and reliably screen suitable DESs in effective recycling of spent LIBs.

Keywords: Deep eutectic solvents; Spent Lithium-ion batteries, Cyclic voltammetry; Lithium; Cobalt.

Segregation and Recycling System of Municipal Waste with Participation of Residents in Minamata City, Japan

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Abstract: Minamata area, located in southern Kyushu of Japan, experienced health hazards and environmental pollution of methyl-mercury discharged from a chemical factory during Japan's rapid industrialization in the 1950s. In Minamata City, which suffered the most casualties, citizens are highly aware of the environment.

In 1992, Minamata City declared an environmental model city as well as decided that health and environmental damages due to the pollution were never repeated. And also for our daily life, we were always considering for water conservation, food safety and waste reduction. Since the disposal capacity of the final disposal site would be reached its limit in a few years at that time, it was decided to separate and recycle garbage with the active participation of the residents.

We held 300 briefing sessions for the residents for 6 months, and with the understanding and cooperation of the residents, we have started sorted collection throughout the city from August 1993. The garbage separation by citizens' cooperation has been continued for 27 years, and improvements have been carried out due to changes of social requirements. So far, 23 kinds of separation have been conducted since 2019.

Recycling rate has reached to about 40% with the separation of garbage, which also contributes to the reduction of garbage. It is linked to collaborative activities of people across generations in the community too. In Minamata City, we are trying to further reduction of kitchen garbage. We are promoting to spread of wooden composters for home use. We are challenging sustainable local communities through reduction of wastes and zero-waste community.

Keywords: Municipal waste; Segregation; Recycling: Residents' participation.

Introduction

Minamata City locates southwest part of Japan faces to Yatsushiro sea surrounded by scenic coast and deep forest, and originally consists of agriculture, forestry and fisheries. The Chisso Cooperation started a hydroelectric power generation in Kagoshima Prefecture and started operation in Minamata City in 1908 to produce chemical fertilizer and chemical materials. The company used inorganic mercury as a catalyst in acetaldehyde producing process and discharged wastewater containing a by-product, methyl-mercury directly into the Minamata Bay.

The first recognized outbreaks occurred in 1956 in the vicinity of Minamata Bay. The patient suffered neurological symptoms and the government has concluded Minamata Disease is a poisoning disease of central nervous system caused by methyl mercury which was produced as by-product in the process of manufacturing acetaldehyde at the factory in 1968. Discharged methyl mercury polluted the environment and through the food chain, it was accumulated in fish and shellfish. Minamata Disease occurred among the inhabitants ate high amount of these seafood [1, 2].

Until now, about 2,300 people have been officially certified as methyl-mercury poisoning by the government in the Minamata area. The environment of Minamata Bay was severely damaged as well as human damage. The restoration of the environment required huge amount of cost and 13 years of time. In addition, various discrimination and prejudice occurred among the people, and it was not easy to eliminate such annoyance.

Based on the lessons of the pollution, Minamata City has declared an environmental model city in 1992. The basic concepts of the environmental model city are: 1) never repeating health and environmental damages due to the pollution, 2) promoting environmentally friendly development, 3) considering for water conservation, food safety and waste reduction in our daily life. As an activity in which the general public can contribute to achievement of environmental model city, Minamata city has started the advanced classification and recycling of municipal waste in 1993 as one of the environmental measures that can contribute at the citizen level. The activity has continued for 27 years.

1. Citizen-participation-type municipal waste recycling

1.1 Background

In addition to increasing peoples' attention to the environment, capacity of the final disposal site for waste in the city was reaching the limit in a few years. There was only one final landfill site in the city, and it has been very difficult to set up new sites in the city because the entire Minamata area can be regarded as one important water source.

1.2 Basic concept of the system

*Separation procedures shoul*d be carried out at the first stage, and recyclable material should be sorted as much as possible. And also, profits from the sale of recyclable are returned to the residents' association. Table 1 lists classification detail of materials as well as collection frequencies.

Table 1. Classification and Frequency of Municipal Waste Collection in Minamata City.

Items	Collection Frequency	Items	Collection Frequency	Items	Collection Frequency
Returnable glass bottles	once a month at 300 stations	Fluorescent tubes/bulbs	once a month at 300 stations	Container and packaging plastics	once a week at 700 sites
Glass bottles (transparent)		Batteries		Kichen garbage	twice a week at 700 sites
Glass bottles (brown)		Electric cords		Burnable garbage	
Glass bottles(others)		Small household appliances		Cooking oil	once a month at 300 stations
Aluminum cans		Newspapers and flyers		Beverage paper pack (white)	
Steel cans		Magazines other papers		Beverage paper pack (silver)	
Spray cans		Cardboard			
PET bottles		Cloth (Clothing)			

1.3 Procedures to start the system

In order to obtain consensus of the citizens, 20 kinds of sorting were started in some model communities. During 6 month 300 town meetings, explanatory meetings were held. And then, the system was started throughout the city from August 1993. Now, separation is carried out into 23 categories as social requirements

2. Effects of the collection system

2.1 Recycling rate and total amounts of municipal waste

As shown in Table 2, before this activity started, recycling amounts was zero, but recently it has maintained a rate of around 40%. And also, total amount of waste has decreased.

Table 2. The Effects of Segregation and Recycle Activity on Total Amounts of Municipal Waste

Fiscal year	Total amounts of waste	Landfilled waste	Recycling rate	Population (persons)
1991	10,926 t	4,013 t	0 %	34,510
1994	8,938 t	1,289 t	16.5 %	33,671
2013	7,838 t	592 t	40.0 %	26,773
2018	7,095 t	650 t	39.4 %	24,769

2.2 Profits from the segregation and recycling

Table 3 listed total benefits produced by selling recyclable materials such as glass bottles, paper, cans, and others. Nearly two million JP yen per year is earned. Half of the profit will be distributed to local residents' associations, and half will be the city's income.

Table 3. Total Benefits of Recycled Resources (2018 FY).

Recyclable item		Shipped weight (t)	Sales (yen)
Bottles	Returnable bottles	19	283,333
	Others	167	8,348
Paper	Newspapers and leaflets	228	5,055,614
	Corrugated cardboard	105	2,046,280
	Others (incl. milk cartons)	249	3,563,400
Clothes		143	71,590
Cans	Aluminum cans	31	4,069,280
	Steel cans	28	752,630
Metals		105	2,669,785
Electric cord		4	397,275
PET bottles		58	126,514
Cooking oil		4	18,811
Total		1141	19,063,860

2.3 Unexpected effects through residents' participation

By continuing these activities, citizens' awareness to the environment continues. In addition, some citizens' groups and sales organization in the city proposed separate collection and recycle of plastic food trays and packing materials. The activity has been started from 1998. The plastic materials are now collected once a week from 700 sites in the city. Collected materials are transported to nearby processing plant where they are sorted by material and reused. This activity is one of the pioneering effort to prevent a recent environmental issues caused by micro-plastics in the environment. In addition, through the activities, exchanges within the community have become popular, and intimate considerations have been given among the communities, especially to the elderly living alone.

2.4 Hazardous waste treatment

Hazardous wastes containing mercury and metals are separately collected, and transported to specific treatment facilities in Japan. Wastes containing mercury are subjected to strict treatment in order to comply with the international convention on mercury, the Minamata Convention[3]. Button batteries, thermometers, etc. containing mercury are transported to a processing plan in Hokkaido, Japan for proper processing and reuse. Used fluorescent tubes are collected in special cartons made of cushioning material and sent to near-by reprocessing plant. Waste batteries containing rare metals and other materials are sent to processing centers in several places in Japan.

2.5 Treatment scheme of municipal waste in Minamata City

Figure 1 shows total material flows of the municipal waste in Minamata City[4]. Since the gasification and melting furnace method is used for the incineration of garbage, the amount of generated ash is suppressed. Nine percent of total waste including collected non-burnables is landfilled.

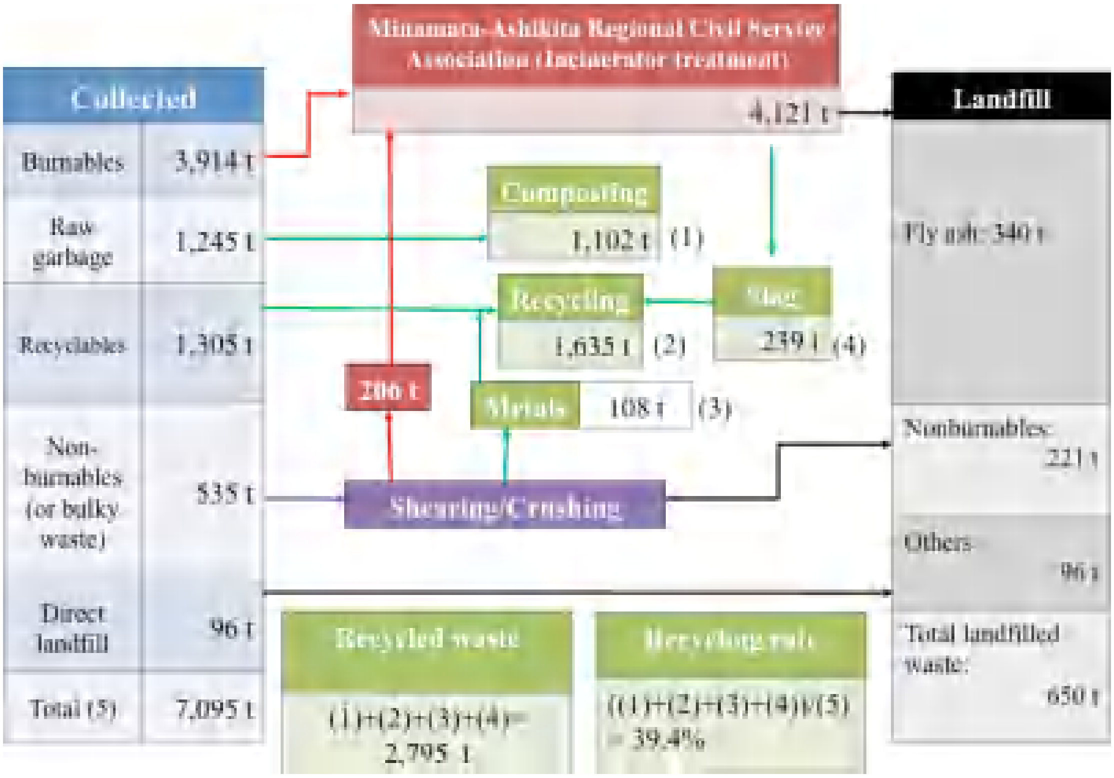

Figure 1. Total Material Flows of Municipal Waste in Minamata City.

2.6 Kitchen garbage treatment at home level

Kitchen garbage is placed in biodegradable plastic bags and collected twice a week for composting. During last some years, Minamata City is promoting the introduction of a composter that can treat food waste at home in order to reduce the amount of garbage. Figure 2 shows a wooden composter in which soil layer of 10 to 20 cm contained. The garbage is digested in 2 or 3 weeks. About 10 % of all households in the city have introduced the composter at home to treat kitchen garbage by themselves. It is expected that transportation costs and processing cost will be reduced.

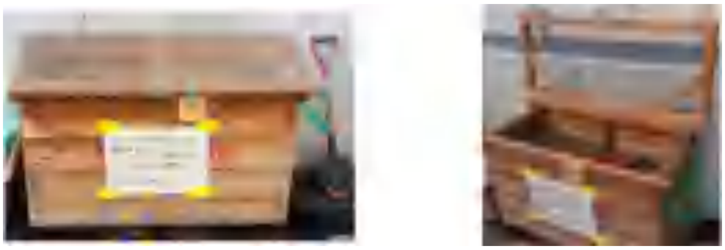

Figure 2. Wooden composter "Kiero" to treat kitchen garbage at home.

2.7 Eco-town project in Minamata City

In Japan, 26 Eco-towns have been assigned by the government and operated based on Zero Emission Concept. Minamata City has an eco-town consisting of seven environment-related companies.

The concepts of Minamata Eco-town are as follows:

1) Become a model for all small and middle size cites in the nation.
2) Promote 4 Rs (Refuse, Reduce, Reuse and Recycle) cooperating with citizens, government and industries.
3) Participation of the citizens.

In Minamata Eco-town, following seven companies related to the environment are operating.

1) Home appliance recycling facility based on Home Appliance Recycle Law[5].

2) Complete circulation model food recycling facility.
3) Used oil recycling facility.
4) Construction material and asphalt composite material manufacturing facility.
5) Fertilizer manufacturing facility using septic material.
6) Used plastic bottle recycling facility.
7) Glass bottle reuse/recycle facility

Even in a local area where it is difficult to provide a place to work, these environment-related companies provide valuable working place and places of life for the local community. Some companies are also active to transfer such environmental technology to the overseas.

Conclusion

Due to the environmental improvement and measures in Minamata area, beautiful sea and river have been preserved. And also, agricultural and marine products produced in the Minamata area are of high quality and safe, and are highly evaluated nationwide.

Minamata City, like other local cities in Japan, faces aging and population decline. Toward a sustainable local community, we have to create technological and social innovation based on our experiences, resources and achievements in the field of the environment. To contribute sustainability of the area, reducing the amount of municipal waste and Zero-Waste are important issues for Minamata City. The city set Zero-Waste as an important target in the 3rd Basic Environmental Plan to be implemented from 2020. Based on the understanding and cooperation of the citizens, we intend to continue the segregation system and improve to the zero-waste. We believe that resilient waste treatment system is essential to the sustainable development of the regions in the world.

Acknowledgements

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Improvement of the overall performance of solidified radioactive resins by a composite mineral admixture

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Abstract（200-400 words）

To improve the overall performance of solidified radioactive resins, a composite mineral admixture prepared using four mineral admixtures was blended in a cementation formula. The efficiency of four mineral admixtures, zeolite, blast-furnace slag, silica fume, and fly ash, for cementation was investigated as single admixtures, and then were compared with that of the composite mineral admixture. A Plackett-Burman design was performed to analyze the effects of single admixtures with the blending amounts from 0 to 10% on the performances of solidified resins. Both silica fume and slag presented significant positive effects on mechanical strength with increasing blending amounts. Fly ash and slag increased the fluidity of mortar, and benefited solidification with appropriate blending amounts. All the four admixtures showed positive effects on the Cs(I) leachability index, enhancing the Cs(I) retention of the solidified resins. Based on the effects of single admixtures, the composite admixture was prepared with the optimized composition of 35.7% slag, 32.0% silica fume, 18.0% zeolite, and 14.3% fly ash. With 10% composite admixture in the cementation formula, the 7d compressive strength was 13.1 MPa, fluidity 216.0 mm, and Cs(I) leachability index 11.72. The overall performance of radioactive resins solidified by sulfoaluminate cement was improved by the composite admixture.

Keywords: adioactive resin; composite mineral admixture; radioactive wastes solidification; Plackett-Burman design

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Stocks of resources and toxic substances in urban mining

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Abstract

With the economic growth and rapidly rising of global population, the increasing depletion of natural resources has become a particularly acute issue. Massive amounts of natural resources have been extracted and then consumed or accumulated in the cities. Urban mining emerged as the times require. Urban mining containing both valuable resources and harmful substances. This study clarified the stocks and trends of valuable metal resources (gold, silver, and copper) and toxic substances (lead) related to urban mining in China. Waste electric and electronic equipment (WEEE) and end-of-life vehicles (ELV), which got the most concern products, were selected as the target, including TVs, refrigerators, air conditioners, washing machines, PCs, mobile phones and passenger vehicles. A population balance model was used to estimate the number of in-use and end-of-life (EOL) products. The substance flow analysis was developed based on the substance concentration and content per product and the estimated EOL product generation. The study demonstrated that more than 6 billion units of products would be stocked in China in 2020. The amounts of EOL products was not significant at first, while in 2020, more than 700 million units (16 million tons) of EOL products would enter into waste streams as urban mines in China, in which the ELVs possess the largest weight. EOL TVs, especially cathode ray tube (CRT) TVs had been considered as the least valued WEEE, while gold and silver stocked in the in-use TVs is the highest. Gold stocked in EOL products accounted ~1/3~1/2 gold demand in China industry during 2007-2016, except the year of 2010, in which the industry demand for gold increased sharply. Copper stored in EOL air-conditioners is the highest, higher than that in all the other EOL products from 2005. In 2013, ~290 thousand tonnes of copper was estimated in EOL products, accounted approximately half of copper production amounts in 2013. Lead accumulated in in-use and/or EOL CRT TVs was the highest before 2010. With the CRT TVs elimination, lead stored more in vehicles. At the time of urban mining, hazardous substances, such as lead, also could release to the environment and need to pay attention.

Keywords: urban mining; valuable resources; toxic substance; substance flow analysis; stocks and trends

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Survey towards tourism waste reduction: tourists' awareness, behavior and discharge status in Kyoto City

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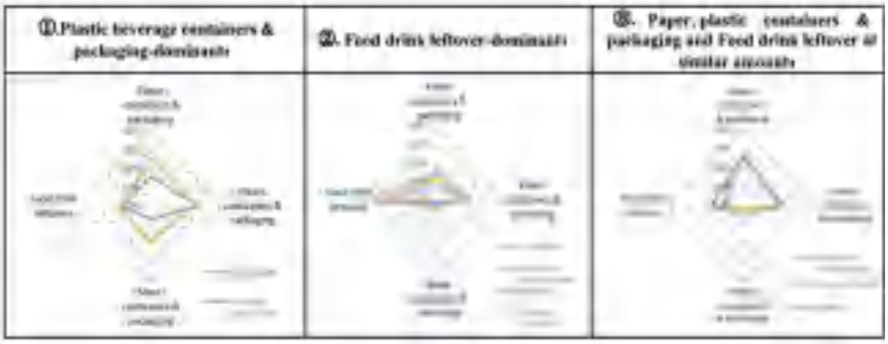
Abstract (200-400 words)

The accelerated development of tourism industry is bringing impacts to Kyoto City on various aspects, with waste management problems being no exception. Nevertheless, there is no systematic information on tourism waste's current situation in Kyoto City. Therefore, this study aims to unveil the current situation of tourism waste in Kyoto and seek for effective short-term countermeasures for tourism waste. Accordingly, this research presents 4 surveys, from summary of current tourism waste situation in Kyoto City to countermeasure recommendations. Firstly, tourism waste 2R (reduce and reuse) schemes in Kyoto City were summarized through interviews with various stakeholders including hotels, NPO, and municipality of Kyoto (2018, 6 groups). Effectiveness of these current efforts was evaluated by foreign tourists through a questionnaire (2018, 126 samples). As a result, the current strategies are claimed to be ineffective; therefore, this research targeted to imply effective 2R strategies for Kyoto City. Specifically, tourism waste composition survey was conducted (November 2018, 6 regions, 93kg) to unveil the waste categories requires reduction, while a second questionnaire for tourists was conducted on their preferences for 2R countermeasures (December 2019, 404 samples). The results show that current countermeasures to tourism waste in Kyoto City summarized in survey 1 is evaluated ineffective in survey 2 due to tourists' limited practices and knowledge. However, tourists' strong intention in plastic waste reduction is discovered. Waste composition surveys demonstrated that plastics and beverage containers are the main challenge for tourism waste 2R management. Regional differences were also revealed in mainly three scenarios due to different business types in region: ①plastic containers & packaging dominant, ②food drink leftovers dominant, and ③paper containers & packaging, plastic containers & packaging, food drink leftovers three-way dominant. Survey 4 illustrated there is high potential for "Kyoto style cooperative tourism on 2R behaviors". To achieve this goal, Kyoto City is expected to encourage tourists more directly and strongly on their 2R behaviors while supporting business through soft incentives. Businesses need to correctly grasp tourists' cooperation willingness and practice 2R efforts accordingly. Specific work focuses are to improve waste separation rate and to reduce plastic waste. Effective strategies selected by tourists including financial incentives, consciousness campaign etc. should be adopted.



Keywords: tourism waste, waste reduction, Kyoto City, discharge status, pro-environment behaviors

Peer-review under responsibility of Tsinghua University/ Basel Convention Regional Centre for Asia and the Pacific.

Selected Proceedings of the Fourteenth International Conference on Waste Management and Technology

The 15th International Conference on Waste Management and Technology (ICWMT 15)

Uncovering the flow of global scarce metals in electric vehicles

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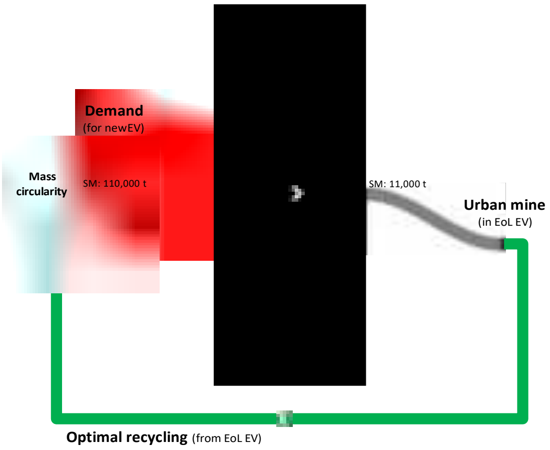
Abstract（200-400 words）



Material extraction has fueled economic progress since the Industrial Revolution; the global use of materials reached 90 billion t in 2017, and will increase to between 170−180 billion t in 2050 by forecasting. Natural reserves are increasingly and acceleratingly transforming into urban mines (e.g. end-of-life products) after the use phase, in particular regarding some scarce metals (SM) essential for emerging “clean” technologies (e.g. renewable power generation, energy storage, and electro mobility). Urban mining of these SM may serve as an important strategy to strengthen the world sustainable development. Accordingly, this study focused on 31 SM: 5 precious metals (PM), 8 rare earth elements (REE), 4 battery ternary compounds, and 14 others in 3 types of electric vehicles (EV): hybrid electric vehicles (HEV), plug-in hybrid electric vehicles (PHEV), and battery electric vehicles (BEV). To explore their global recycling potentials, we developed a substance flow analysis based on estimations of SM contents per EV and end-of-life EV generation in 2018; furthermore, their mass circularities (i.e. recycled materials/materials demand) in EV were assessed. The study estimates that the global EV in use in 2018 exceeded 18 million units (72% HEV, 10% PHEV, and 17% BEV), meanwhile, the end-of-life EV generation researched 0.6 million units (90% HEV, 3 PHEV, and 7% BEV). The associated SM stock were 400,000 t worldwide, among, top three holders are Japan (shared the largest proportion of HEV), the US, and China; the associated recycling potentials of PM, REE, and battery ternary compounds from end-of-life vehicle parts (e.g. catalytic converter, electronics, motors, and batteries) were estimated as 4 t, 2,000 t, and 9,000 t, respectively. The results also show that, in EV, the global mass circularities (considering collection and recycling efficiencies in optimal situations) of PM, REE, and battery ternary compound could meet 10%, 16%, and 9% in 2018.

Keywords: Urban mining; Scarce Metals; Electric Vehicles; Material Flow Analysis; Circular economy

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Towards a more circular economy using the example of plastics beverage packaging recycling in Austria

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Abstract

The European Commission's single-use plastic directive stipulates the ’separate collection‘ of plastic beverage packaging with a share of at least 90 % by 2029. At the same time, newly produced and marketed bottles must contain at least 30 % recycled plastic. In Austria, about 70 % of plastic beverage packaging is collected separately. Hence, this paper presents alternatives that are capable of meeting a 90 % ’separate collection rate focusing on possibilities and limits of different alternatives - including mixed municipal waste and commercial waste. Based on the market volume and existing regional collection rates, possible achievable collection rates are presented using material flow analysis and ensuring to maintain the existing separate collection of light packaging waste. The alternatives include solutions with deposit and predominant return at retail as well as alternative solutions without deposit. Based on the material flow analysis for each alternative, necessary changes to the infrastructure such as take-back systems, collection systems, waste sorting and recycling are described and evaluated including the comparisons of ecological effects and costs. Additionally, possible effects on multiple use of refillable beverage packaging are described but in particular, the expected contribution of the alternatives to reduce littering is addressed.

Besides the targets from the single-use plastic directive, effects and contributions of the alternatives on other objectives such as minimum recycling quotas for mixed municipal waste and minimum recycling quotas for plastic packaging are taken into accounts within a time horizon up to the year 2025 and 2029 respectively.

Keywords: Circular economy; single-use plastic; plastics beverage packaging; deposit; recycling.

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Risk management of chemical substances from the perspective of risk/risk trade-offs

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Abstract（200-400 words）

One of the challenges in risk management of chemicals is to address their interconnected multiple risks. There are issues such as local risk versus global impact, human risk versus ecosystem risk, and risks from different life cycle phases. A trade-off involves creating new risks while solving existing ones. Sound decision making should always attempt to mitigate risk/risk trade-offs. However, the current situation is that most evaluations are single risk assessment. There are knowledge gaps in multiple risks assessment and risk/risk trade-offs analysis. Here, we characterize and quantify multiple risks and trade-offs by integrating material flow analysis (MFA), risk assessment (RA), and life cycle assessment (LCA) by several case studies. It concluded that the countervailing risk must be addressed as well when attempting to reduce the target risk. The results also suggest a life cycle control strategy avoiding risk transfer or transform from one life cycle phase to another life cycle phase. Moreover, phasing out of a chemical with potential harm is just one important first step. The subsequent stock and waste management also should be tackled with proper countermeasures. A risk/risk trade-off diagram with two newly proposed indicators was developed providing a holistic perspective informing chemical risk management policies. Integration of MFA, RA, and LCA contributes to broad decision making in a dynamic manner, promoting efficient and effective chemical management towards sustainability.

Keywords: Risk assessment, risk management, chemical substitution, flow and stock, risk/risk trade-offs;

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Ex-ante LCA of an Cl recovery process for advanced PVC wastes recycling based on up-scale experiments

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Abstract

To achieve sustainable development goals, implement of advanced recycling technologies will be one of the essential tasks. Because the design of technology at the laboratory experiment stage will decide most of the environmental impacts during the industrial application, ex-ante life cycle assessment will be a promising tool to predict the potential impacts and suggest an environmentally-friendly design of emerging technology. In this case study, we focused on a Cl recover process for Poly (vinyl chloride) (PVC) wastes. Owe to its excellent stability, PVC is widely applied in modern society, and it is the third-largest produced plastic resin in the world. As PVC resin containing 56.8 wt% of Cl, the production of PVC is the biggest consumer of the Cl from the chlor-alkali industry. However, the PVC wastes are commonly treated by thermal treatments, resulting in the formation of undesired Cl-compounds. A Cl recovery process was developed to recycle Cl from PVC wastes and valorize the hydrocarbon. First, PVC wastes are dechlorinated in ethylene glycol (EG)/NaOH solvent with ball milling at 190 ºC and electrodialysis. Cl is accumulated in the solvent as salt, and the dechlorinated hydrocarbon (Cl content < 0.5 wt.%) can be used for feedstock recycling. Then, the solvent is proceeded to electrodialysis for the separation and recycling of EG and salt. To suggest the optimal design of the Cl recovery process in terms of environmental impacts, the life-cycle energy consumption and greenhouse gas (GHG) emissions of current PVC waste treatments in Japan were investigated as the benchmark. The potential energy consumption and greenhouse gas (GHG) emissions of the Cl recovery process was modeled based on the operation of the ball mill reactor and the kinetic model of dechlorination reaction. Based on the up-scale experiment and the simulation of the ball milling process, it is suggested that the control on the impact energy of ball milling and NaOH concentration is essential for reaching a high dechlorination efficiency and low environmental impacts of Cl recovery process.

Keywords: ex-ante life cycle assessment; polyvinyl chloride; dechlorination; Cl recovery; recycling

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Characteristics of material flow in the whole management of oily sludge in China

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Abstract

China's relevant laws and regulations have classified oily sludge as hazardous waste, being listed in China's "National Hazardous Waste List". Therefore, if not treated properly, oily sludge will bring harm to human health and ecological environment. However, with the development of the petroleum industry, oily sludge is gradually increasing. Uncertain data reveals that China produces over 3 million tons of oily sludge per year, most of which comes from crude oil extraction procedures in oil fields.

In this study, China's production of oily sludge from different oil fields will be estimated, different treatment methods used in China will be presented, and its comprehensive utilization potentials will be introduced. Further on, two of the most common treatment methods will be selected, and through data collection, the database will be created. Using the research method of material flow analysis, the processes of oily sludge production, consumption, utilization and disposal of the two selected technologies will be revealed. Followed by the analysis of the two case studies, an estimated material flow analysis of oily sludge in China will be made, discovering the typical flow characteristics of valuable resources and pollutants during the process, providing guidance for future related policy formulations. Lastly, by using the material flow analysis research method, China's industrial waste treatment's main challenges will be presented and China's industrial waste management will be discussed.

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Keywords: oily sludge; material flow analysis; hazardous waste; industrial waste management; China

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Zero Waste: Sustainable Approaches and Practices

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Abstract

To achieve local or regional sustainability, one approach towards a sound waste management is to drive for zero waste goal, which entails elimination of waste and maximization of resource efficiency. This however requires a fundamental change in our mindset, that is: waste is simply a misallocated resource and nothing can be called waste. A paradigm shift is also needed in the implementation system, that is: advancing from waste management to resource circulation.

It is noted that, zero waste goal can be achieved in stages of increasing difficulty: initially, zero waste to landfill; then, zero waste from the production to consumption process; and finally, zero waste generation at source. Nevertheless, zero waste system at all stages necessitates appropriate technologies and systems. Further, a successful implementation of zero waste system needs to be sufficed by environmental and socio-economic soundness. A sustainability index is henceforth required for evaluation of the planned zero waste system, incorporating thoughtful consideration of all environmental, social, and economic factors.

This paper will address the sustainability issues associated with zero waste system. Approaches of various practitioners will be shared, with a view of sharing viewpoints and suggestions towards reaching a better understanding of the implication and implementation of zero waste system.

An introduction will first be given to address the zero-waste approach, followed by the discussion about the necessary and sufficient conditions for implementing zero waste systems. A sustainability index incorporating the economic, environmental and social indicators will be presented, to illustrate the evaluation method and its usefulness in planning the targeted zero waste system.

Successful zero waste practices will be shared, to demonstrate practical approaches to plan and implement the zero waste systems. Cases will include: an integrated approach for beneficial use of sludge, biosolid and wood wastes, in an economically and environmentally sustainable manner; industry’s approach applying industrial ecology concept, to develop a metal-based a circular economy system; taking a cleaner technology approach to converting waste to value-added biofuel and renewable chemicals, hence achieved a zero waste system. Lastly, an overview will be presented respecting the role of zero waste in the New Green Deal, with consumption and climate implications.

This presentation will provide the zero waste researchers, planners and practitioners an insight view of promising opportunities and inherent challenges. It is hoped that this inspire them to think and work collectively to search for innovative technologies and strategies, so as to further advance the accomplishment of zero waste goals in various fronts.

Experimental Study on Recovery of Au, Ni, Cu from Waste Printed Circuit Board

Qianxia Li, Zhenfeng Xiong, Ying Huang*

Abstract: E-waste is considered one of the fastest growing municipal solid wastes. Printed circuit boards are the core components of electronic products. They contain a large amount of metals and have high resource recycling value and economic recovery benefits. In this paper, trichloroisocyanuric acid was used as a leaching agent to efficiently extract Au, Ni, Cu from the "golden fingers" of waste printed circuit boards. The effects of leaching agent concentration, time, temperature, and pH are studied experimentally. During the investigation, it was found that the molar concentration of trichloroisocyanuric acid was 25 mmol/L, the leaching time was 10h, the temperature was 30°C, and the pH was 1, the leaching rate of gold was 60.15%, nickel was 74.69%, copper was 75.53%. In this study, a single organic reagent was used to extract metals from waste printed circuit boards to provide a basis for the wet recovery of metals.

Keywords: Waste printed circuit boards, Trichloroisocyanuric acid, Metal recycling

Preparation of high wear-resistant sulphoaluminate cementitious materials using steel slag

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Abstract: The iron and steel industries discharge a huge amount of steel slag every year. Due to its high hardness and instability, only 30% is utilized. In China, the slag accumulation is up to 2 billion tons, which has caused severe financial and environmental burdens to the industries and the society. It is urgent to find a new solution which could consume steel slag in large scales and produce high value-added materials/products. This study aims to prepare high-performance sulphoaluminate cementitious materials using steel slag, flue gas desulfurization gypsum, aluminium ash and carbide slag. The steel slag could take up to 30% in the raw materials and the utilization of natural resources, such as limestone, is significantly reduced. The calcination temperature is 100 ℃ lower than that in the traditional process. Thus, carbon-dioxide emission could be dramatically reduced. Moreover, the mineralogical composition of the clinker is C4A3S, C2S and C4AF, and the material shows great wear-resistant properties. It is a promising marine engineering material, and could be used to build long-life seawalls and artificial islands.

Keywords: Steel slag, sulphoaluminate clinker, wear-resistant, mechanical strength

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Microplastic abundance and distribution in sandy beaches of Malaysian Islands

Fauziah S.H., Nurul N. A.

Abstract: No marine environment is devoid of marine debris pollution particularly due stranded plastic waste, which inevitably leads to the accumulation of microplastics. Accordingly, risks of contamination to the food-web too have become a distressing issue of concern. This study aimed to correlate the abundance of macroplastics with microplastics distribution in recreational sandy beaches in Malaysia. The collected marine debris was segregated into 27 types, while microplastics were sampled from triplicates 12.5L sand samples from selected beaches. Hard plastic, film, and polystyrene are predominant (60-80%) in the marine debris stream, while, the most abundant microplastic were foam and fragments. A positive correlation (0.917) $R^2 = 0.841$) was found between the abundance of macro and microplastics on the selected beaches of Malaysian islands. This highlights that macroplastic abundance has significant contribution to the presence of microplastics that appropriate strategy for plastic waste management is crucially needed to lessen the problem of microplastic pollution.

Key words: Macroplastics, Microplastics, recreational beaches, plastic waste, Malaysia.

Current Status and Future Plan of Plastic Waste Management in Korea (Republic of)

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Abstract（200-400 words）

In Korea, generation of plastic waste is increased from about 14,153 ton/day in 2011 to 22,107 ton/day in 2017 with a compound annual growth rate of 7.7% for the period of 2011 to 2017. In 2017, treatment of plastic waste was 62% of recycling, 33% of incineration and 5% of landfill. Even though the recycling of plastic waste is very high, the amount of plastic waste used as energy resources has been decreased recently because the facilities for waste to energy were not operated properly due to heavy fine dust in Korea. Hence, the cost of waste to energy on plastic wastes has been increased significantly. As a result, the treatment cost on plastic wastes in incineration and landfill was increased overall so that collectors refused to collect plastic wastes because of the market led to a decrease in the price of plastic waste in 2018. The Korean government has set a goal of 50% reduction in the generation of plastic waste by 2030. In order to achieve this goal, the improvement plan according to stakeholder related to plastic products and their waste was established. The government has tried to increase the capacity of the public waste treatment facilities and to amend law on recycling of plastic waste. Producers of plastic products is being conducted to improve design of plastic products and to use alternative. Consumers should be reduce the use of single-use plastic such as plastic bags and the separate and discharge by plastic materials. The scientific and technological community is working with the plastics industry to develop plastic separation and recycling technologies including alternative plastics.

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Keywords: Plastic wastes, Improvement plan, Waste management

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Plastic Economy and Waste Management in India

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President, International Society of Waste Management, Air and Water (ISWMAW)
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Abstract（200-400 words）

Among the fastest-growing industries in India, plastics are experiencing a double-digit growth rate on an average and host more than 2,000 exporters. It employs about 4 million people and comprises more than 30,000 processing units, 85-90% of which are small and medium-sized enterprises (SMEs). Study revealed that, plastics formed 2.80% of India's overall merchandise exports during April – September 2018 (H12018-19). Plastics exports had a growth of 31.6% at $4.59 billion during the 1st quarter of 2018-19 as against $3.48 billion in the same period during 2017-18. Nearly 707 million tons/year plastic products are produced in India with 9.7 kg per capita consumption and 80% for packaging applications. The annual plastic consumption is expected to reach to 20 million tons by 2020. Due to the pandemic outbreak of COVID 19 the targets of all the industries throughout the word in early FY 2020 have been affected which is evident in India too. It is uncertain at this stage that when the upward tendency in business will achieve coming out of the ill effects of COVID19. However, the major portion of wastes generated from plastics is from packaging sectors and consumer products. Around 4059 tons/day of plastic waste is generated from 60 major cities and nearly 25,940 tons/day with highest plastics recycling rate (47%) in the world and huge demand for recycled plastics. The fraction of plastic in MSW varies from 3.10% to 12.47% with an average of 6.92%. Nearly 94% waste comprises of recyclable thermoplastic content, e.g., PET, LDPE, HDPE, PVC and remaining 6% is non-recyclable thermoset and others. Major cities, Delhi, Chennai, Kolkata, Mumbai and Bengaluru generate more than 50% of the total plastic waste.

India has voluntarily committed to eliminate single-use plastic by 2022 being the host of World Environment Day 2018 with the slogan "Beat the Plastic Pollution". India has banned plastic carry bags up to 50 micron thickness of specified sizes and levied on the use of plastics bags on higher thickness. Sikkim banned plastic bags in 1998. The Plastic Waste Management (Amendment) Rules, 2018 were notified in India introducing extended producer responsibility (EPR) for producers, importers and brand owners to ensure environmentally sound management of plastic products in their life cycle, focusing source segregation of waste, awareness generation, organizing the informal sectors of waste handlers with the ambition to follow a waste-to-wealth pathway via recovery, reuse and recycling. Indian cement plants are becoming a new destination of a major portion of non- recyclable waste plastics for co-processing through regulatory framework.

Technological intervention and innovation in plastics recycling have been practiced and encouraged in India since long back, namely, mechanical recycling, energy recovery, plastics to oil, Co-processing of plastic in cement kilns as AFR, pyrolysis, plastics in road making, pave making process etc. LVPs and multi-layered plastic are recycled to make furniture, handicraft & home décor items etc. This study will present an overview of current trends and future plans of the plastics waste management in India focusing resource recovery and circular economy.

Keywords: Plastics waste management, Resource recovery, plastics recycling, Rules, Circular Economy, Plastic Economy, India

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Plastic/ Plastic Waste Management-An Overview

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Abstract（200-400 words）

Generation of plastic waste is associated with the affluence of a country, and with majority of countries striving towards development, the amount of plastic waste generation is increasing exponentially. Production of plastic globally has reached almost 400 million tonnes per year, however only 9% of the total of 9 billion tonnes of plastic waste generated over the years has been recycled. Packaging plastics account for 40% and it is estimated that only 14% is recycled, although effectively is it only 2% that is recycled clean. As a result of the large quantity of generation with low recycling, plastics imposed several issues. Plastic recycling in developed countries is not a big problem. For instance, in European Union, 69.2% of plastic waste generated is either sent for recycling or waste-to-energy. However, plastic waste recycling poses the biggest challenge in developing countries where approximately 88% Municipal Solid Waste (MSW) is sent to landfill. Plastic recycling has generally been discovered to be uneconomical without significant subsidies due to high process costs incurred to produce monomers from plastic waste.

Plastic commodities are part of every sector of human life, from packaging, consumer products to building and constructions, electrical and electronics and automotive industries. Consequently, plastic waste is also being generated in staggering numbers as well. In 2016 alone, 241 million tonnes of plastic waste was generated globally. In consequence, 5 to 13 million tonnes of plastics, 1.5 to 4% of the total global plastic production, ends up in the oceans every year and hence plastic accounts for 60 – 80% of marine litter

One of the most significant impacts is in the ocean. About 12 million tonnes of plastics enters the ocean annually. Of course, this will generate microplastics and its consequences. Contamination of plastic waste is one challenge in recycling plastic waste, the other challenge is posed by mixed polymer waste since reprocessing of mixed polymer waste poses some challenges as compared to mono-plastic. Now-a-days, the concept of plastic circular economy is being tossed around. While, contamination of plastic waste, unknown composition and mixed plastics hinders recycling, which is a component of circular economy, lower price for virgin raw material makes recycling economically non-feasible. Other impacts of plastics include adverse effects in landfilling, blockage of drains, scavenging, beach pollution, open burning and illegal recycling.

China's ban on imports of plastic waste since January 2018 has serious consequences in plastic exports and imports, particularly in Developing countries. Illegal recycling plants have mushroomed in many Developing countries and these became a serious source of environmental problems.

Circular Economy, Extended Producer Responsibility, Deposit System and other incentives have encouraged plastic recycling to a reasonable quantity.

Recycling and management practices of polyethylene terephthalate (PET) plastic bottles in South Korea

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ABSTRACT

Recently, many problems caused by disposal of single-use plastics (e.g., PET, plastic cups, plastic bags) have emerged as an urgent agenda around the world, resulting in marine pollution, breaking of terrestrial and marine ecosystems, and generation of microplastics. Recycling and proper management of PET bottles is needed to avoid plastic pollution as well as to achieve plastic circular economy. In this study, we examined the recycling system and material flow of PET bottles by life cycle stage (production, consumption, collection and recycling and disposal). In South Korea, the PET bottle recycling has been managed by the expanded producer responsibility (EPR) system. The PET bottle consumption was estimated by available statistics and reports. As a result, annual usage of PET drinking water bottles per capita in South Korea is estimated to be approximately 96 units, which is equivalent to 4.9 billion units per year from the country. Recycling rate of PET bottles put on the market was 81% (232,000 tons) in 2017. The trend of the recycling rate is slightly increasing over the past decade due to tightened regulations and recycling target goals of packaging materials by the government. Most recycled PET materials as flake are used for textiles and sheets. In 2020, manufacturing of colored PET bottles is prohibited for better recycling and material recovery. Recycled PET bottles should be developed by producers using recovered PET pellet in cost-effective way toward a plastic circular economy.

Keywords: PET, Single-use plastic, EPR, Plastic waste, Recycling

1. Introduction

The large consumption of single-use plastics has become an issue of concern due to improper disposal of plastic waste, resulting in ecological damages and pollution in ocean and rivers. Based on the recent survey for marine litters in 2018 from 40 monitoring sites in South Korea1), plastic waste accounted for the largest portion 80%, and the most frequently found plastics include ropes, shredded plastic particles, bottles and lids, styrofoam, bags, strings, food containers, and cigarette butts. This indicates that the appropriate collection of PET plastic bottles generated from lands must be prioritized to avoid marine pollution.

In this study, we examine the current recycling and management practices of PET in South Korea by extended producer responsibility (EPR), discuss the recycling methods and technology of PET, and provide material flow of PET. Current efforts and future challenges of PET collection and recycling are presented toward a plastic circular economy in South Korea.

2. Methodology

In this study, statistical data from the Korea Ministry of Environment (Korea MOE), the Korea Environment Corporation (KECO) and research reports were used as shown in Table 1.

Table 1. Data collection and analysis for PET recycling and MFA.

18. Data source	19. References
20. Research reports	21. Study of single-use plastics (2019), plastic strategy toward circular economy in South Korea (2019)
22. Statistics	23. Annual report of plastics production, import and export, Statistics of MSW generation and treatment in Korea MOE
24. KECO (Korea Environment Cooperation)	25. Waste PET bottle generation, collection, and recycling method
26. Korea MOE	27. Production, material recovery, and incineration, landfilling of plastics

Data for material flow analysis (MFA) for PET bottles were collected from various sources (e.g., available statistics of production, use, recycling rate of PET and plastics published by Korea MOE (Table 2). Research reports are also reviewed for checking the data. Some unknown data (e.g., disposal rate, generation of PET) were assumed by consultation and interviews with industry experts. Table 2 shows the data collection method and source by life cycle of PET.

Table 2. Data collection and sources for MFA of PET.

28. Life cycle of PET	29. Data	30. Statistics	31. Survey	32. Literature	33. Assumptions
34. Production	35. PET production, import and export	36. O	37.	38. O	39.
40. Consumption	41. Plastic bottles by industry, Plastic packaging association	42. O	43.	44. O	45.
46. Waste generation	47. MSW generation rate	48. O	49.	50. O	51. O
52. Recycling	53. Plastic recycling statistics	54. O	55. O	56.	57. O
58. Disposal	59. MSW treatment data	60. O	61.	62.	63. O

3. Results and Discussion

3.1 Production and Consumption of PET

PET plastics bottles production for domestic demand has been increasing. In 2018, approximately 301,000 ton of PET plastic for drink bottles and containers were sold. Figure 1 shows the domestic sales volume according to the color of PET bottles. Colorless PET bottles have been widely used for drinks, while colored PET bottles have been decreasing due to regulations.

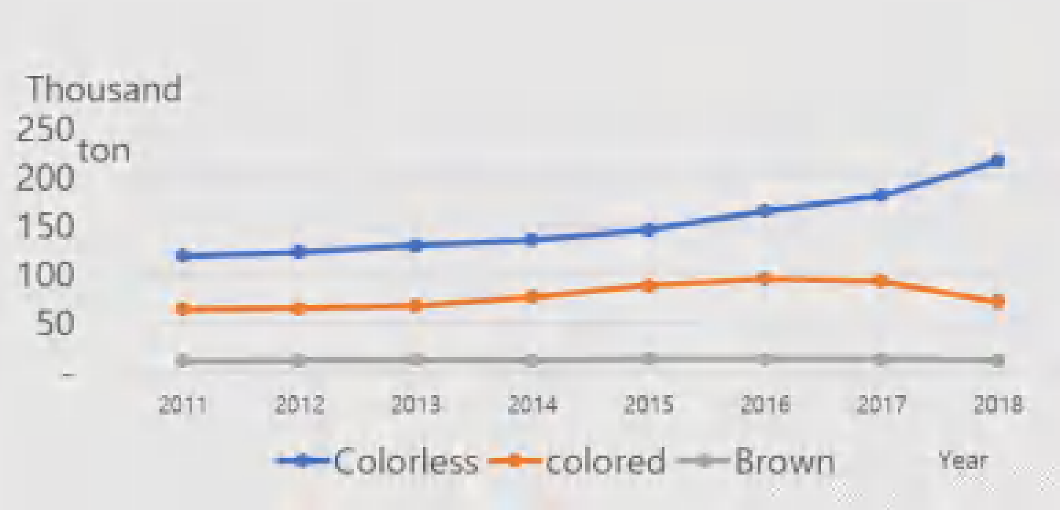

Fig. 1. Domestic sales volume of PET bottles by color

In 2018, several surveys were reported in South Korea to drink approximately 48L of PET bottle water per person per year. It also consumes 5 billion bottles per year, which is equivalent to 96 bottles per person per year. Based on the assumption of 500 ml water bottle with 15 g, approximately 73,400 tons of PET resin is used per year.

3.2 PET recycling rates by EPR in South Korea

Producers and imports by extended producer responsibility (EPR) in South Korea must collect and recycle assigned quantities of their products by national government, based on certain percentages of annual products produced. Otherwise, they must pay more than the fee for recycling their products. The packaging materials for EPR are metal cans, glass bottles, carton packs, PET bottles, synthetic resin packaging materials that are used to pack food and beverages, agriculture, fishery and livestock products, cleansers, medicines and cosmetics, and others. Figure 2 shows the material and financial flows by the EPR system in South Korea. In 2020, the recycling targets by the EPR are 80.0% for colorless PET bottles, 80.2% for colored PET bottles, and 80.3% for composite PET bottles.

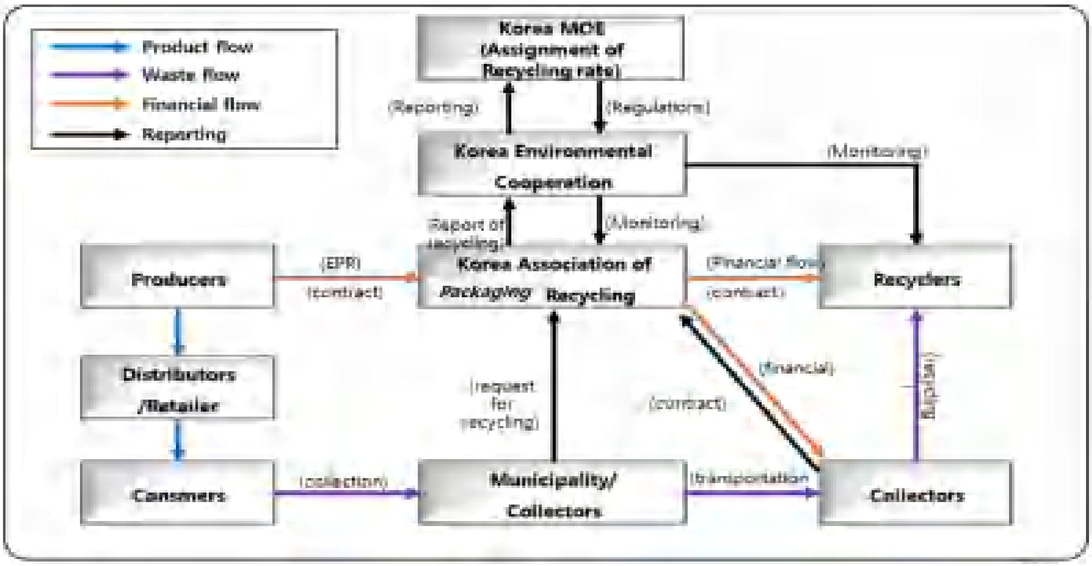

Fig. 2. Packaging waste by EPR system in South Korea.

Figure 3 shows the sales volume of PET bottles, the target recycle rates, the actual recycling amounts achieved between 2010 and 2017. The target rates of PET by the EPR are mostly achieved over the years, although the colorless PET underachieved the rates in 2016 and 2017.

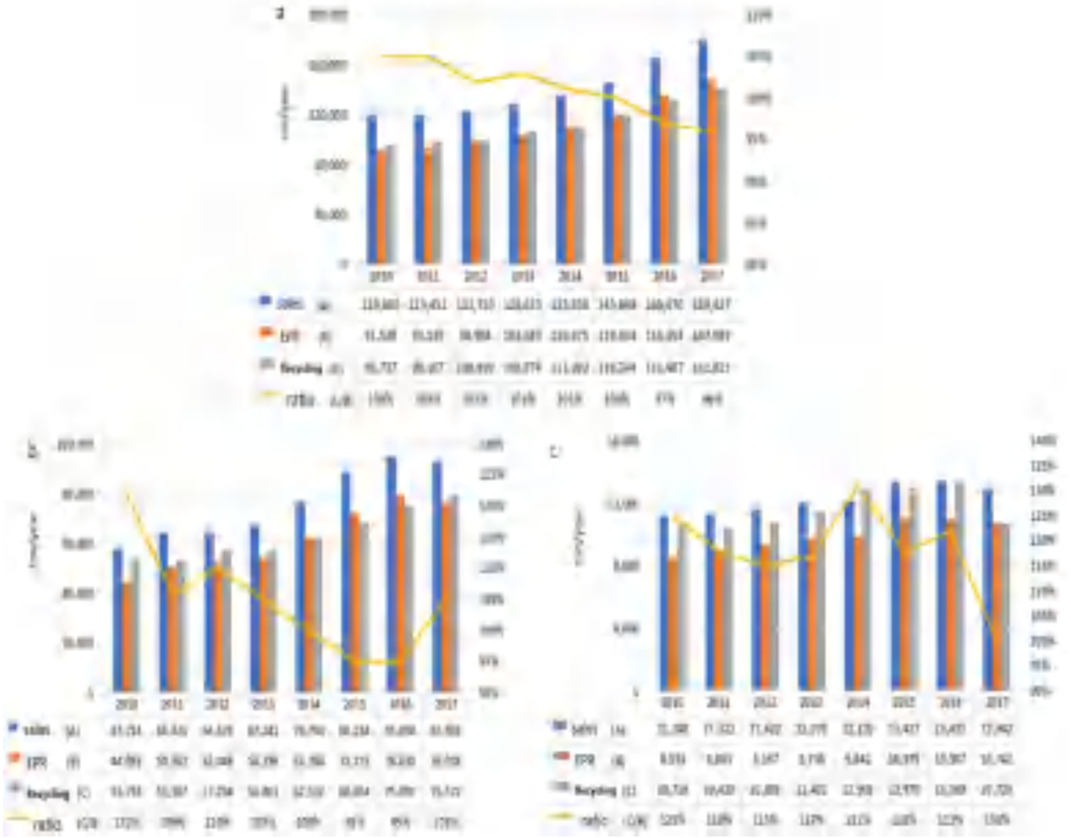

Fig. 3. Recycling rates of PET by EPR in South Korea: (a) Colorless PET; (b) Colored PET; (c) Composite PET.

3.3 *Sorting and recycling methods*

The collected PET bottles are brought to a recycling facility, sorted by color, and the labels removed. Pretreatment processes include crushing, washing, dewatering, and drying. The final product of PET is commonly PET flake, which is used for fibers, textiles, sheet, and PET wires. Figure 4 shows the common sorting and recycling process of PET waste bottles.

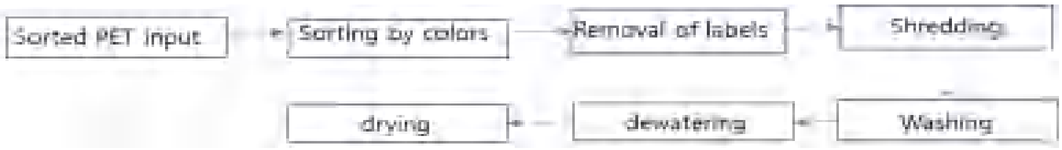

Fig. 4. Recycling process of PET bottles.

3.4 *Material flow of PET in South Korea*

The material flow of PET in Korea for 2017 is shown in Figure 5. The material flow was presented in five stages: A. Domestic use stage, B. Generation stage, C. Collection and sorting stage, D. Recycling and disposal stage, E. Stages of using recycled raw materials.

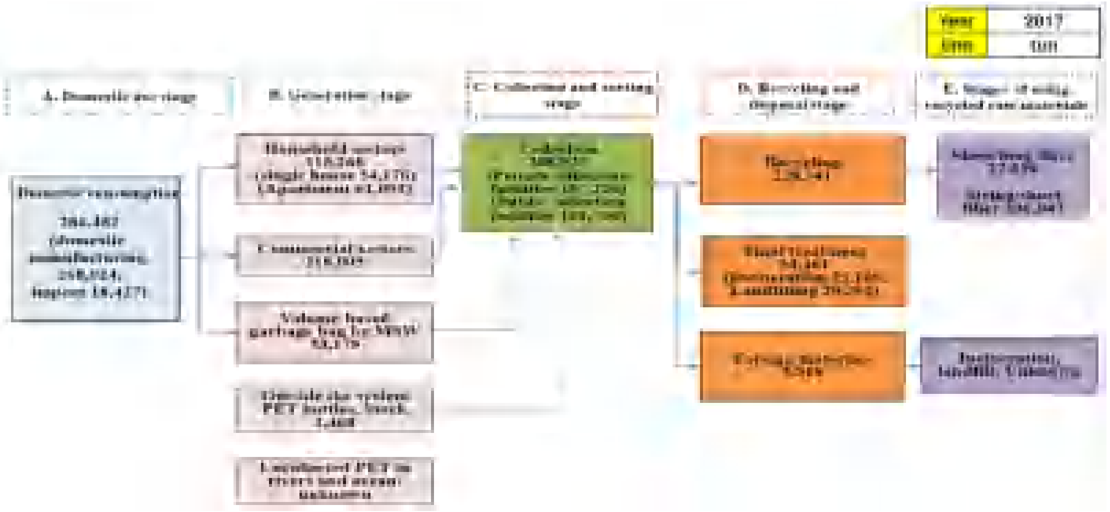

Fig. 5. Material flow of PET in South Korea.

3.5 Challenges and future direction

Six local governments are conducting pilot projects of separated PET collection at source. Households dispose of the colored PET bottles in mixed plastic collection box, while only colorless PET bottles are collected in a PET collection box. By such implementation, more than 100,000 tons of PET waste bottles can be collected and recycled as high quality recycled raw materials for the use of textiles and recycled PET by 2022 and plan to gradually restrict the import of waste PET bottles.

Currently, recyclability of all packing materials in 2020 is being evaluated. Such policy is aimed to promote plastic recycling. It is mandatory to evaluate packaging materials for recyclability in four classes: best, good, normal, and difficult. Producers contribute different costs by the EPR system according to the levels of easy recycling. In the case of PET bottles, it is evaluated by dividing it into body, label, cap for evaluating the use of colorless PET, labels with easily removal by consumers, less amount use of adhesives, and labels and stoppers with specific gravity (<1.0).

4. Conclusion

Based on this study, the following conclusions are made.

- There are more than 300,000 tons of PET produced and consumed each year in South Korea.
- PET bottle waste is managed by the EPR system by achieving 76% recycling rate (228,000 ton).
- There is an urgent need to better cost-effective recycling technology with source separation of PET bottles.
- As a result of material flow analysis of PET bottle in 2017, recycled amount of PET was 228,941 tons from the collected PET of 288,920 tons.

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Systems Integration for Global Sustainability: Focused on SDG 15 (Life on Land)

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Abstract

Systems integration is holistic approaches to integrating various components of coupled human and natural systems, in which human and natural components interact. Wastes are part of coupled human and systems. They are generated within and across adjacent and distant systems. They change over time and across local to global levels. Wastes affect SDG 15 (life on land) in many direct and indirect ways. The processes of generating, transporting, and treating wastes consume energy, emit greenhouse gases, occupy land, convert natural habitat, and pollute the environment (e.g., air, water, and soil). Achieving global sustainability such as SDG 15 requires systems integration of waste prevention, generation and management over time, at all organizational levels, and across space worldwide.

Enhance the role of ecosystem management towards green economy and SDGs

Guoqin Wang

International Ecosystem Management Partnership, United Nations Environment Programme (UNEP-IEMP), Beijing, PR China

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Abstract（200-400 words）

Ecosystems are the basis of human civilization and natural capital for green economy development. Ecosystem management, “an integrated process to conserve and improve ecosystem health that sustains ecosystem services for human well-being,” is a critical approach to realize a green economy and SDGs 2030. Ecosystems have been profoundly degraded over the last 50 years and pressure on them continues unabated. Ecosystem management plays a critical role in halting and reversing this ongoing degradation, and also provide economic and job opportunities, particularly for developing countries. This presentation will share on-going global calls and UN resolutions for ecosystem management, and showcase ecosystem management experiences and lessons from the different developing countries, particularly these from the Chinese Ecosystem Research Network in the past 30 years.

Peer-review under responsibility of Tsinghua University/ Basel Convention Regional Centre for Asia and the Pacific.

Food loss and waste ~ Linkage to SDG 2 'Zero Hunger' and SDG 12 'Responsible Consumption and Production'

Dong Le

Poverty Reduction and Innovation Officer, Food and Agriculture Organization (FAO),
Beijing, PR China

Abstract（200-400 words）

World Hunger is on the rise; yet, an estimated 1/3 of all food produced globally is lost or goes to waste. FAO is partnering with governments, international organizations, the private sector and civil society to raise awareness on the issues and to implement actions to address the root of the problem. This presentation introduces FAO's work in this regard at the global level and particularly in China. For instance, FAO China organized the first Hackathon for reducing food loss and waste in Beijing in November 2019, in partnership with Tsinghua University, Swiss Agency for Development and Cooperation, and Messe Dusseldorf.

Peer-review under responsibility of Tsinghua University/ Basel Convention Regional Centre for Asia and the Pacific.

KPI and MRV system to evaluate the waste management under SDG 11.6 and SDG 13

Nina Mitiaieva

Deutsche Gesellschaft für Internationale Zusammenarbeit (GIZ) GmbH,
Beijing, PR China

Abstract（200-400 words）

The presentation will give an overview of approaches applied by China Integrated Waste Management NAMA Support Project (China IWM NSP) to monitor the progress of its demonstration municipalities towards low-carbon integrated solid waste management (ISWM). Given the need to not only ‘capture’ the level of ISWM implementation, but to also consider its effects on the intensity of greenhouse gas emissions, the project has been using both KPI and MRV systems and, thus, can share its insights on how both systems complement each other and which synergies they offer when applied together.

Peer-review under responsibility of Tsinghua University/ Basel Convention Regional Centre for Asia and the Pacific.

The 15th International Conference on Waste Management and Technology (ICWMT 15)

Encouraging Cool Choices and Decisions for SDG14 in SIDS – Consideration on technical assistance in Federated States of Micronesia –

Kikuko Sakai

OFCF-FSM Office (Overseas Fishery Cooperation Foundation of Japan, Federated State of Micronesia)

Abstract（200-400 words）

Achieving SDG14 is the heart of resilience building in Small Island Development States (SIDS), while they are also particularly vulnerable to extreme weather events, climate change, ocean pollution and acidification. This presentation is based on a case in Federated States of Micronesia (FSM), through the implementation of a technical assistance program toward FSM Strategic Development Plan for fisheries as well as SDG14. The program has been conducted by Overseas Fishery Cooperation Foundation of Japan (OFCF) in targeting 9 Pacific countries for over 30 years to repair and restore the artisanal fisheries facilities, mainly for small vessels and ice making machines. Appropriate refrigeration systems would contribute to SDG14 through improvement of local fishers' livelihood in keeping fish quality and reducing post-harvest loss. Therefore, both donors and recipient countries are encouraged to make cool choices and decisions for refrigeration systems in SIDS in line with Nationally Determined Contributions on Climate Change.

Peer-review under responsibility of Tsinghua University/ Basel Convention Regional Centre for Asia and the Pacific.

The 15th International Conference on Waste Management and Technology (ICWMT 15)

Financing waste management infrastructure – challenges in implementing a transition towards a Circular Economy

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Abstract

Currently, the world is on a trajectory where the generation of municipal solid waste still outpaces population growth. Although improvements and innovations are detected globally, waste management is a complex issue and consumes a large portion of municipal budgets. The characteristics of waste management systems in EBRD's 39 countries of operation are quite different, therefore investments in upgrading waste management systems need to be carefully prepared. Beside the preparation of solid waste projects, the implementation of these projects is no less complex, especially the COVID-19 pandemic puts pressure on cities and municipalities. This paper describes a general path of development in waste management in EBRD's geographical region and the major challenges and lessons learned regarding financing solid waste infrastructure. Important issues from an international financial institution's point of view are the acceptance of new waste infrastructure, economic feasibility and affordability and in parallel a commitment to support clients moving from disposal-oriented to resource conservation-oriented societies. The paper provides insights regarding a stepwise implementation approach, the necessary capital expenditures and why infrastructure provision alone is not creating sustainable solutions. In addition, experiences regarding implementing waste infrastructure are grouped and guidelines for potential project developers are presented.

Keywords: municipal solid waste, circular economy, infrastructure, finance, investment, international financial institutions

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A New Approach to Measuring Effective Linkage Formation in China's Industrial Symbiosis Parks

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Abstract

The present article centres on the concept of institutions, i.e. systems of rules that guide behaviour and interaction of socio-economic actors, and their role in advancing China's Circular Economy (CE). Since the early 2000s, state and non-state actors in China have began to experiment with the CE in various domains, such as waste management and industrial symbiosis. As a result, the country now features a multitude of CE patterns and systems which in some cases performed more, in others less successful. Part and parcel behind the effectiveness of such CE applications and schemes are the institutional arrangements within. Based on various research projects in China over several years, the article highlights what I believe to be key institutional ingredients for effective outcomes. Hereby, particular focus will be put on information provision, the congruence of interests among involved actor groups and the dynamics of imitation and experimentation. The significance of these key elements will be demonstrated on the basis of findings from case studies in Beijing, Shenzhen and Changchun as well as from secondary literature.

Keywords: Circular economy; China; Institutions; Waste collection; Informal Recycling Sector.

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The 15th International Conference on Waste Management and Technology (ICWMT 15)

A New Approach to Measuring Effective Linkage Formation in China's Industrial Symbiosis Parks

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Abstract

This paper presents a work in process methodology for evaluating the Industrial Symbiosis (IS) performance in China's Eco-Industrial Parks (EIPs) and Circular Economy parks (CEPs). Over more nearly two decades, China has been most actively exploring IS formation development in its industrial parks. Based on findings from secondary literature on the domestic and international contexts, parks in China have achieved the status of an international frontrunner, being on a par with IS activities in Japan, South Korea or England. One evidence of the effort to continuously improve performances in China is demonstrated by several instances of adjusting and innovating key evaluation indicator frameworks for EIPs and CEPs. However what has as of now not been included in these official frameworks are indicators that address how the particular institutional scaffolding in parks, e.g. fiscal policy measures per year, information provision mechanisms, environmental regulations, has influenced IS development in parks. This stands in contrast to findings from literature on IS parks in China and abroad, which shows that such institutional elements have a significant impact on the formation of IS-linkages in park estates. The article therefore sets out to discuss relevant literature on the topic and thereof derive an alternative indicator framework that measures institutional effectiveness for promoting IS-linkage building in Chinese park estates.

Keywords: Industrial Symbiosis, China; Institutions; Eco-Industrial Parks; Waste recycling;

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天然气开采水基钻井固废处理处置技术及应用研究进展

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摘要：天然气水基开采过程产生大量的钻井固体废弃物，包括钻井岩屑和钻井泥浆，近年随着天然气需求量的增大，钻井固废污染防治形势越发严峻。为降低钻井固废对环境的影响，提高利用率，多种无害化处理技术和资源化途径被提出并研究。系统地分析和总结了水基钻井固废的污染特征，国内外钻井固废的无害化处理技术（包括：固化稳定化技术、生物降解技术、化学淋洗技术、井下回注技术、焚烧技术）与资源化利用途径（包括：免烧砖、路基土、沙漠改良土），并阐述了各技术的特点、处理效果，以及处理达标后钻井固废的资源化利用状况。结果表明：水基钻井固废的污染性取决于前端钻井液的添加剂，污染性低于油基固废；多种无害化处理技术均能有效地降低重金属及有机物的浓度，达到一般工业固废Ⅰ类的要求；多元化的资源化途径可大幅提高固废的利用率，具有较好的发展前景。但在实际推广应用中仍面临较多的问题，包括：固化稳定化技术可有效去除重金属，但不能去除有机污染物，只能包裹，存在再次浸出的风险；生物降解技术受菌种、气温、污染物组份影响较大，不能适用所有地域的固废；井下回注技术、化学淋洗法在国外应用较广，但在国内处于初步实验阶段；焚烧技术处理效果较好，但成本较高；资源化利用与当地产业特征结合不紧密，仅处于示范阶段，处理量还处于较低的水平。为使钻井固废处理处置尽快形成工程化、规模化的模式，建议下步从以下几点进行深入研究：加大两种或多种处理处置技术的联合研究，发挥协同作用；从源头上对钻井固废产生特征进行研究，降低固废产生量；探索钻井固废作为路基土使用的技术及工艺 。

关键词：天然气开采；水基钻井固废；无害化处理；资源化利用；研究进展

Research progress of solid waste treatment and disposal technology of water-based drilling for natural gas exploitation and its application

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2. Ordos haoxin green environmental engineering co. LTD

Abstract: large amount of drilling solid wastes, including drilling cuttings and drilling mud, are produced during water-based exploitation of natural gas. In recent years, with the increasing demand for natural gas, the prevention and control of drilling solid waste pollution becomes more and more serious. In order to reduce the impact of solid waste on the environment and improve the utilization rate, a variety of harmless treatment technologies and resource recovery approaches have been proposed and studied. Systematically analyzes and summarizes the water-base drilling solid waste pollution characteristic of drilling solid waste harmless treatment technology at home and abroad (including: curing stabilization technology, biological degradation, chemical leaching technology, downhole reinjection technology, incineration technology) and the resource utilization way (include: baking-free brick, subgrade soil, the desert, improved soil), and expounds the characteristic, the treatment effect of each technology and processing standards after drilling solid waste resource utilization. The results show that the contamination of solid waste in water-based drilling depends on the additives in the front-end drilling fluid, and the contamination is lower than that in oil-based solid waste. A variety of harmless handling technology can effectively reduce the concentration of heavy metals and organic compounds, reached the requirements of general industrial solid waste Ⅰ class; The utilization rate of solid waste can be greatly improved by diversified resource recovery methods, which has a good development prospect. However, there are still many problems in practical application, including: curing and stabilization technology can effectively remove heavy metals, but can not remove organic pollutants, can only be wrapped, there is a risk of re-leaching; Biodegradation technology is greatly affected by bacteria, air temperature and pollutant composition, and can not be applied to solid waste in all regions. Downhole reinjection technology and chemical leaching are widely used abroad, but they are in the preliminary experimental stage at home. The incineration technology has good treatment effect but high cost. Resource utilization is not closely combined with local industrial characteristics, and the treatment capacity is still at a low level. In order to form an engineering and large-scale model of solid waste treatment and disposal in drilling as soon as possible, it is suggested to carry out in-depth research from the following steps: to increase the joint research of two or more treatment and disposal technologies, to give play to the synergistic effect; Study the characteristics of drilling solid waste from the source to reduce the production of solid waste; To explore the technology and technology of solid waste used in drilling as subgrade soil.

Keywords：natural gas exploitation；solid drilling waste；harmless treatment；resource utilization；research progress

中国城市矿产上市公司投资价值分析

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摘要：在我国工业化和城镇化快速推进的过程中，城市矿产蓄积量不断增加。城市矿产区别于自然矿藏，是蕴藏于城市废弃产品中能够再生利用的资源，对其开发和利用作为战略性新兴产业，是保障资源安全、减轻环境污染的重要途径，同时也是发展循环经济的关键环节。城市矿产上市公司是城市矿产开发状况的晴雨计。本文给出城市矿产上市公司的界定标准，以沪深两市 18 家城市矿产上市公司作为研究对象，从成长能力、可持续发展能力、盈利性等多维度评估企业投资价值，通过因子分析和熵值法提取度量上市公司投资价值的特征指标变量，对各公司进行综合评价和排名。同时将城市矿产代表性企业与循环经济板块其他子领域代表性企业进行对比分析，运用估值模型发现它们的潜在投资价值，一方面帮助投资者提高投资效率，另一方面也有利于上市公司扩大融资规模，推动城市矿产业成为新的经济增长点。

关键词：城市矿产；上市公司；因子分析；熵值法；投资价值

Analysis on the investment value of Listed Companies in China's urban mineral industry

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Abstract: In the process of rapid industrialization and urbanization in China, the stock of urban mineral has been increasing. Urban minerals, as recyclable secondary resources contained in urban waste products, are different from natural minerals. Urban mining has become an emerging industry of strategic importance. It is not only an important way to ensure resource security and reduce environmental pollution, but also a key link to develop circular economy. The urban mineral listed company is a barometer of the state of urban mineral development. This paper illustrates the definition criteria of urban mineral listed companies. With the research object of 18 urban mineral listed companies in Shanghai and Shenzhen stock exchange, the investment value of companies is evaluated from the growth ability, sustainable development ability, profitability and other dimensions. Through factor analysis and entropy method to extract the characteristic index variables, comprehensive evaluation and ranking of each company are made to determine the investment strategy. At the same time, the representative listed companies of urban mineral industry and other sub-industries of the circular economy are compared and analyzed by using the valuation model to find their potential investment value. On the one hand, it helps investors improve investment efficiency, on the other hand, it is also conducive for listed companies to expand their financing scale and operating capital, thus promoting the urban mining industry to become a new economic growth point.

Keywords: Urban mineral; Listed company; Factor analysis; Entropy method; Investment value

一、 引言

城市矿产区别于自然矿藏，是一种载能性、循环性、战略性的资源[1]。原生矿藏经过逐年开采，资源趋于枯竭，矿石品位下降，需求缺口逐年扩大。世界上大部分可供工业开采的矿产资源已经从自然界提取出来，经过

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加工制造形成产品和材料，并以在用存量或废弃物的形态堆积在城市地区，形成城市矿产。城市矿产作为一种再生资源，既源于原生资源，又与之具有相同的市场竞争目标，两者处于相互竞争、相互替代又相互补充、相互耦合的复杂系统之中[2]。城市矿产往往品种繁多，不同的产品对应着不同的再生资源[3]。对城市矿产进行规模化、产业化、专业化地回收利用，挖掘和整合有价值的资源，是缓解资源约束和环境危机的有效途径。

据测算，中国将分别于 2020 年和 2030 年产生电子废弃物 1550 万吨和 2840 万吨，超过美国成为世界上最大的电子废弃物产生国。从经济角度讲，电子废弃物中蕴藏的大量资源也提高了回收价值，测算结果表明，我国电子废弃物中平均回收价值将从 2010 年的 160 亿美元增加到 2020 年的 420 亿美元和 2030 年的 734 亿美元[4]。可见我国城市矿产资源开发潜力巨大，发展城市矿产产业迫在眉睫。

就我国目前的回收情况来看，从 2014 年到 2018 年，我国废钢铁、废有色金属、废塑料、废轮胎、废纸、废弃电器电子产品、报废机动车、废旧纺织品、废玻璃、废电池十大类别再生资源回收总量增长迅速，从 2.45 亿吨增长到 3.22 亿吨，增长幅度为 31.43%。从回收资源构成上看，废钢铁、废纸、废塑料三类资源占比较大，从增长幅度来看，废电池的增幅最为显著，高达 98.95%。再生资源回收总值由 6446.9 亿元增长到 8704.6 亿元，增长了 35.02%。废钢铁和废有色金属回收价值之和连续五年占据 60%以上[14]。

城市矿产资源的开发也引起了政府的高度重视。自 2010 年起，我国已分六批建立了 49 个城市矿产示范基地，建设城市矿产示范基地是树立节约集约循环利用资源观的重要举措，能够有效缓解我国战略资源短缺的现状，保障国家资源安全。

城市矿产企业在有效开采城市矿产资源、引领产业变革、转变经济增长方式上，正发挥越来越重要的作用。作为具有融资优势的上市公司，其发展状况和潜力备受关注。尽管国内外对于城市矿产的研究已经十分丰富，但是关于城市矿产企业在资本市场上投资价值的研究却非常少。本文以我国城市矿产上市公司作为研究对象，选用上海、深圳证券交易所城市矿产上市公司数据，通过因子分析和熵值法对上市公司绩效进行分析，同时探究城市矿产与循环经济其他子领域代表性上市公司的差异，以客观准确地衡量上市公司的投资价值，评估城市矿产业的发展潜力。

二、　文献综述

（一）城市矿产相关概念的演变

美国社会学家 Jacobs（1961）认为可以从城市固体废弃物中开采大量原材料，以某纸张再循环公司为例，提出“城市是未来的矿山”的观点[5]。我国学者杨显万等（1985）通过对废旧金属等资源回收利用的分析首次使用“城市矿山”概念[6]。日本东北大学南條道夫教授（1988）首次将“都市矿山”的概念定义为废旧机电设备等再生资源的蓄积场所[7]。我国学者张汉民（1989）也采用这种表述，将“都市矿山”比喻成“静脉”，认为它是实施资源再循环的理想场所[8]。日本学者白鸟寿一等（2006）将所有可以循环利用的资源都视为“人工矿床”，并提

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[14] 来源：http://ltfzs.mofcom.gov.cn/article/ztzzn/an/201910/20191002906058.shtml。2020 年 1 月 10 日引用。

出了对其进行开发的设想[9]。山末英嗣等（2010）把废旧电器、汽车等蕴含金属的废旧产品称作“城市矿石”[10]。

学界对城市矿产、矿山、矿床、矿石这几个概念做出明确辨析。城市矿产聚焦循环物质，而城市矿山和城市矿床强调蓄积场所[11]。城市矿山是指城市矿产蓄积与开发利用的场所，如废弃设备拆解设施[1]。城市矿床是指城市中某一特定的具有明显区域界线的功能分区，不同的功能区内矿体种类是不同的[12]。而城市矿石是城市矿物的集合体，如报废电脑零部件。

2010 年，国家发改委下发《关于开展城市矿产示范基地建设的通知》[15]，第一次正式提出“城市矿产”明确的官方定义。即工业化和城镇化过程中产生和蕴藏在废旧机电设备、电线电缆、通讯工具、汽车、家电、电子产品、金属和塑料包装物以及废料中，可循环利用的钢铁、有色金属、稀贵金属、塑料、橡胶等资源。郑龙熙等（1997）和 Brunner 等（2011）认为，城市矿产包含的范围还应该更为广泛，不仅仅是材料，能量也应该被视为可以回收利用的对象[13、14]。

（二）城市矿产研究热点

学者们多是从城市矿产资源的发展潜力、开发价值、开采技术、回收网络以及政策工具 5 个方面展开研究。

对城市矿产资源发展潜力的分析主要是计算并预测城市矿产社会蓄积量，其中，物质流分析是最主要的方法之一，它是一种对有特定时空边界的系统中物质和能量的输入、转移、聚集、输出进行定量分析的方法，具体又分为“由上至下”计算方法和“由下至上”计算方法[1]。大量的物质流研究集中在电子垃圾、报废汽车等废弃物上。Dwivedy 等（2010）通过对印度目前和未来的电子废物量进行测算，认为 2007-2011 年期间，废弃电子电器总量估计约为 250 万公吨，来自电脑的废物量占所产生的废电子电器量的 30%[15]。Yu 等（2010）运用物质流方法测算得出中国 2008 年废弃手机量约为 7700 万台[16]。何朋蔚等（2018）运用动态物质流方法，测算出废弃手机数量及其所含的高技术矿产社会存量[17]。系统动力学是另一种研究方法，它通过系统内部各组成部分的交互反馈来发掘产生变化的原因。Karavezyris 等（2002）以柏林为例，基于系统动力学研究了各种因素对城市矿产量的显著影响，预测了柏林城市矿产资源潜在的长期产量[18]。还有部分学者将 Logistic 模型用于各种城市矿产蓄积量的预测[19-21]。

城市矿产的开发价值包括经济、环境和社会价值。Pimenteira 等（2005）分析了里约热内卢城市矿产资源利用的社会经济价值，通过将废金属、废塑料、废玻璃和废纸四个城市矿产回收利用部门添加到投入产出表中，使城市矿产资源重新输入经济生产过程，最终通过资源替代效益计算出 45 个行业由于使用城市矿产而产生的污染物减排和能源节约量[22]。Liang 等（2012）利用实物投入产出模型和情景分析研究了废弃物回收利用对城市代谢的影响，对 2015 年中国苏州城市代谢进行了预测，阐述了四种废弃物回收利用的资源环境影响[23]。Krook 等（2010）分析了城市矿产开发的经济价值，认为现阶段，城市矿产开发的经济性不容乐观，主要的成本制约因素是技术[24]。薛菲等（2014）利用机会成本法对城市矿产开发利用的环境效益进行了量化，结果证明了某城

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[15] 来源：http://www.gov.cn/zwgk/2010-05/27/content_1614890.htm。2020 年 1 月 10 日引用。

市矿产示范试点基地具有良好的环境效益[25]。

研究表明，使用先进的技术可以更彻底地拆解电子产品，获得更高的效益[26]。Kang 等（2005）研究了美国电子垃圾回收的基础设施建设与回收技术的选择问题，重点分析了从电子垃圾中回收玻璃、塑料与金属的处理方法，综述了铜、铅、银、金、铂、钯等金属的回收工艺[27]。Bhat 等（2012）结合湿法冶金和生物吸附法从电子废弃物中回收贵金属[28]。Brandl 等（2001）采用微生物学方法，利用细菌对电子垃圾处理过程中产生的灰尘和微粒进行生物技术回收，取得了较好的效果[29]。Macaskie 等（2007）用一种生物气体从电子废弃物浸出液中回收贵金属[30]。

针对城市矿产的回收，国内外学者进行了多方面的研究。在回收网络的研究方面，多数学者运用逆向物流网络优化[31-35]。在回收决策模型方面的研究也取得了丰硕的成果[36-39]。近年来也出现了关于回收交易平台、软件工具运用方面的研究[40、41]。

在政策工具层面，国外学者证明了生产者延伸责任制（EPR）这一环境政策原则应用于废弃物管理的重要性[42-44]。我国学者在对国内政策的实施效果、存在的问题、国外政策经验借鉴等方面展开了讨论。陈德敏等（2013）研究了城市矿产再生利用的立法现状，通过对日本、德国及其他国家再生资源产业法律保障机制的考察对构建我国法律制度提出相关建议[45]。彭花等（2016）认为我国应该对关于城市矿产的回收市场政策、产业政策、技术管理政策和绿色财税扶持政策进行创新[46]。姚海琳等（2017）系统地收集了 1987-2015 年中央政府制定的关于城市矿产资源的相关政策，运用政策文件的定量分析方法，从发文时间、发行主体、政策工具、政策作用对象等四个维度对 77 篇政策文本进行了计量分析，揭示了我国城市矿产政策的一般特征和发展过程，指出了政策中存在的问题[47]。姚海琳等（2018）通过搜集 2003－2016 年中央政府颁布的 148 项与城市矿产相关的政策，从政策力度、政策措施和政策目标三个方面对城市矿产政策的效力及实施效果进行了量化评估[48]。

（三）上市公司投资价值评估方法

上市公司投资价值评估多采用多目标决策模型，单一指标不能全面评估股票的投资价值。在评价方法的选取上具有多样性。其中，因子分析和熵值法都是客观赋权的方法，其优点在于不需要事先设定权重，能够有效降低主观性。

因子分析是一种多变量统计分析方法，根据原始指标相关矩阵的内部结构特征重现指标与综合因子的关系，并按相关程度对变量进行划分。在经济研究中因子分析可以从复杂的经济环境中筛选少数几个主要因素，以简化经济问题。Eminocal 等（2005）选取了 1998-2001 年土耳其国内建筑行业上市公司的 25 个财务指标，利用因子分析法从流动性、资本结构和盈利能力、活动效率、利润增长率以及资本结构对上市公司进行评价，认为流动性和盈利能力对上市公司的投资价值影响最大[49]。Das（2009）以美国非盈利医院作为研究对象，选取相应的财务比率，运用因子分析法从资本结构、盈利能力、营运能力、资金流动性和相关活动五个方面评价非盈利医院的投资价值，结果表明资本结构、营运能力和盈利能力对非盈利医院的评价影响较大[50]。陈智玲等（2006）利用因子分析法对计算机行业上市公司的内在价值进行衡量评分，证明了该评价方法具有一定的综合评估作用

[51]。

熵是信息论中对系统不确定性的度量。信息量越大，不确定性就越小，熵也越小；反之，熵值越大。熵值法是一种依据各指标值所包含的信息量的大小确定决策指标权重的客观赋权法。高立辉等(2005)介绍了熵权系数法的基本原理，并采用该方法从成长性、收益性及风险性方面对股票投资价值进行量化[52]。陈敬武等(2008)运用熵值法和灰色系统理论对上市公司的投资价值进行客观地衡量[53]。

三、 城市矿产上市公司界定和样本选择

（一）城市矿产上市公司界定

城市矿产业并不是一个独立的产业，而是一个范围广、跨行业、跨区域的产业体系。对城市矿产资源的回收利用首先是依附于某一个主体产业，其主营产品也服务于主体产业的发展。但是，随着工业化的进程和市场的需求，城市矿产业逐渐成为一个复合型产业，越来越多的综合回收利用城市矿产资源的企业开始出现。

上市公司的行业分类一般以其营业收入等财务指标作为划分依据，根据其主营业务划入该业务相应的行业。股票板块主要是按行业、概念、地区进行分类。由于国内城市矿产业正处于起步阶段，对城市矿产资源进行开发和利用的产业化水平不高，所涉及的相关上市公司并不多，目前学术界及证券研究机构都没有对城市矿产上市公司进行过明确地界定及划分。本文从城市矿产的概念出发，以废弃物回收对象种类作为划分依据，对城市矿产业上市公司进行分类，以明确城市矿产板块究竟涉及哪些领域，理清上市公司的类型和数量，方便投资者科学决策。具体可分为以下五类：废金属（如废钢、废铜、废铝、废铅等）回收冶炼类；废机电产品（如废电线电缆、废家电、废电池、报废汽车等）拆解加工类；废造纸原料（如废纸、废棉等）回收利用类；废轻化工原料（如废橡胶或轮胎、废塑料等）回收再造类；多种城市矿产资源综合回收利用类。具体内容如表 1 所示。

表 1 城市矿产上市公司构成

类型	主要内容
废金属回收冶炼类	在资源开采过程中对伴生矿进行综合开发和合理运用，废旧钢铁、稀贵金属回收处理，废杂铜铝等有色金属回收利用及深加工等。
废机电产品拆解加工类	废电线电缆、废电子产品及其零部件、报废汽车、废弃船舶、废旧家电的拆解回收处理等。
废造纸原料回收利用类	废纸、废纺织品回收制造再生纤维等。
废轻化工原料回收再造类	对旧轮胎进行翻新，对废橡胶裂解、再生橡胶制造，对废塑料薄膜、泡沫塑料、塑料包装等进行回收再生，回收废酒瓶等。
综合回收利用类	对多种城市矿产资源进行回收，以城市矿产为原料进行加工利用，从事城市矿产资源加工利用的机械制造业务以及从事城市矿产资源市场交易组织、科研及信息等服务性工作。

（二）样本选择

根据上文中对城市矿产上市公司的界定标准，对上海、深圳证券交易所 A 股股票进行筛选（截至 2020 年 1 月 10 日止），选取从事城市矿产资源回收利用业务且该业务在 2016 年对本公司营业收入、营业利润或净利润产生 10%以上影响的上市公司，同时剔除特别处理的公司以及涉足城市矿产业但仍未取得一定收益的公司，最

终确定 18 家城市矿产上市公司。其中，废金属类 5 家，废机电产品类 3 家，废造纸原料类 1 家，多种城市矿产综合回收利用类 9 家。对废弃轻化工原料进行回收再造的上市公司虽然有，但并没有达到界定标准所限定的规模，因此样本中只涉及四类城市矿产上市公司。如表 2 所示。

表 2　城市矿产上市公司样本选择

类型	上市公司
废金属类	豫光金铅（600531）、贵研铂业（600459）、赤峰黄金（600988）、驰宏锌锗（600497）、楚江新材（002171）
废机电产品类	南都电源（300068）、赣锋锂业（002460）、骆驼股份（601311）
废造纸原料类	山鹰纸业（600497）
综合类	格林美（002340）、中再资环（600217）、华宏科技（002645）、怡球资源（601388）、东江环保（002672）、天奇股份（002009）、金圆股份（000546）、启迪环境（000826）、葛洲坝（600068）

总的来说，目前我国城市矿产上市公司数量还比较少，主要是因为资源回收利用产业集中度不高，大多数企业规模较小，产能不大，深加工技术薄弱，二次污染控制能力较差，龙头企业少。而专门对某一类城市矿产资源进行回收利用的上市公司更是少之又少，这类企业多是在主营业务的基础上开始转型，回收的材料多用于主营产品制造，如汽车制造企业开始回收报废汽车，家电生产企业开始回收废家电，但由于起步较晚，没有形成一定的规模，与主营业务收入相比差距较大。如在国内塑料、橡胶回收利用领域，小企业、游商小贩占据了大部分市场，它们多集中在城乡接合部及周边，尚没有达到一定规模的上市公司出现。

四、　实证分析

（一）评价指标体系的构建

考虑到数据的有效性、可获得性和指标间的可比性，本文选取 2016-2018 年 18 家城市矿产上市公司相关指标作为评估上市公司经营绩效的依据，从成长能力、可持续发展能力、盈利能力、股本扩张能力、营运能力五个方面选取 12 个指标建立指标体系。

营运能力和盈利能力反映企业经营状况和经济效益。同时，城市矿产业作为战略性新兴产业，发展潜力巨大，因此需要考虑企业的成长能力和股本扩张能力。劳动和技术投入是公司可持续发展的重要支撑因素。城市矿产上市公司通常要进行资源回收和加工利用两项工序，由于资源的回收、初级分类、拆解等工作需要大量的人力，用员工人数代表劳动投入，对城市矿产进行再生加工利用需要技术支持，因此很多企业不断引进和研发新技术，本文用研发支出总额、研发人员数量代表技术投入。具体评价指标如图 3 所示。

表 3　城市矿产上市公司评价指标体系

一级指标	二级指标	变量名
盈利能力	总资产净利率	X_1
	营业净利率	X_2
	每股收益	X_3
营运能力	总资产周转率	X_4
	应收账款周转率	X_5
股本扩张能力	每股净资产	X_6

成长能力	每股未分配利润	X_7
	营运总收入增长率	X_8
	净利润增长率	X_9
可持续发展能力	员工人数	X_{10}
	研发人数	X_{11}
	研发支出总额	X_{12}

（二）因子分析

1.适用性检验

本文运用 SPSS25.0 软件对样本数据进行因子分析，在这里以 2018 年数据为例展示分析过程，数据来源于各公司年报及 Wind 数据库。为了确定因子分析法的适用性，选用 KMO 和 Bartlett 检验法对样本数据进行检验，检验结果如表 4 所示。

由表 4 可知，KMO 值为 0.612，大于 0.5 的判别标准，Bartlett 球形检验统计量为 154.874，p 值为 0.000，在显著水平 5%的情况下拒绝原假设，即本文样本适合进行因子分析。

表 4　KMO 和 Bartlett 检验

取样足够度的 Kaiser-Meyer-Olkin 度量		0.612
Bartlett 球形度检验	近似卡方	154.874
	自由度	66
	显著性	0.000

2.提取公因子

本文运用主成分分析法提取公因子，通过特征值大于 1 和累计方差贡献率大于 75%的原则来确定公因子个数，运用 SPSS25.0 软件得到解释的总方差，如表 5 所示，在保留前四个因子时，累计方差贡献率已达到 81.783%，即原始数据信息量的 81.783%已被提取，可以将这四个公因子作为研究城市矿产上市公司投资价值的代表指标。

表 5　方差分解表

成分	初始特征值			提取载荷平方和			旋转载荷平方和		
	总计	方差百分比	累积 %	总计	方差百分比	累积 %	总计	方差百分比	累积 %
1	4.424	36.867	36.867	4.424	36.867	36.867	3.309	27.577	27.577
2	2.975	24.795	61.663	2.975	24.795	61.663	2.862	23.852	51.429
3	1.386	11.551	73.214	1.386	11.551	73.214	2.292	19.096	70.525
4	1.028	8.569	81.783	1.028	8.569	81.783	1.351	11.257	81.783
5	0.743	6.191	87.974						
6	0.703	5.862	93.836						
7	0.377	3.138	96.974						
8	0.137	1.145	98.119						
9	0.106	0.88	99						
10	0.051	0.424	99.424						
11	0.045	0.375	99.799						
12	0.024	0.201	100						

为了明确各公因子代表的含义，采用最大方差旋转法进行旋转，使因子载荷尽可能向两级分化，以对各因子进行区分，表 6 显示的是因子载荷矩阵旋转后的结果。

表 6　旋转后的因子载荷矩阵

	成分			
	1	2	3	4
X_1	0.941	0.047	-0.028	-0.138
X_2	0.784	0.094	0.081	-0.528
X_3	0.627	0.645	0.348	-0.102
X_4	0.039	-0.018	-0.209	0.863
X_5	-0.342	0.124	-0.635	0.008
X_6	-0.009	0.562	0.755	-0.011
X_7	0.195	0.277	0.802	-0.188
X_8	0.698	-0.347	0.145	0.243
X_9	0.826	0.149	0.139	0.382
X_{10}	-0.279	0.349	0.633	-0.226
X_{11}	-0.079	0.94	0.201	-0.07
X_{12}	0.069	0.937	0.145	0.045

公共因子 F_1 在总资产净利率、营业净利率上的载荷值分别为 0.941 和 0.784，这两个指标主要反映盈利能力，因此定义 F_1 为盈利因子。公共因子 F_2 在研发人员数量、研发支出总额载荷值较大，其作用在第二个公因子上的载荷分别为 0.940 和 0.937，因此认为 F_2 为可持续发展因子。公共因子 F_3 在每股未分配利润、每股净资产上的载荷分别为 0.802 和 0.755，所以将 F_3 命名为股本扩张因子。F_4 在总资产周转率上有较大比重，认为其是营运因子。提取公因子后，根据主因子得分系数矩阵可以得到样本在各因子上的得分，如表 7：

表 7　上市公司公因子得分表

	F_1	F_2	F_3	F_4
金圆股份	0.7044	-0.54144	0.50781	0.58779
启迪环境	-1.08062	-0.18742	2.61437	-0.73495
天奇股份	0.2711	-0.68361	0.81635	0.61227
楚江新材	0.32531	0.15644	-0.50575	1.45496
格林美	0.13453	-0.0404	-0.58132	0.04666
赣锋锂业	1.52549	0.09728	-0.28802	-1.92771
华宏科技	0.86095	-0.68361	0.13705	0.18634
东江环保	0.31065	-0.28374	0.25818	-1.23797
南都电源	-1.15799	-0.32021	0.33374	-0.28644
葛洲坝	-0.36101	3.62335	0.52981	-0.09824
中再资环	0.86979	-0.68475	-0.55678	-0.31861
贵研铂业	0.00552	0.13885	0.26922	2.5535
驰宏锌锗	-0.91016	0.52882	-1.87409	-0.73738
豫光金铅	-0.9086	0.14871	-1.51591	0.59038
山鹰纸业	1.81771	0.43354	-0.39794	-0.24922
赤峰黄金	-2.05851	-0.78697	-0.33564	-0.78115
骆驼股份	0.32057	-0.02492	1.14577	0.14603
怡球资源	-0.66914	-0.88992	-0.55686	0.19375

盈利因子得分大于 0 的上市公司有 11 家，其中 2 家为废机电产品回收利用类，6 家为综合回收利用类，表明废机电产品回收利用类和综合回收利用类上市公司盈利能力较强。可持续发展因子得分大于 0 的上市公司有 7 家，其中 4 家为废金属加工冶炼类上市公司，表明废金属加工冶炼类上市公司可持续发展能力较强。股本扩张

因子得分大于 0 的上市公司有 9 家，营运因子得分大于 0 的上市公司有 9 家。在 9 家综合回收利用类上市公司中，6 家盈利因子得分大于 0，1 家可持续发展因子得分大于 0，5 家股本扩张因子得分大于 0，5 家营运因子得分大于 0。从整体上看，城市矿产上市公司的盈利能力普遍较强，但可持续发展能力相对较差。

（三）熵值赋权法

本文运用熵值赋权法对上文提取的四个代表性的因子指标进行赋权，假设第 i 个样本公司在第 j 项公因子下的指标值为X_{ij}，运用 Excel 软件对四个公因子数据进行标准化处理，设标准化后的指标值为Y_{ij}，之后分别计算信息熵和指标权重，设信息熵为E_j，指标权重为w_j。

$$Y_{ij}=\frac{X_{ij}-\min(X_{1j},X_{2j},\ldots,X_{nj})}{\max(X_{1j},X_{2j},\ldots,X_{nj})-\min(X_{1j},X_{2j},\ldots,X_{nj})} \tag{1}$$

$$E_j=-\frac{1}{ln\,n}\sum_{i=1}^{n}p_{ij}\,ln\,p_{ij} \tag{2}$$

$$p_{ij}=Y_{ij}/\sum_{i=1}^{n}Y_{ij} \tag{3}$$

$$w_j=(1-E_j)/\sum_{j=1}^{m}(k-E_j) \tag{4}$$

其中，n 为样本公司个数，k 为公因子个数。若$p_{ij}=0$，则定义$\lim\limits_{p_{ij}\to 0}p_{ij}=0$。根据公式得到计算结果，如表 8 所示。

表 8 公因子熵值与权重

	F_1	F_2	F_3	F_4
信息熵	0.95257	0.8504	0.94649	0.950263
权重	0.157955	0.498207	0.178203	0.165635

由熵值赋权法的原理可知，信息熵越大，权重越小，对整个评价体系的贡献就越小，反之则对评价体系的贡献就越大。由表 8 可知，F_2和F_3的权重分别为 0.498207 和 0.178203，即可持续发展因子和股本扩张因子对综合得分的贡献较大。

（四）2016—2018 年城市矿产上市公司综合得分及排名

通过因子分析和熵值赋权法得到了公因子及其权重，由此可以得到各上市公司综合得分的表达式：

$$Z=0.157955F_1+0.498207F_2+0.178203F_3+0.165635F_4 \tag{5}$$

根据建立起的综合得分函数，可以计算出各上市公司的最终得分及排名。类似地，运用 18 家上市公司 2016 年和 2017 年的相关指标数据，通过同样的方法计算出各公司在 2016 年和 2017 年的综合得分及排名，将 2016—2018 三年的得分及排名汇总如下：

表 9　2016—2018 年城市矿产上市公司综合得分及排名

上市公司	2018 年得分	2018 年排名	2017 年得分	2017 年排名	2016 年得分	2016 年排名
金圆股份	0.047207	11	0.041869	12	0.034202	15
启迪环境	0.055422	6	0.094782	3	0.100935	2
天奇股份	0.042685	13	0.03403	16	0.04404	10
楚江新材	0.066081	4	0.047818	9	0.0757	5
格林美	0.052024	9	0.051856	8	0.036774	12

赣锋锂业	0.054361	8	0.099	2	0.035912	14
华宏科技	0.039578	15	0.043333	11	0.045978	8
东江环保	0.043509	12	0.052467	7	0.037635	11
南都电源	0.041056	14	0.046203	10	0.060871	7
葛洲坝	0.169039	1	0.133771	1	0.120276	1
中再资环	0.033504	16	0.037442	14	0.020851	18
贵研铂业	0.073509	2	0.040525	13	0.088175	3
驰宏锌锗	0.054703	7	0.035265	15	0.033967	16
豫光金铅	0.051118	10	0.017332	18	0.083232	4
山鹰纸业	0.073496	3	0.075031	4	0.044214	9
赤峰黄金	0.016802	18	0.032885	17	0.035933	13
骆驼股份	0.062897	5	0.062498	5	0.071322	6
怡球资源	0.023008	17	0.053893	6	0.029984	17

由上表可知，2016年城市矿产上市公司投资价值综合排名前三名分别是葛洲坝、启迪环境和贵研铂业，2017年前三名分别是葛洲坝、赣锋锂业和启迪环境，2018年前三名分别是葛洲坝、贵研铂业和山鹰纸业。葛洲坝连续三年综合排名位居榜首，表现出良好的经营绩效和稳定的投资价值，综合实力极强。其综合得分在这三年分别为0.120276、0.133771和0.169039，作为城市矿产业龙头企业，该得分也代表了城市矿产发展的最高水平，可以看出2016到2018年的发展状况越来越好，城市矿产板块值得投资者关注。其次，启迪环境、骆驼股份、楚江新材在近三年的排名均位于前十位，经营绩效较好，但楚江新材投资价值的稳定性不佳，从2016年的第五名直接滑落至2017年的第十名，2018年又上升第四名。反观排名靠后的上市公司，赤峰黄金、金圆股份、中再资环在这三年的综合实力均排在后十位，投资价值较低，但金圆股份的排名一直在上升，由2016年的第15名到2017年的第12名，再上升至2018年的第11名，有一定的发展潜力。

废金属回收类的上市公司整体经营业绩不佳，投资价值不高。贵研铂业的稳定性较差，由第三名直接滑出前十名，之后又上升至第二名；楚江新材同样是稳定性不强；豫光金铅近两年的业绩都较差且不稳定；赤峰黄金的排名一路下滑；只有驰宏锌锗的综合得分在不断提高，但整体排名依旧靠后。废纸回收利用类上市公司山鹰纸业综合排名持续上升，由第九名上升至第四名再到第三名，业绩良好，投资价值较高，长远来看潜力依然很大。而综合回收利用类上市公司分化较为严重。从投资价值持续、稳定地增长和发展的角度看，葛洲坝、启迪环境都是城市矿产产业的龙头企业，表现出具有持续性的投资价值。但也有部分企业情况较差，华宏科技在这三年的综合排名一路呈下降趋势，公司的投资价值大打折扣，中再资环的三年排名均位于后五名，整体实力处在样本平均水平之下。

五、 城市矿产与循环经济

（一）城市矿产与循环经济的关系

循环经济又称资源循环型经济，是涉及到社会再生产各个环节的经济运作模式，包括对于自然资源的合理开发和利用、在生产过程中原材料的减量化和现场回用、消费过程中尽可能多次地使用物品和尽可能少地产生废弃物、废弃资源回收再加工等。发展循环经济的核心内容是资源的循环利用，而在再生资源中最重要的构成

部分就是城市矿产。对城市矿产资源的开发和利用是发展循环经济的必经之路。

城市矿产开发是循环经济系统的一个子系统，开发城市矿产和发展循环经济是从属关系，循环经济遵循“减量化、再利用、再循环”的原则，把传统的“资源——产品——废弃物”的线性模式转变为“资源——产品——再生资源”的闭合反馈模式。城市矿产是从循环经济大概念下聚焦具体几类重要资源的循环利用，通过再利用、再循环达到减量化这一更高层次的要求；满足循环经济发展要求的城市矿产业，也是转变粗放型经济增长方式、实现可持续发展的重要途经。

城市矿产是循环经济中最具价值的部分。在各种废弃资源中，城市矿产在总量和开发价值上都有着绝对的优势。城市矿产作为自然矿产的空间转移，利用价值高，效益成本比率高，能够有效弥补原生矿产资源的不足。充分挖掘其中的价值，通过技术提高回收率，是发展循环经济很好的切入点。城市矿业是最重要的贯彻循环经济理念的产业。

对城市矿产的循环利用刺激了相关产业的发展，进一步促进了我国循环经济的发展。我国工业化和城镇化的进程加快，城市矿产资源蓄积量逐渐增加，开发价值巨大。为了有效利用城市矿产这一蓄积量庞大的资源，就必须促使设备制造、垃圾回收、污染治理、网络电商等相关产业科学技术的进步，物流运输业的提升，贸易的发展，从而有效拉动需求和就业，促进经济的发展。因此，加强城市矿产的开发利用，不仅可以缓解大量开发自然资源所带来的资源和环境压力，减轻环境污染；而且可以提升就业率，培育新的经济增长点，促进循环型社会和生态文明建设。

（二）城市矿产与循环农业

我国在循环经济发展规划中提出了四项重点任务：构建循环型工业体系、构建循环型农业体系、构建循环型服务业体系、推进社会层面循环经济发展[16]。循环经济是一个系统性的概念，在不同的领域有不同的运作方式，这些不同的方式实际上是一个有机统一体，只有在整个社会层面系统性地协调，才能实现资源的高效循环利用。

城市矿产是对城市中废弃资源进行规模化、产业化开发利用的形象比喻，相比于循环经济更为宽泛的概念，城市矿产在循环经济发展理念的基础上，更加关注城市中蕴藏资源的循环利用，主要涉及采掘业、制造业等循环工业体系建设，范围缩小，目标更加明确具体。除了城市中蕴藏的废弃资源利用，农村中农业资源的再利用也是循环经济的重要组成部分，城市矿产概念应该延伸到农村。本文选取城市矿产和循环农业代表性上市公司进行对比分析，探索两种经济运作模式各自的特点。

（三）城市矿产与循环农业代表性上市公司

由上文分析可知，葛洲坝和启迪环境都是城市矿产的龙头企业，由于葛洲坝仍然是以建筑为主营业务，城市矿产业务所占比例不高，所以这里选取启迪环境作为城市矿产业的代表性企业。启迪环境长期致力于综合环境服务及城市矿产系统开发，公司线下实体产业涉及电子垃圾处置、报废汽车拆解及再制造、危险废物处置、

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[16] 来源：http://www.gov.cn/zwgk/2013-02/05/content_2327562.htm。2020 年 1 月 10 日引用。

产业园区运营、废塑料和废轮胎深加工等，线上不断优化和完善易再生 O2O 平台。通过商业模式创新、管理创新和技术创新，公司走出了一条线下资源与线上平台互通互联、各主营业务打通交互、多业务领域布局、全产业链发展的创新之路和崛起之路。

农业循环经济将循环经济思想应用于农业经济生产活动中。对农村中各种生产要素进行统筹规划、系统开发和深度利用，是发展社会主义新农村的重要方式。目前，我国循环农业上市公司主要包括畜禽养殖废物资源化利用类、农副产品综合开发类和标准化清洁化生产类。畜禽养殖废物资源化利用类上市公司主要通过现代养殖设施和养殖模式，将畜禽养殖废弃物就地就近用作农用有机肥，推进区域生态农业新模式的发展，形成种养结合的农村生态系统营养物质闭合循环。农副产品综合开发类上市公司主要利用现代生物工程技术，在农副产品深加工过程中进行原料循环利用和产品梯次开发。标准化清洁化生产上市公司主要涉及从事清洁生产的农业机械制造业务、化肥农药研发业务等。山东民和牧业股份有限公司是循环农业龙头企业，公司在原有的畜牧业基础上，通过种养结合的方式实现农业经济产业化，形成了“鸡—肥—沼—电—生物质”的循环经济业务链，创建了以生物产业为中心的新型工业化农业。因此本文选取民和股份作为循环农业板块代表性企业。

在分析各企业经营模式的基础上，运用市盈率模型评估股票价值。本文根据公司的经营范畴和股本规模选择同行业的四只股票为可比公司，以五只股票的平均市盈率作为标准市盈率。数据来源于 Wind 数据库。

启迪环境在 2018 年 12 月 28 日的收盘价为 10.36 元，每股收益为 0.48 元，可计算出市盈率为 21.58 倍。

表 10　城市矿业上市公司股票市盈率比较

	启迪环境	格林美	东江环保	怡球资源	中再资环
价格	10.36	3.81	11.30	1.92	4.09
每股收益	0.48	0.19	0.53	0.05	0.38
市盈率	21.58	20.05	21.32	38.40	10.76
平均市盈率	22.42				

通过对这五家公司股票市盈率的比较分析，可以看出城市矿产行业的平均市盈率为 22.42 倍。将城市矿产业平均市盈率作为基准市盈率，可以得出 2018 年 12 月 28 日启迪环境股票的理论价值估值为 10.76 元。而当日该股票的收盘价为 10.36 元，可见，启迪环境股票具有一定的升值空间。根据发行股票数量 1430578784 股计算，启迪环境公司的企业价值为 15393027716 元。

山东民和牧业股份有限公司是生态循环农业龙头企业，民和股份在 2018 年 12 月 28 日的收盘价为 11.45 元，每股收益为 1.26 元，可计算出市盈率为 9.09 倍。

表 11　循环农业上市公司股票市盈率比较

	民和股份	圣农发展	华英农业	益生股份	博世科
价格	11.45	14.04	5.16	8.15	9.84
每股收益	1.26	1.25	0.36	1.07	0.65
市盈率	9.09	11.22	14.38	7.64	15.12
平均市盈率	11.49				

通过对五家循环农业公司股票市盈率的比较分析，我们发现行业平均市盈率为 11.49 倍。以之作为基准市盈率，可以得出 2018 年 12 月 28 日民和股份的股票内在价值为 14.48 元。而当日该股票的收盘价为 11.45 元，

可见，民和股份股票具有一定的升值空间。根据发行股票数量 302046632 计算，民和股份的企业价值为 4373635231 元。

由上文分析可知，城市矿产强调资源再利用、再循环，使废弃物能够重新进入社会再生产；循环农业强调资源减量化，注重资源合理利用，追求以较少的投入获得较高的产出和效益。城市矿产在回收阶段需要一定的成本消耗，在深加工和利用阶段获得收益；而循环农业通过建立农业产业循环链，在每个环节都能取得一定的收益。根据市盈率估值模型，启迪环境和民和股份股票在 2018 年 12 月 28 日都有一定的升值空间，但是，市盈率估值模型在反映公司成长性、风险性方面还存在一定的局限性，所以投资者在投资时，还应结合该公司的基本面和行业背景、与同行业其他企业的比较优势、整体市场的系统风险等情况来综合判断其投资价值。

六、　总结与启示

本文给出城市矿产上市公司的界定标准，以 2016—2018 年沪深两市 18 家城市矿产上市公司作为研究对象，从成长能力、可持续发展能力、盈利能力、股本扩张能力、营运能力五个方面选取 12 个指标建立指标体系，通过因子分析和熵值法确定度量上市公司投资价值的特征指标变量及权重，完成对样本的综合评价和排名。从整体上看，城市矿产上市公司的盈利能力普遍较强，但可持续发展能力相对较差。可持续发展能力对上市公司投资价值综合得分的贡献较大。废金属回收类的上市公司整体经营业绩不佳，投资价值不高。而综合回收利用类上市公司经营绩效分化较为严重。从投资价值持续、稳定地增长和发展的角度看，葛洲坝、启迪环境都是城市矿产产业的龙头企业，表现出具有持续性的投资价值，但也有部分综合回收类企业表现较差。同时将城市矿产回收利用代表性企业与循环经济板块另一子领域——循环农业代表性企业进行对比分析，探究两大产业各自的运作模式，运用估值模型发现两个代表性企业都具有一定的投资价值。根据研究结论，我们可以得出以下启示：

（一）我国城市矿产上市公司数量不多，资源回收利用产业集中度不高，小企业往往技术水平低，二次污染严重。因此，应该建立完善的废旧资源回收渠道，推进市场有效整合，建立废物交换系统、企业间的闭路循环和生态链等，形成一批具有典型示范效应的城市矿产示范基地，实现行业经济效应的整体提升。同时对回收流通过程中存在的非法行为进行严厉打击，促进大规模、高起点、高水平地开发利用城市矿产资源。

（二）可持续发展能力对上市公司投资价值综合得分的贡献较大，因此应该大力提高企业科研技术水平和员工素质。资源回收利用的技术是城市矿产开发中最重要的生产力，加强关键技术的研发与应用，不仅能提高资源利用率，还能保证在开发过程中废物的零排放。鼓励科研机构突出自主创新，同时在企业内部，要对生产人员进行严格管理和培训，提高工人的技能和素质，建立激励机制，鼓励工人积极参与技术创新。

（三）城市矿产业是循环经济的重要组成部分，部分城市矿产上市公司具有诱人的发展前景，值得投资者关注。对城市矿产上市公司投资价值的分析要立足长远，投资者要根据公司的基本面和行业背景、与同行业其他企业的比较优势、整体市场的系统风险等情况进行综合分析和长期跟踪。科学合理地投资一方面帮助投资者提高投资效率，另一方面也拓展了上市公司的融资渠道，从而带动城市矿产行业良性发展。

（四）循环经济按照物质循环和能量转换规律来重构经济形态和经济发展模式，涉及工业、农业、服务业

等各领域。循环经济系统是由企业、技术、资源、环境、经济和社会构成的大系统。在我国，循环经济的发展仍然具有广阔的空间，循环经济的实现离不开各个产业和企业。因此，应该推进循环经济运作过程中不同层面的共同发展，通过企业内生产物流循环和产业链闭合延伸进行多领域合作，使各个环节形成一个有机统一体，只有通过整个社会再生产系统的全面协调，才能真正实现人类技术经济思维方式的革命、技术经济范式革命和环境保护范式革命。

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城市污泥林地利用过程中重金属的生态风险评价

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摘要：随着城市化进程的加速，污泥处理处置问题成为关注焦点。污泥林地利用能够增加土壤肥力，促进林木增长，具有广阔的应用前景，但污泥中所含有的重金属进入环境后引起的风险问题备受关注。本文连续 5 年监测了污泥堆肥产品施用于林地后土壤中重金属含量的变化情况，采用单因子指数法和潜在生态危害指数法分析评价了污泥堆肥泥质、污泥堆肥不同施用比例以及连续施肥等对土壤重金属环境风险的影响，并利用相关性分析阐述了土壤重金属来源与施用污泥的关系。研究结果表明，污泥堆肥中 Hg、Cd、Zn、As、Pb 存在较大风险；污泥堆肥施用比例为 10%和 20%时产生的环境风险较低，而施肥比例为 30%和 40%时环境风险较大。连续 5 年的监测结果表明土壤中重金属含量具有一定的累积效应，但均未超过《土壤环境质量标准 农用地土壤污染风险管控标准（试行）》（GB 15618-2018）（$6.5\leq pH<7.5$）。通过土壤污染物累积模型预测后发现，施肥比例为 10%的林地第 11 年时土壤重金属含量将会超标，10 年内施肥较为安全。通过重金属相关性分析发现，土壤中重金属并非全部来源于施肥污泥，大气沉降、降水、土壤母质等因素也影响了土壤重金属含量。

关键词：污泥堆肥；重金属；风险评价；相关性分析；土壤污染物预测模型

Eco-environmental risk assessment of urban sludge application in forest land

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Abstract With the acceleration of urbanization, the problem of sludge treatment and disposal has become the focus of attention. The use of sludge forest land can increase soil fertility and promote forest growth, so it has broad application prospects, but there are still unclear about the environment risks caused by the heavy metals introduced along with sludge. In this paper, based 5 consecutive years measurement heavy metal content in the soil of fertilized forest land, though the single factor index method and the potential risk hazard index method, the influence of the characteristic of applied sludge, the application ratios and continuous fertilization on environmental risk of heavy metal in soil were evaluated, and use the correlation analysis was conducted to elaborate the relationship between the sources of heavy metal risks in soil and fertilizing sludge. The results showed that Hg, Cd, Zn, As, Pb in sludge were likely to bring greater environmental risks. It indicated that applied sludge with proportion of 10% and 20% lead to lower risk. However, the risk to the environment is greater when the fertilization ratio is 30% and 40%. The monitoring results showed that the heavy metals in the soil has accumulated but not exceeded the soil environmental quality risk control standards for soil contamination of agricultural land (GB 15618-2018) ($6.5 \leq pH < 7.5$) in 5 years. Through the prediction of the soil pollutant accumulation model, it was found that the soil heavy metal content exceeded the standard in the 11th year for the application of sludge with 10% proportion, so it was suggested to be safety to fertilize within 10 years. In addition, correlation analysis showed that except for fertilized sludge. Factors such as atmospheric deposition, precipitation, and soil parent material also affect the content of heavy metals.

Key words compost sludge；heavy metals；risk assessment；correlation analysis；soil pollutant prediction model

随着城市化进程的加速，污水处理率逐年提高，随之带来污水处理厂大量剩余污泥的产生。城市污泥的处理处置已经成为全国性的难题。以北京 2017 年数据统计为例，城市污泥的最终处置方式主要为土地利用、焚烧、填埋、建材利用等，占比分别为 78%、11%、3%、2%。污泥林地利用具有诸多优势，可以充分利用污泥中营养元素及有机质，增加土壤肥力，改善植物生长状况[1,2]，同时避开食物链，减少对人体健康的影响[3]。但是，城市污泥中存在的重金属是制约其土地利用的主要因素[4,5]。有研究表明，城市污泥中的重金属会以不同的形态存在于土壤环境中，其中 Cu、Cd 以及 Hg 等毒性较强的重金属以残渣态存在，Zn 和 Ni 主要以不稳定态存在[6]。但重金属在土壤中的累积可能导致超标，危及到土壤环境安全。因此污泥产品施用于林地后带来的重金属环境风险问题不容忽视。

为评价污泥产品在林地中长期施用可能带来的环境风险，课题组连续 5 年将城市污水处理厂污泥堆肥产品施用于白皮松林地。本文结合施肥过程中连续 5 年监测的土壤重金属（Cu、Zn、Hg、Cr、Cd、Pb、As、Ni 等）含量变化数据，分析污泥堆肥泥质、不同的施肥比例以及连续追肥等因素对土壤重金属产生的环境风险影响，并依据模型预测多年连续施肥给土壤带来的环境风险，为城市污水厂污泥林地利用提供参考。

1 材料与方法

1.1 实验区域与施肥过程

实验区域位于北京市大兴区永定河沙荒地平原造林场地，以该区域种植的白皮松作为研究树种，采用北京市某污水处理厂经过堆肥处理后的污泥堆肥产品（含水率 40%）进行林地施肥，施肥方式采用环状沟施，即距树基（滴水线树冠垂直下来到地面的线）40-60cm 处分别挖出深度为 20cm、30cm、40cm、50cm 的施肥环进行施肥。

白皮松林地分为 4 个地块，设置 4 个施肥比例，施用污泥堆肥产品与表层土壤的掺混质量比为 10%、20%、30%、40%，施肥后均用表土覆盖，每个施肥比例的地块设置 10 棵样树。

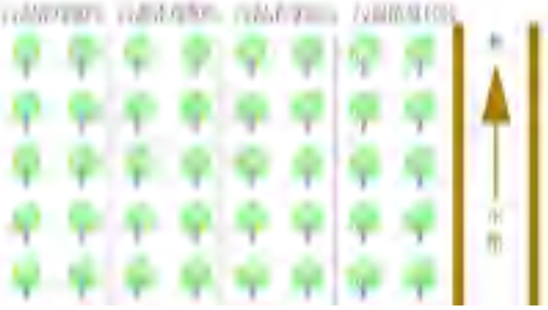


图 1 实验区域示意图

Fig. 1 Schematic diagram of the experimental area

1.2 样品采集与预处理

林地每个地块采用 S 形布点方式选择 3 棵样树进行取样，采集后混匀合为一个土壤样品，避免土壤重金属含量的不均质性所带来的误差。

利用土钻采集 0-20 cm 深度的土壤样品，装入样品袋。将湿的土壤样品摊成 2 cm 厚的薄层于阴凉通风处风干，拣出碎石、砂砾及植物残体等杂质。再将风干样品用研磨棒压碎，拣出杂质并用四分法分取压碎样，全部过 20 目尼龙筛，再过 100 目尼龙筛后待测。土壤样品按不同污泥堆肥施用比例、不同取样深度进行编号存放。

1.3 样品处理与测定

准确称取土壤样品 0.1 g，置于溶样杯后，用少量水润湿，在通风橱中逐步缓慢加入 4 ml 浓盐酸，2 ml 浓硝酸，2 ml 氢氟酸。样品与消解液充分混匀后移至消解管中，加盖置于微波消解转盘上，采用梯度升温的方法（第一步 10 min 从室温中升温至 100 ℃，保持 3 min；第二步 10 min 从 100 ℃升温至 150 ℃，保持 3 min，第三步 5 min 从 150 ℃升温至 190 ℃，保持 45 min；第四步风冷 15 min）进行消解。待管内温度降至室温后从通风橱中取出，缓慢泄压放气，打开消解管盖。将消解后的混合液倒出后，用去离子水清洗消解罐 2-3 次并收集清洗液，用 0.45 μm 的聚四氟乙烯膜过滤，收集滤液用去离子水定容至 50 ml，于 4 ℃下保存待测，重金属检测方法见表 1。

表 1 土壤样品重金属检测方法

Table 1 Method for detecting heavy metals in soil samples

重金属	方法	参照标准
Zn、Cu、Pb、Cd、Cr、Ni、As	微波消解-电感耦合等离子体质谱（ICP-MS）	《城市污水处理厂污泥检验方法》（CJ/T 221-2005），HJ 683-2013，HJ 491－2009 ，GB/T17139-1997，GB/T 15618-2018
Hg	微波消解-原子荧光法（AFS）	

1.4 评价方法

1.4.1 评价依据

研究区域白皮松林地施用的污泥堆肥采用《城镇污水处理厂污泥处置林用泥质标准》（CJ/T 362-2011）进行评价[7]。自 2015 年 5 月-2018 年 10 月每年施肥一次，共施肥 4 次，至 2019 年 5 月共连续监测 5 次，监测施肥前后林地土壤重金属含量，所得结果参考《土壤环境质量标准 农用地土壤污染风险管控标准（试行）》（GB 15618-2018）（6.5<pH<7.5）[8]进行评价。

表 2 土壤环境质量及污泥泥质标准

Table 2 Soil environmental quality and sludge mud quality standards

标准（单位：mg/kg）	Zn	Cu	Cr	Cd	Ni	Pb	As	Hg
《土壤环境质量标准 农用地 土壤污染风险管控标准（试行）》（GB 15618-2018）6.5≤pH<7.5	250	100	200	0.3	100	120	30	2.4
《城镇污水处理厂污泥处置 林用泥质标准》（CJ/T 362-2011）	3000	1500	1000	20	1000	200	75	15

1.4.2 单因子评价法

本文采用单因子指数法对林地土壤进行环境质量评价。单因子评价计算公式如下[9]：

$$P_i = \frac{C_i}{S_i} \qquad (1)$$

式中，C_i为单项指标 i 在不同环境介质中的监测数据；

S_i为单项污染指标 i 的环境质量标准。

当P_i值大于 1 时，认为存在一定的环境影响；当P_i值小于 1 时，认为在该指标方面不存在环境影响；当P_i值介于 0.7 与 1 之间时，则认为该指标处于警戒范围。如表 3 所示。

表 3 单因子指数与污染级别

Table 3 Single factor index and pollution level

单项 Pi 值	0.7<Pi<1	＜1	≥1
污染等级	警戒限	无污染	有污染

1.4.3 潜在生态危害指数法

为进一步探究施肥林地土壤中重金属产生的潜在生态风险，本文采用潜在生态危害指数法对连续 5 年监测的施肥林地土壤中重金属污染水平进行分析评价。

潜在生态危害指数法评价公式如下[10]：

$$RI = \sum EI_r^i = \sum T_r^i \frac{C_r^i}{S_r^i} \qquad (2)$$

其中：RI为综合生态风险指数；

EI_r^i为重金属 i 的潜在生态风险指数；

T_r^i为重金属 i 的生物毒性响应系数，可通过计算或查阅文献得到该值，如表 4 所示[11]；

C_r^i为表层土壤重金属 i 的环境暴露值；

S_r^i为重金属 i 的参比值，参比标准选用《土壤环境质量标准 农用地 土壤污染风险管控标准（试行）》中土壤污染风险筛选值（见表 2）。

计算之后，得到EI和RI值，参照风险等级标准（见表 5）进行评价。

表 4 不同重金属的生物毒性响应系数

Table 4 Biotoxicity response coefficients of different heavy metals

重金属	Cu	Zn	Pb	Cr	Ni	As	Hg	Cd
生物毒性响应系数	5	1	5	2	5	10	40	30

表 5 潜在生态危害系数和危害指数与污染程度关系

Table 5 Relationship between potential ecological hazard coefficient and hazard index and pollution degree

	低	中等	可接受	高风险	非常高
EI	≤40	40~80	80~160	160~320	＞320
RI	≤150	150~300	300~600	600~1200	＞1200

潜在生态危害指数法以定量的方法划分出重金属潜在危害的程度，综合考虑了重金属的毒性以及重金属区域背景值的差异，可综合反映土壤中重金属对生态环境的影响。

1.4.4 土壤污染物预测模型

本文采用了土壤中常见的污染物残留量预测模型，通过模型来预测长期施用污泥堆肥后土壤中重金属的残留量，进而预测长期施肥后土壤中重金属的环境风险。

土壤污染物在土壤中年残留量（年积累量）的计算模式如下[9]：

$$W = K(B + R) \tag{3}$$

式中：W 为污染物在土壤中年残留量（mg/kg）；

B 为区域土壤背景值（mg/kg）；

R 为土壤污染物对单位土壤（kg）的年输入量（mg/kg）；

K 为土壤污染物的残留率（年累积率，%）。

若污染年限为 n，每年的 K 和 R 不变，则污染物在土壤中 n 年内的累积量为：

$$W_n = BK^n + RK\frac{1-K^n}{1-K} \tag{4}$$

其中，

$$R = \frac{XM}{G} \tag{5}$$

式中：X 为污泥中污染物含量（mg/kg）；

G 为耕作层单位（m^2）土壤质量（kg/m^2）；

M 为污泥施用量[$kg/(m^2 \cdot a)$]，依照前期盆栽试验所得不同重金属的年残留率如表 6 所示[12]。

表 6 土壤中重金属年残留率

Table 6 Annual residual rate of heavy metals in soil

项目	Cu	Zn	Pb	Cr	Ni	As	Hg	Cd
残留率（%）	99	95	99	99	99	99	86	99

1.5 数据处理

采用 office 2013、origin 2018 对数据进行处理制图，通过 SPSS 2013 对重金属进行相关性分析，并数通过统计软件 R version 3.6.1 进行聚类分析。

2 结果与讨论

2.1 林地施用污泥堆肥产品泥质分析

本文以污泥堆肥产品或者土壤中重金属含量与标准值的比值（Pi 值）为纵坐标，以施肥时间为横坐标作图。研究区域连续 4 年施用的污泥堆肥中重金属含量变化如图 2 所示，参考的标准为《城镇污水处理厂污泥处置林用泥质标准》（CJ/T 362-2011）。图 3 为林地施用污泥堆肥产品的风险图，以综合生态风险指数为纵坐标。

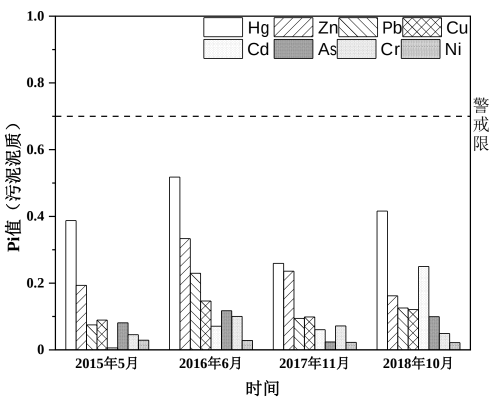


图 2 污泥重金属 Pi 值变化图

Fig.2 Pi change in heavy metal of sludge

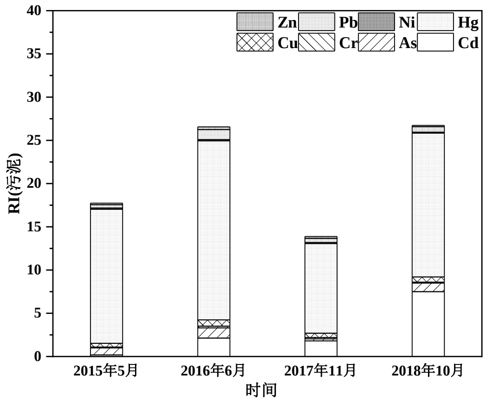


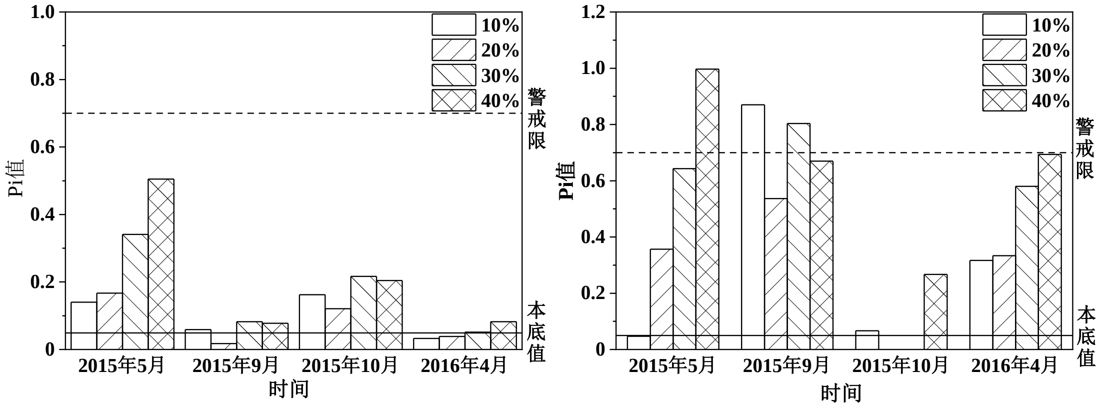
图 3 污泥重金属潜在风险图

Fig.3 Potential risk map of sludge heavy metals

由图 2 可以看出，Cu、Zn、Hg、Cr、Cd、Pb、As、Ni 等 8 种重金属的 Pi 值均小于 1，表明重金属的含量均未超过《城镇污水处理厂污泥处置林用泥质标准》（CJ/T 362-2011）的标准值。此外，堆肥污泥中重金属含量基本稳定，其中 Hg 的 Pi 值处于 0.26~0.52 之间，Pi 值小于 1，表明 Hg 未产生污染。但是由图 3 可以看出，Hg 在 8 种重金属之间产生的潜在生态风险的贡献率最大，最高可达 87.35%。Cd 的 Pi 值范围在 0.06~0.25 之间，其对重金属综合生态风险的贡献率也逐年增加，在 2018 年高达 28%。因此，污泥施用到林地后，需重点关注 Hg 和 Cd 可能带来的污染和风险。此外，根据 Pi 值排序：Hg>Zn>Pb>Cu>Cd>As>Cr>Ni，说明 Hg、Zn、Pb 的 Pi 值相对较高；而根据潜在生态风险贡献率排序：Hg>Cd>As>Pb>Cu>Zn>Cr>Ni 来看，Hg、Cd、As、Pb 的潜在风险相对较大，其贡献率分别为 75.56%、12.53%、3.60%、3.46%。

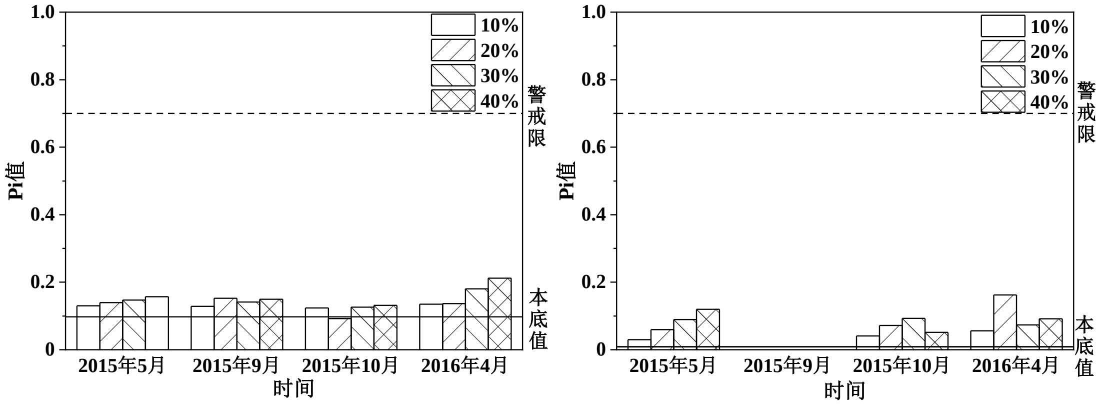
2.2 不同施肥比例地块中重金属风险评价

研究区域在 2015 年 5 月首次施肥，施用不同比例堆肥污泥后的林地土壤中重金属 Pi 值变化如图 4 所示，参考标准为《土壤环境质量标准 农用地 土壤污染风险管控标准（试行）》（GB 15618-2018）（6.5≤pH<7.5）。



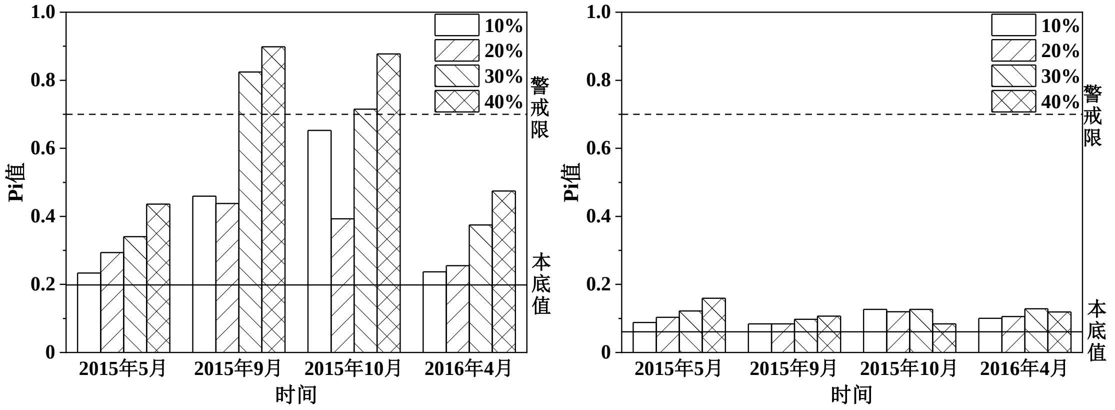
（a）Hg含量的Pi值

（b）Cd含量的Pi值



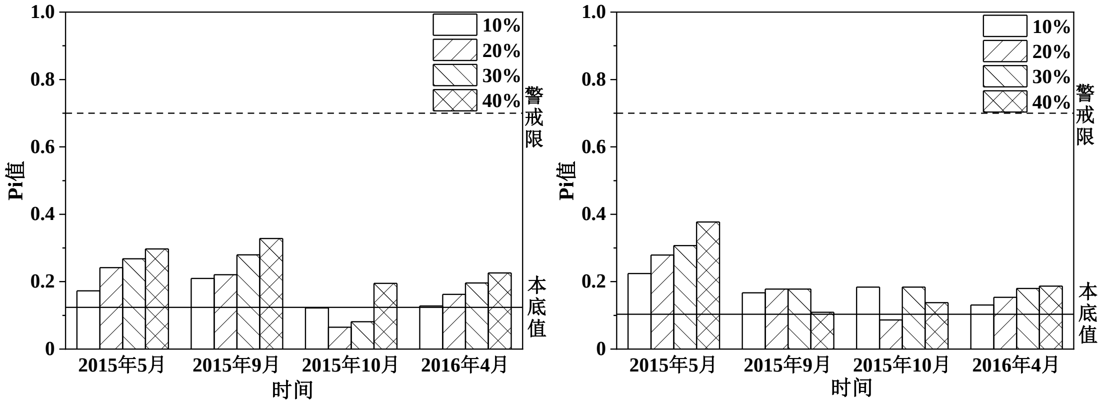
（c）As含量的Pi值

（d）Pb含量的Pi值



（e）Zn含量的Pi值

（f）Cr含量的Pi值



（g）Cu含量的Pi值

（h）Ni含量的Pi值

图 4 白皮松林地施用不同比例污泥的重金属 Pi 值变化图

Fig.4 Pi Change in heavy metal caused by application of different proportions of sludge in forest land

由图 4 可以看出，施肥之后土壤中 8 种重金属的 Pi 值基本都高于本底值，说明污泥堆肥产品的施用会导致土壤中重金属含量的增加。但是 8 种重金属的 Pi 均小于 1，表明首次施肥后的一年内重金属的含量均未超标，符合土壤环境质量标准的要求。值得注意的是，Cd 和 Zn 的含量超过了警戒限，表明堆肥污泥的施用对土壤中 Cd、Zn 含量影响较大，可能产生风险。在 2015 年 5 月与 2016 年 4 月的监测结果中可以看出，土壤中重金属含量随着施肥比例的增加而递增，其中 2015 年 5 月 Cd 含量增长最为明显。在 4 种施肥比例下，Cd 的 Pi 值分别为 0.047、0.357、0.643、0.997，虽未造成污染，但 Cd 的 Pi 值在 40%的污泥施用比例下已接近 1，可能产生污染风险。4 次监测结果表明，施用污泥比例较高（30%和 40%）的地块，重金属 Pi 值均较高，可能产生风险。此外，8 种重金属中 Hg、Zn、Cd 的 Pi 值相对较高，最高值分别达到了

0.505、0.898、0.996。

为进一步确认土壤中重金属的潜在风险，对首次施肥的土壤进行潜在生态风险评价，结果如图 5 所示。不同灰度代表的是施用不同比例的堆肥污泥产品，而不同纹路则代表不同重金属的潜在生态危害指数 EI。

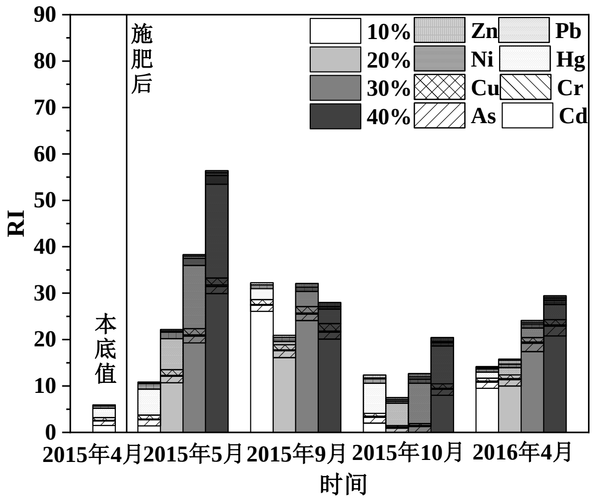


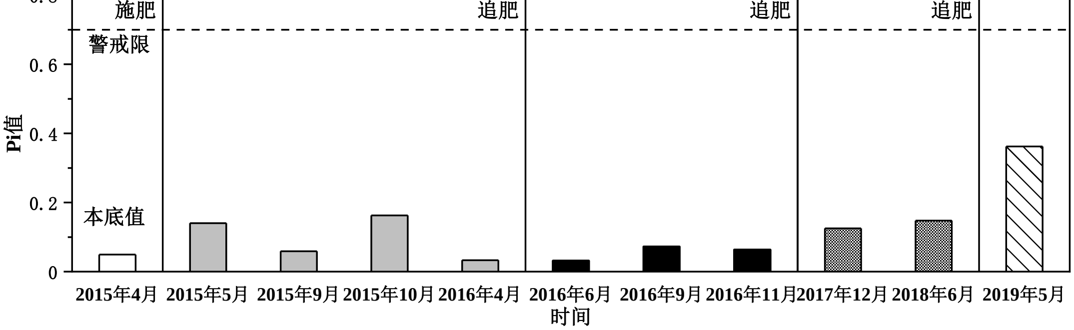
图 5 林地施用不同比例污泥的重金属潜在风险图

Fig.5 Potential risk of heavy metals caused by different proportions of sludge applied in forest land

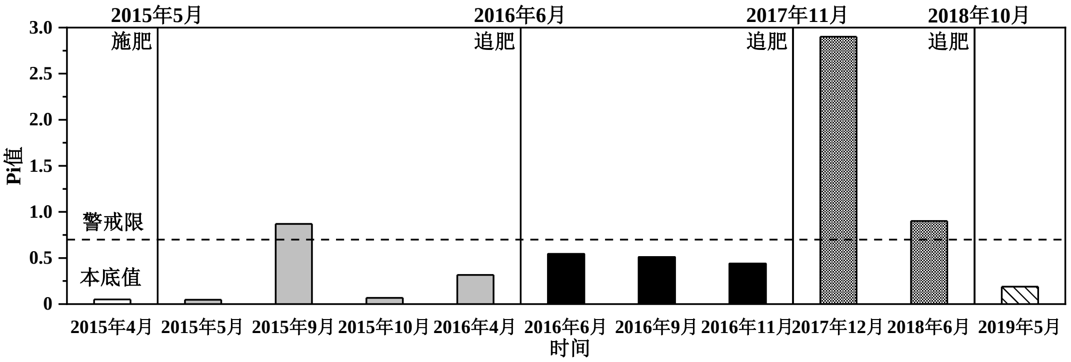
由图 5 可以看出，综合生态风险指数 RI 值均远小于 150，各重金属的 EI 值均小于 40，表明首次施用污泥堆肥产品后土壤重金属处于低风险阶段，但施肥地块 RI 值均高于土壤本底 RI 值，表明污泥的施用会导致土壤中重金属的累积。与图 4 规律相似，在刚施肥和施肥一年后，重金属潜在生态风险随着污泥施用比例的增加而增加，在施用比例为 30%和 40%的地块中重金属综合生态风险相对较大，其 RI 最大值分别为 38.31、56.39，而施肥比例为 10%和 20%的地块中最大 RI 值为 32.24 和 22.16。此外，在土壤本底值中 Cd 的潜在风险贡献为 25.25%，而在施肥后 Cd 的潜在风险贡献率高达 80.94%，Hg 的贡献率从 33.10%增长至 68.33%，表明污泥施用前后 Hg、Cd 产生的风险变化较大。综上所述，当施肥比例为 10%和 20%时潜在风险相对较低，可以进行连续施肥，而施肥比例为 30%和 40%时潜在风险较大，不宜连续施肥。

2.3 林地连续施肥地块重金属风险评价

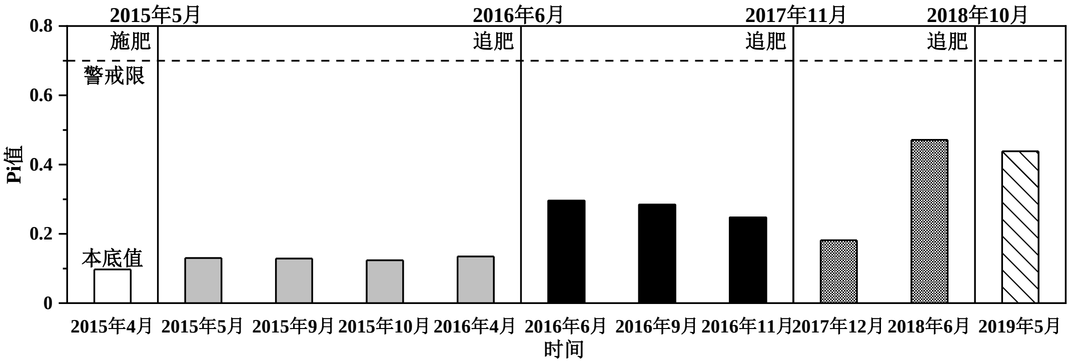
自 2015 年施用堆肥污泥开始，于 2016 年-2018 年连续追肥 3 次，每年施肥一次，施肥具体时间如图 6 所示，不同纹路代表施肥后土壤中重金属的变化施肥比例为 10%的白皮松林地连续 5 年监测的土壤重金属的 Pi 值如图所示。



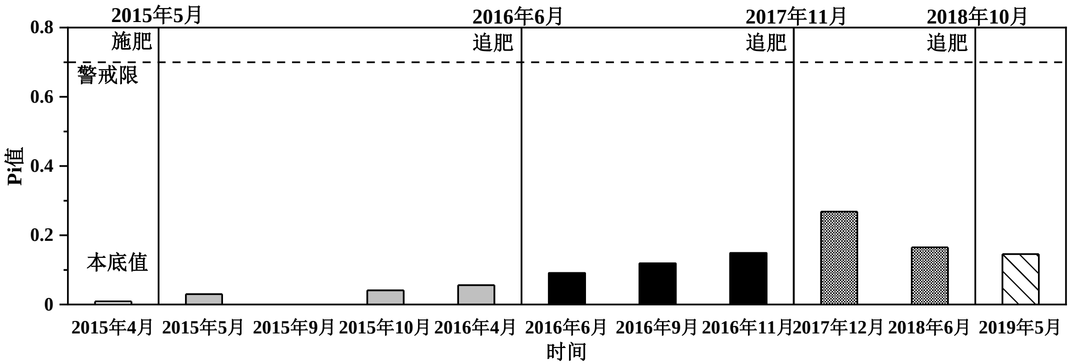
（a）Hg的Pi值



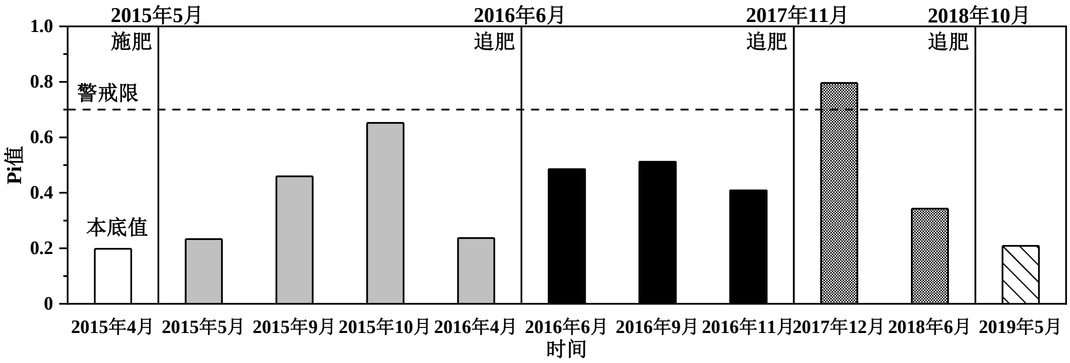
（b）Cd的Pi值



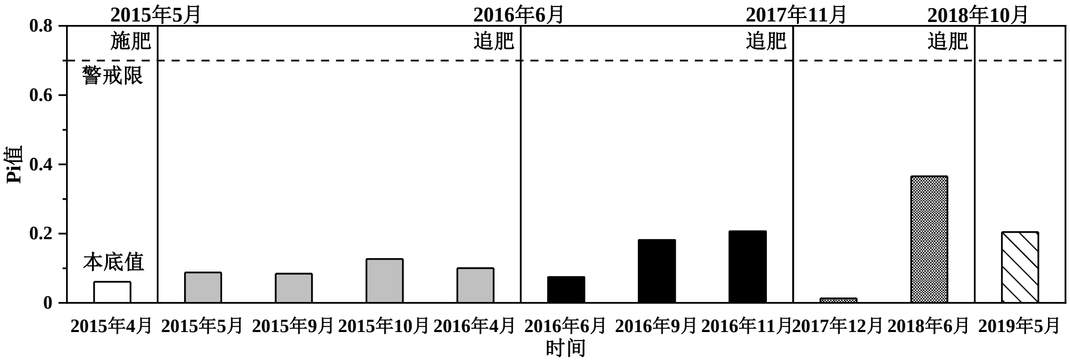
（c）As的Pi值



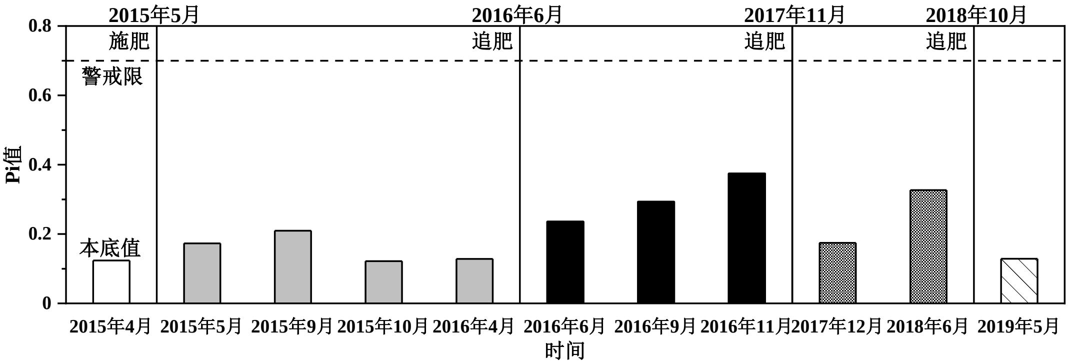
（d）Pb的Pi值



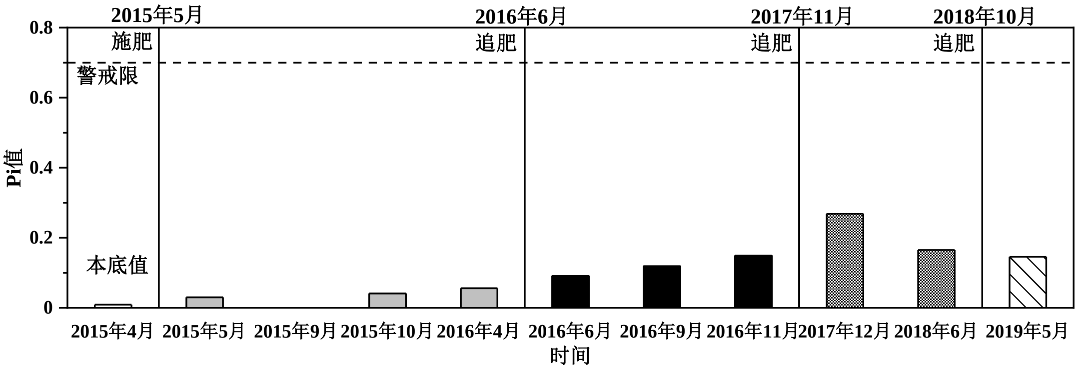
（e）Zn的Pi值



（f）Cr的Pi值



（g）Cu的Pi值



（d）Pb的Pi值

图 6 连续 5 年施用 10%配比污泥林地的重金属 Pi 值变化图

Fig.6 Pi Change of heavy metal in forest land with 10% continuous application of sludge in 5 years

图 6 中每条竖线代表每年的施肥时间，虚线代表警戒限。图中 Cd 的 Pi 值在 2017 年 12 月超过了 1，此外 8 种重金属的 Pi<1 满足标准要求。但 Cd 和 Zn 在 2017 年和 2018 年均出现 Pi 值大于 0.7 超过警戒限，说明堆肥污泥的施用对土壤中 Cd 和 Zn 含量影响较大。此外，从长期来看重金属 Pi 值基本全部大于本底 Pi 值，且重金属含量呈现递增趋势，表明污泥的施用确实是土壤中重金属累积的重要原因之一。

堆肥污泥的施用虽然并未使得重金属含量超标，但从图 6 中可以发现 Cd、As、Hg、Zn 的 Pi 值较高，需进一步评价这些重金属存在的潜在生态风险。上述重金属的综合风险 RI 值随时间变化如图 7 所示，不同纹路则代表不同重金属的潜在生态危害指数 EI。

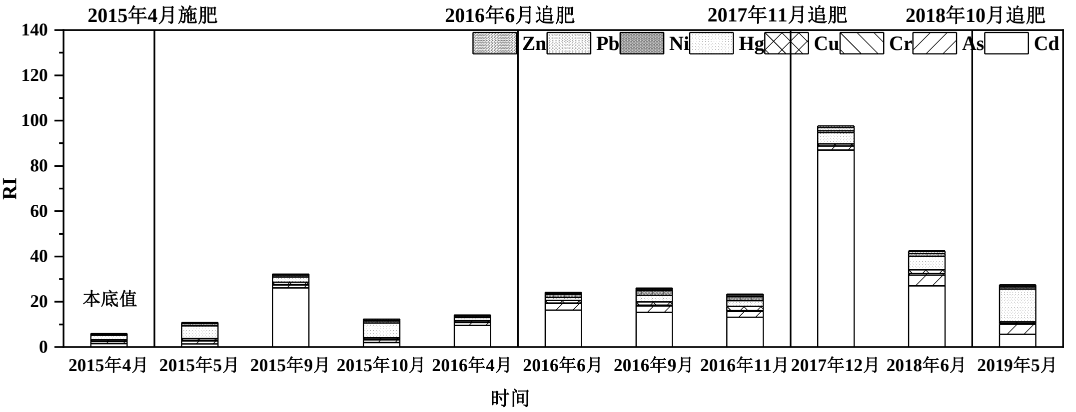


图 7 连续 5 年施用 10%配比污泥的林地重金属潜在风险图

Fig.7 Potential risk of heavy metals in forest land with 5% continuous application of sludge for 5 years

从图 7 中可以看出，各重金属潜在生态风险指数 EI<40，8 种重金属的综合生态风险指数 RI<150，表明其处于低风险阶段，但连续 5 年的监测结果可以看出风险总体呈现增加趋势，表明重金属在表层土壤中产生了累积，但仍处于低风险范围。综合生态风险在施肥当年呈现先增后减的趋势（如 2015 年 5 月-2016 年 4 月），推测是降水导致重金属向外迁移所致。8 种重金属潜在风险贡献率的顺序为：Cd>Hg>As>Ni>Cu>Zn>Pb>Cr，其中 Cd、Hg、As 的贡献率相对较大，平均可达 50.74%、22.09%、10.41%。堆肥污泥施用后 Cd 的贡献率从未使用污泥前的 25.25%增加到了施肥后高达 89.07%，表明施肥对重金属中 Cd 含量的影响很大，施肥后土壤中 Cd 可能产生风险。

2.4 连续施肥后土壤中重金属含量预测结果及风险分析

以林地土壤重金属本底值为背景值，采用常见的土壤污染物累积模型对施肥比例为 10%的林地土壤中重金属含量随施用年限的累积情况进行预测。施肥前 4 年采用实际污泥堆肥泥质预测重金属含量，而后采用其中含量最高一年的重金属进行预测。结果如表 7 所示。

可以看出，在连续施用堆肥污泥产品后第 11 年，土壤中 Zn 和 Cd 的含量超过了 2018 年发布的《土壤环境质量标准 农用地土壤污染风险管控标准（试行）》（GB 15168-2018）（6.5<pH<7.5），可能存在污染风险。由此得出，施肥比例为 10%配比污泥在 10 年之内风险较小。预测值和前 4 年实测值对比发现， Cu、As、Hg、Cr 4 种重金属预测值与实测值相近或略低，但 Zn、Cd、Ni、Pb 4 种重金属的实测值均高于预测值。研究区域中人为影响较小，推测 Zn、Cd、Ni、Pb 这 4 种重金属除受施肥影响之外，大气沉降、降水以及土壤介质的不均匀等因素也是影响其含量变化的因素之一。因此，对于其来源需进行进一步相关性分析。

表 7 10%配比污泥堆肥施用后土壤重金属含量预测

Table 7 Prediction of soil heavy metal content after application of 10% proportioned sludge compost

	时间	Zn	Cd	Hg	Pb	As	Cr	Cu	Ni
预测值	1 年（2015）	64.28	0.02	0.26	1.52	3.08	13.40	16.38	11.13
	2 年（2016）	78.19	0.02	0.38	1.96	3.24	14.67	20.33	11.91

	3 年（2017）	91.41	0.03	0.48	2.41	3.39	15.92	24.25	12.69
	4 年（2018）	103.96	0.03	0.57	2.84	3.55	17.16	28.13	13.46
	5 年	128.29	0.07	0.70	4.23	3.78	20.09	34.62	14.20
	6 年	151.41	0.12	0.81	5.60	4.01	22.98	41.03	14.93
	7 年	173.37	0.16	0.90	6.96	4.24	25.84	47.39	15.65
	8 年	194.23	0.20	0.98	8.30	4.47	28.68	53.68	16.37
	9 年	214.05	0.24	1.05	9.63	4.70	31.48	59.91	17.08
	10 年	232.87	0.28	1.11	10.95	4.92	34.26	66.08	17.78
	11 年	250.76	0.32	1.16	12.25	5.14	37.01	72.18	18.48
标准	GB15618-2018	250	0.3	2.4	120	30	200	100	100
	本底值	49.63	0.02	0.12	1.07	2.92	12.13	12.38	10.34
实测值	2015 年 5 月	58.32	0.01	0.34	3.58	3.91	17.60	17.29	22.40
	2016 年 6 月	121.21	0.16	0.08	10.92	8.88	14.88	23.61	26.89
	2017 年 12 月	199.08	0.87	0.30	32.21	5.45	2.56	17.45	16.45
	2019 年 5 月	76.53	0.08	0.99	20.10	15.52	51.48	17.33	24.88

2.5 重金属相关性分析

为研究土壤中重金属是否全部来源于施肥污泥，对土壤中各重金属含量进行相关性分析（方差齐性时（P>0.05），采用 Pearson 积差相关；方差非齐性时，采用 Spearman 等级相关），结果见表 8。

由表 8 可知，林地土壤中重金属之间具有较强的相关性。其中，As 与 Cr 具有极显著的正相关性；Cd 与 Zn、Cu 具有较为显著的正相关性；Hg 与 Pb 具有极显著的相关性，表明 As 与 Cr 之间，Cd 与 Zn、Cu 之间以及 Hg 与 Pb 之间的来源相似。值得注意的是 Ni 与 Cd、Cu、Pb、Hg 之间、Cr 与 Cd、Cu 之间及 As 与 Cu 之间以及 Cd 与 Pb 之间具有负相关性，其他重金属之间呈现正相关，表明 Ni、Cr、As 与 Cd、Cu、Pb、Hg 之间以及 Cd 与 Pb 之间的来源差异极大。

此外，Hg 与其他重金属之间的相关性较差，表明 Hg 与其他重金属的来源差异较大。主要由于林地土壤黏性较差，孔隙度大，Hg 易释放到空气中所致[13]。

污泥堆肥的连续施用是导致表层土壤中重金属累积的重要因素之一，但不排除其他因素也会对表层土壤重金属产生影响。因此利用表 8 中相关系数对表层土壤中重金属进行聚类分析，结果如图 8 所示。

表 8 白皮松林地土壤中重金属的相关性

Table 8 Correlation of heavy metals in the soil of Pinus bungeana forest

	Cd	As	Cr	Hg	Ni	Pb	Zn	Cu
Cd	1	0.046	-0.233	0.124	-0.06	-0.072	.734*	.686*

As	0.046	1	.783**	0.468	0.524	0.485	0.548	-0.139
Cr	-0.233	.783**	1	0.591	0.344	0.504	0.249	-0.27
Hg	0.124	0.468	0.591	1	-0.277	.818**	0.366	0.131
Ni	-0.06	0.524	0.344	-0.277	1	-0.066	0.299	-0.141
Pb	-0.072	0.485	0.504	.818**	-0.066	1	0.319	0.168
Zn	.734*	0.548	0.249	0.366	0.299	0.319	1	0.461
Cu	.686*	-0.139	-0.27	0.131	-0.141	0.168	0.461	1

注：*在置信度（双侧）为 0.05 时，相关性是显著的

**在置信度（双侧）为 0.01 时，相关性是显著的

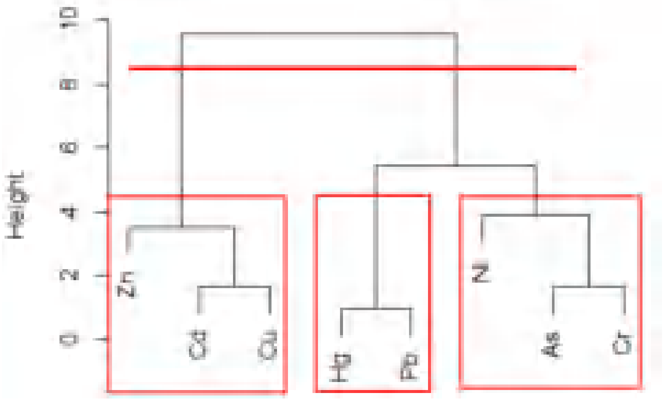


图 8 林地土壤中重金属聚类图

Fig.8 Heavy metal clustering map in forest soil

由图 8 可以看出，聚类分析树状图中土壤重金属可分为三类，第一类是 Zn、Cd、Cu；第二类是 Hg、Pb；第三类是 Ni、As、Cr。结果说明 Zn、Cd、Cu 之间具有相似性，Hg、Pb 之间具有相似性，Ni、As、Cr 具有相似性。有研究发现国内土壤中 Zn、Cd、Cu 主要来自于施肥等农业活动，部分地区还来源于工业活动，甚至以其为主；Hg 则主要来源于工业活动及其产生的大气沉降，局部地区叠加高 Hg 农药的贡献；Pb 的来源则比较复杂，主要来自工业、交通和垃圾堆肥等；As、Cr、Ni 则主要受土壤母质控制[14,15]。根据本研究对林地施肥土壤重金属的相关性和聚类分析，可推测林地土壤中重金属的来源：Ni、As、Cr 的含量主要受土壤母质的影响，叠加施肥的影响；而 Hg、Pb 则主要是受到污泥施用、大气沉降等多因素作用的共同影响；Zn、Cd、Cu 在污泥中含量相对较高，且林地受人为影响较小，因此 Zn、Cd、Cu 在土壤中的含量主要是受到施肥的影响。

3 结论

通过污泥堆肥产品泥质分析以及堆肥污泥不同施用比例、连续施肥因素下对林地土壤重金属的风险评价，得出以下结论：

（1）通过对污泥堆肥产品泥质分析发现污泥中 Hg、Cd、Zn、As、Pb 可能存在污染风险。

（2）施肥比例为 10%和 20%时产生的潜在生态风险较低，可进行连续施肥，而施肥比例为 30%和 40%

时产生的潜在生态风险较大，不宜连续施肥。

（3）连续 5 年施肥林地土壤中除 Cd 在 2017 年 12 月超标外，其余重金属均未超标，但重金属含量呈累积趋势。经模型预测，在施肥比例为 10%的林地土壤中，连续施用 10 年是安全的。

（4）对重金属进行相关性及聚类分析，发现重金属来源并非全部源于施肥污泥。土壤中 Zn、Cd、Cu 含量主要受施肥影响， Hg 和 Pb 受施肥以及大气沉降等综合作用影响，而 Cr、Ni、As 主要来源于土壤母质。

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济南市建筑废物综合式资源化模式全生命周期环境评价

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摘要：随着城市化进程持续加速，济南市建筑废物体量也飞速激增。目前采用直接填埋的模式，带来许多环境问题，且已不能满足消纳建筑废物的需要。而常用的建筑废物资源化模式，都有各自的弊端。为了科学有效地解决济南市建筑废物问题，构建了符合济南市实际的综合式建筑废物资源化模式，并运用生命周期评价理论，与直接填埋模式和集中式资源化模式进行了对比分析。结果显示直接填埋式环境影响当量为 6.19E-11 kg，集中式为 9.13E-12 kg，综合式为 7.28E-12 kg。验证了综合式资源化模式在环境影响方面，要优于其他两种处理处置模式。

关键词：建筑废物，生命周期评价，资源化，济南

Life cycle assessment of Jinan construction waste comprehensive recycling model

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Abstract: with the continuous acceleration of urbanization process, the volume of construction waste in Jinan City is also increasing rapidly. At present, the mode of landfill has brought many environmental problems, and can not meet the needs of building waste consumption. However, the commonly used construction waste recycling models have their own disadvantages. In order to solve the problem of building waste in Jinan City, this paper constructs a comprehensive model of building waste recycling, which is in line with the actual situation of Jinan City, and uses the theory of life cycle evaluation to compare with the direct landfill model and the centralized recycling model. The results show that the environmental impact equivalent of direct landfill is 6.19E-11kg, that of centralized landfill is 9.13E-12kg, and that of comprehensive landfill is 7.28E-12kg. It is verified that the comprehensive resource-based model is superior to the other two disposal models in terms of environmental impact.

Key words: Construction waste;LCA; recycling; Jinan

自 2019 年起，“无废城市”建设成为我国解决固体废物问题的主要手段。建筑废物是大宗废物主要一类，是“无废城市”建设着重考虑的重要方向。国务院办公厅发布的《“无废城市”建设试点工作方案》中提出了“摸清建筑废物产生现状和发展趋势，加强建筑废物全过程管理”[1]。针对固体废物的管理，济南市政府制定了《济南市生活垃圾分类工作总体方案（2018—2020 年）》，于 2018 年 7 月中旬强制推行，并要求到 2020 年底垃圾分类覆盖率达到 100%。

1、研究背景

1.1 济南市建筑废物处理处置现状

随着城市化进程持续加速，济南市的建筑废物体量也飞速激增。但是目前济南市采用露天堆放和直接填埋的处理处置方式，会使有害化学物质渗入到空气、土壤和水中，从而造成不可逆转的环境破坏。而且运输途中及堆放填埋过程中，出现撒漏和扬尘等二次污染。此外，经过调研，就济南建筑废物的增长量而言，济南市消纳能力不足四年。因此如何科学有效地处理处置建筑废物是济南市迫在眉睫需要解决的问题。

1.2 建筑废物资源化模式分析

国内外解决建筑废物问题，都在大力推广新型的建筑废物资源化的方法。根据处理形式的不同，建筑废物资源化处理模式分为集中式资源化和就地式资源化两种处理模式。集中式资源化模式主要是将建筑废物由现场运至固定的资源化工厂内统一再生资源化处理的模式。但是其缺点是前期投资大，占地规模大，由于运输距离长和运输量大从而运输费用高，而且还会造成二次污染环境等问题。就地式资源化模式，即在建筑废物现场使用移动式建筑废物处理设备，对现场已分类的需再生利用的建筑废物进行加工生产，生产出的再生建筑材料直接使用到现有工程项目中，从而达到建筑废物减量化和循环再利用的目的。该模式的缺点在于，只适用大规模资源化项目，对于产生量小和产生过程长的项目则不适用，而且还受到资源化场地的限制。综上所述，单独采用某一种资源化模式，都有不可避免的弊端。本次研究根据济南市建筑废物不同的产生情境，综合使用集中资源化模式和就地资源化模式，构建附合济南市实际的建筑废物分类处理处置模式，以期达到济南市建筑废物分类处理处置的最佳效果。

2、构建济南市建筑废物综合式资源化模式

2.1 济南市建筑废物的特点

表 1　2017 年济南市建筑废物组成成分含量估算表（单位：万 t）

Tab.1　2017 Jinan construction waste component content estimation table (unit: 10000 t)

年份	建筑废物类　别	混凝土砂浆	砖等块状物	废钢筋废钢材	木材	塑料	玻璃	其他	合计
2017	新建施工类	124.40	46.44	7.52	17.27	1.56	0.63	5.34	203.17
	装修类	20.52	35.00	0.59	1.11	0.12	0.18	1.11	58.63
	两类汇总	144.92	81.45	8.10	18.38	1.68	0.81	6.46	261.80
	两类成分占比（%）	16.63	9.35	0.93	2.11	0.19	0.09	0.74	30.04
	旧建拆除类	262.16	246.92	20.73	37.19	3.66	6.71	32.31	609.67
	旧建成分占比（%）	30.08	28.33	2.38	4.27	0.42	0.77	3.71	69.96
	三类汇总	407.08	328.36	28.83	55.57	5.34	7.51	38.77	871.47
	三类成分占比（%）	46.71	37.68	3.31	6.38	0.61	0.86	4.45	100.00

经过调研发现，济南市建筑废物组成成分呈现以下特点：

（1）混凝土和砂浆、砖、砌块、陶瓷和瓦片、废钢筋、废塑料、废玻璃、废木材等六种主要可再生利用的建筑废物成分产量占到总产量的 95%以上；

（2）其中混凝土、砂浆、砖、砌块、陶瓷和瓦片等成分含量占到总含量的 84%以上，且年产量在 700 万 t 以上，这些组成成分可以可以作为再生骨料再生利用；

（3）通过对比旧建筑拆除固体废物、新建筑施工固体废物和建筑装修固体废物的年产量可以发现：旧建筑拆除固体废物占到济南市建筑废物年总产量的 70%左右，是济南市建筑废物的主要组成部分，其他两类建筑废物只占到 30%左右；

（4）旧建筑拆除固体废物中混凝土、砂浆、砖、砌块、陶瓷和瓦片等产量占到年相同成分总产量的 60%左右，约在 400 万 t 以上，且具有规模大、产量多、产生集中和施工作业面大等特点。

2.2 济南市建筑废物综合式资源化模式的建立

根据以上济南市建筑废物产量的特点，构建以下济南市建筑废物分类处理处置模式：

（一）旧建筑拆除固体废弃物资源化采用就地式资源化模式。

基于旧建筑拆除固体废物是特点，应采用就地资源化的方式在拆除现场处理这些建筑废物。应在济南市分区布置 24 套时产 50t 的移动建筑废物破碎设备和配套移动式建材生产系统。每套时产 50t 的移动建筑废物破碎设备，可以年处理 15 万 t 建筑废物；24 套可以共处理 360 万 t 建筑废物，此产量可以消化大部分旧建筑拆除固体废弃物中的混凝土、砂浆、砖、砌块、陶瓷和瓦片等。现场人工分拣出的废钢筋、废钢材、木材、塑料和玻璃等属于直接回收再利用类建筑废物可以直接由施工现场，运往回收再利用场所。余土运至建筑废物消纳场，无害化处理后进行填埋处理。

采用此种模式，首先现场消化大量建筑废物，不需占用土地，可以随着拆除工程同时进行建筑废物资源化，有利于促进旧建筑拆除工程。其次，由于现场处理建筑废物，可以节省建筑废物运输费用。同时生产出的再生资源化产品可以在拆除现场存放，节省了土地占用。待新建筑施工开始，再生资源化产品直接使用，这也节省了再生产品的运输费用。另外，根据旧建筑物拆除工程规模大小和施工时间的不同，24 套移动式建筑废物处理设备可以灵活组合调配，便于旧建筑物拆除工程的不同需求。

（二）新建筑施工固体废物和装修固体废物采用集中资源化模式。

新建筑施工固体废物和装修固体废物产量远没有旧建筑拆除固体废物产量大。其中可以作为再生骨料的建筑废物两者之和占济南市建筑废物总产量的比例不足 16%。而且两种建筑废物产生的时间不集中，往往是伴随着工程进度不断产生，地点也很分散。如果单个工程运用就地资源化处理模式，满足不了移动式建筑废物资源化设备生产需求，会造成设备使用的浪费。另外，现场也没有多余场地可供移动式建筑废物资源化设备生产和存放再生资源化产品。因此，就地资源化处理模式不适用于这两种建筑废物。

根据表 1 中所体现的新建筑施工固体废物和装修固体废物的年产量，可在济南市设置 3 座年处理量在 100

万吨的集中式建筑废物资源化处理中心。具体做法是，首先在现场人工分拣出的废钢筋、废钢材、木材、塑料和玻璃等属于直接回收再利用类建筑废物，将其直接由施工现场运往回收再利用场所。被分类的混凝土、砂浆、砖、砌块、陶瓷和瓦片等加工后再生利用类建筑废物，集中运输至集中式建筑废物资源化处理中心集中资源化处理。余土运至渣土消纳场，无害化处理后进行填埋处理。

集中式资源化处理模式可以有效解决这两种建筑废物单个项目产量不足、地点分散和生产场地不足的问题。可以集中全市的产量于一处，集中处理这两种建筑废物。而且还可以运用就地资源化未能处理的旧建筑拆除固体废弃物余量，保证集中式资源化处理模式生产的连续运行和弥补就地资源化的产能不足。

3、济南市建筑废物处理处置模式生命周期评价模型

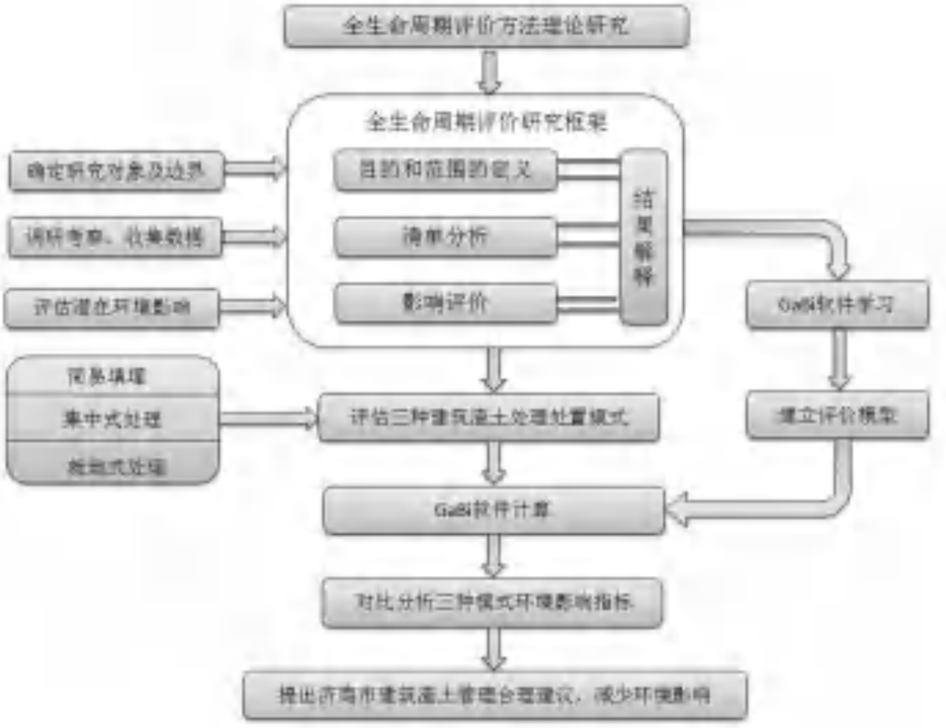

图 1　济南市建筑废物管理生命周期评价研究框架

Fig.1 Research framework of LCA of construction waste management in Jinan

3.1 目的与范围

（1）济南市建筑废物处理处置模式的生命周期评价的目的

基于生命周期评价理论的框架结构，本文建立了三类建筑废物处理处置模式环境评价系统模型，并且阐述系统内各个模块的相互作用和联系。由于生命周期评价可以量化每一类建筑废物处理处置模式对环境的负荷，所以可以将对比分析三类建筑废物处理处置模式对环境的影响程度，从而为济南市在选择建筑废物处理处置模式上提供环境影响基础数据和决策参考。具体研究框架如图 1 所示。

（2）确定济南市建筑废物处理处置模式的功能单位

功能单位是生命周期评价中所采用的特定计量单位。固体废物生命周期评价研究中，功能单位都是采用质

量或者体积作为计量单位。由于建筑废物密度的差异，因此本文使用质量作为功能单位，即以处理处置1t建筑废物作为功能单位。

表1显示了2017年济南市建筑废物各组成成分的含量。本次研究以2017年济南市建筑废物各组成成分百分比作为研究标准。即功能单位1t建筑废物中含有混凝土和砂浆467.1kg，砖、砌块、石材、陶瓷和瓦片376.8kg，废钢筋、废钢材33.1kg、木材63.8kg、塑料6.1kg、玻璃8.6kg、其他成分44.5kg。

（3）确定济南市建筑废物处理处置模式的系统边界

本次研究针对不同的建筑废物处理处置模式，采用的建筑废物生命周期的终点是不同。如果采用填埋的方式，建筑废物生命周期终点就是当建筑废物被填埋厂处理的那一刻。如果采用资源化的处置处理方式，建筑废物生命周期终点就分为两类情况。一类是建筑废物还存在某些循环再利用的价值，这是建筑废物生命周期终点就是从回收站被出售的时间点。另一种是建筑废物被资源化再加工，当建筑废物成为再生产品的那一刻，即为建筑废物生命周期终点。就系统输出而言，它的产品都是可以再生循环的，除此之外，还有排放的各类污染物和惰性填埋物质。

3.2 清单分析

济南市建筑废物处理处置模式全生命周期清单分析是指在整个建筑废物处理处置模式中，每个研究阶段所需的能源和物质，进入研究边界范围内的输入和输出的汇总统计，以及因此排放的对环境影响的污染物数量的量化分析。本次研究的基础数据，主要通过调研收集、文献查阅和通用生命周期评价数据库等方式获得的。国内外开发了各类与固体废弃物相关的数据库，例如国外的Boustead，Franklin等和中国的CLCD数据库[2,3]。本次研究采用GaBi软件的数据库。GaBi软件数据库是将不同国家的相关研究机构和产业界的数据库汇集在一起，几乎包括了欧洲所有相关工业生态和包装材料的相关数据。GaBi软件将数据库划分为物质流与能源流和生产技术两大类别。该软件数据库总共包括了1250个工艺和94个方案的相关数据[4]。但是由于建筑废物的相关研究数据有限，所以在使用该数据库时，需要进行必要的修正。

显而易见，济南市建筑废物处理处置模式生命周期评价的研究数据具有自身的独特性，本次研究所用的数据并非是最丰富和最完美的，其中的不完善之处，会影响到最终分析结果。

3.3 影响评价

（1）影响类型以及参数选择

生命周期评价方法一般分为中间点法和终结点法两大类[5]。中间点法是面向问题的评价方法，主要针对酸化（Acidification Potential，简称：AP）、全球变暖（Global Warming Potential，简称：GWP）、富营养化（Eutrophication Potential，简称：EP）、人类毒性（Human Toxicity Potential，简称：HTP）、光化学臭氧合成（Photochemical Ozone Creation Potential，简称：POCP）等相关环境影响进行评价，常使用EDIP97、EDIP2003、MPACT2002+和CML2001等体系作为评价体系[5]。

本次研究采用国际通用的GaBi 8.0教育版建立生命周期评价模型。在GaBi 8.0软件提供的评价模型库中，选择CML2001模型作为基本研究模型。该模型将环境影响类型分为三类：物质资源耗竭、生态危害和人类健康。CML2001模型应用于面向问题的方法。由于列表分析的传统特征和标准研究方法，该模型易于操作，减少了假设的数量和模型的复杂性。但是，由于某些化学物质的生态毒性难以确定和缺乏排放特性数据，一定程度

上影响了评价结果的不确定性[6]。CML2001 模型包含 10 余种环境影响评价，本文只选择常用酸化（AP）、富营养化（EP）、全球变暖（GWP）、人类毒性（HTP）、光化学臭氧合成（POCP）等五类指标进行研究。

①酸化潜值（AP）

来自于化石燃料燃烧产生的酸化物质 SO_2、NO_X、CO_2 及其他有机酸会造成水体和土壤的酸化[7]。这将对生态系统产生很大影响。酸化潜值是以 SO_2 为当量因子，将不同类型的酸化污染物质换算成为以 SO_2 基准的环境影响效果，计算公式如下所示[5]：

$$AP=\sum AP_i\times M_i=\sum\frac{v_i/M_i}{v_{so_2}/M_{so_2}}\times M_i \qquad (1)$$

式中：M_i 表示第 i 类物质质量，单位：kg；v_i 表示单位质量下第 i 类物质与 H^+ 结合的速度。

②富营养化潜值（EP）

富营养化是指工业生产中产生的大量含氮、磷等营养物质排放到自然水体中，致使其中的水生生物，尤其是藻类的大量繁殖，从而造成水肿溶解氧含量大量降低，最终破坏水体。一般以磷酸盐（PO_4^{3-}）作为富营养化潜值的当量因子，以此指标将各类富营养化污染物换算成以磷酸盐（PO_4^{3-}）标准的环境影响效果。计算公式如下所示[5]：

$$EP=\sum_{\mathrm{j}=1}^{\mathrm{m}}W_{\mathrm{j}}\times TLI(j)=\sum_{j=1}^{m}\frac{r_{ij}^2}{\sum r_{ij}^2}\times TLI(j) \qquad (2)$$

式中，m 为引起富营养化作用的 m 类物质，r_{ij} 指的是第 j 种参数与基准参数的相关系数，W_{j} 和 $TLI(j)$ 指代的是第 j 种物质的营养状态指数的相关权重和营养状态指数。

③全球变暖潜值（GMP）

在工业生产中，排放了大量的温室气体造成全球气候变暖。一般将一百年内的时间范畴纳入考虑，各种由温室气体引发的温室效应。由于影响全球变暖的最大因素是二氧化碳，所以将 CO_2 作为当量因子，其他各类温室气体产生的温室效应都将换算成 CO_2 为基准的等量环境影响效果。计算公式如下所示[5]：

$$GWP=\sum GWP_{\mathrm{i}}\times M(kg)=\frac{\int_0^T a_i c_i(t)dt}{\int_0^T a_{CO_2}c_{CO_2}(t)dt}\times M(kg) \qquad (3)$$

式中，T 为第 i 种气体引起温室效应的时间，a_i 和 c_i 分别代表单位浓度下第 i 种温室气体经过 T 时间的热吸收度及热辐射，CML2001-June.2016 模型一般将 T 值按 100 年计算。

④人体毒性潜值（HTP）

人体毒性潜值指自然界中的污染物对人体的潜在影响，一般以每 kg 体重所能承受毒害量的极限值。通常以二氯苯（Dichlorobenzene，简称：DCB）作为各类污染物毒性的标准参照物。各类污染物毒性换算成二氯苯造成的人体潜在毒性影响。计算公式如下所示[5]：

$$HTP = \sum HCA_{\mathrm{i}} \times M_{i1}(kg) + \sum HCW_{\mathrm{i}} \times M_{i2}(kg) + \sum HCS_{\mathrm{i}} \times M_{i3}(kg) \qquad (4)$$

式中，$HCA_{\mathrm{i}}, HCW_{\mathrm{i}}, HCS_{\mathrm{i}}$，分别代表单位质量下第 i 种毒性物质在大气、水体和土壤中的毒害系数，毒害系数的数值高低与暴露系数和影响系数有密切关系。M_{i1}、M_{i2}、M_{i3} 分别表示第 i 种毒害物质对大气、水体和土壤中排放的质量。

⑤光化学臭氧形成潜值（POCP）

自然界中，当紫外光照射到 NO_x 气体与可挥发性有机物（Volatile Organic Compounds，简称：VOC）以及其他挥发性有机物的混合物时，将产生臭氧，生成光化学烟雾。光化学臭氧形成潜值以乙烯（Ethene）作为当量因子。将不同污染物换算成乙烯为标准的等量环境影响效果。计算公式如下所示[5]：

$$\mathrm{pocp} = \sum \mathrm{pocp}_{\mathrm{i}} \times M_i(kg) = \frac{a_i / b_i}{a_{C_2H_2} / b_{C_2H_2}} \times M_i(kg) \qquad (5)$$

式中，a_i、b_i 分别代表一个单位质量中的第 i 种具有挥发特点的有机物质引起臭氧的变化值以及 T 时间段内 VOC 的排放含量。VOC 产生化学作用，是引起臭氧发生变化的主因。

（2）济南市建筑废物处理处置模式生命周期评价特征化

经过上述处理后，需要将每个类型的排放物进行特征化。通过与特征化因子相乘，将每种排放物所得出的环境影响值汇总折算为同一单位的影响类别特征化指标。本次研究采用 GaBi 8.0 教育版软件自带 CML2001 模型作为特征化模型[8-11]，进行济南市建筑废物生命周期评价特征化研究。该模型中运用当量因子法，借助不同的环境影响因子对该类别的环境影响差异，从而找到以参照排放物为标准的当量大小。

表 2　CML2001-Jan.2016 模型下环境影响类型典型污染物与标准当量物

Tab.2　Typical emissions and standard references in CML2001-Jan.2016 method

环境影响类型	主要影响物质	标准当量物
酸化（AP）	SO_2, HCI，NOx，NHa^+	SO_2
水体富营养化（EP）	PO_4^{3-}，NOx，NHa-N，硝酸盐	PO_4^{3-}
温室效应（GWP 100 year）	CO_2, CH_4, CH_3Br，CFCs	CO_2
人体潜在毒性（HTP）	进入人体的有毒物质	二氯苯（DCB）
光化学毒性（POCP）	NMHC	乙烯（Ethene）

数据来源：文献【12】

计算公式[13]如下所示：

$$EV(j) = \sum EV(j)_i = \sum \left[EF(j)_{\mathrm{i}} \times Q_i \right] \qquad (6)$$

式中，EV(j)是指研究系统中对第 j 种环境影响类型的环境影响总值；$EV(j)_{\mathrm{i}}$ 是指第 i 种排放物对第 j 种环境影响类型潜在影响贡献值；$EF(j)_{\mathrm{i}}$ 是指第 i 种排放物对第 j 种环境影响类型的当量因子；Q_i 是指第 i 种排放物的产生量。

（3）济南市建筑废物处理处置模式生命周期评价标准化

在完成济南市建筑废物生命周期评价特征化计算后，为了更好地评估济南市建筑废物处理处置模式中的每种环境影响类型数据的高低，需要特征化结果进行标准化处理。济南市建筑废物生命周期评价标准化是指通过量化处理所有环境影响分类特征化的影响因子，转换成统一值，以便在相同范围内比较各个济南市建筑废物处理处置模式的环境影响，并且综合评估各个济南市建筑废物处理处置模式的环境影响。本文选择 CML2001-Jan.2016，world 评价标准对特征化结果进行标准化。

表 3　CML2001-Jan.2016 模型下环境影响类型量化基准值

Tab.3 CML2001-Jan.2016 Environmental impact type quantitative reference value

序号	环境影响类型	标准参照物	单位	量化基准值
1	CML2001-Jan.2016 酸化（AP）	SO_2	kg	2.39×10^{11}
2	CML2001-Jan.2016 富营养化（EP）	磷酸盐（PO_4^{3-}）	kg	1.58×10^{11}
3	CML2001-Jan.2016 全球变（GMP）	CO_2	kg	4.22×10^{13}
4	CML2001-Jan.2016 人体毒性（HTP）	二氯苯（DCB）	kg	2.58×10^{12}
5	CML2001-Jan.2016 光化学毒性（POCP）	乙烯（Ethene）	kg	3.68×10^{10}

数据来源：（GaBi 8.0 教育版）

3.4 结果解释

结果解释，是指比较分析各种可行方案的环境影响结果，从而得到环境影响评价和相关管理建议。就本次研究而言，结论解释是基于前三个研究阶段的成果基础上，针对济南市建筑废物采用不同的处理处置模式而进行环境影响评估，再比较分析出不同处理处置模式对环境影响最小的一种模式，从而在环境影响角度确定适合济南市建筑废物处理处置模式。

4、济南市建筑废物处理处置模式数据收集

4.1 生命周期评价对比分析的管理模式

本部分研究主要针对济南市建筑废物三种不同处理处置模式做出环境影响的对比分析。这三种建筑废物处理处置模式是：济南市目前使用的直接填埋模式、目前常用的集中式建筑废物资源化模式和本次研究提出的综合式建筑废物分类处理处置模式。

4.2 直接填埋模式的环境清单分析

经过现场实际调研，济南市目前建筑废物处理的主要方式是直接填埋。直接填埋范围为从建筑废物装车运输开始，指导填埋完成为止。主要包括运输阶段和填埋阶段两个部分。尽管建筑废物中绝多数都是惰性成分，在进行填埋处理的时候，仅仅会出现一些污染；但是直接填埋的还包括非惰性的组成成分在内，而此部分产生的污染是必须要考虑的。综上所述，完整的清单分析系统应包括填埋方式对环境的影响和过程能源的输入两个部分。

（一）运输阶段的环境分析

根据表中所示，济南市现在运行的建筑废物收纳场的服务半径都控制在 20 公里范围内。本次研究假定建筑废物的运输距离为 20 公里。通过现场调研，济南市建筑废物运输车辆主要是荷载 25 吨的重型渣土运载车，所

使用能源为柴油。本次研究借鉴 GaBi 软件数据库中相关数据标准作为运输阶段能耗标准。

（二）填埋阶段的环境分析

经查询文献和现有环境数据库，均未发现有关济南市建筑废物填埋时的所排放的污染物种类和排放量的具体数据。而文献【2】中计算出了大连市的建筑废物直接填埋所排放的气体和渗透液的污染物成分和含量。由于济南市和大连市同为国家的 15 个计划单列市，经济发展进度相当；同属北方城市，建筑特点和所用材料近似。借鉴采用大连市建筑废物直接填埋式的数据，对济南市建筑废物直接填埋式环境影响研究具有相当重要的研究价值和借鉴意义。因此本文借鉴文献【2】中有关大连市建筑废物直接填埋时所排放的填埋气体和填埋渗透数据作为济南市渣土建筑直接填埋式的污染物的排放数据。填埋气体排放量如表 4 所示，填埋渗透液如表 5 所示。

表 4　1t 建筑废物填埋气体排放量（单位：kg/t　建筑废物）

Tab.4 Gas emission of 1t construction waste landfill (Unit: kg/t construction waste)

成　分	CO_2	CH_4	CO	H_2S	HCL	HF	NH_3
产　量	117.04	51.23	0.16	0.46	1.01	8.55×10^{-3}	1.71×10^{-3}

数据来源：文献【2】

表 5　1t 建筑废物渗滤液各物质含量

Tab.5 Output of each substance of 1t construction waste leachate

成　分	产生量　单位：kg/t 建筑废物	成　分	产生量　单位：kg/t 建筑废物
COD	0.755	CL^-	0.158
TOC	0.307	Mg^{2+}	0.118
碱度($CaCO_3$)	0.965	K^+	0.101
氨氮	0.0204	SO_4^{2-}	0.163
Ca^{2+}	0.274	Na	0.254
Pb	3.7×10^{-5}	Cd	8.13×10^{-6}
Cr	3.2×10^{-6}	Hg	3.49×10^{-7}

数据来源：文献【2】

（三）建立直接填埋式清单的 GaBi 软件方案

根据上文所得出的建筑废物直接填埋模式的环境清单数据，在 GaBi 软件中济南市建筑废物直接填埋模式方案（Plans）、工艺过程（Process）和基础流（Flow），方案如图 2 所示。

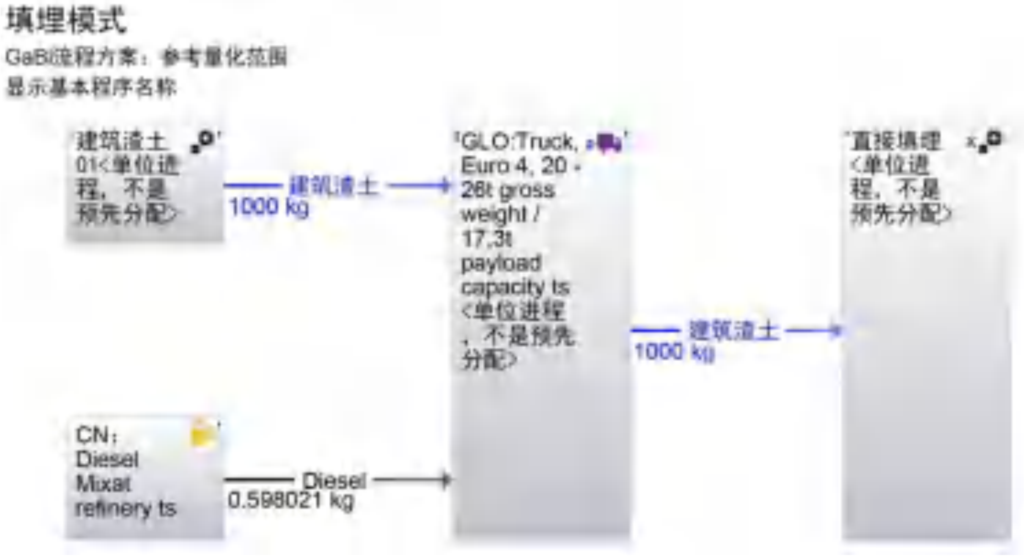

图 2　直接填埋模式的 GaBi 软件方案

Fig.2 The GaBi plan of landfill mode

4.3 集中资源化模式的环境清单分析

据第 2.2 节介绍，集中式建筑废物资源化模式研究范围是从建筑废物装车运输开始，到加工出建筑废物再生产品为止。主要包括运输阶段、预处理阶段、建筑废物资源化阶段、残土处置阶段等四个阶段。建筑废物中木材、玻璃、废塑料、废钢筋、废钢材等可再生利用的部分，本次研究视为其在施工现场人工分拣后，作为原材料汇集运输到另一个生产系统中。因其在建筑废物组成部分占比过小，且再生利用后与相应生产工艺所需原材料无异，因此本次研究不将其纳入环境影响范围内。

（一）运输阶段的环境清单

集中式资源化模式，为节约土地占用，就假设在原有建筑废物填埋场建设相关处理设施和设备。因此建筑废物产生后，与直接填埋式相似，先要运输至集中式资源化处理中心，再进行再生资源化处理。因此集中式建筑废物资源化模式运输阶段的环境影响分析数据与直接填埋阶段的一致，也是按 20 公里计算运输距离，采用 25t 渣土运输车进行运输，同时借鉴 GaBi 软件数据库中全球通用的相关运输车辆和燃油排放数据标准作为运输阶段能耗标准。与直接填埋不同的是运输量上，由于运输之前已将废钢筋和废钢材、木材、废塑料、废玻璃已分类处理，建筑废物中的混凝土和砂浆，砖、砌块、石材、陶瓷和瓦片，以及其他类建筑废物参与运输及以后资源化的生产活动。按照表 1 中 2017 年济南市建筑废物组成成分比例，可以推算出 1t 建筑废物中有混凝土和砂浆 467.1kg,砖、砌块、石材、陶瓷和瓦片 376.8kg 与其他类建筑废物 44.5kg，共计 888.4kg 进入到集中式资源化过程中。

（二）预处理阶段的环境清单

表 6　预处理阶段设备表

Tab..6 Equipment in pretreatment stage

序号	设备名称	单位	数量	单位功率 单位：kw	合计功率 单位：kw	备　注
1	给料料斗	台	2	–	–	4m^3
2	振动给料机	台	2	5.5	11	R×28145-0100
3	反击式破碎机	台	2	94	188	PF-1210

4	1 破碎物输送机	台	2	4	8	R×28145-0200
5	2 破碎物输送机	台	2	4	8	R×28145-0300
6	振动筛分机	台	2	7.5	15	R×28145-0400
7	筛下物输送机	台	10	2.2	22	R×28145-0500
8	旋风除尘器	台	2	5.5	11	R×28145-0600
9	风机	台	2	5.5	11	含减震座
10	星型卸灰阀	台	2	1.1	2.2	R×28145-0600

续表 6. 预处理阶段设备表

序号	设备名称	单位	数量	单位功率单位：kw	合计功率单位：kw	备　注
11	电磁除铁器	台	2	1.1	2.2	−
12	钢平台	台	2	−	−	R×28145-0700
13	电器箱	台	2	0.6	1.2	−
14	反料输送机	台	2	2.2	4.4	R×28145-0700
15	颚式破碎机	套	2	75	150	R×28145-0700
16	单机除尘器	套	2	22	44	袋式
17	装载机	台	6	−	−	ZL50
	合　计				478	

数据来源：文献【14】

预处理阶段主要是将运到资源化处理厂的建筑废物，预先筛分出其中的竹木、塑料、包装纸袋等块状杂质并分类存放；随后按照强度的不一样，进行类型划分，破碎为四类不同粒径的再生骨料备用。经分类后的备用骨料进入资源化利用流程，其余残土和其他有机物进入填埋场填埋。从表 6 中可以看出，预处理阶段能源消耗主要是预处理设备的电力消耗和装载机的燃油消耗。

（1）电力能源消耗

按照年消化 100 万 t 建筑废物的规模设计，相关于一年有 84.39 万 t 混凝土和砂浆、砖、砌块、石材、陶瓷和瓦片等进入到预处理阶段。每年除去检修停工时间，按照 330 天生产，预处理阶段日处理规模为 2557t，表 4.5 中预处理阶段设备每天工作时间按 8 小时计算，则预处理 1t 混凝土和砂浆、砖、砌块、石材、陶瓷和瓦片等所消耗电能：

W_1=预处理设备总功率×设备工作时间÷建筑废物日处理量

=478×8÷2557=1.50kw·h/t。

因此 1t 建筑废物预处理所消耗电能为：

1.50kw·h/t×84.39%=1.266kW·h/t。

（2）燃油消耗

表 7　常用装载机耗油量统计表

Tab.7 Fuel consumption statistics of common loaders

品牌型号	山工 652b	国机常林 955N	龙工 855b	山东临工 L956F	柳工 ZL50CNX
额定功率单位：kW	154	162	162	162	162
单位时间耗油量单位：L	13～14	13～15	13～15	13～16	13～17

数据来源：中国路面机械网

经调研得知，所用装载机一般选用功率为 162kw 的装载机。每台工程在满负荷工作工作的情况下油耗约为 13～17L，如表 7 所示。本次研究按照 15L 计算耗油量。根据以上条件可知预处理 1t 混凝土和砂浆、砖、砌块、石材、陶瓷和瓦片等所消耗燃油：

装载机燃油消耗量=单位时间耗油量×工作时间×台数÷建筑废物日处理量=15×8×6÷2557=0.282L/t。

因此 1t 建筑废物预处理所消耗电能为：0.282L/t×84.39%=0.238L/t

（三）资源化处理阶段的环境清单

资源化处理阶段研究范围是建筑废物制备再生免烧免蒸砖生产过程中所产生的直接环境影响和所消耗能源产生的的间接环境影响。本次研究按照惯例，不考虑生产所用机械设备、基础设施和场内生活等所产生的环境影响。资源化处理阶段的研究对象为建筑废物制备的免烧免蒸砖，研究功能单位为 1t 建筑废物。根据再生免烧免蒸砖制作工艺流程[15]，可知资源化处理阶段包括物质消耗和能源消耗两个部分。

（1）物质消耗

为了再生产品的品种多样化和满足不同的需要，设计只有预处理生产出的一半再生骨料用于生产再生免烧免蒸砖。另根据文献【2】和文献【13】的研究，资源化处理 1 吨建筑废物，会产生不能利用的残土 76.5kg 需要填埋。因此本次研究按照 1t 建筑废物中相当于 383.37kg 进入到集中式资源化过程中。结合文献【15】对于生产 1 块再生免烧免蒸砖需要建筑废物和各种原材料消耗量及所占质量百分比，如表 8 所示。综上所述，最终由表 8 可得处理 1t 建筑废物用于生产免烧免蒸砖材料消耗清单，如 8 表所示。

表 8　建筑废物制免烧免蒸砖原材料用量清单(单位：kg/块标准砖)

Tab.8 List of raw material consumption of non fired and non steam brick made from construction waste (Unit: kg / standard brick)

原材料名称	再生骨料	硅酸盐水泥	矿　渣	石　膏	水
1 块标准砖消耗量 单位：kg	2.7	0.369	0.057	0.028	0.41
1t 建筑废物用于再生砖消耗量 单位：kg	383.37	52.45	8.07	4.03	58.27
固体用料百分比	85.60%	11.70%	1.80%	0.90%	0.13
备　注					水固比

数据来源：（文献【15】）

（2）能源消耗

从表 9 中可以看出，资源化处理阶段能源消耗主要是建筑废物再生产品设备的电力消耗与搬运设备装载机和叉车的燃油消耗。

①电能消耗

再生免烧免蒸砖生产线是按照年消化 50 万吨建筑废物的规模设计，每年除去检修停工时间，按照 330 天生产，资源化处理阶段日处理规模约为 1278t。表 10 中资源化处理阶段设备按照每天工作时间按 8 小时计算，则实际每 t 建筑废物资源化处理所消耗电能：

W2=资源化处理设备总功率×设备工作时间÷建筑废物日处理量

=651.2×8÷1278=4.076kw·h/t。

因为再生免烧免蒸砖生产消化建筑废物的数量只是设计消化能力一半。所以本次研究中，功能单位 1t 建筑废物中所消耗电能应按实际的一半计取，即为：4.076kw·h/t×84.39%×0.5=1.720 kw·h/t

②燃油消耗

此处燃油消耗计算与预处理阶段计算方式相同。参照表 7 所示，本次研究将按照 15L 计算装载机和叉车耗油量。结合表 9 中装载机和叉车数量可知资源化处理阶段燃油消耗为：

装载机燃油消耗量=单位时间耗油量×工作时间×台数÷建筑废物日处理量=15×8×4÷1278=0.376L/t。

与电能消耗原因一致，本次研究中，功能单位 1t 建筑废物中所消耗应按实际的一半计取，即为：0.376L/t×84.39%×0.5= 0.158L/t

表 9　资源化处理阶段设备表

Tab.9 Equipment list of recycling processing stage

序号	设备名称	单位	数量	单位功率 单位：kw	合计功率 单位：kw	备注
1	RTQT9 砌块成型机	台	4	48	192	
2	面料装置	台	4	1.5	6	
3	湿产品输送机	台	4	5.5	22	
4	产品刷	台	4	2.2	8.8	
5	升板机	台	4	5.5	22	
6	降板机	台	4	5.5	22	
7	降板节距输送机	台	4	3	12	
8	全自动码垛机	台	4	30	120	
9	栈板刷	台	4	2.2	8.8	
10	栈板翻转装置(翻板机)	台	4	3	12	
11	栈板仓	台	4	-	-	
12	栈板浸油装置	台	4	2.2	8.8	
13	成品板式输送机	台	4	5.5	22	
14	配料搅拌系统	台	4	7.5	30	
15	骨料仓(底料)3×12m^3	台	4	-	-	
16	称重皮带(底料)	台	4	5.5	22	
17	骨料提升机(底料)	台	4	5.5	22	
18	搅拌机(底料)	台	4	5.5	22	
19	底料水泥秤重	台	4	2.2	8.8	
20	搅拌平台	台	4	-	-	
21	出料皮带机（底料）	台	4	5.5	22	
22	骨料仓(面料)1×12m^3	台	4	0	0	

续表 9 资源化处理阶段设备表

23	称重皮带（面料）	台	4	2.2	8.8
24	骨料提升机(面料)	台	4	2.2	8.8
25	搅拌机（面料）	台	4	3	12
26	出料皮带机（面料）	台	4	3	12
27	注水与测湿系统	套	6	-	-
28	水泥筒仓	个	8	-	-
29	螺旋输送机	台	8	2.2	17.6
30	面料水泥称重	台	4	2.2	8.8
31	电器控制系统	套	4	-	-
32	气动系统	套	4	-	-
33	模具	套	16	-	-
34	生产线用栈板（钢栈板）	块	8000	-	-
35	轨道	m	3600	-	-
36	装载机	台	2	-	-
37	叉车	台	2	-	-
	合计				651.2

数据来源：文献【14】

（四）残土处理阶段的环境清单

残土处理阶段主要是将建筑废物资源化后，不能被资源化的残土和残渣的填埋处理。功能单位1t建筑废物中需要填埋的主要包括建筑废物中其他类44.5kg和资源化后产生的残土76.5kg，共计121kg。残土填埋是按照GaBi软件数据库中欧盟28国（EU-28）垃圾填埋场处理城市固体废物工艺标准考虑的，包括了填埋气体和渗滤液处理。

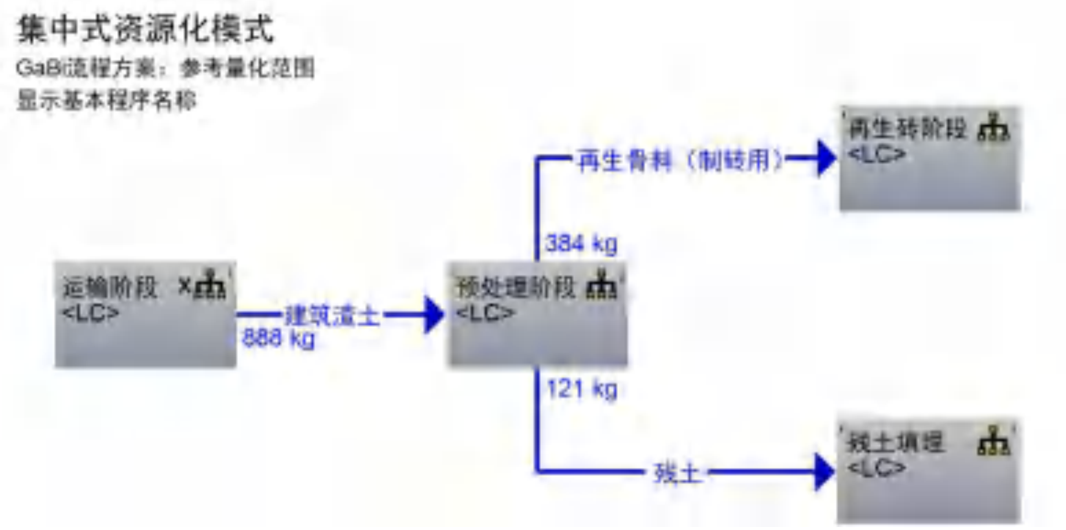

图3　集中式资源化模式的GaBi软件方案

Fig.3　The GaBi plan of Centralized recycling mode

（五）建立集中式资源化模式清单的 GaBi 软件方案

根据上文所得出的建筑废物集中式资源化模式的环境清单数据，在 GaBi 软件中建筑废物集中式资源化模式方案（Plans）、工艺（Process）和基础流（Flow），方案如图 3 所示。

4.4 综合资源化模式的环境清单分析

根据第 2.2 节所构建的济南市建筑废物综合式分类处理处置模式，济南市建筑废物资源化处理分为两种模式：一种是旧建筑拆除固体废弃物资源化采用就地式资源化模式；另外一种是新建筑施工固体废弃物和装修固体废弃物采用集中资源化模式。依据这种模式设置，综合式建筑废物资源化模式的研究范围是从建筑废物就地破碎开始，到加工出建筑废物再生产品为止。主要包括就地资源化阶段、运输阶段、固定式资源化阶段、残土处置阶段等四个阶段。

按照表 1 中 2017 年济南市三类建筑废物年产量的占比计算，研究系统中的功能单位为 1t 建筑废物中，约占全部建筑废物 70%的旧建筑拆除固体废弃物采用就地式资源化模式；约占全部建筑废物 30%采用新建筑施工固体废弃物和装修固体废弃物采用集中式资源化模式。即功能单位为 1t 建筑废物中，700kg 建筑废物采用就地式资源化模式，300kg 建筑废物采用集中式资源化模式。

与集中式建筑废物资源化假设一致，将其中建筑废物中木材、废塑料、废钢筋、废钢材等可再生利用的部分，视为其在施工现场人工分拣后，作为原材料汇集运输到另一个生产系统中。因其在建筑废物组成部分占比过小，且再生利用后与相应生产工艺所需原材料无异，因此本次研究不将其纳入环境影响范围内。

（一）就地资源化阶段的环境清单

表 10 就地式资源化模式主要设备概况

Tab.10 General situation of main equipment of local recycling mode

设备系统名称		单位	数量	额定功率 单位：kw	工作时长 单位：h/台班	耗电总量 单位：kWh	额定处理量 单位：t/h	备注
移动式建筑渣土破碎站		套	1	300	8	1800	50	电力
移动式再生制品生产系统	制砖生产线	套	1	200	8	1200	-	电力
	栈板	块	3000	-	-	-	-	-
	模 具	付	2	-	-	-	-	-

数据来源：文献【16】

就地资源化处理阶段研究范围是从建筑物和构筑物被拆除成为建筑废物开始，直接在拆除现场利用移动设备生产再生建筑材料生产过程中所产生的直接环境影响和所消耗能源产生的的间接环境影响。本文按照研究惯例，不考虑生产和运输所用机械设备、基础设施和场内生活等所产生的环境影响。就地资源化处理阶段的研究对象为由建筑废物生产的再生建筑材料。根据文献【16】所述移动设备生产再生建筑材料工艺流程，可知就地资源化处理阶段包括物质消耗和能源消耗两个部分。

（1）物质消耗

按照文献【16】的研究，50 t/h 移动式建筑废物资源化系统生产出来的再生骨料，一半直接出售用于再生混凝土的制备或用于路基回填等；一半用于现场制备尺寸为 240 mm×115 mm ×53 mm 的再生实心砖。由于功能单位 1t 建筑废物中只有 700kg 旧建筑拆除固体废弃物进行就地式资源化。并且按照表 1 中，700kg 旧建筑拆除固体废弃物中，只有混凝土和砂浆 300.8kg 与砖、砌块、石材、陶瓷和瓦片 283.3kg，共计 584.1kg，可以采用移动式建筑废物资源化设备生产再生产品。根据文献【16】研究，该套系统的合格出骨料率为 80%。由表 9 可以得知，使用 292.05kg 的建筑废物的材料消耗为 233.64kg 再生骨料，31.93kg 硅酸盐水泥，4.91kg 矿渣，2.46kg 石膏，35.48kg 水。并产生 58.41kg 不能利用的残土，本文假设这些残土用于本地开发项目回填料使用。

（2）能源消耗

①电力消耗

从表 10 中可以看出，就地资源化处理阶段能源消耗主要是建筑废物再生产品设备的电力消耗。功能单位 1t 建筑废物只有 584.1kg 的建筑废物参与就地式资源化模式。则采用就地资源化方式处理所消耗电能：

（1800kWh+1200 kWh）÷（50t/h×8h）×58.41%=4.38kWh/t

②燃油消耗

就地资源化处理阶段能源消耗另一组成部分为装载机和叉车的燃油消耗。参照表 7 所示，本次研究将按照 15L 计算装载机和叉车耗油量。功能单位 1t 建筑废物只有 584.1kg 的建筑废物参与就地式资源化模式。则采用就地资源化方式处理所消耗柴油：

（15L/h×8h×2）÷（50t/h×8h）×58.41%=0.351L

（二）运输阶段的环境清单

综合式资源化模式运输阶段与直接模式的处理模式是一致的，只是运输数量发生变化。按照综合式资源化模式设计，需要运输的建筑废物主要包括两个部分：一个部分是旧建筑拆除固体废弃物中其他类 31.15kg；另一部分就是需要集中式资源化的新建筑施工固体废弃物和装修固体废弃物，约计 300kg。运输过程同样是按 20 公里计算运输距离，采用 25t 渣土运输车进行运输，同时借鉴 GaBi 软件数据库中全球通用的相关运输车辆和燃油排放数据标准作为运输阶段能耗标准。

（三）集中资源化阶段的环境清单

综合式资源化模式集中资源化阶段与集中式建筑废物模式的处理模式是一致的，只是数量发生变化。按照综合式资源化模式设计和表 1 中，可以得知功能单位 1t 建筑废物中有 266.52kg 的建筑废物需要运输至集中资源化场地进行处理。主要包括两个环节，全部 266.52kg 的建筑废物要经过预处理环节，除 13.35kg 其他类建筑废物需要填埋处理外，其余的一半约 129.9kg 的建筑废物都必须要通过采取集中资源化的方法进行处理。

（1）物质消耗

就集中资源化的过程里，物质消耗主要存在于生产再生免烧免蒸砖工艺上。由表 8 可以得知，使用 129.9kg

的建筑废物的材料消耗为 119.97kg 再生骨料，17.755kg 硅酸盐水泥，2.73kg 矿渣，1.365kg 石膏，19.725kg 水。并产生 9.935kg 不能利用的残土。

（2）能源消耗

集中资源化阶段的能源消耗主要是预处理和再生资源化两个环节产生的。每个环节的能源消耗都包括电力消耗和燃油消耗两种类型。

①电力消耗

由第 4.3 节可知处理 1t 建筑废物用于生产免烧免蒸砖，预处理环节需要消耗电力为 1.266kWh，资源化环节需要消耗电力为 1.720kWh。按照生产质量比例换算为：

预处理环节需要消耗电力为 1.266kWh×（259.80÷843.90）=0.462kWh；

资源化环节需要消耗电力为 1.720kWh×（129.90÷405.95）=0.550kWh

因此，固定资源化阶段的电力消耗合计为：1.012kWh。

②燃油消耗

由第 4.3 节可知处理 1t 建筑废物用于生产免烧免蒸砖，预处理环节需要消耗燃油 0.238L，资源化环节需要燃油为 0.158L 按照生产质量比例换算为：预处理环节需要消耗燃油为 0.238L×（259.8÷843.90）=0.073L；

资源化环节需要消耗燃油为 0.158L×（129.9÷405.95）=0.051L；

因此，集中资源化阶段的电力消耗合计为：0.073L+0.051L=0.124L。

（四）残土处理阶段的环境清单

综合式资源化模式残土填埋与集中式建筑废物模式的处理模式是一致的，只是数量发生变化。功能单位 1t 建筑废物中需要填埋的主要包括建筑废物中其他类 44.5kg 和集中资源化后产生的残土 19.87kg，共计 64.37kg。同样是借鉴 GaBi 软件数据库中相关建筑废物填埋数据标准作为填埋阶段的能耗标准。

（五）建立综合式资源化模式清单的 GaBi 软件方案

如前文所述，济南市建筑废物综合式分类处理处置模式分为就地式资源化和集中资源化两个互不干涉和同时进行的部分。根据这个特点，综合式资源化模式的 GaBi 软件方案也分为就地式资源化和集中资源化两个部分分别计算。其中包含了两个部分所涉及运输环节和各自的残土处理。具体方案如图 4 和图 5 所示。

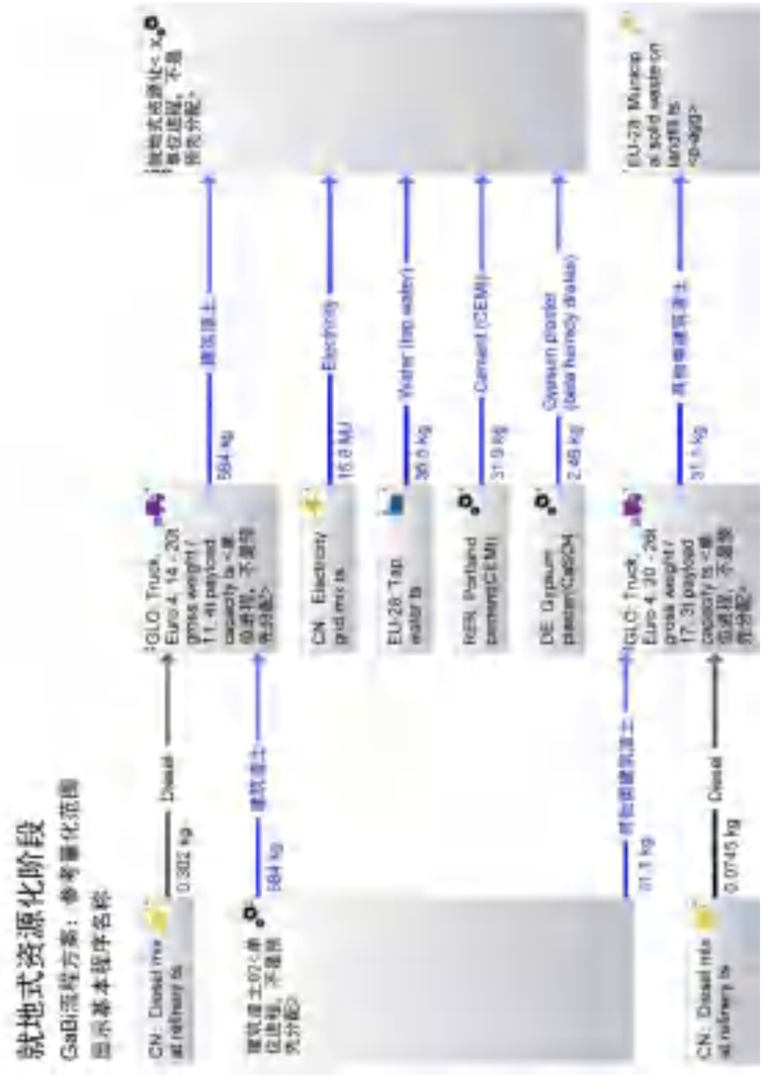

图 4　就地式资源化阶段的 GaBi 软件方案

Fig.4　The GaBi plan of Local recycling stage

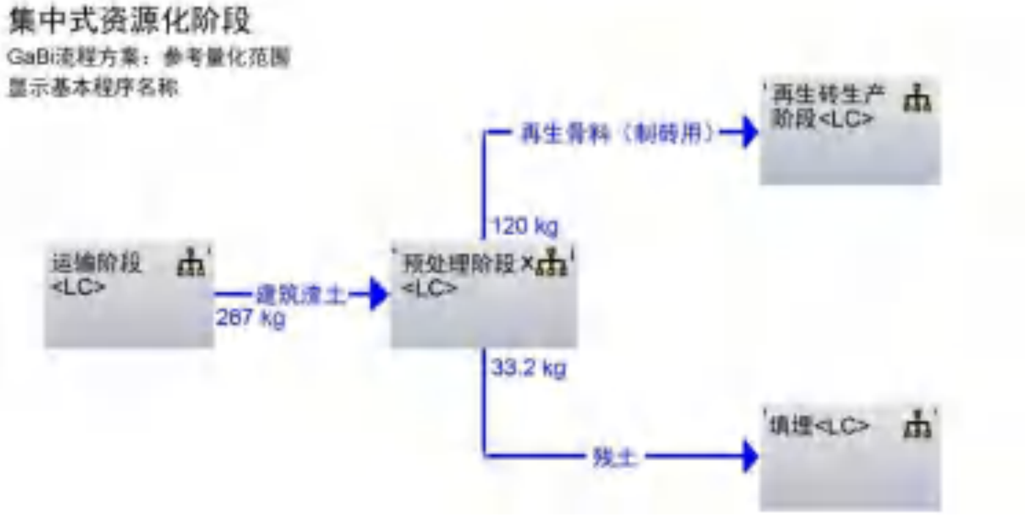

图 5　集中式资源化阶段的 GaBi 软件方案

Fig.5 The GaBi plan of Centralized recycling stage

5、济南建筑废物处理处置模式全生命周期环境影响研究结果

结合第 4 节对三种建筑废物处理处置模式清单分析结果，运用 GaBi 软件分析三种建筑废物处理处置模式的进行生命周期评价结果。按照第 4.2.3 节所建立的济南市建筑废物处理处置模式生命周期评价模型，首先对三种建筑废物处理处置模式选定酸化（AP）、富营养化（EP）、全球变暖（GWP）、人类毒性（HTP）、光化学臭氧合成（POCP）等五类指标进行研究；其次将每个类型的排放物进行特征化换算；最后再将特征化结果进行标准化处理，比较出三种建筑废物处理处置模式生命周期评价结果的优劣。

5.1 特征化

特征化的目的在于将不同排放物对环境影响的差异，比照相应环境影响类型下的参照物，统一转化成可以比较的环境影响值。特征化主要与污染物排放量与参照物的当量因子有关。本次研究采用 CML2001-Jan.2016，world 评价标准中的特征因子，运用生命周期评价特征化方法分析了三种建筑废物处理处置模式的环境影响，其分析结果如表 11 所示。

表 11 综合式资源化模式特征化结果

Tab.11 Characteristic results of comprehensive recycling model

序号	环境影响类型	标准参照物	单位	就地式阶段	集中式阶段	综合式资源化
1	CML2001-Jan.2016 酸化（AP）	SO_2	kg	0.100323	0.0512029	0.1515259
2	CML2001-Jan.2016 富营养化（EP）	磷酸盐（PO_4^{3-}）	kg	0.0360308	0.0199451	0.0559759
3	CML2001-Jan.2016 全球变暖（GMP）	CO_2	kg	61.7266	33.3962	95.1228
4	CML2001-Jan.2016 人体毒性（HTP）	二氯苯（DCB）	kg	6.00221	3.06001	9.06222
5	CML2001-Jan.2016 光化学毒性（POCP）	乙烯（Ethene）	kg	0.0122274	0.00698326	0.01921066

表 12 特征化结果

Tab.12 Characterization results

序号	环境影响类型	标准参照物	单位	直 接填埋式	集中式资源化	综合式资源化
1	CML2001-Jan.2016 酸化（AP）	SO_2	kg	1.51608	0.163823	0.1515259
2	CML2001-Jan.2016 富营养化（EP）	磷酸盐（PO_4^{3-}）	kg	0.1440935	0.122295	0.0559759
3	CML2001-Jan.2016 全球变暖（GMP）	CO_2	kg	1553.66	164.694	95.1228
4	CML2001-Jan.2016 人体毒性（HTP）	二氯苯（DCB）	kg	25.0552	8.80241	9.06222
5	CML2001-Jan.2016 光化学毒性（POCP）	乙烯（Ethene）	kg	0.308372	0.0346856	0.01921066

5.2 标准化

表 13　综合式资源化模式标准化结果
Tab.13 Normalization results of Comprehensive recycling model

序号	环境影响类型	标准参照物	单位	就地式阶段	集中式阶段	综合式资源化
1	CML2001-Jan.2016 酸化（AP）	SO_2	kg	4.1976E-13	2.14238E-13	6.33998E-13
2	CML2001-Jan.2016 富营养化（EP）	磷酸盐（PO_4^{3-}）	kg	2.28043E-13	1.26235E-13	3.54278E-13
3	CML2001-Jan.2016 全球变暖（GMP）	CO_2	kg	1.46272E-12	7.91379E-13	2.25410E-12
4	CML2001-Jan.2016 人体毒性（HTP）	二氯苯（DCB）	kg	2.32644E-12	1.18605E-12	3.51249E-12
5	CML2001-Jan.201 光化学毒性（POCP）	乙烯（Ethene）	kg	3.32266E-13	1.89762E-13	5.22028E-13
6	合计		kg	4.76923E-12	2.50766E-12	7.27689E-12

表.14　标准化结果
Tab.14 Normalization results

序号	环境影响类型	标准参照物	单位	直接填埋式	集中式资源化	综合式资源化
1	CML2001-Jan.2016 酸化（AP）	SO_2	kg	6.34343E-12	7.03523E-13	6.33998E-13
2	CML2001-Jan.2016 富营养化（EP）	磷酸盐（PO_4^{3-}）	kg	6.79073E-13	6.57613E-13	3.54278E-13
3	CML2001-Jan.2016 全球变暖（GMP）	CO_2	kg	3.68165E-11	3.56043E-12	2.25410E-12
4	CML2001-Jan.2016 人体毒性（HTP）	二氯苯（DCB）	kg	9.7113E-12	3.41929E-12	3.51249E-12
5	CML2001-Jan.2016 光化学毒性（POCP）	乙烯（Ethene）	kg	8.37967E-12	7.88211E-13	5.22028E-13
6	合计		kg	6.19300E-11	9.12907E-12	7.27689E-12

得出特征化值后，需要将特征化结果进行标准化处理，以便比较三种建筑废物处理处置模式环境影响的优劣。本次研究采用表 3 中所列的 CML2001-Jan.2016，world 评价标准中的量化基准值，将酸化（AP）、富营养化（EP）、全球变暖（GWP）、人类毒性（HTP）、光化学臭氧合成（POCP）等五类指标归一量化，以便进行比较。具体结果如表 13 和表 14 所示。

6、济南市建筑废物处理处置模式全生命周期结果分析与讨论

从表 12 中可以看出三种建筑废物处理处置模式在各个环境影响的特征值大小。通过对比可以发现，直接填埋造成环境影响最严重，而本文构建的济南市建筑废物综合式处理处置模式造成的环境影响最小。按照处理处置功能单位 1t 建筑废物计算，与直接填埋模式相比，综合式资源化模式可以减少酸化气体排放 1.365Kg（SO_2当

量），富营养化物质 0.088Kg（PO_4^{3-}当量），温室气体排放 1458.537Kg（CO_2当量），人体毒性物质 15.993Kg（DCB 当量），光化学毒性物质 0.289kg（Ethene 当量）。与集中式资源化模式相比，综合式资源化模式可以减少酸化气体排放 0.012Kg（SO_2当量），富营养化物质 0.066Kg（PO_4^{3-}当量），温室气体排放 69.571Kg（CO_2当量），人体毒性物质-0.260Kg（DCB 当量），光化学毒性物质 0.015kg（Ethene 当量）。

经过标准化处理后，三种建筑废物处理处置模式处理处置功能单位为 1t 建筑废物的全生命周期的总环境负荷指数分别是直接填埋模式为 6.19×10^{-11}；集中式资源化模式为 9.13×10^{-12}；综合式资源化模式为 7.27×10^{-12}。针对三种建筑废物处理处置模式所造成环境负荷值进行排序为：直接填埋模式>集中式资源化模式>综合式资源化模式，具体详见表 3.14。这充分说明在环境影响方面比较三种建筑废物处理处置模式，综合式资源化对环境影响最小。采用综合式资源化模式，相对直接填埋模式，可以有效降低酸化物质排放（AP）90.01%；富营养化物质排放（EP）47.83%；全球变暖物质排放（GMP）93.88%；人体毒性物质排放（HTP）63.83%；光化学毒性物质排放（POCP）93.77%。相对集中式资源化模式，可以有效降低酸化物质排放（AP）9.88%；富营养化物质排放（EP）46.13%；全球变暖物质排放（GMP）36.69%；人体毒性物质排放（HTP）-2.73%；光化学毒性物质排放（POCP）33.77%。由此可见采用综合式资源化模式对减少环境影响最大的贡献是能有效减少全球变暖物质、酸化物质和光化学毒性物质排放。

针对综合式资源化模式，比较不同环境影响类别所造成的环境影响标准值，然后进行排序得到：酸化物质>光化学毒性物质>富营养化物质>人体毒性物质>温室气体，具体详见表 14。说明综合式资源化模式在造成的环境影响中对酸化物质的影响是最大的，其次是光化学毒性物质和富营养化物质。从清单分析中可以看出，水泥是造成综合式资源化模式对环境排放酸化物质和光化学毒性物质的主要原因。今后应改进再生资源化工艺，尽量减少水泥用量，以降低对环境的影响。

综上所述，通过对比三种常用的建筑废物处理处置模式生命周期评价结果发现，建筑废物综合式资源化模式是一种最为环境友好的建筑废物处理处置模式。

7、小结

（1）本章基于济南市建筑废物年产量的特点和所构建的济南市建筑废物综合式分类处理处置模式，运用生命周期评价法，建立了济南市建筑废物处理处置模式生命周期评价模型。

（2）针对目前常用的直接填埋模式和集中式资源化模式，以及本文构建的综合式资源化模式，进行对比分析。经过目标和范围确定、清单分析、环境影响评价和结果解释各个生命周期评价环节，得出了对比结果。

（3）通过运用 GaBi 软件计算，得出三种建筑废物处理处置模式处理处置功能单位为 1t 建筑废物的全生命周期的总环境负荷指数分别是直接填埋模式为 6.19×10^{-11}kg；集中式资源化模式为 9.13×10^{-12} kg；综合式资源化模式为 7.27×10^{-12} kg。最终得出从环境影响方面，本文所构建的综合式资源化模式是目前最适合济南市建筑废物处理处置的环境友好型的方式。

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中国钢结构产业可持续性分析

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摘 要：随着社会的进步和经济的发展，钢结构建筑得到了快速普遍应用，成为主流的建筑类型。但是，过去对于钢结构产业发展的可持续性缺乏系统性评估，对其环境影响及资源产率也有待进一步挖掘。本文选择全国西部、东北和中部地区 15 个钢结构建筑设施，首先基于物质流分析理论，剖析钢结构建筑物质流动过程中输入、输出物质种类和质量。结合钢结构建筑所产生的经济价值，揭示钢结构资源产率。利用灰色模型对未来钢结构中关键物质钢铁需求量进行预测，确定未来钢结构发展潜力。生命周期评价是一种评价产品从“摇篮到坟墓”整个生命周期过程对环境影响的方法。基于钢结构生命周期物质输入和物质输出的种类和质量，并借助 Gabi 软件中的 CML 方法估算钢结构生命周期对环境影响的种类和特征化值。结果显示，我国西部地区、东北地区、中部地区钢结构建筑资源产率分别为 1354.3 元/t、978.7 元/t、1432.2 元/t；生命周期评价表明钢结构对环境的影响有四类，分别为环境酸化、富营养化、温室效应、光化学氧化剂产生能力。钢结构建筑中关键物质钢铁不回收利用，钢结构生命周期对环境影响最大阶段发生在钢铁生产阶段；如果实施循环经济回收利用钢铁，钢结构生命周期对环境影响发生在钢结构加工阶段。通过对钢结构中关键物质钢铁进行回收再利用和不回收进行情景对比，发现将钢结构中钢铁回收再利用，钢结构产业生命周期对环境的影响可显著降低。

关键词：可持续性；钢铁；废物管理；循环经济;中国

Measuring the Sustainability of China’s Steel Structure

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Abstract: With the development of the human society and economy, the buildings, which are closely related to human life, have developed into a diversified direction. The materials used in the earliest buildings were mainly wood or clay. Up to now, it has undergone tremendous change and includes concrete buildings, reinforced concrete buildings, and steel structure buildings. The steel buildings are rapidly applied, due to its high strength and conveniently installation. However, there is still lack of the systematical evaluation about sustainability of steel structure buildings in terms of environmental and economic performance. Therefore, it is crucial to investigate the efficiency of steel structure resources and the environmental impact of steel structure life cycle.

Material flow analysis is conducted to analyze the types and quality of materials input and output during the material flow of steel structure buildings. Combined the economic value generated by steel structure buildings, the efficiency of steel structure resources is revealed. Life Cycle Assessment is a method to study the environmental impact of the whole life cycle process from cradle to grave. Based on the analysis of the steel structure life cycle material input and output, the type and characterization value of the steel structure life cycle environmental impact are calculated using the CML method in Gabi software to calculate.

According to the calculation results, the resource productivity of steel structure buildings in northwest China, northeast China and central China is 1354.3 yuan/t, 978.7 yuan/t and 1432.2 yuan/t, respectively. Depending on the Gray Model, the demand of steel in China's steel structure would exceed 100 million tons in 2023. The results of Gabi calculations indicate that the environmental impact of the steel structure includes four types, such as environmental acidification, eutrophication, greenhouse effect and photochemical oxidant production capacity. If the key steel material in the steel structure buildings is not recycled, the most important stage of the life cycle environmental impact of the steel structure occurs in the steel production stage. Otherwise, it occurs during the steel structure processing stage. Through the comparative analysis of the recycling and non-recycling of the key steel materials in the steel structure, the impact of the steel structure life cycle on the environment would be greatly reduced when the steel in the steel structure is recycled. In this study, the efficiency of steel structure resources in northwest, northeast and central regions of China were calculated. Moreover, the factors which affect the efficiency of steel structure resources were evaluated by the sensitivity analysis. The study on the environmental impact of steel structure life cycle indicate that the main source of the environmental damage is caused by the stage of steel production. Effective recycling of steel in steel structure buildings is helpful to reduce life cycle environmental hazards.

Key words: sustainability; steel; waste management; circular economy; China

我国目前正处在快速工业化和城镇化阶段，对资源的需求巨大，以往我国用大量的资源消耗来换取经济发展。随着现代化进程的推进，我国面临的资源和环境问题更加严峻，为实现可持续发展的战略目标，必须提高自然资源的效率，追求用少的资源投入，获得更高的经济价值[1, 2]。在尽可能减少资源消耗，同时获得最大经济效益产出和最少的废物排放，减小给自然环境带来的负担。

钢铁的生产属于高耗能、高污染产业。在满足我国人民生活需求的前提下，避免我国矿产资源被过度开发，符合国家对环境保护重视的要求，提高钢铁资源产率是最有效的方法[3]。为了钢结构企业的稳定发展并且获得一定的经济利润，必须提高钢结构建筑的资源产率，包括材料资源、人工资源、机械资源和物流资源等[4, 5]。经济的发展与人均钢铁需求量具有一定的关系，目前我国的发展现状决定了未来几年我国的钢铁需求量仍然很大。国家“十三五规划”中提出，钢铁去产能的一种方式是发展钢结构建筑，实现供给侧改革，同时提出 2020 年钢结构建筑钢铁使用量占新增建筑总用钢量的 25%，而目前仅占 10%[6]。从国家的政策来看，未来我国钢结构建筑将会得到大力推广。欧洲等发达国家随着经济的增长钢铁的需求量反而有下降趋势，与我国随着经济的发展钢铁需求量持续增加相比较，说明我国钢铁资源产率低于发达国家钢铁的资源产率[7]。钢结构建筑与传统的混凝土建筑或者钢筋混凝土相比较属于绿色建筑，我国近年来对环境的重视进一步促使钢结构建筑的发展。

综上所述，探索钢结构建筑的发展，对钢铁资源产率的提高和环境效益的改善具有重大意义。本文将研究钢结构建筑的资源产率和钢结构建筑生命周期内对环境的影响，我国钢结构建筑与国外钢结构建筑相比较资源利用效率、产业结构和质量效益等方面还有一定的差距[8]。所以提高钢结构建筑资源产率和确定钢结构建筑生命周期环境影响，对推动钢结构发展具有积极意义。

1 数据和方法

1.1 数据收集

我国钢结构中轻钢钢结构占钢结构总量约为 60%，大跨度空间钢结构占钢结构总量约为 30%，其他种类钢结构占钢结构总量约为 10%，因此本文选取轻钢钢结构建筑为例研究我国钢结构建筑资源产率和环境影响。本文作者张元林参与了我国实际钢结构建筑行业的 15 个案例，获得了一手的资料，其中我国西部、东北和中部各 5 个项目。各项目的相关数据如表 1 所示。

表 1 我国 15 个钢结构建筑行业的实际数据

区域	项目	面积（m^2）	经济利润（元）	资源消耗量（t）					
				化石能源	矿物	生物质	氧气	水	总和
西部地区	X_1	2594	313000	16.3	197.9	7.8	39.1	154.3	415.4
	X_2	8880	693000	50.3	430.7	15.6	120.7	399.5	1016.8
	X_3	3600	327000	22.6	201.7	8.7	54.2	178.2	465.4
	X_4	3467	255000	12.4	156.6	5.5	29.7	154.2	358.4
	X_5	1387	243000	17.3	196.5	7.5	41.5	136.1	398.9
东北地区	X_6	6715	931000	59.4	608.3	16.7	142.6	539.9	1366.9
	X_7	1080	135000	5.9	157.2	3.8	14.2	177.9	359
	X_8	2520	324000	7.6	249.1	8.1	18.2	350.5	633.5
	X_9	1050	101000	5.6	139.5	2.6	13.4	156.7	317.8
	X_{10}	4620	572000	28.1	293.6	11.1	69.8	444.7	847.3
中部地区	X_{11}	4831	609000	47.3	369.8	13.5	113.5	336.4	880.5
	X_{12}	3730	428000	29.6	279.3	9.2	71.1	211	600.2
	X_{13}	4550	585000	32.5	344.7	11.2	78	228.6	695
	X_{14}	7000	787000	53.7	520	15.2	128.8	369.9	1087.6
	X_{15}	1795	17000	8.5	93.12	7.6	20.4	83.6	213.22

本文基于 Gabi 计算钢结构生命周期对环境产生的影响，Gabi 计算所需要的钢铁生产过程和环境影响数据来源于我国研究者王腊芳和张莉沙等收集数据[9]以及炼钢工业大气污染物排放标准；岩棉生产过程清单和环境影响清单采用我国研究者刘富成和赵薇等收集的数据以及国家关于工业炉窑大气污染物排放标准和大气污染物综合排放标准；钢结构建筑加工数据来源于企业内部；其它非主要数据采用 Gabi 数据库中数据，例如生命周期各阶段运输数据。

1.2 研究方法

（1）物质流分析（Material Flow Analysis）：本文研究钢结构建筑物质输入的空间边界为项目的“围墙”，即整个项目为边界。钢结构建筑物质输入的时间边界有三种尺度：（1）由原材料生产加工至成品；（2）成品到报废回收，包括产品的使用、产品维修、产品的回收利用等；（3）生命周期，包括原材料加工至成品、产品使用、产品维修、产品回收利用等。本文研究钢结构建筑的时间边界为（1），为了满足由原材料生产加工至成品与自然资源经济系统的物质交换，包括投入物质、储存物质、输出物质。钢结构建筑物质流分析框架如图 1。物质随着钢结构建筑加工工艺流动而“向下流动”，不断有新物质输入到经济系统中，同时排放出有害物质到自然环境

中。左端为输入端，包括化石燃料、矿物质、生物质、隐藏流以及水分和氧气；中间部分为经济系统的储存；右端为输出端，包括废水污染物、废气污染物、固体污染物、废钢、隐藏流以及氧气和水分。针对物质流分析指标进行分类，首先要了解都有哪些物质输入，物质伴随着钢结构建筑加工工艺流动，每一步工序都有物质的输入、储存、输出。

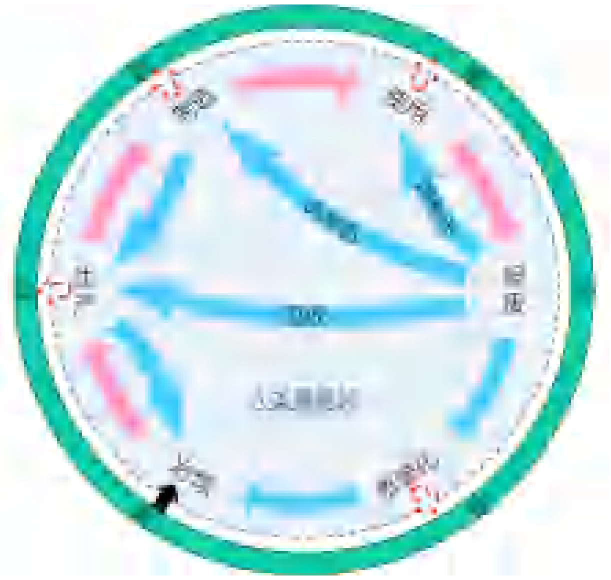

图 1 钢铁生产加工的全生命周期

Figure 1 The whole life cycle steel product. Note: adapted from Zeng and Li (2018) [10].

（2）资源产率（Resource Productivity）评估：资源产率的概念在不同的场合意义略有不同，这里我们采用联合国普遍的定义，资源产率是单位质量资源投入带来的经济增长贡献，单位为元/t 物质，与资源强度（Resource Intensity）成反比[11, 12]。

（3）生命周期评价（Life Cycle Assessment）：生命周期评价适用于制造业决策者关于产品、过程或者政策的合理制定[13]。本文针对钢结构建筑生命周期环境影响评价借助 Gabi 进行，计算钢结构生命周期各类环境影响特征化值。本文研究钢结构建筑对环境的影响，研究范围为钢结构建筑生命周期对环境影响（图 1）。生命周期评价研究是原材料生产过程、产品制作过程、产品使用过程、产品报废过程以及整个生命周期对环境的影响，从而确定生命周期各阶段给环境带来的负担，并针对环境危害较大的阶段加以控制，实现可持续发展。

2 结果分析

2.1 钢结构建筑中关键资源的物质流分析

通过数据收集和转化计算，钢结构建筑中关键物质为钢铁。钢铁由钢厂生产后，经过运输阶段和钢结构加工阶段，最终形成钢结构建筑成品。对西部地区 5 个案例（建于 2010-2015 年）进行分析，得到钢铁生产、加工、消费、废弃的物质流如图 2 所示，共有 1185t 的钢铁流向加工生产阶段，其中接近 95%进入钢结构建筑中使用，5%成为废钢铁（New scrap）。

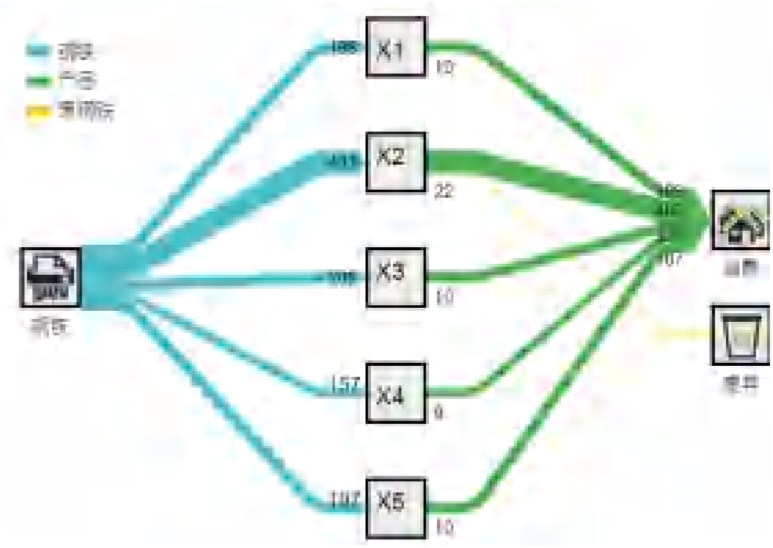

图 2 中国钢结构建筑中钢铁生产消费废弃的物质流分析图（t）

Figure 2 Analysis of steel material flow in Chinese steel structures

考虑钢结构建筑中的所有材料消耗，如矿物、化石能源、生物质、氧气和水（表 1），物质流分析主要体现了钢结构建筑过程中对资源消耗的程度。矿物与水是生产钢结构建筑的主要原料，平均消耗量在 200t 以上，其中中部地区的矿物资源平均利用量略高于东北地区和西北地区，生物质与化石能源消耗最少，平均都低于 20t 以下（图 3a）。从全国来看，钢结构建筑中单位建筑面积资源消耗量中，从高到低排序为矿物、水、氧气、化石能源、生物质，因为矿物及化石能源为不可再生资源，格外受到关注，单位面积矿物的消耗量为 240kg，化石能源的消耗量为 20kg（图 3b）。

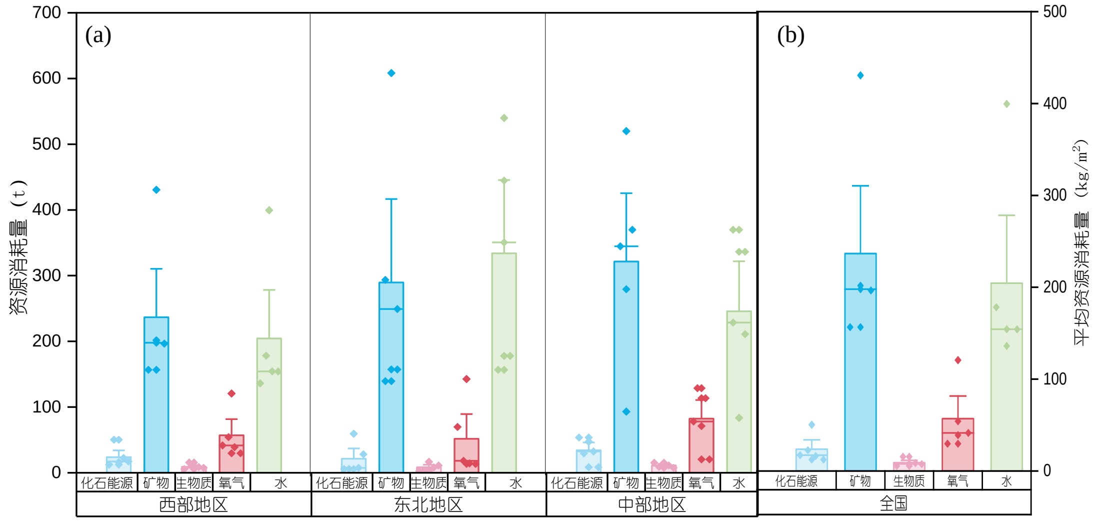

图 3 钢结构建筑的各种资源消耗. （a）不同地区资源消耗量；（b）全国单位面积资源消耗量.

Figure 3 The consumption of various resources in the steel structure building. (a) resource consumption in different regions; (b) average resource consumption per area.

进一步分析发现，每百平方米东北地区的矿物质消耗量最大为 10.68t，产生这种现象的原因有两种，第一种是结构设计不合理，从而导致不必要的材料浪费；第二种是施工过程中管理比较低下，造成过多的材料浪费。

单位面积东北地区化石能源消耗量最小为 0.75t，因为钢结构建筑建造所使用的材料运输距离比较短，运输所使用的化石能源较少。单位面积上东北地区物质的消耗量最大为 25.47t 且其数值是另外两地区 1.6 倍，其他两地区数值比较接近。

2.2 我国不同区域钢结构建筑资源产率评估

通过上述计算，得到了东北地区、西部地区和中部地区钢结构建筑资源产率；不同地区钢结构建筑矿产资源、化石能源和生物质的所占比例。根据东北地区、西部地区和中部地区钢结构建筑直接输入物质所占比例绘制出占比图形（图 4），结果显示，我国西部和中部地区钢结构建筑资源产率接近，分别为 1354.3 元/t 和 1432.2 元/t,。但是，东北地区钢结构建筑资源产率比较低为 978.7 元/t。这种结果与国家推行西部大开发相关，西部地区大部分钢结构工程项目都是由东部地区钢结构公司来承接，导致两地区钢结构建筑资源产率比较接近。

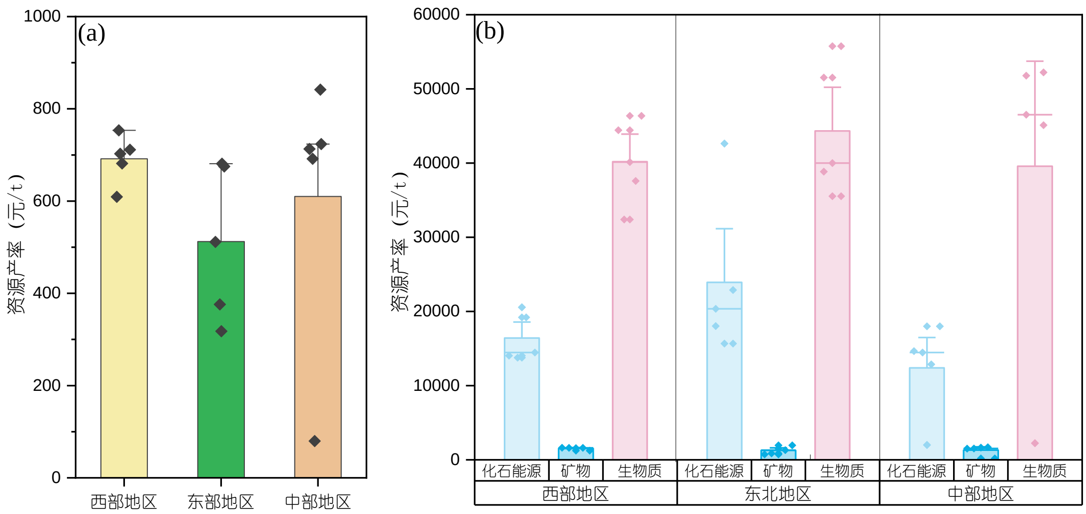

图 4 不同地区钢结构建筑资源产率. (a) 总资源产率；（b）三种物质的资源产率.

Figure 4 Resource productivity of the steel structure building in various regions. (a) total resource productivity; (b) resource productivity of three materials.

直接输入物质有化石能源、矿物和生物质这三种，其中矿物所占的比例最大（图 4）。钢结构建筑建设过程，主要消耗的矿物质是钢铁，钢铁的用量直接决定了钢结构建筑资源产率的高低。三个地区相比较，相同建筑面积条件下，东北地区钢铁用量最高。钢铁用量取决于设计水平、加工制作技术水平和管理能力。所以东北地区目前应该采取相应措施减少钢铁的使用量。西部地区和中部地区钢结构建筑资源产率比较接近。但是，钢铁的使用量有一定的差距，这种现象的产生与进入厂区原材料的结构形式有一定的关系。化石能源占比最小的是东北地区，中部地区和东部地区化石能源占比接近，所以中部地区和西部地区应当减少钢铁的运输距离和项目建设过程中能源消耗。

2.3 钢结构生命周期环境影响

环境影响归一化结果表明（图 5）：第一，钢结构建筑生产加工过程环境影响总量为 1.74E-9，其中酸化潜力为 1.77E-10、富营养化潜力 3.95E-10、全球变暖潜力 1.89E-10、光化学氧化剂生成潜力 7.36E-10；第二，钢结构

建筑生命周期过程，对环境影响最大阶段为钢铁生产阶段，对环境潜在影响占比 73.15%。其次岩棉生产和钢结构加工安装过程对环境的影响基本相当，分别为 12.41%和 13.70%；第三，生命周期过程对环境影响从大到小分别为全球变暖潜力、酸化潜力、光化学氧化剂生成潜力、富营养化潜力（图 5），其中对环境影响最大的全球变暖占比 41.26%，其次为酸化潜力和光化学氧化剂生成潜力占比分别为 25.73%和 24.97%，环境影响最小的为富营养化潜力占比 8.04%；第四，全球变暖影响阶段主要在钢铁生产和岩棉生产阶段，酸化影响阶段主要在钢铁生产和钢结构加工安装阶段，光化学氧化剂生成影响阶段主要在钢铁生产和钢结构加工安装阶段，富营养化影响阶段主要在钢铁生产和钢结构加工阶段。

通过上述分析，钢结构生命周期环境危害最大的阶段发生在钢铁生产过程中。因此，为减小钢结构生命周期对环境的危害，应该控制钢铁生产阶段对环境的危害。其主要的环境危害是全球变暖，引起全球变暖主要原因为 CO_2 的超量排放，应该控制该气体向大气中排放。控制钢结构生命周期对环境危害，除了采取必要的环保措施外，满足使用条件前提下，用高强度钢铁 Q345 替代 Q235，达到减少钢铁使用的目的。

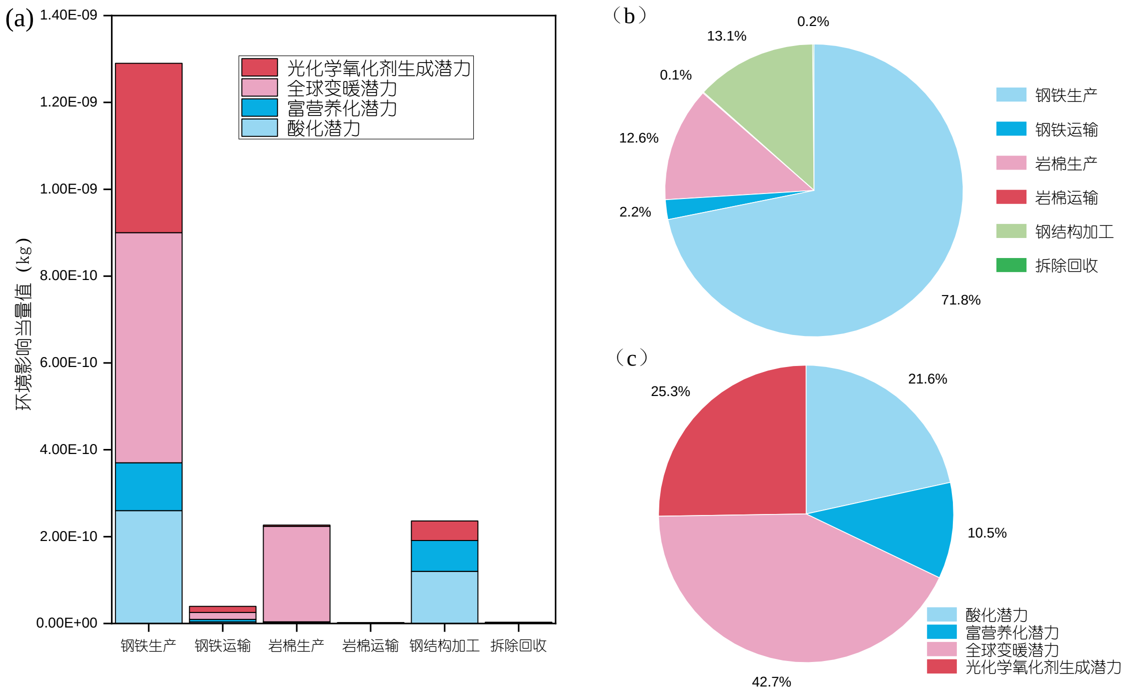

图 5 钢结构建筑生命周期环境影响. （a）归一化结果；（b）不同阶段环境影响占比；（c）不同环境影响占比

Figure 5 The environmental impact of the steel structure building life cycle. (a) Normalized results; (b) Environmental impacts at different stages of the life cycle; (c) Percentage of environmental impacts.

如果对钢铁进行回收再利用，钢结构建筑生命周期环境影响归一化结果（如图 6）：第一，钢结构建筑生产加工过程环境影响总量为 6.93E-10，其中酸化潜力为 1.33E-10、富营养化潜力 9.65E-11、全球变暖潜力 3.19E-10、光化学氧化剂生成潜力 1.01E-11；第二，环境影响最大的为钢结构加工安装过程，占环境影响总量的 34.49 %；第三，环境影响由大到小分别为全球变暖潜力 GWP、酸化潜力 AP、富营养化潜力 EP、光化学氧化剂生成潜力 POCP（图 6），其中影响最大的为全球变暖潜力占比 46.04%；第四，全球变暖主要发生在岩棉生产阶段，酸化主要发生在钢结构加工阶段，富营养化发生在钢结构加工安装过程，光化学氧化剂生成钢结构加工安装阶段。

钢结构建筑钢铁不进行回收利用与回收利用对环境的影响相比较，钢结构建筑建筑材料钢铁进行回收再利用可以大幅降低钢结构建筑对环境的影响总量。其中引起环境危害降低的原因主要钢铁生产过程中产生的环境负担减小。所以为了进一步减小环境的危害，钢结构建筑应该注意钢铁材料的回收或者钢结构建筑的重复利用。钢结构建筑的钢铁进行回收利用前提下，钢结构建筑生命周期对环境影响比较大的为钢结构建筑加工过程和岩棉的生产过程，在此情况下，我们应该关注岩棉生产和钢结构建筑加工过程带来的环境危害。

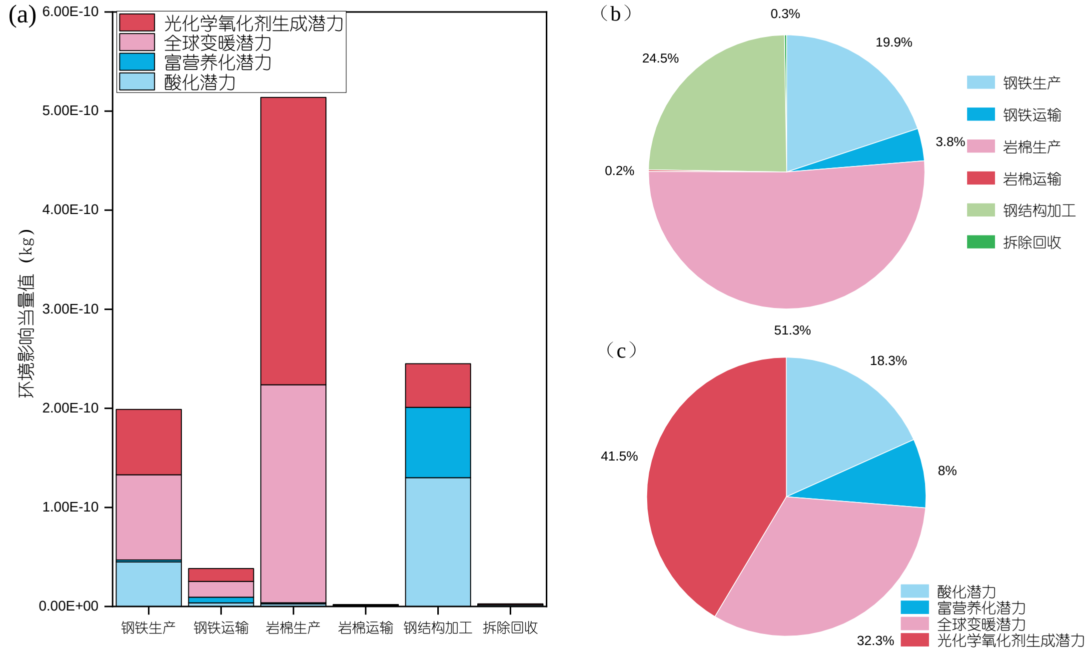

图 6 考虑钢铁回收利用的钢结构建筑生命周期环境影响. （a）归一化结果；（b）不同阶段环境影响占比；（c）不同环境影响占比

Figure 6 The environmental impact of the steel structure building life cycle with the recycling. (a) Normalized results; (b) Environmental impacts at different stages of the life cycle; (c) Percentage of environmental impacts

3 讨论

3.1 钢结构产业环境影响

本文研究钢结构建筑生命周期对环境的影响以轻型钢结构为例进行研究，与早期研究者研究钢结构建筑（大跨度钢结构、桥梁钢结构）对环境的影响和钢结构建筑与混凝土建筑进行比较分析，发现无论何种钢结构建筑对环境的影响比混凝土建筑对环境的影响小。无论何种钢结构建筑对资源的消耗比较大，能耗相对较小，对环境的影响主要发生在材料准备阶段和钢结构加工制造阶段。与早期学者王侠[14]等研究混凝土结构环境影响相比较，单位面积钢结构建筑化石能源消耗量是混凝土建筑的 91.4%，单位面积钢结构 CO_2 排放量是混凝土结构的 58.6%，单位面积钢结构含硫化合物排放量是混凝土结构的 90.1%，单位面积钢结构氮氧化合物排放量是混凝土结构的 63.9%。全现浇框架结构建筑、砖混结构建筑、钢结构建筑 A 与本文研究钢结构建筑 B 钢铁不回收利用和钢结构建筑 C 钢铁回收利用生命周期材料生产阶段、建造阶段、拆除回收阶段对环境影响特征化值如表 2 所示。

表 2 环境影响特征化值对比

Table 2 Comparison of characteristic values of environmental impact

建筑类型	材料准备阶段	建造阶段	拆除回收阶段	单位面积值
现浇框架结构	*3.98E-008*	*2.60E-009*	*1.17E-008*	*1.21E-011*
砖混结构	*5.04E-008*	*2.90E-009*	*7.08E-008*	*1.27E-011*
钢结构建筑 A	*5.19E-008*	*3.10E-009*	*6.76E-008*	*1.15E-011*
钢结构建筑 B	*9.00E-009*	*2.40E-010*	*2.70E-012*	*1.14E-011*
钢结构建筑 C	*4.40E-010*	*2.40E-010*	*2.70E-012*	*6.83E-012*

通过对表 2 钢结构与传统建筑生命周期各阶段环境影响特征化值，对比分析得出，如果钢结构建筑使用的钢铁不进行回收利用，生命周期内钢结构建筑 A 和钢结构建筑 B 在材料准备阶段、建造阶段、拆除回收阶段单位面积给环境带来负担略低于现浇筑框架结构和砖混结构，并没有较大的优势。但是钢结构建筑 C 是将钢铁回收利用生命周期给环境带来的负担远远小于现浇框架结构和砖混结构。所以钢结构相对于混凝土建筑来说，钢结构建筑对环境的危害小于混凝土建筑。这说明了从长远的角度来看，我们应该采用钢结构建筑替代传统的建筑，钢结构建筑属于绿色建筑。

3.2 钢结构建筑回收利用

目前我国关于钢结构建筑钢铁回收利用主要有两种方式，第一种方式由一些小型企业将钢结构建筑拆除并将其零部件进行翻新之后重新售卖；第二种回收方式和其它企业所产生的废旧钢铁一样进行回炉重新生产钢铁[15]。基于以上两种回收方式，我国目前关于钢结构建筑的回收利用还欠缺很多。针对于第一种由小型企业进行回收，回收技术比较落后主要采用火焰切割的方式将钢结构进行分割，分割过程中会造成部分组件的破坏，从而造成资源的浪费[16]。小型企业缺乏严格的质量检测能力，钢结构建筑再次利用存在严重的质量风险，国家应该制定相应法律制度和标准来约束钢结构建筑的回收。钢结构建筑所采用钢铁质量好于“地条钢”，如果将其混杂在一起进行回收利用，将会造成优质钢铁资源浪费[17]。近些年，我国大力推广钢结构建筑，未来若干年我国关于钢结构建筑所产生的废旧钢铁数量将会大大增加，按照目前钢结构建筑中钢铁回收方式必将无法满足未来需求。

为了使钢结构建筑中钢铁得到有效回收利用，建造过程中将非关键受力部件由焊接改为机械连接，不但可以减少建造过程中人力资源的消耗，还可以减少拆除过程中人力资源的消耗和提高部件再次使用效率。钢结构建筑设计采用标准化和工厂定制化生产，提高了零件部件的可替换性，从而使钢结构建筑钢铁的重复使用率得到提高。

4 结论

我国西部地区钢结构建筑资源产率为 1354.3 元/t，东北地区钢结构建筑资源产率为 978.7 元/t，中部地区钢结构建筑资源产率为 1432.2 元/t。提高钢结构建筑资源产率可以从设计出发合理布局结构减少钢铁使用，采用高强度材料减少材料的使用，加强生产过程管理，减少资源的浪费，循环利用自然资源，从而提高资源产率。

不考虑钢结构建筑中钢铁回收利用前提条件下，钢结构建筑生命周期过程中给环境带来的负担总量为1.74E-9，其中最大危害是全球气候变暖，占比达到41.26%，其次是酸化；考虑钢结构建筑钢铁回收再利用，钢结构建筑生命周期给环境带来的负担总量为 5.76E-10，其中最大的危害是全球变暖占比 47.32%，其次是酸化。减少对环境危害最有效的方法是控制钢铁材料的使用量或者加强钢结构建筑钢铁回收重复利用。

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废塑料废轮胎等化学降解成有机小分子化学品技术

Technology of Chemical Decomposition of Waste Plastics and Tires into Organic Small Molecular Chemicals

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摘要:

废塑料废轮胎等化学降解技术能将废塑料、废轮胎、废电线电缆料和废化纤纺织品等高分子废弃材料，采用温和化学降解的方法，逆向降解变成有机小分子化学品，从而使高分子废弃材料的处理实现无害化、资源化和循环化。

关键词:**废塑料，废轮胎，废电线电缆料，废化纤纺织品，高分子废弃材料，降解，无害化，资源化，循环化**

Abstract

Chemical decomposition technologies such as waste plastic, waste tires, waste wires and cables, waste chemical fiber textiles and other polymer waste materials can be decomposed into organic small molecule chemicals by mild chemical decomposition, so that the treatment of polymer waste materials can be harmless, resourceful and recycling.

Key words:**Waste plastics, waste tires, waste wires and cables, waste chemical fibers textiles, polymer waste materials, decomposition，harmless，reusable, recycling**

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0 引言

废旧的塑料、轮胎、化纤纺织品和电线电缆料等高分子废弃材料是恶化自然环境、破坏植被生长、影响人类健康、危及生态环境的**“白色污染”**（废塑料污染）、**“黑色污染”**（废轮胎污染）和**“彩色污染”**（废化纤纺织品和电线电缆料污染），这些高分子废弃材料在自然界中极难降解。如何处理这些高分子废弃材料呢？基本上是回收再生利用一部分，多数还是填埋、热解、焚烧。用这些方法处理，利用价值低、环境污染高、资源浪费大。当前，国家大力提倡发展循环经济，建设资源节约型和环境友好型社会，废塑料、废轮胎、废电线电缆料和废化纤纺织品等虽说是“白色污染”物、“黑色污染”物和“彩色污染”物，但这些高分子废弃材料也是可资利用的宝贵资源。我们采用温和化学降解的方法，可将这些“白色污染”物、“黑色污染”物和“彩色污染”物进行逆向化学降解无害化处理，并将其变废为宝，得到有机小分子化学品，得到新的化工原料，实现“原料==>产品==>消费==>废物==>**逆向化学降解**==>原料==>产品==>……”无限循环，实现“资源再生”和“循环利用”，完全符合国家大力提倡的发展循环经济，建设资源节约型和环境友好型社会，从而使**高分子废弃材料的处理做到无害处理零污染、变废为宝价值高、资源利用循环化**。

1、 试验

1.1 主要原材料及试验方法

主要原材料为废塑料、废轮胎、废电线电缆料和废化纤纺织品等高分子废弃材料，还有温和化学降解用的专用化学制剂。

试验方法为将废塑料、废轮胎、废电线电缆料和废化纤纺织品等高分子废弃材料，分别与各种高分子废弃物相适用的专用化学制剂加到反应釜中，在温度 350℃左右，压力为常压条件下，进行逆向化学降解反应，反应生成的蒸汽进入冷凝器冷凝成液体，此液体为以芳烃为主的有机小分子原料产品。反应釜中最后还剩有固体粉末状的有价值的炭类产品。

1.2 试验过程

1.2.1 试验工艺流程方块图

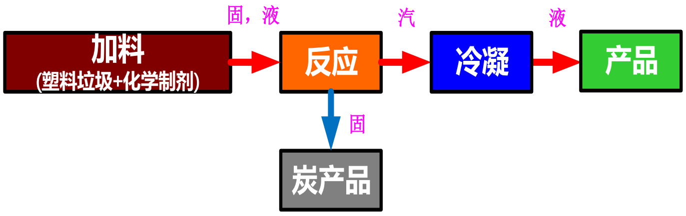


图 1、 试验工艺流程方块图

试验工艺流程主要有加料工序、反应工序、冷凝工序。

1.2.2 试验装置

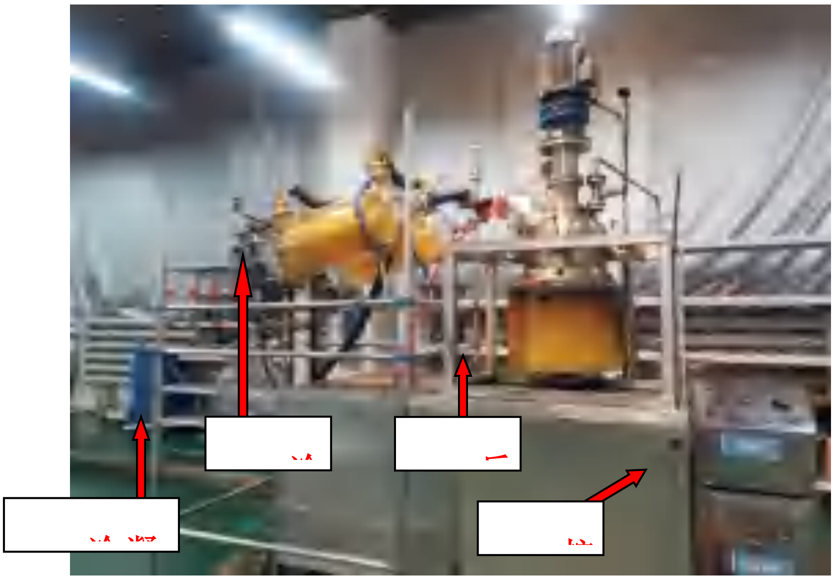


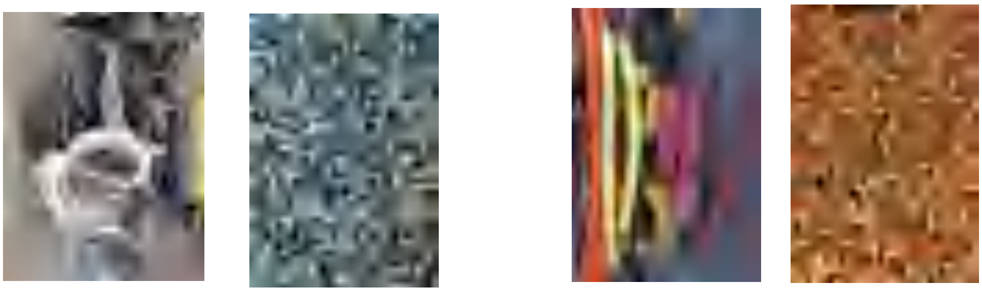
图 2、 试验装置

试验装置主要有反应釜、冷凝器、冷凝液储罐和控制台。其中，反应釜采用电磁加热方式加热；冷凝器采用制冷机组冷凝。

反应釜上部设有人工加料口，反应釜下部设有人工卸料口。试验物料和专用化学试剂均从反应釜人工加料口由人工加入；试验结束后的固体剩余物由反应釜卸料口人工卸出。

1.2.2 试验说明

1、将废塑料、废轮胎、废电线电缆料和废化纤纺织品等高分子废弃材料分别粉碎至不大于粒径 5mm；



废电线电缆料 A 粉碎前　　废电线电缆料 A 粉碎前　　废电线电缆料 B 粉碎前　　废电线电缆料 B 粉碎后

图 3、 试验原材料

2、将废塑料、废轮胎、废电线电缆料和废化纤纺织品等高分子废弃材料分别与各种高分子废弃物相适用的专用化学制剂按一定比例投入到试验装置的反应釜中；

3、将废塑料、废轮胎、废电线电缆料和废化纤纺织品等高分子废弃材料分别与各种高分子废弃物相适用的专用化学制剂在试验装置的反应釜中浸泡约 60 分钟；

4、试验装置的反应釜通过控制台开始用电磁加热方法按程序加热，直至加热到约 350℃左右；

5、试验装置的反应釜产生的蒸汽经冷凝器冷凝后送至冷凝液储罐，此即为降解所得的以芳烃为主的有机小

分子原料产品；

6、试验装置的反应釜加热到最后只剩余固体粉末状产品。

有机小分子原料产品 A　有机小分子原料产品 B　固体粉末状产品 A　固体粉末状产品 B

图 4、 试验结果所得的液体产品和固体粉末状产品

1.3 试验记录

1、试验物料有废混合塑料 A 、废混合塑料 B、废电线电缆料 A 和废电线电缆料 B 等，其中各种试验物料的组成成分会有所不同，因此，试验剩余固体物会有所不同，从而计算出来的降解率也会有所不同。废轮胎和废化纤纺织品降解试验时也同样会有这种情况，见表 1、试验物料降解率。

表 1、试验物料降解率

序号	试验原材料			试验条件		试验结果	
	原材料名称	原材料量 kg	化学制剂量 kg	最高压力 MPa	最高温度 ℃	剩余固体物量 kg	计算降解率 %
1	废混合塑料 A	10	10	0	387	2.17	78.30
2	废混合塑料 B	10	5.25	0	340	2.90	71.00
3	废电线电缆料 A	10	10	0	330	3.91	60.90
4	废电线电缆料 B	10	10	0	315	2.58	74.20
5	废轮胎	5	5	0	351	1.97	60.60
6	废化纤纺织品	5	5	0	349	1.49	70.20

注：计算降解率(%)=(原材料-试验剩余固体物)/原材料*100 (%)

2、在表 2、试验物料降解为芳烃化学品含量中，废混合塑料 A、废混合塑料 B、废混合塑料 C 和废混合塑料 D 各个试验物料的成分会有所不同，因此，降解所得的芳烃化学品含量会有所不同。

3、在表 2、试验物料降解为芳烃化学品含量中，序号 5、6、7 的废电线电缆料系同一试验物料，而送检样品是从降解所得芳烃化学品储罐中的上层、中层和下层分别取样的。

表 2、试验物料降解为芳烃化学品含量

序号	试验原材料	样品日期	芳烃化学品含量	分析化验单位
1	废混合塑料 A	2018-07-05 样品	42.30 %	中科院化学所质谱中心
2	废混合塑料 B	2018-10-30 样品	42.47 %	中科院化学所质谱中心
3	废混合塑料 C	2018-12-05 样品	61.32 %	中科院化学所质谱中心
4	废混合塑料 D	2018-12-12 样品	44.93 %	中科院山西煤化所
5	废电线电缆料	2019-08-24 样品上层	40.74 %	中科院宁波材料所
6	废电线电缆料	2019-08-24 样品中层	37.65 %	中科院宁波材料所
.7	废电线电缆料	2019-08-24 样品下层	46.60 %	中科院宁波材料所
8	废轮胎	2019-06-30 样品	36.86 %	内蒙古汇邦化验
9	废化纤纺织品	2019-10-16 样品	44.00 %	中科院化学所质谱中心

2 试验结果与分析

(1) 废塑料、废轮胎、废电线电缆料和废化纤纺织品等高分子废弃材料，采用温和化学降解的方法，分别与各种高分子废弃物相适用的专用化学制剂进行逆向降解后变成有机小分子化学品，其降解率的计算为：

降解率(%)=(原材料-试验剩余固体物)/原材料*100 (%)

(2) 废混合塑料、废电线电缆料、废轮胎和废化纤纺织品的成分不同，其降解率也会不同。由表 1、试验物料降解率可见，废混合塑料的降解率为 70%以上；废电线电缆料的降解率为 60% 以上；废轮胎的降解率为 60% 以上；废化纤纺织品的降解率为 70% 以上。

(3) 废混合塑料和废电线电缆的成分不同，降解所得的芳烃化学品含量也会有所不同。 由表 2、试验物料降解为芳烃化学品含量可见，废混合塑料降解所得的芳烃化学品含量为 40% 以上；废电线电缆料降解所得的芳烃化学品含量为 35% 以上。

(4) 废轮胎和废化纤纺织品，也采用温和化学降解的方法，分别与专用化学制剂进行了逆向降解后变成有机小分子化学品试验，其降解所得的芳烃化学品含量分别为 35% 以上和 40% 以上。

3 讨论

（1）特别值得指出的是，在采用温和化学降解法降解废塑料时，废塑料中含有热固性塑料，如热固性聚氨酯(PU---polyurethane)也能降解回收，这是废塑料回收处理这一领域的重大突破，**突破了学术界公认的“热固性塑料‘不溶不熔’理论”**。

对比国内外废塑料回收利用技术，绝大部分技术都只能针对某一种或某一类塑料进行处理。其中，最难以克服的技术难关在于品种繁多、成分复杂的各种不同垃圾的分拣工作。虽然出现了各种各样的自动分拣设备，但多是不太实用。废塑料的分拣还是必须由人工来完成。可是人工分拣的工作环境非常恶劣，人工进行塑料识

别非常困难。正是有了突破“不溶不熔”定论的、性能优异的全新的专用化学制剂，即使包含有交联结构的品种繁多、成分复杂的各种废塑料等，也可以**不必分类、混合一起、同时处理**，省去了废塑料人工分类分拣的步骤，这样的“**不必分类、混同处理**”方法可使废塑料等的处理工艺非常简单，非常环保，投资也非常节省，是其他废塑料等的处理方法无法相比的。

（2）“**不必分类、混同处理**”的方法不仅适用于处理废塑料，同样适用于处理废轮胎、废电线电缆料和废化纤纺织品。

废塑料中可能有各种各样成分的，甚至如餐盒有剩饭菜等，均可“不必分类、混同处理”。

废轮胎中有天然橡胶，也有合成橡胶，但也可以“不必分类、混同处理”。

电线电缆绝缘及护套用塑料俗称电缆料，其中包括了橡胶、塑料、尼龙等多种成份，仍然可以“不必分类、混同处理”。

纺织品很多是混纺或混织的。废纺织品中可能有天然纤维和合成纤维，有可能有丝、毛、棉、麻、皮、化纤等，仍然可以“不必分类、混同处理”。

（3）将废旧化纤纺织品降解转化为有机化工原料，降解转化率 70% 以上，剩余的降解固体物转化为发热量很高、含水量很低的“类同优质电煤”，完美地解决了废旧化纤纺织品难以降解处理和无法循环利用的世界难题。

据了解，“十二五”期间，我国废旧纺织品累计产生量达 1.4 亿吨，预计到“十三五”末，废旧化纤纺织品的产生量可达近 2 亿吨。目前我国废旧化纤纺织品的回收总量目前不足 10%，而且主要集中在纯聚酯纺织品，主要回收对象是废旧工装、制服及加工过程中的边角料。目前废旧化纤制品，大多被当作垃圾进行填埋或焚烧等简单处理。这样简单处理实在太可惜了，那是巨大的宝藏啊！

废旧化纤纺织品降解剩余固体物样品化验结果見表 3。

表 3 废旧化纤纺织品降解剩余固体物样品化验结果

样品日期	全水	分析水	硫	发热量低位	发热量高位	挥发	灰分	焦渣特征	固定碳	化验单位
2019-01-09	1.04	0.65	0.10	4921	5119	29.48	25.86	1	44.01	东方化验
2019-01-10	0.89	0.75	0.09	5910	6096	23.21	18.95	1	57.09	东方化验
2019-01-11	1.00	0.97	0.10	4871	5051	28.99	26.37	1	43.67	东方化验

4 结论

(1) 废塑料、废轮胎、废电线电缆料和废化纤纺织品等高分子废弃材料采用温和化学降解的方法能够逆向降解。废混合塑料的降解率为 70% 以上；废电线电缆料的降解率为 60% 以上；废轮胎的降解率为 60% 以上；

废化纤纺织品的降解率为 70% 以上。

(2) 废塑料、废轮胎、废电线电缆料和废化纤纺织品等高分子废弃材料采用温和化学降解的方法能够逆向降解变成可以再重新利用的有机小分子化学品。废混合塑料降解所得的芳烃化学品含量为 40% 以上；废电线电缆料降解所得的芳烃化学品含量为 35% 以上。

(3) 废轮胎和废化纤纺织品，采用温和化学降解的方法，也能分别与专用化学制剂进行逆向降解，降解后也变成有机小分子化学品，其降解所得的芳烃化学品含量分别为 35% 以上和 40% 以上。

(4) 废塑料中含有热固性塑料，如热固性聚氨酯(PU---polyurethane)也能降解回收。

(5) 废塑料、废轮胎、废电线电缆料和废化纤纺织品等高分子废弃材料采用温和化学降解的方法能够使高分子废弃材料的处理做到无害化、资源化和循环化。

(6) 废塑料、废轮胎、废电线电缆料和废化纤纺织品等高分子废弃材料温和化学降解条件为温度 350℃左右，压力为常压。

农业农药包装废弃物管理模式研究[17]

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摘要：农业农药包装废弃物为典型的社会源废物，其特点决定了收集回收难、管理难，故我国大部分地区未开展该类废物的管理。发达国家虽有一套成熟的农业农药包装废弃物管理经验，但是并不适合我国国情；部分经济发达地区虽然开展了农业农药包装废弃物的管理实践，但管理模式与现行有关法律法规相矛盾。鉴于此，探索符合现有法律法规规定且适合我国国情的农药包装废弃物管理模式势在必行。通过多方调研，本文提出了受益者担责原则，并探讨了该原则在农业农药包装废弃物管理中的应用。在受益者担责原则下，农药生产者、经营者、使用者利用各自优势分别承担相应责任，共同完成农业农药包装废弃物回收处置义务；同时满足现行法律法规要求，具有普遍适用性和可持续性等优势。

关键词：农业农药包装废弃物，受益者担责，管理模式

Discussion on the management mode of agricultural pesticide packaging waste

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Abstract: Agricultural pesticide packaging waste is a typical social source, its characteristics determine difficulty of collection and recovery, management difficulty, so most of our country did not carry out the management. Developed countries have a set of mature agricultural pesticide packaging waste management experience, but it is not suitable for China's national conditions. Although the management of agricultural pesticide packaging waste has been carried out in some economically developed areas, the management contradicts the existing laws and regulations. In view of this, it is imperative to explore a pesticide packaging waste management mode that conforms to the existing laws and regulations and is suitable for China's national conditions. This paper puts forward the principle of beneficiary responsibility and discusses its application in agricultural pesticide packaging waste management. Under the principle of beneficiary responsibility, pesticide producers, operators and users should take their respective advantages to assume corresponding responsibilities and jointly fulfill the obligation of recycling and disposing agricultural pesticide packaging wastes，adapting to existing laws and regulations, with universal applicability and sustainability and other advantages.

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Key words: agricultural pesticide packaging waste, beneficiary responsibility, management mode

农药包装废弃物主要产生于农药生产、农业生产（农药使用）两大领域，其中农药生产领域产生的农药包装废弃物集中，易收集处置，且责任主体明确，法律依据充足，故易于管理；而农业生产领域（使用领域）产生的农药包装废弃物与农药生产领域产生的有很大不同，决定了该类废弃物收集回收难度大，管理难。为了与农药生产领域产生的农药包装废弃物区别，把农业生产（农药使用）领域产生的农药包装废弃物称之为“农业农药包装废弃物”，并定义为“农药废弃物一种，是指农业生产中产生的、与农药直接接触或含有农药残余物的废弃包装物、容器”。该概念涵盖了农药包装废弃物中残留的农药。

1. 农业农药包装废弃物的特征

文献【1】给出了农业农药包装废弃物基本无残余价值、降解难、收集回收难与集中贮存、运输难等特点，除此之外，农业农药包装废弃物还有以下特征：

（1）数量庞大。文献显示我国每年产生的农业农药包装废弃物在80亿-100亿[2][3]。产生数量如此庞大的农业农药包装废弃物的原因主要是用药量大（内在因素）决定的，其次是农药包装容积极小、小（外在因素）决定的。

（2）包装容积以极小、小为主。笔者调研了农药生产企业，农药产品容积在20mL或者20g及以下占总产品数量的60-70%，以极小包装为主。林漫莎等对回收后的农药包装废弃物进行统计，最小容积为3mL或者3g，容积在30mL或者30g以下的占48.6%，100mL或者30g以下占63.5%[4]；王俊伟等调研显示北京市农药包装废弃物的容积以10g以下为主[5]。这种以极小、小容积农药包装现状的设计依据是亩农药使用量，与传统农业种植相适应，决定了废弃后收集难。但事实上，由于“三权分置”的推行，农村土地得到一定程度的流转，新型农业经营主体种植面积多在百亩以上，甚至更大，再继续以亩农药使用量为农药包装容积设计依据则与现实不符。

（3）典型的社会源废物。零散的分布在人数庞大的农业经营主体（农药使用者）手中，属于典型的社会源废物，且具危害性；最大特点是基本无残余价值导致的收集回收难，涉及主体较多带来责任主体不明晰，加上相关法律法规的缺失，故管理难，以至于实施农业农药包装废弃物有效管理的地区较少。故农业农药包装废弃物应成为后续管理重点。

（4）属于危险废物。农业农药包装废弃物与其他农业包装废弃物不同，因含有或沾染有农药，具有一定的危害性，被明确列入《国家危险废物名录》，应按照危险废物管理；但其收集过程被豁免。农业农药包装废弃物内残余农药对环境影响大，是主要的农业面源污染来源。

2. 发达国家管理经验

日本、法国、巴西、加拿大、比利时等国家开展农业农药包装废弃物的回收管理工作较早[3]。

德国在农业农药包装废弃物回收处置方面经验成熟，本文以德国回收实践为例分析发达国家农药包装

废弃物回收处置的经验。德国的农业农药包装废弃物回收处置由农药工业协会（IVA）管理、PAMIRA 系统承担、RIGK 企业具体实施[6]。

PAMIRA 回收系统是德国农药生产者和批发商在自愿的基础上成立，是一简单、安全、环保的农业农药包装废弃物回收处理系统，不包含残留农药。农业种植者将农业农药包装废弃物洗净晾干并收集好，在特定时间交送任一收集点（即农药出售点）免费回收。在确认满足回收条件后收回，按其能量或材料价值进行分类打包，妥善处置或资源化。农药包装废弃物的收集、运输、回收等所需费用由农药生产者承担、CWFG 负责项目资金管理。为了安全环保地回收、处置农业农药包装废弃物，PAMIRA 系统对包装物明确提出“六必须”交付要求：带有 PAMIRA 商标；清洗干净；干燥；按照塑料、金属分类；包装物上的固定件分开交付；50L 以上的容器切开交付。另外也接收柔性包装，如塑料或纸的袋或箱。在收集点交付农药包装废弃物时，由专门工作人员检查；拒收不符合要求的农药包装废弃物。PAMIRA 系统成功地将农业种植者、经销商和农药生产者联系起来。农业种植者交送 PAMIRA 系统后可得到合格处理农业农药包装废弃物的证明文件以满足《商业废物管理》要求。2017 年全国范围内有 360 个收集点，回收了 3050 吨；2018 年增加到 365 个收集点。[7]

德国农药包装废弃物能高效回收基于一前提：德国土地集中、耕地面积大，使用机械化喷洒农药，故使用的农药包装容积较大，基本为 5L 以上的包装桶，大者可达 50L 以上，本身便于清洗、收集与回收。大多数发达国家如此。显然这与我国的实际国情大不同，我国耕种地相对分散，农药包装物以极小、小包装为主，100mL 以下占绝大多数，不利于收集、清洗，具有农药残留，不适于打包压缩贮存与运输等。国情不同决定了发达国家管理经验可借鉴之处不多。

3. 我国部分经济发达地区管理实践

3.1 现有管理模式

在我国部分经济发达地区，开始了对农业农药包装废弃物管理探索。如上海、北京、浙江、安徽等地开展了农业农药包装废弃物的管理实践[1][8][9][10][11]，实施管理的地区多以有偿回收方式进行回收，所涉收集、回收、运输、处置费用均为地方各级政府财政资金；在县级辖区内一般建立了两级回收网络，实施回收与管理单位多为农业主管部门下属单位等[1]。这种农业农药包装废弃物回收处置模式暂称之为政府主导模式。政府主导模式有其优势：如回收处置率高，回收到农药包装废弃物废物均能得到无害化安全处置等。

3.2 现有模式存在的问题

政府主导模式虽然回收处置率高，但问题非常突出：（1）该模式与现行法律法规规定相冲突。2019 年 1 月 1 日实施的土壤法第 30 条规定“农业投入品生产者、销售者和使用者应当及时回收农药等农业投入品的包装废弃物，并将农药包装废弃物交由专门的机构或者组织进行无害化处理”，显然土壤法中把回收处置责任分配给农药生产者、销售者和使用者，而非政府；同样政府主导模式也与农药管理条例的规定相矛

盾。管理实践与现行法律法规不符，显然与依法行政相违背。（2）该模式普遍适用性与可持续性值得关注。对于经济发达地区，政府主导模式有其适用性，但是对于经济欠发达地区，该模式就会出现问题，因为农药包装废弃物收集、回收、处置产生的费用财政经费难以持续承担；即使可临时拨付或筹措一定的财政资金，但持续下去也很困难，而农业农药包装废弃物是每年都要产生的。故政府主导模式难以在全国范围内推广。

4. 受益者担责原则的管理模式

在农业农药包装废弃物管理上，即无发达国家管理经验可借鉴，也无现成管理实践可参考，自行探索符合现有法律法规规定且适合我国国情的农业农药包装废弃物管理模式势在必行。

4.1 受益者担责原则的提出

4.1.1 广义的受益者担责原则

日本在 1993 年制定的《环境基本法》中提出了受益者负担原则理念：从环境或资源的开发、利用过程中获得实际利益者，均应就环境与自然资源价值的减少付出应有的补偿费用，而不局限于开发者和污染者【12】。张洋洋认为受益者负担原则是要求从自然环境中实际获益者履行治理污染、恢复生态、保护环境的义务，否则要承担相应的责任；受益者负担原则的义务主体不再局限于自然资源的开发者和排污者，而扩展到所有的自然环境获益者【13】。显然上述理念属于广义的受益者负担原则，该理念比较超前，并不适用于我国国情。

4.1.2 狭义的受益者担责原则

在广义的受益者担责原则理念下，结合农药包装的生命周期与农业农药包装废弃物的特征，通过对农药生产者（包括进口分装者）、经营者、农药包装生产者、农药使用者（包括传统农业经营者：农户，新型农业经营者：农业企业）、农业农药包装废弃物管理者（包括镇级、县级、地市级、省级）等多角度的调研，并对现行法律法规规章梳理，提出了适合现行法律法规要求的、狭义的受益者担责原则，并适用于农业农药包装废弃物的管理。

（1）主要受益者与责任分担分析

农业农药包装废弃物的产生是整个农药生命周期环节中的一环，是不可避免的必然的产物，是农药包装物的归宿。

从农药的生产，到农药储存、运输、销售和使用等环节，每个环节均存在经济受益者。农药生产者属于农药生命周期中的主要受益者，根据生产者责任延伸制度，理应承担农业农药包装废弃物的回收处置义务；农药经营者，即农药销售者，属于农药生命周期中的受益者，他们与使用者的距离最近，农药销售场所是最佳的回收场所，具有回收农业农药包装废弃物的独有优势，宜承担农药包装废弃物的回收处置义务；农药使用者属于农药生命周期中的终极受益者，是农业农药包装废弃物的直接产生者，收集交送最为方便，宜承担农药包装废弃物的收集交送义务。这三类主体均为农药生命周期中的主要受益者，且各自拥有农业

农药包装废弃物收集、回收的优势，由他们来承担农业农药包装废弃物的治理责任有利于农业农药包装废弃物回收与无害化处置。这种责任分配，称之为受益者担责原则。

（2）狭义受益者担责定义

在农药包装生命周期中的主要受益者与其在农业农药包装废弃物中的责任承担分析的基础上，给出狭义受益者担责的定义。所谓受益者担责是指产品生命周期中主要经济利益受益者承担产品生命周期中产生废物的治理责任。对农业农药包装废弃物的治理责任应由农药生命周期中的主要经济利益受益者承担。

这里的“受益者担责”取狭义概念，于广义的受益者担责不同。受益者担责原则下的农业农药包装废弃物管理完美地契合了现行法律法规的要求，并符合我国国情。

4.2 受益者担责原则下的管理模式

把受益者担责原则应用于农业农药包装废弃物管理中，可以把各义务主体的责任/义务有机组合起来，把农业农药包装废弃物相关管理制度串在一起，形成一种农业农药包装废弃物管理模式（见图 1）。

在受益者担责原则管理模式下，农药生产者（包括进口者）应对使用的农药包装进行源头控制，以便从源头上减少包装物的产生量以及尽可能使用易回收处置的材料，同时应按照数量缴纳回收处置基金；对于农药经营者，未纳入回收体系者应履行缴纳回收处置基金义务，已纳入回收体系者应承担回收义务；对于农药使用者，应履行其产生的农业农药包装废弃物的交送义务，但最好配套一定的激励政策鼓励农药使用者实施送交义务，以保证回收率。鉴于农药生产者、经营者、使用者间的关系是松散的，需要权威部门把他们有机联系起来，该工作可以在政府协调下由行业协会等组织承担，形成类似于德国的 PAMIRA 系统。

图 1 受益者担责管理模式

4.3 受益者担责原则管理模式的优势

相较于政府主导模式，在农业农药包装废弃物管理中采用受益者担责管理模式契合了现行法律法规，在全国范围内具有普遍适用性和可持续性；同时最为经济、高效且具有可操作性等优势。

在受益者担责管理模式下，有助于实施以旧包装换新农药（简称以旧换新）等利于农业农药包装废弃物回收政策实施。

建议把受益者担责原则上升为国家对农业农药包装废弃物管理的基本原则，并通过法律法规予以固化。

受益者担责原则管理模式适用于大多数社会源产品类废弃物的管理。

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奥.穆萨尔裂解气化“三废”超低排放装置

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摘要：危险废物（含工业危废、医疗废弃物）处理不当将会污染大气、水体和土壤，破坏生态环境，还有可能通过生态链和食物链等各种渠道侵害人类身心健康，甚至不可逆转的危害。现行的处理技术及设施普遍存在处置成本高，二次污染等弊病，与快速增长的固体废物市场需求和国家对环境保护的要求不相匹配。在吸收国际先进技术的基础上开发的垃圾裂解气化处理技术及相关设备，填补了国内空白，实现低成本处理危险废物（含工业危废、医疗废弃物），达到无害化、减量化、资源化及废气、废水、废渣的超低排放目的。

关键词：裂解气化　低成本 超低排放

一、导引

废弃物是因人类生产和生活而产生的，它有很多种，如生活垃圾、餐厨垃圾、电子垃圾等等。其中危险废物是非常难以处理的一种，它具有毒性、易燃性、爆炸性、腐蚀性、化学反应性、传染性及潜伏性，不但污染大气、水体和土壤，破坏生态环境，而且还通过生态链和食物链等各种渠道侵害人类身心健康，导致中毒、癌变及畸形，造成长久的、甚至不可逆转的危害。

我国现行的危险废物（含工业危废、医疗废弃物）处理技术及设施，如填埋、固化、焚烧等，普遍存在处理手段单一、废弃物减量率低、资源利用率低，处理处置成本高、产生二次污染等弊病，且与目前快速增长的固体废物市场需求和国家对环境保护的要求不相匹配。特别是这次新冠病毒疫情以来，疫情期间全国医疗废物生成量比疫情前以 25%速度增加。而湖北省医疗废物生成量是疫情前的 3.7 倍；武汉市是疫情前的 5.6 倍。原有的处理设施处理能力明显不够，临时上的一些处置设施，超负荷运行，同时也造成超标排放，进一步暴露了目前危险废弃物处理处置技术的弊端。

党的十八大以来，中央明确提出建设生态文明和美丽中国的目标要求，积极倡导“绿水清山，就是金山银山”的理念，已成为全民的共识和向往。中小城市（垃圾日产量小于 300 吨）的生活垃圾大部分还在填埋。由于多种因素，特别是处置技术上的原因，国有大型企业和上市公司基本都没有涉足中小城市垃圾处理项目，这也是摆在各级政府面前的一道难题。

鉴于我国传统危险废物处置技术普遍存在上述问题，及处理与排放标准提升的严峻现状。要应对日益严重的环境污染问题，要实现无害化、减量化、资源化和低成本处理及低排放的目标，当务之急就是要研究和开发符合国情、集成大量现代高新技术、节能环保、经济实用、安全高效的新技术和新装置。因此，创新和提升危

险废物的处理处置技术水平已势在必行。

二、奥.穆萨尔裂解气化技术

奥.穆萨尔热解气化技术于 1999 年从俄罗斯引进我国后，在积极消化和吸收的基础上，研究适合我国不分类的“混合型”垃圾特征的——垃圾热解气化处理技术与装置，并基于该项技术而开发出第一代生活垃圾热解气化处理设备。第一代技术设备示范项目于 2000 年在长春设备运行现场通过中国环境保护产业协会专家组评审及通过二恶英检测。专家组认为：在吸收国际先进技术的基础上开发的垃圾热解处理技术及相关设备，技术路线正确，**填补了国内空白**，符合国家产业政策，具有较好的发展应用前景。

20 多年来，针对不同行业的各种废弃物，不断进行技术创新，优化工艺，升级和完善各类处置装备。由第一代单一技术产品发展到第三代复合集成技术产品。如**第二代技术产品——医疗废弃物裂解气化处理装置**，2003 年在包头医疗废物处理厂投入运营，中国环境保护产业协会固废处理利用委员会专家组现场评审认为：采用热解方式处理医疗垃圾或生活垃圾，符合减量化、无害化、资源化的固废发展方向，具有能源回收率高，产生的二次污染小，综合经济效益好等优点，**研究成果属于国内首创。**比较完善的垃圾热解处理和热解气回收成套设备，其设计合理，自动化水平高，占地面积少，设备运转正常。具备工程应用及市场转化条件，具有广阔的推广应用前景。

系统采用废弃物自身产生的热解气体实现能量循环，降低能耗和处理成本，具有较好的经济效益，是本技术的突出特色。

第三代技术产品——移动式医疗废物热解处理车，在 2010 年已通过解放军总后卫生部专家评审，认为移动式医疗废物热解处理车**填补了国内与我军的空白。**移动式医疗废物热解处理车于 2013 年装备**国家、军队应急中心和部分野战医院。**

国家工信部与财政部将移动式医疗废物热解处理车与生活垃圾热解处理设备已列入国家【“环保装备‘十二五’发展规划”】及【国家鼓励发展重大环保技术装备目录】（附件序号：30，95）。

奥.穆萨尔裂解气化技术已经过了干馏裂解、气化分解、废渣熔融、催化反应、单一技术向复合技术集成、设备的大型化向小型化转变、小型化向微型移动化转变、间歇运行向连续运行、低成本实现超低排放等各技术阶段十几种炉型的上千次历练，从第一代技术产品（2000 年）处理 1 吨垃圾的直接运行费用 120 元/吨，辅助能源消耗 120 公斤煤炭/吨。发展到第三代技术产品（2016 年）处理 1 吨垃圾的直接运行费用 40 元-60 元/吨，能源消耗无需外部辅助能源，实现能量自我循环及超低排放。

奥.穆萨尔第三代裂解气化处理技术，以无氧高温裂解、高温气化分解和高温催化反应与熔融技术为核心，集成了热解（干馏）产生的可燃气体品质高的优势，气化分解处理能力大的特点，熔融灰渣彻底特长及无氧高温催化反应资源转化率高等优势有机结合，融为一体。将热解、气化产生的混合可燃气体和炭渣熔融产生的烟气经催化反应，使气体中的焦油、水、二氧化碳等转化为以甲烷、一氧化碳、氢为主的燃料气体，在减少废气、

废水、废渣产生、排放与治理的同时，提高裂解气的质量与产量。经过催化反应的裂解气体热值在 8000 千焦/m³-11000 千焦/ m³，经简单净化后可作为工业用清洁燃料进行发电或供热。

改变烟气排放路径，解决二噁英处理难题，实现超低排放环境效益。在不增加尾气处理系统设备和运行费用的情况下，将烟气二次引回加热室内的特殊烟气氧化箱净化，利用烟气氧化箱的温度、时间、涡流、供氧量等关键控制工艺，使烟气中存留的微量有害物质二次氧化，从源头抑制二噁英类污染物的产生与二次合成，实现低成本环境效益和超低排放。经中国检科院检测，医疗废物裂解气化处理废气排放中的二恶英类污染物含量仅为 0.013ngTEQ/ m³，低于国家现行标准 38.46 倍。（医疗废物焚烧处理二恶英类污染物排放量为 0.5ngTEQ/ m³）

奥.穆萨尔第三代裂解气化处理技术与传统的焚烧技术相比，节约电能约 60％，节约辅助燃料约 80％，节约用水量约 50％，节省运行费用约 50-70％，减少二氧化碳排放量约 70%，这为在垃圾处理领域率先实现节能减排和控制 PM2.5 与雾霾有着现实的重大意义。

第三代裂解气化集成技术有效解决了热解、气化、焚烧等单一技术处理垃圾存在的不足及运行的不稳定性。创新解决热解、气化领域尚未解决的三大难题：

一是热解（干馏），外加热热能利用率低，耗能高，设备处理能力小，炭渣需二次处理难题；

二是气化分解，产生的混合燃气热值低，一般只有 3500-5000 千焦/ m³，不能作为单一燃料使用，未加工的混合物料（特别是生活垃圾）在气化炉内不均匀，易出现烧穿事故，运行不稳定难题；

三是热解（干馏）与气化过程中产生的焦油、积碳和有机酸难处理，易堵塞管道难题。

三、奥.穆萨尔第三代裂解气化处理技术工艺过程

奥.穆萨尔第三代裂解气化处理技术工艺过程分四个阶段：

1．第一阶段，无氧裂解（也称干馏炭化）

加热室内的高温气体对裂解仓加热，裂解仓外表温度达到 900-1000 度，裂解仓内部温度达到 830-930 度，同时有部分高温气体进入到裂解仓内的热传导管内，热传导管在垃圾层内，使垃圾均匀受热，通过热辐射的方式对垃圾进行裂解。垃圾有机物在高温、无氧条件下分解，有机物的分子链断裂、分解，产生含有甲烷、一氧化碳、氢、二氧化碳、有机酸、焦油等组成的混合气体；在此阶段，垃圾在炉内停留约 90 分钟，干馏分解转化率为 100%。

在裂解仓内分解转化的主要产物：

（1）混合可燃气体；
（2）轻质焦油；
（3）有机酸液；
（4）垃圾炭。

2．第二阶段，气化分解

裂解后的垃圾已转化为以碳元素为主的固体物-垃圾炭（垃圾中的大部分有害物质如重金属、硫等被固定在垃圾炭中），垃圾炭进入到气化分解仓进一步进行气化分解。裂解气化炉加热室产生的高温气体，部分进入到气化分解仓内的U型热传导管内（U型热传导管在炭层内），通过热辐射的方式对垃圾炭进行加热分解，垃圾炭在800-950度高温条件下，将分解出氢和甲烷可燃气体。

在气化分解仓转化的主要产物：

（1）混合可燃气体；

（2）未完全气化的垃圾炭和不能气化的无机物。

3．第三阶段，垃圾炭熔融焚烧

在气化分解仓内未完全反应的垃圾炭和不能气化的无机物，进入熔融室进行熔融焚烧，垃圾炭中的有害物质在高温下完全氧化，重金属都富集和浓缩于固体残渣中，残渣呈惰性状态，化学性能稳定，很难再次析出或迁移。

在炭渣熔融室主要转化的产物：

（1）无毒无害的炉渣。

（2）垃圾炭熔融焚烧时产生的烟气。

4．第四阶段，催化反应

裂解气化炉无氧裂解仓、气化分解仓内产生的混合气体和炭渣熔融室产生的烟气进入催化反应仓进行催化反应，混合气体和烟气中的二氧化碳、有机酸、焦油（此时为蒸汽态）等在催化反应仓内发生反应，

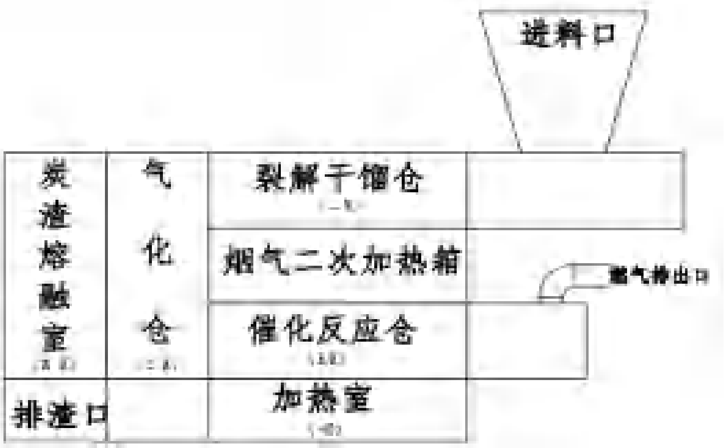
（$C + 1/2\ O_2 \longrightarrow CO$ ，$C + CO_2 \longrightarrow 2CO$）。产生以一氧化碳、氢、甲烷为主的可燃气体。

催化反应仓主要产物：

（1）一氧化碳、氢、甲烷及其他烷烃类为主的可燃气体；
（2）炭灰。

在上述过程中，它包含了许多复杂物理化学过程。

裂解气化工作原理图



在裂解气化炉实际的运行过程中，上述四个阶段有明确的功能边界，但又相互渗透和交错。

四、主要技术工艺创新

1．消除二噁英的技术创新

从源头控制二噁英生成，裂解气化处理采用非直接焚烧工艺，是利用中间介质传热方式对裂解反应器加热，使垃圾在无氧条件下进行高温热分解。因而，没有二噁英形成的基本元素（碳、氧、氯、氢）条件。其次，经过净化处理后的裂解气不存在具有催化作用的物质（金属或其氧化物），裂解气体高温燃烧过程是一个彻底而洁净的氧化过程。为了防止垃圾自身携带有二噁英类污染物在后期再合成，改变烟气排放路径，在裂解气化炉内加装了特制的烟气氧化箱，将烟气二次引回加热室的烟气氧化箱净化，运用烟气氧化箱温度、时间、涡流、供氧量控制技术工艺，从源头上控制氯苯的合成和炭灰参与燃烧，切断二噁英再次形成的条件，并在尾气处理系统中采用急冷、曝气净化与过滤相结合的工艺，在不增加尾气处理设备和运行费用的情况下，实现尾气达标排放。

2．控制污染物产生与排放技术创新

垃圾有机物在无氧裂解和气化分解及残渣熔融焚烧处理过程中产生混合气体中含有大量焦油、积碳、灰尘、二氧化碳和水蒸气，排出炉外极易污染环境和堵塞、腐蚀管路，是热解气化技术尚未解决的一大难题。第三代技术处理装置创新采用催化反应技术与裂解气化技术相结合的新工艺，有效解决焦油与积碳堵塞管路难题，是裂解气化处理技术工艺重大突破。混合气体在催化反应转化仓内进行二次催化和还原反应，水蒸气反应转化为氢，焦油二次反应转化为不可逆转的高热值的燃料气，二氧化碳反应还原为一氧化碳。因此，有效**控制污染物产生与排放，**在减少废气、废水、废渣的产生、排放与治理的同时，又增加了燃气的产量与质量。

3．热能共享，超低排放技术的创新

依据裂解、气化、熔融、催化反应各技术功能与效率规律、最小和最大产气量与持续燃烧的关系的基础上，探索和创新提出“五区”理念，并在裂解气化装置内部设计五个功能区。第一区为空气加热区，第二区为无氧裂解区，第三区为气化分解区，第四区为废渣熔融区，第五区为混合气体催化还原反应区。在二、三、四区产生的混合气体通过第五区催化与还原处理后产生完全可利用的可燃气，可燃气作为清洁能源进入一区进行燃烧产生热能，热能再进入二、三、四、五区参与工作，实现闭路循环。“五区功能”是热能共享技术的创新，提高装置的热能利用率和工作效率，实现装置内部能源自我循环利用，降低处理成本，实现超低排放，提高资源化综合效益。

4．热传导技术创新

在裂解气化功能区外部间接加热，会导致装置内热传导不均匀，出现局部物料不能完全裂解气化的现象，处理时间长，耗能高。通过技术创新，把外部间接加热方式与反应仓内部间接与直接加热的方式相结合，通过加热室和气体热传导管道直接向垃圾层传热。在裂解仓内部还设计增加了物料搅拌机。热传导方式的改变与物料搅拌机的增加，大大加快了热能传递的速度，缩短了垃圾的处理时间，提高了装置的处理能力 2-3 倍。

5．装备“E”型设计，热效率最大化技术创新

裂解气化炉的热效率表现在它的吸热效率，吸热效率越高，则表明它的热能利用率越高。因此，传热率最大化表现在裂解气化炉高温气体停留时间上，时间越长则表示热量利用率和垃圾热解吸收率越好，所以裂解气化炉在设计时必须考虑使裂解气化炉传热时间最大化。第三代技术处理装置内部结构设计呈 E 型，是一大科技创新。即装置内的无氧裂解仓和催化反应仓采用横向设计，而且都设计有吸热板，无氧裂解仓下部是烟气二次氧化加热箱，催化反应仓下部是加热室。无氧裂解仓一端和催化反应仓一端与立式气化分解仓连接；残渣熔融焚烧室在加热室一端外侧。加热室产生的热能依次加热催化反应仓、裂解仓、气化仓和残渣熔融室，在装置内热能高温辐射轨迹形成了 E 字型，延长高温气体在炉内停留时间，使各功能仓有足够的吸热时间，使热能利用率尽可能最大化。

6．装置小型移动化技术的创新

垃圾处理装置小型化、移动化，一直是垃圾处理技术的“瓶颈”，也是垃圾处理行业长期以来面临的困境。要实现危险废物小型移动化处理装置，需要技术的高度集成，使其能够适应实施公路、铁路、水路等机动运输，装置外部没有高耸的烟囱（烟气排放设施），也没有庞大的尾气处理装置。能够在突发事件或自然灾害发生时，快速到达事发地点，就地处理可能造成疫情发生或污染环境的物质。小型车载化技术解决了炉体内炉膛容积有效匹配、燃烧室耐热材料应用、炉整体质量控制、推料机构密封设计、烟气及二噁英排放控制、炉体安全性设计、炉温检测与控制设计、防震减震、重心动态平衡等多项技术关键。

小型车载化装置平时可根据用户需求，将装置移动到任意地点进行危险废物处理作业，减少或节省废物的运输及收集成本及收集与运输过程中产生二次污染。小型化设备也可作为产废单位的环保设施，安装在产废企业、工业园区、车站、港口、机场、旅游景区、海岛及边防部队营区等地，就地处理废弃物，并做到日产日清。

7．防爆安全技术的创新

防爆安全历来都是装备制造业关注的重点。危险废物处理装置采用防爆安全与出渣机构合二为一的创新设计理念，将水封防爆安全泄压机构与螺旋出渣机构有机结合，简化了工艺，提高了装置防爆的可靠性与安全性能，同时增大了装置内部的空间，有效解决了装置出渣时出现扬尘现象。

五、主要功能

1．用于危险废物处理

包括医疗废物 HW01；医药废物 HW02；废药物、药品 HW03；农药废物 HW04；木材防腐剂废物 HW05；废有机溶剂与含有机溶剂废物 HW06；废矿物油与含矿物油废物 HW08；水、烃/水混合物或乳化液 HW09；精（蒸）馏残渣 HW11；染料、涂料废物 HW12；有机树脂类废物 HW13；感光材料废物 HW16 等。及海关、商检罚没的其它有毒有害物品。

2.用于工业废物处理

包括石油、化工、汽车、造纸、纺织、印刷、包装、电子等行业的废塑料、橡胶及产品边角废料。

3.用于生活垃圾处理

包括城乡生活垃圾可燃物、农业废弃物和各类秸秆，旧的垃圾填埋场可燃物。

六、主要结构

1．上料系统：

有两套上料装置，一套用于颗粒状物料或油泥类物料；一套用于非颗粒状物料，如医疗废物、纺织制衣类边角余料等。

2．一体化裂解、气化、熔融、催化反应系统：

有加热室、裂解仓、气化仓、残渣熔融室、催化还原仓及出渣装置。

3.尾气净化处理系统：

有尾气二次氧化箱、急冷塔、曝气塔、冷凝塔、过滤塔及排放烟筒。

4.自动化控制系统：

电源柜、控制柜、操作台。

结束语

2020 年 4 月 26 日，《固体废物污染环境防治法（修订草案）》三审稿提请十三届全国人大常委会第十七次会议审议。加强了医疗废物特别是应对重大传染病疫情过程中医疗废物的管理，并明确了医疗废物按照国家危险废物名录进行管理。疫情过后，为巩固疫情防控的成果，积极顺应疫情防控常态化的形势，各地将完善医废处理处置应急预案，小型化与移动式设备或模块式裂解气化处理装置契合了医疗废物产量较小、产生分散、收运时限短的特征，将迎来更广阔的发展机遇。

第三代裂解气化技术与装置能够在垃圾减量、减排处理控制环节，确保垃圾无害化处理，且以裂解气化工艺技术严控控制二噁英的生成最小量化，同时以裂解气化技术充分裂解出可燃气体进行循环再利用作为燃料补充与能耗而降低等，确保系统高效节能，在无废城市建设、危废、工业固废、中小城市生活垃圾处理中发挥重要的作用。

设备照片

废旧锂离子电池正负极混合物氨浸液电沉积研究

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摘要：利用电沉积法处理废旧锂离子电池正负极混合物氨浸液，考察了电流对电沉积过程中金属钴、锂、镍、铜的回收率、阴极金属粉末中金属分布率、物相与形貌影响。结果表明，随着电流的升高，金属钴、镍和铜的回收率总体呈现升高趋势，而锂的回收率总体较低，当电流为 1.0 A 时，钴、镍、铜和锂的回收率分别为 98.15%、99.11%、99.91%和 15.36%。阴极金属粉末中钴的占比最大，最高占比可达 80.71%。电流大小对阴极金属粉末的 XRD 物相影响不大。从阴极金属粉末微观形貌来看，提高电流有利于减小阴极粉末的粒径。

关键词：锂离子电池；氨浸液；电沉积；回收率

Ammonia leaching solution of waste Lithium ion batteries cathode and anode mixture recovery by electro-deposition

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Abstract: Ammonia leaching solution of waste Lithium ion batteries (LIBs) cathode and anode mixture was recovered by electro-deposition. The effects of current on cobalt, nickel, copper and lithium recovery rate and distribute rate, the obtained phase and micromorphology during the electro-deposition were investigated in detail. The result showed that the recovery rate of cobalt, nickel and copper increased with the increase of the current. However, lithium was the opposite. When the current was 1.0 A, the recovery rate of cobalt, nickel, copper and lithium was 98.15%, 99.11%, 99.91% and 15.36%, respectively. Co in the obtained metal powders were the highest, 80.71%. The current had little effect on XRD patterns of the obtained metal powders. Based on the micromorphology of the obtained metal powders, increasing the current was beneficial to reducing its particle size.

Key words: LIBs; ammonia leaching solution; electro-deposition; recovery rate

锂离子电池具有能量密度高、自放电性能小、无记忆效应、可循环使用等优点，在便携式移动电源、笔记本电脑、移动通讯设备、摄影设备及常规测量仪器中得到了广泛应用，而且锂离子电池也是新能源汽车首选的动力电池之一[1,2]。然而，锂离子电池的使用寿命有限，一般为 2~3 年[3]；此外，储能技术的发展导致电池技术更新换代速度加快，从而导致锂离子电池大量废弃[4]。

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废旧锂离子电池成分复杂，兼具有毒性及有价值性[5,6]。一方面，废旧锂离子电池中的金属钴、镍及锰等有一定的致癌性，易引发皮肤发生过敏等炎症反应[7]。同时，其中的钴、镍、锂、铜等为有价金属，其品味远高于一般矿石中的含量[8]。因此，废旧锂离子电池的处理对环境污染控制及有价资源回收均有重要意义。

现有的废锂离子电池处理技术主要分为机械物理法[9]、生物法[10]、湿法[11,12]和电解法[13]。机械物理法虽操作简单，但存在处理效率低、高污染等缺点。生物法目前仍处于实验室研究阶段。湿法的浸出剂一般为酸性，对金属的回收效率高，但对金属的浸出选择性差。在课题组前期研究中，提出了一种高效处理废旧锂离子电池正负极混合物还原氨浸体系，可实现对有价金属有选择性的浸出，钴和锂的浸出率可分别达到 91.16% 和 97.57%[14]。然而，氨浸液中选择浸出的有价金属仍以离子状态存在，需进一步提取。电沉积技术具有成本投入低、回收效率高、二次污染少等优点[15]。然而，以往研究中，电沉积技术主要应用于酸性体系中，对于碱性的氨浸液电解体系回收锂离子电池中有价金属的研究却很少。

本次以课题组前期最佳氨浸条件下的氨浸液为研究对象，考察电流对电沉积过程中金属钴、锂、镍、铜的回收率、得到的阴极金属粉末中金属分布率、物相与形貌影响。

1 材料与方法

1.1 样品预处理

在本次实验中，收集的废旧锂离子电池均来自于某具有回收资质的电子废弃物回收处理公司。对收集得到的废旧锂离子电池进行预处理，主要包括 NaCl 盐溶液放电、烘箱干燥、机械破碎、筛分等步骤，得到粒径小于 0.45 mm 的样品颗粒。采用 HNO_3-$HClO_4$-HF 电热板消解法消解得到的金属颗粒[16]。然后对消解后获得的溶液使用电感耦合等离子体发射光谱仪（ICP-OES）对其中的金属成分及含量进行测定，测定结果见表 1。从图 1 样品 XRD 结果可以看出，样品中主要的成分为锂离子电池正负极材料钴酸锂与石墨。

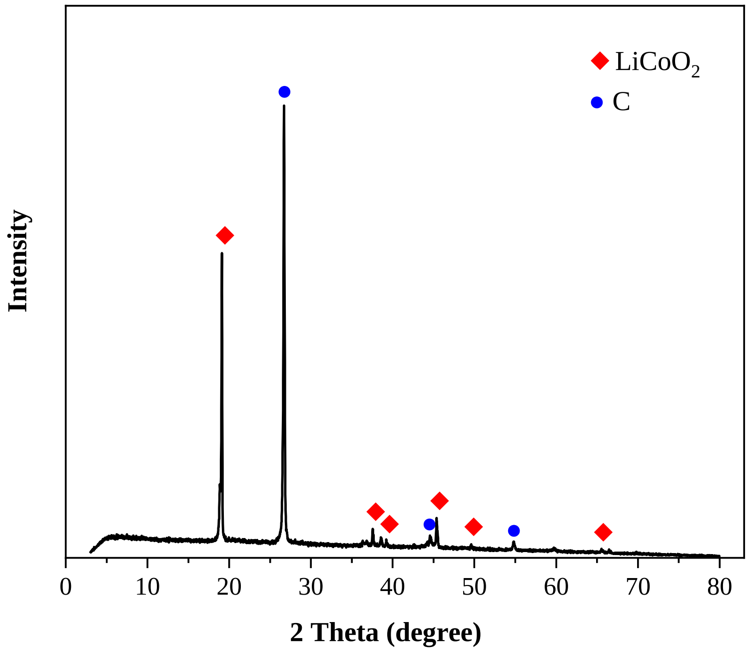

图 1 样品 XRD 结果

Fig. 1 XRD result of sample

表 1 样品中的主要金属及含量

Table 1 Chemical composition of specimen

元素	Co	Li	Mn	Ni	Al	Cu	Fe
含量（wt.%）	24.40	4.18	6.76	2.40	1.83	1.79	0.08

1.2 浸出液获取

基于课题组前期研究的最佳的浸出条件 $NH_3 \cdot H_2O$ 120 g/L、NH_4HCO_3 75 g/L 和 (Na_2SO_3): n (Co) =2:1，反应温度为 353 K，反应时间 240 min，配置 300 mL 一定浓度的 $NH_3 \cdot H_2O$、NH_4HCO_3 和 Na_2SO_3 浸出液到入 500 mL 烧杯中。覆盖多层保鲜膜，防止浸出过程中氨水挥发而造成损失。将容器放入集热式恒温加热磁力搅拌器中，待容器中浸出液温度到指定温度后，称取 6 g 废旧锂离子电池粉末物料置于容器中，搅拌(400 rpm) ，240 min 后，过滤，收集滤液。

1.3 电沉积实验

废旧锂离子电池正负极粉末混合物氨浸液电沉积实验装置为实验室自制，尺寸为 9×8×8 cm，材质为聚四氟乙烯。阳极板采用高纯度的镀钌钛板，阴极板采用 99.9%的钛板，极板间距为 8.5 cm，极板实际参与反应的截面积为 35.30 cm^2。

将上述收集的289 mL滤液迅速倒入电沉积实验装置中，覆盖保鲜膜，成分见表2。置放集热式恒温加热磁力搅拌器中，接通电源，考察电流（0.1~4.5A），对电沉积过程中各金属的迁移转化规律。反应3h后，关闭电源，取出阴阳极板，收集电解产生的金属粉末及电解液。将电解得到的金属采用苯并三氮唑钝化、去离子水洗涤、超声，60℃下干燥；将电解残液转入500 mL的容量瓶中进行定容，待测。XRD、SEM等分析所得金属粉末。消解并用ICP-OES测定电解所得的浸出渣中金属Co、Li、Ni及Cu的含量，探究电解过程中各个金属的迁移转化规律进行探究。

表2 氨浸液主要成分

Table 2 Chemical composition of ammonia leaching solution

元素	Li	Cu	Ni	Co	Mn	Al
浓度（mg/L）	718.20	278.90	386.40	3291.00	0.40	0.90

金属回收率的计算公式如下：

$$D_i = \frac{w_i}{W_i} \times 100\% \tag{1}$$

式（1）中，D_i是金属回收率，%；w_i是在得到的阴极粉末中金属质量，g; W_i是浸出液中金属的质量，g。

2　结果与分析

2.1 电流对电解过程中金属钴回收率的影响

图2表示电流在0.3~4.5 A条件下时，金属钴、锂、镍和铜在电沉积过程中回收率的变化。从图中可以看出，金属钴的回收率随着电流（0.3~4.5 A）的增加逐渐升高。当电流为0.3 A时，金属钴的回收率较低，为28.2%；当不断提高电流到4.5 A时，金属钴的回收率达到99.98%。这表明适当提高电沉积过程中的电流，有利于金属钴在阴极的沉积。Prabaharan等采用先酸浸后电解的方法研究了锂离子电池正极材料中Co的电化学浸出过程，其回收率与本次结果相近，在适当的电流密度下，Co的回收率高达96%[17]。

金属锂的回收率整体较低。当电流为1.0 A时，金属锂的回收率最低，仅为15.36%；提高电流到1.5 A时，此时金属锂的回收率最高，为48.66%。从浸出结果可以看出，金属锂主要以离子形式存在于电解液中，这是因为金属锂作为一种较活泼金属，其标准电极电势极负，为-3.0401 V，较难以沉积下来。Li等也对废旧锂离子电池正极材料硝酸浸出液中$LiCoO_2$的电化学回收过程进行了研究，并指出过量的OH^-是$LiCoO_2$电沉积的必要条件[18]。从总体趋势可以看出，在碱性环境下，适当提高电流有利于金属锂的沉积。

随着电流的升高，金属镍的回收率呈现先升高后降低再升高的趋势。当电流为0.3 A时，金属镍的回收率为78.48%；当不断提高电流到1.0 A时，金属镍的回收率升高到99.11%，几乎全部以阴极粉末的形式得到回收；当继续提高电流到4.5 A时，金属镍的回收率达到99.99%。从总体趋势可以看出，适当提高电流有利于金属镍的沉积。

金属铜的回收率整体较高，且随着电流的升高整体呈现升高趋势。当电流为0.3 A时，金属铜的回收率就达

到了 90.97%；当不断提高电流到 1.0 A 时，金属铜的回收率升高到 99.91%，可以看出金属铜几乎全部沉积在了阴极板上；再继续提高电流时，金属铜的回收率均可达到 100%。Veit 等人采用先酸浸再电沉积的方法对废旧印刷线路板中的铜进行回收，铜可被有效地回收，回收得到铜的纯度高达 98%[19]。

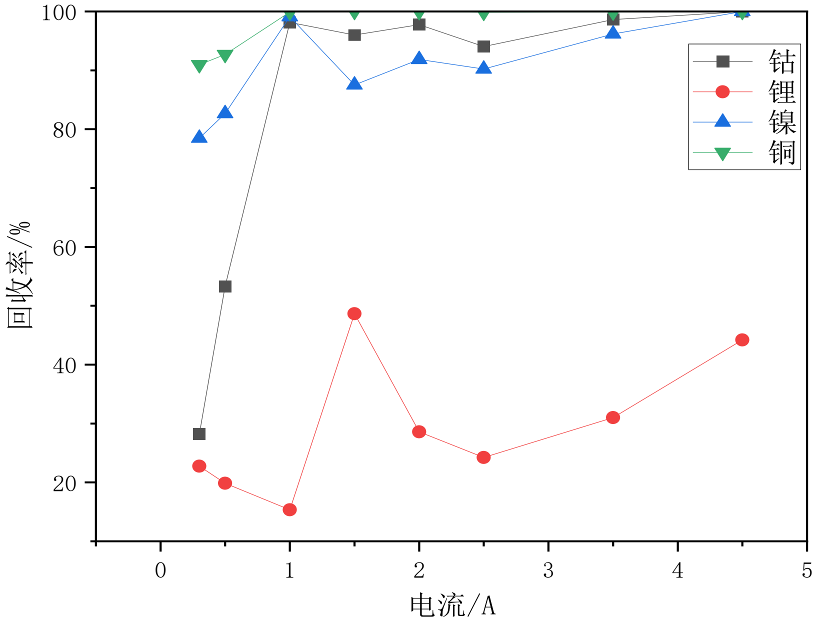

图 2　电流对电解过程中金属回收率的影响

Fig. 2 Effect of current on metals recovery rate in electrolysis

2.2　电流对电解过程中阴极粉末中金属分布的影响

图 3 是电流对得到的阴极粉末中金属分布规律的影响。从图中可以看出，在得到的金属粉末中存在的主要金属有钴、镍、铜及锂，其中金属钴在金属粉末中占比最大。当电流为 0.3 A 时，金属钴、铜、镍及锂占比分别为 56.29%、18.4%、15.39%及 9.92%。当电流提高到 1.0 A 时，金属钴在阴极金属粉末中含量最高，为 80.71%，其余依次为镍 9.57%、铜 6.96%及锂 2.76%。这表明通过提高电流，有利于金属钴在阴极沉积。当电流继续提高到 4.5 A 时，阴极金属粉末中金属钴含量有轻微下降，为 77.01%，然而金属锂的含量升高到了 7.43%，镍与铜的含量变化不大，分别为 9.04%和 6.52%。

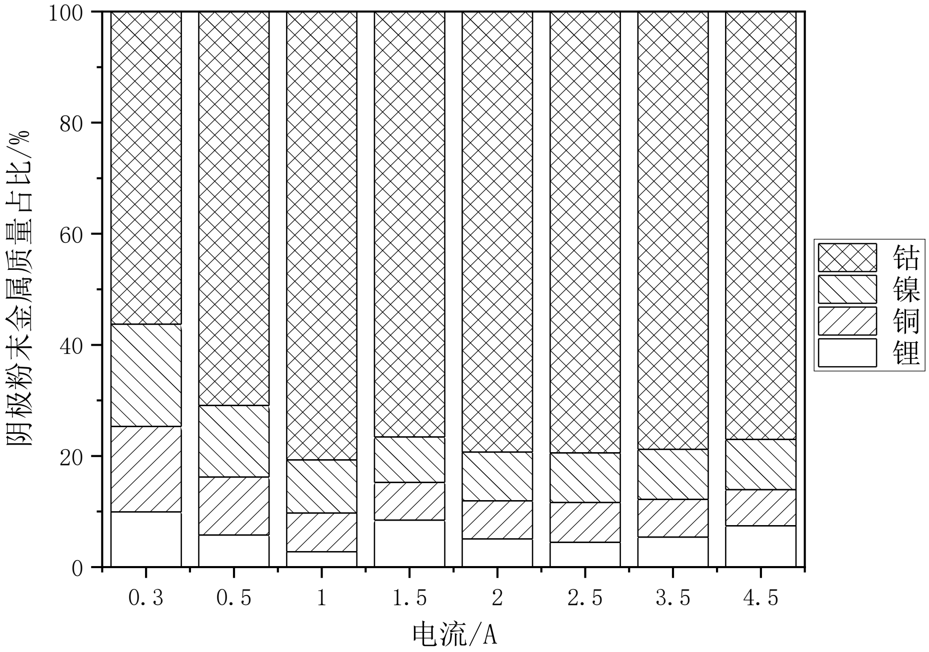

图 3 电流对电解过程中阴极粉末中金属分布的影响

Fig. 3 Effect of current on mass contribution of cathode metal powder in electrolysis

2.3 阴极金属粉末物相分析

图 4 是电流对阴极金属粉末 XRD 结果的影响。如图 4 所示，当电流为 0.3 A 时，得到的阴极金属粉末的物相组成主要为金属铜。随着电流的提高，可以看出得到的阴极金属粉末的 XRD 结果变化不大。此外从图中可以看出，电流在 0.5~4.5 A 条件下，得到的阴极金属粉末的 XRD 图谱表现为非晶质的衍射图，并且在 XRD 物质卡片上没有对应的物质与之匹配。造成这个现象的原因可能是得到的阴极金属粉末的晶粒非常细小，导致晶体的衍射峰极大地宽化并相互重叠，进而产生模糊化结果[20]。

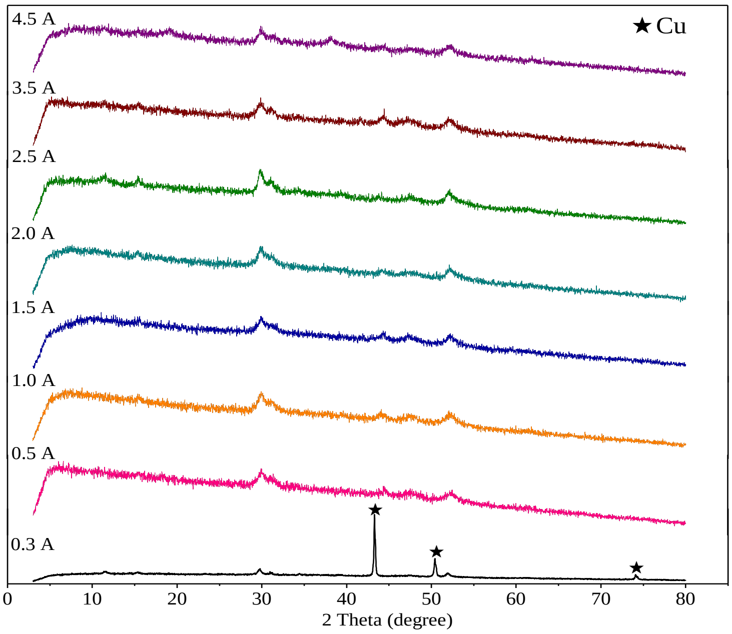

图 4 电流对电解过程中阴极金属粉末 XRD 结果的影响

Fig. 4 Effect of current on XRD results of cathode metal powder in electrolysis

2.4 阴极金属粉末形貌分析

图 5 表示电流对电沉积过程中得到的金属粉末的扫描电镜图与能谱图结果。为了更加全面地分析电流变化对金属粉末微观形貌的影响，这里选取了 0.3 A 和 4.5 A 电流条件下获得的阴极粉末为表征对象。其中，图 5（A_1）和图 5（A_2）为电流 0.3 A 时，不同倍镜下的扫描电镜图，EDS-A 为对应的能谱图；图 5（B_1）和图 5（B_2）为电流 4.5 A 时，不同倍镜下的扫描电镜图，EDS-B 为对应的能谱图。在低倍镜下，当电流从 0.3 A 提升到 4.5 A 时，可以看到得到的金属粉末由大颗粒的团聚体慢慢变成粒径越来越小粒径的颗粒团聚体，这表明提高电流条件，有利于形成减小阴极金属粉末粒径。在高倍镜下，观察到在图 5（A_1 和 A_2）中，0.3 A 的条件下获得的粉末形貌是鳞片状，结合对应的能谱图（EDS-A）得知这鳞片状的物质主要成分为铜，另含有少量的钴等金属，这与图 4 中得到的阴极金属粉末 XRD 结果一致。然而随着电流的升高，在高倍镜下观察到 4.5A 条件下的阴极粉末的形貌均变为了粒径较小的颗粒团聚体，结合对应的 EDS-B 能谱图，得知含有的主要金属成分为钴，其他较高的成分为镍与铜，这与金属的分布结果一致。另外可以看到 S 的含量也很高，这主要与体系中含有的硫酸根有关。

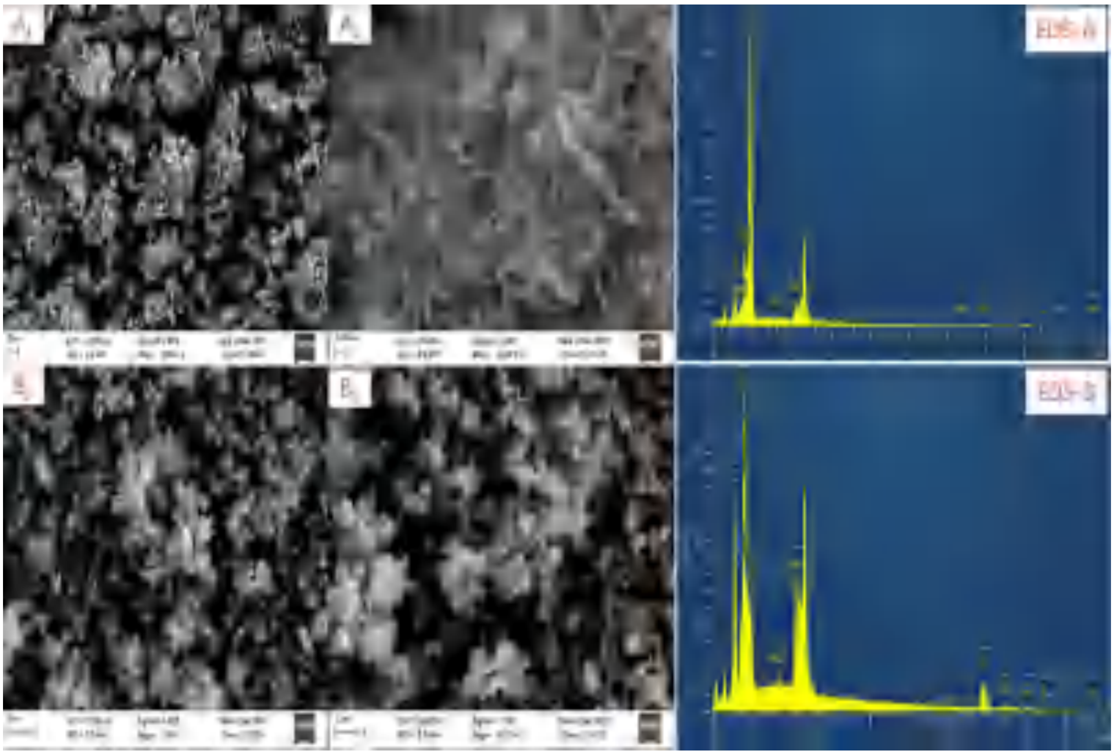

图 5 电流对电解过程中阴极金属粉末微观形貌和 EDS 结果的影响

Fig. 5 Effect of current on morphologies and EDS of cathode metal powder in electrolysis

2.5 阴极金属粉末后续处理回收

阴极粉末中金属钴的含量占比较高，最高可达 80.71%。所以，可以对阴极粉末进一步处理得到较高含量的钴产品。首先，使用硫酸对阴极粉末进行溶解，加入铁粉沉铜、黄钠铁矾除铁；然后，使用价廉易得的氨水来

调节酸浸液的 pH，使得镍离子和铝离子完全析出，使酸浸液纯化，并使用碳酸氢铵对酸浸液进行中和；最后，再用化学沉淀和萃取等方法进一步使钴富集和提纯即可得到含量较高的钴产品。

3 结论

1）电沉积法处理在较佳浸出条件下氨浸液时可以成功地以金属粉末的形式回收了废旧锂离子电池中的有价金属。随着电流的升高，金属钴、镍和铜的回收率不断升高，当电流为 1.0 A 时，回收率分别为 98.15%、99.11%及 99.91%，而金属锂的回收率先下降后上升，在 1.0 A 电流下回收率最低，为 15.36%。当继续提高电流为 4.5 A 时，金属钴、镍和铜几乎全部得到回收。

2）得到的金属粉末中存在的主要金属有钴、镍、铜及锂，其中金属钴在金属粉末中占比最大，且提高电流，有利于金属钴在阴极沉积。当电流为 1.0 A 时，金属钴在阴极金属粉末中含量最高，为 80.71%，其余依次为镍 9.57%、铜 6.96%及锂 2.76%。

3） 电流大小对得到的阴极金属粉末的 XRD 物相影响不大。从得到的阴极金属粉末微观形貌来看，在低电流条件下的阴极金属粉末形貌为鳞片状，高电流条件下得到的阴极金属粉末为小颗粒的团聚体。综合来看，提高电流有利于减小阴极粉末的粒径。

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电解锰渣建材资源化研究现状与展望[19]

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摘　要：电解锰渣已成为制约电解锰行业发展的瓶颈问题，建材可以实现电解锰渣的大规模消纳，但电解锰渣含水率高导致其氨氮和可溶性硫酸盐处理处置难，目前尚无经济稳定运行的工业化案例。为实现电解锰渣建材资源化，系统梳理了电解锰渣理化特性、生态环境特征、减量化和资源化现状，重点分析了近年来电解锰渣建材资源化研究现状以及产业化应用实施案例，结合目前的经济、技术和市场因素，探讨了电解锰渣制备水泥混合材和蒸压加气混凝土的可行性，以期为解决电解锰渣资源化利用与无害化处理提供新的思路，从而推动电解锰行业的可持续发展。

关键词：电解锰渣；理化特性；生态环境特征；建材；资源化

Current status and future prospects of electrolytic manganese residue Reuse as Building Materials

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Abstract: Electrolytic manganese residues (EMRs) significantly blocked the development of electrolytic metal manganese industry. Although building materials could efficiently reutilize these EMRs in large-scale, no economically and stable running cases could be found in the market because of NH_4^+-N and soluble sulfates caused by its high-water content. To better EMRs reutilization in building materials, first, its physical/chemical characteristics, eco-environmental characteristics, reduction and decontamination methods are reviewed, then the research status and perspectives of EMRs for building materials as well as their industrialization implementation cases are discussed, finally, the feasibility of EMRs for cement mixture and autoclaved aerated concrete are analyzed, aiming to provide a new idea for EMRs reuse and decontamination and to ensure the sustainable development of electrolytic metal manganese industry.

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Keywords: electrolytic manganese residue; characterizations; eco-environmental compact; building materials; reuse

锰是重要的战略金属，主要用于冶金、电子和化工等领域，其中钢铁行业锰需求量占锰总需求量的 90% 以上，素有“无锰不成钢”之说[1]。炼钢时，锰既是脱硫剂又是脱氧剂，可显著提高钢的强度、硬度和韧性[2]。目前，锰的主要生产方法是电解法，此法生产的锰常被称为电解金属锰。我国是电解金属锰的最大生产国、消费国和出口国。2018 年，我国电解金属锰产能达 226 万 t、产量约 140 万 t，约占世界总产量的 97%[3]。电解锰渣是电解金属锰生产过程中，锰矿石经酸解、中和、除杂、压滤产生的酸性废渣，主要成分为 SiO_2 和 $CaSO_4 \cdot 2H_2O$，具有含水率高、粘度大和活性低等特点。随着锰矿资源的日益枯竭，锰矿品位急剧降低，生产 1 t 电解金属锰将会产生 8-12 t 电解锰渣[4]。截至 2018 年，全球电解锰渣总量约为 1.5 亿 t，并以 1000 万 t/年的速度增加[5]。

电解金属锰生产过程添加了硫酸、氨水、SeO_2 和 $K_2Cr_2O_7$ 等化学药剂，同时锰矿中含有的 Co、Pb、Zn 等伴生元素会随着锰矿浸出。因此，电解锰渣含有大量的 NH_4^+-N、Mn^{2+}、Cu^{2+}、Zn^{2+}、Cr^{6+}、Cd^{2+}、Se^{4+}、Pb^{2+}和 Ni^{2+}等污染物。由于历史与技术问题，这些污染物在减量化、无害化和资源化处置过程中，容易发生迁移，破坏周围生态环境。目前，电解锰渣的主要处置方式是堆存，部分渣场防渗措施不当，导致电解锰渣中的污染物容易进入水体、土壤和空气，破坏生态平衡，危害人体健康。同时，高含水率的电解锰渣具有良好的流动性和迁移性，容易引起溃坝事故。2009-2012 年，湖南和贵州先后发生了电解锰渣渣库溃坝事故，共造成超过 9 人死亡的安全事故。新产生和堆存的电解锰渣缺乏成熟的减量化措施，资源化综合利用方法尚不成熟，导致目前电解锰渣的堆存量越来越大，潜在生态和环境危害越来越严重，成为制约电解锰行业发展的瓶颈。

国家和各级地方政府先后推行了一系列政策整治电解锰渣，但并无突破性进展和成熟的处置方案。新一轮环保政策对电解锰渣综合整治提出了更高的要求，开展电解锰渣减量化、无害化和资源化利用技术研究刻不容缓。研究开发锰矿选矿富集技术和锰矿中 Mn^{2+}的低成本高效浸出技术，引进国外高品位优质锰矿与国内低品位锰矿混合使用，可以减少电解锰渣的产生量，在一定程度上可以实现电解锰渣的减量化。采用碱性物质、化学药剂、微生物、电场强化和电动力修复等方法在一定程度上可以实现电解锰渣中 Mn^{2+}的固化和 NH_4^+-N 的脱除，但缺乏低成本高效的电解锰渣无害化技术。一些消纳电解锰渣的企业仅考虑电解锰渣的资源化，常常忽略电解锰渣堆存过程和电解锰渣相关产品产生的二次污染。此外，电解锰渣的资源化主要有回收有价物质、制备肥料和生产建材产品等。然而，回收有价物质过程中耗水量大、浸取周期长，仅适用于回收可溶性 Mn^{2+}、NH_4^+-N、Fe^{3+}和 Mg^{2+}等物质，同时需对回收过程产生的大量废水和废渣进行二次处理。回收有价元素后，还会残余大量废渣，并不能实现电解锰渣的规模化利用；所制备的肥料肥效不足，肥料中所含的重金属离子会破坏植物根系，植物会富集肥料中的重金属，目前尚未实现产业化。相反，电解锰渣主要氧化物组成为 SiO_2、Al_2O_3、Fe_2O_3 和 CaO 等，可用于制备路基、蒸压砖、蒸压加气混凝土、玻璃陶瓷、水泥熟料、吸附剂、填料等建材产品实现电解锰渣规模化利用，具备良好的经济效益、社会效益和环境效益。

虽然国内外研究者针对电解锰渣建材资源化利用开展了大量研究，并进行了一些产业化示范，但电解锰渣综合利用量小、利用率低，未见经济稳定，可推广应用的成功案例。主要原因是高含水率电解锰渣中氨氮和硫酸盐含量较高，目前的脱氨、脱硫工艺不成熟，预处理成本较高，电解锰渣中的有害物质难以解毒，所生产的产品容易产生二次污染，危害生态环境。同时，受限于工艺，电解锰渣生产过程中无法实现深度资源化，甚至资源化过程中还会产生更多的废弃物，导致电解锰渣的减量化和无害化也难以实现。加之直接排放的电解锰渣处理处置难度大、运输困难；相关产品附加值低，市场竞争力弱；相关产业政策执行难、落地难，综合利用企业不愿大规模利用电解锰渣。只有资源化才能真正实现电解锰渣的规模化处置，但电解锰渣资源化必须结合其减量化和无害化，建材作为电解锰渣消纳的主要途径，可以实现电解锰渣的规模化消纳。因此，结合电解锰渣的理化特性、生态环境特征、减量化和资源化研究现状，系统梳理目前电解锰渣建材资源化利用的途径和存在的问题，并针对性地提出相应的解决方案，对实现电解锰渣规模化利用，确保电解锰行业可持续发展具有重要意义。

本文系统整理和分析电解锰渣的基本理化特性、生态环境特征、减量化和资源化技术研究现状。在此基础上，总结了近年来电解锰渣建材资源化研究现状和产业化实施案例，分析了各种电解锰渣建材资源化途径的利弊，分析了电解锰渣制备水泥混合材和蒸压加气混凝土的可行性，旨在从建材角度明确电解锰渣的资源化途径。最后，结合技术、经济、市场和政策因素对电解锰渣的建材资源化利用未来发展进行了展望，为电解锰渣的规模化处置提供了研究和产业化思路，对电解锰渣的规模化处置和电解锰行业的可持续发展意义重大。

1　电解锰渣理化特性

由于锰矿来源和品位不同，各地电解锰渣的化学成分也有差异，但均以 SiO_2、Al_2O_3、Fe_2O_3 和 CaO 为主，是潜在建材和工业生产原料。如表 1 所示，电解锰渣中上述四种主要化学成分的总含量为 43.76%-56.36%，但 MnO 可高达 3.35%、SO_3 高达 37.31%，在利用时应严格控制。

表 1 电解锰渣的化学成分（wt.%）

地域	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	MnO	SO_3	K_2O	Na_2O	TiO_2
重庆	22.03	8.54	19.16	3.09	8.83	3.35	30.37	0.73	0.24	0.18
湖南	26.95	2.27	7.82	6.27	3.74	2.09	11.95	1.58	0.75	0.26
贵州	31.38	4.82	10.71	9.45	7.53	1.61	18.58	3.40	0.77	0.57
宁夏	27.93	5.08	15.39	5.78	5.29	NA	37.31	1.14	0.56	0.32
广西	23.41	4.80	14.96	2.46	8.57	1.24	27.58	0.60	0.05	0.15

NA: 信息未提供.

电解锰渣的主要矿物组成为石膏（$CaSO_4 \cdot 2H_2O$）、石英（SiO_2）、钠长石（$(Na, Ca)AlSi_3O_8$）、白云母（$KAl_2Si_3AlO_{10}(OH)_2$）、高岭石（$Al_2Si_2O_5(OH)_4$）、铁矾土（FeS_2）、黄铁矿（$(NH_4)_2(Mg, Mn, Fe)(SO_4)_2 \cdot 6H_2O$）、$MnSO_4 \cdot H_2O$、$(NH_4)_2SO_4$ 和 $MgSO_4$[6]。堆存时，易溶的 $MnSO_4 \cdot H_2O$、$(NH_4)_2SO_4 \cdot H_2O$、$MgSO_4$ 等物相会消失，形成难溶的$(NH_4)_2Mn(SO_4)_2 \cdot 6H_2O$、$(NH_4)_2Mg(SO_4)_2 \cdot 6H_2O$、$MnO_2$、$MnFeO_x$ 等物相，锰和氨氮的浸出浓度随堆存时间延长而逐渐降低[7]。堆存电解锰渣的危害程度较刚产生的电解锰渣小，但脱硫脱氨难度更大。电解锰渣呈酸性

（pH =4.00-6.40）、比表面积较大（3.00-9.66 m^2/g）、粒径较小（17.37-80.00 μm）、含水率较高（18.60-30.00%）[8-11]。在资源化利用时，需调整 pH 值，解决由电解锰渣比表面积大、粒径小和含水率高带来的粘度大和难分散问题。

几种典型电解锰渣的浸出毒性结果如表 2 所示。由表 2 可知，电解锰渣中的 Mn^{2+}、NH_4^+-N、Cr^{6+}和 Ni^{2+}均超过污水综合排放标准（GB 8978-1996），尤其是 Mn^{2+}和 NH_4^+-N 可高达 2057.00 mg/L 和 815.31 mg/L，分别为 GB 8978-1996 中规定值的 1029 和 54 倍，成为限制其建材资源化利用的关键因素和研究重点。

表 2 电解锰渣的浸出毒性(HJ 557-2010) (mg/L)

地域	Mn^{2+}	NH_4^+-N	Cu^{2+}	Zn^{2+}	Cr^{6+}	Cd^{2+}	Se^{4+}	Pb^{2+}	Ni^{2+}
重庆	2057.00	186.00	0.19	0.75	0.11	0.054	0.061	0.35	0.74
湖南	1300.12	650.85	0.051	1.14	NA	0.036	NA	NA	0.75
贵州	1321.61	815.31	NA	0.015	0.34	0.006	NA	0.14	0.22
宁夏	1820.00	NA	0.062	1.34	NA	0.036	NA	NA	4.83

NA: 信息未提供.

2 电解锰渣生态环境特征

目前，电解锰渣的主要处置方式是堆存，部分渣场防渗措施不当甚至未做防渗处理。雨季时，电解锰渣中的 Mn^{2+}、NH_4^+-N、其他重金属离子和小颗粒物质容易进入水体、土壤和空气，造成严重的环境污染，破坏周边环境的生物多样性，进而影响人体健康。

电解锰渣对农田、土壤、地下水、地表水和植物有严重影响。段宁[12]和降林华等[13]系统分析了电解金属锰行业的硒污染，表明电解锰渣中的硒具有显著的环境和生态风险。杨爱江等[14]发现，距电解锰渣渣场 50 m 的农田中，Mn 和 Cr 含量分别高达 287.00 mg/kg 和 233.70 mg/kg，超过或接近土壤环境质量标准的规定值（均为 250 mg/kg）。徐龙君等[15]发现电解锰渣中的水溶性 Mn 含量为 310.70-314.70 mg/L，pH 值为 5.00，均超过了 GB 8978-1996 的限值（2.00 mg/L 和 6-9 ），容易对土壤和水体造成污染，导致溪流和河道淤积，甚至造成人身伤亡。李昌新等[16]系统评估了电解锰渣渣场对人体健康和生态系统的潜在风险。结果表明，基于风险评估模型，电解锰渣中重金属对渣场的潜在风险顺序为 Mn > Co > Zn > Cu > Cr = As = Pb。根据修正后的潜在生态风险指数，电解锰渣对人类健康和生态系统的风险依次为 As > Cu > Mn > Co > Pb > Cr > Zn。沈华等[17]分析了湘西地区电解锰渣渣库周边的水质，发现水中 Mn^{2+}和 NH_4^+-N 可高达 537.00 mg/L 和 795.77 mg/L，周边的土壤也遭到严重污染。陆凤等[18]发现电解锰渣和浸出液对植物根伸长的抑制率超过 42.50%，甚至高达 100.00%。 王加真等[19]发现，经 6% 和 9% 的电解锰渣浸出液处理 12 d，黑麦草的总叶绿素含量分别降低了 47.50% 和 70.87%，类胡萝卜素含量分别降低了 77.80% 和 83.90%。曹建兵等[20]发现，玉米植株会富集电解锰渣中的重金属，影响其生长。电解锰渣对人体有潜在危害。人体摄入过量锰时，会损害神经系统，导致帕金森病甚至死亡。过量的镉会损害人体的肝、肾等器官。此外，水体中的 NH_4^+-N 容易被微生物转变为亚硝酸盐，从而毒害人体甚至导致癌症。硒过多会引起消化不良、四肢麻木、脱发和指甲变形等不良症状。

从上述研究可知，未经严格处置的大量高含水率电解锰渣在堆存过程中所释放的 Se^{4+}、Mn^{2+}、NH_4^+-N 等有害

离子有显著的生态环境风险，导致水体和土壤重金属超标，影响植物的生长，危害人体健康。高含水率电解锰渣具有良好的流动性和迁移性，容易引起溃坝事故，造成严重生态环境问题，带来巨大的经济损失。因此，寻找有效途径实现电解锰渣资源化利用，缓解其大量堆存带来的生态环境风险迫在眉睫。

3 电解锰渣减量化和无害化研究

3.1 电解锰渣减量化

电解锰渣堆存量巨大、Mn^{2+}和NH_4^+-N等污染物含量多、含水率高、环境风险大；雨季时，堆存的高含水率电解锰渣容易发生迁移和流动，存在溃坝风险。从无害化和资源化角度看，电解锰渣处置首先要解决的问题是源头减量。目前，电解锰渣的减量化主要包括三方面：（1）锰矿的选矿富集，以获得品位较高的锰矿生产原料。主要包括磁选、重选、化学药剂浮选和物理选矿等。Wu[21]等发现通过高强度磁选可以获得品位为22.75%的锰矿，锰矿回收效率为89.88%。Muriana[22]发现利用重选法锰矿的回收效率为91.11%。Zhou[23]等发现以亚油酸异羟肟酸为浮选药剂可以获得品位为18.30%等锰矿，锰矿回收效率为97.00%。Mishra[24]等利用带式磁选机获得了品位为45.00%的锰矿，锰矿回收效率为69.00%。（2）锰的高效浸出。采用稀硫酸[25]、稀盐酸[26]、木质素[27]和SO_2[28]等化学药剂浸出，微波[29]、电场强化[30]和生物浸出[31]等方法，Mn^{2+}的浸出效率为96.21%、97.10%、91.00%、95.50%、98.60%、98.20%和98.00%。（3）引进国外高品位优质锰矿与国内低品位锰矿复配，实现锰矿原料品位的优化。宁夏天元锰业、广西中信大锰和贵州部分锰生产企业通过引进南非和加纳等地的高品位优质锰矿，实现了锰矿原料的优化，降低了电解锰渣的排放量。

虽然研究者针对电解锰渣减量化开展了大量研究，并取得了一系列成果。但电解锰渣的减量化仍然存在以下问题：（1）因为菱锰矿的本身特性，选矿方法难以提高锰矿品位，传统的浸出工艺很难进一步提高Mn^{2+}浸出率；（2）电解锰渣颗粒细、比表面积大、粘度大，导致电解锰渣含水率居高不下，其中夹带大量有价资源和污染物，即使采用先进的压滤工艺和设备，也难以降低电解锰渣含水率。

3.2 电解锰渣无害化

电解锰渣无害化的实质是将其所含的Mn^{2+}和NH_4^+-N等污染物固化或脱除，主要有化学方法（CaO[32]、臭氧[33]、CaS[34]、磷酸盐+镁盐+碳酸盐[35]和磷石膏[36]等）、电化学方法（电场强化[30]和电动力修复[37]）、生物浸出[31]、焙烧和水洗等。研究表明以CaO为处理药剂，Mn^{2+}和NH_4^+-N的脱除率可达99.98%和99.21%；以臭氧为处理药剂，Mn^{2+}的脱除率可达99.90%以上；以CaS为处理药剂，Mn^{2+}的脱除率可达99.90%以上；以MgO + CaO + 磷酸盐为处理药剂，Mn^{2+}和NH_4^+-N的脱除率可达100.00%和84.89%；以磷石膏协同处置，Mn^{2+}和NH_4^+-N的脱除率可达99.94%和96.36%；采用电场强化方法，Mn^{2+}和NH_4^+-N的脱除率可达98.60%和99.80%；采用电动力修复方法，以太阳能为能源，Mn^{2+}和NH_4^+-N的脱除率可达99.49%和99.70%；采用生物浸出方法，Mn^{2+}和NH_4^+-N的脱除率可达98.00%和99.00%。

虽然研究者针对电解锰渣无害化开展了大量研究，并取得了一系列成果。但电解锰渣的无害化仍然存在以

下问题：（1）电解锰渣的分散设备欠缺，难以实现处理药剂和电解锰渣的充分混合；（2）目前的电解锰渣无害化技术难以同时实现 Mn^{2+}和 NH_4^+-N 的低成本高效脱除；（3）现有的无害化处置后的电解锰渣长期稳定性差，存在二次污染风险。

4 电解锰渣建材资源化研究

电解锰渣建材资源化利用方式见图 1，包括水泥、混凝土、墙体材料、玻璃陶瓷、陶粒、路基和聚合物等。

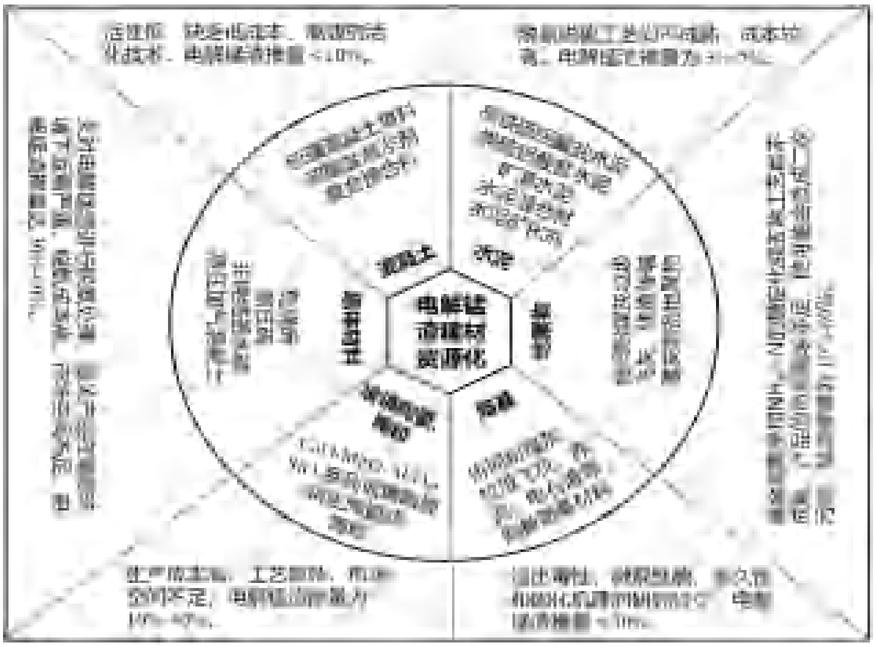

图 1 电解锰渣的建材资源利用方式

由图 1 可知，电解锰渣可用作水泥矿化剂、混合材和特种水泥原料，掺量为 3-5%；可用作混凝土复合掺合料、硫酸盐激发剂和硫磺混凝土填料，掺量＜10%；可制备免烧砖、蒸压砖、非烧结透水砖和蒸压加气混凝土等墙体材料，掺量为 30%-60%；可制备玻璃陶瓷和陶粒，掺量为 10%-40%；可协同粉煤灰等废渣制备路基材料，掺量＜30%；可协同垃圾飞灰等废渣制备地聚物，掺量为 10%-80%。但由于高含水率的电解锰渣氨氮和硫酸盐含量较高、脱氨脱硫工艺不成熟、处置成本较高，受市场等因素限制，其建材资源化利用并无可推广应用的成功案例。

4.1 水泥和混凝土

电解锰渣硫酸盐含量较高，可用作水泥矿化剂，掺加 2%-8% 的电解锰渣时，水泥熟料煅烧温度可降低 100 ℃，熟料中 C_3S（硅酸三钙）含量有所增加[38]。电解锰渣的主要氧化物与水泥一致，辅以粘土、石灰石、硅质和铝质校正原料，在适当的煅烧温度煅烧可生产水泥。侯鹏坤等[9]利用电解锰渣制备了 56 d 抗压强度为 36-65 MPa 的类硫铝酸盐水泥。雷杰等[39]利用电解锰渣制备了 3 d 抗压强度达到 49.80 MPa 的高铁硫铝酸盐水泥。此外，电解锰渣中的石膏、石英、钠长石、白云母、高岭石等主要矿物在直接煅烧或改性煅烧时，会脱水或发生晶型转变，使其活性得到增强，电解锰渣中的石膏在水泥水化时起缓凝作用，因此电解锰渣可用作水泥混合材和缓凝组分。程淑君等[40]发现电解锰渣经 1200 ℃ 煅烧，活性指数可达 95%。此外，经碳、煤、焦炭等还原剂脱硫、NaOH 激发和灼烧生料陈化预处理的电解锰渣均具有良好的活性，可用作水泥混合材。林明跃等[41]发现掺入 30%

的经高温脱硫的电解锰渣时，水泥强度可达到P·S·A 32.5级。黄川等[42]研究发现当NaOH : 电解锰渣 = 15 : 85时，电解锰渣的碱激发效果最佳。金胜明等[43]提出将电解锰渣与碳粉或铝粉混合，经900-1400 ℃ 煅烧20 min，再与水泥熟料和石膏混合、球磨可制得水泥，28 d抗压强度达到53.63 MPa。蒋勇等[44]研究发现利用灼烧生料对电解锰渣进行预处理，电解锰渣活性得到增强，可用作水泥混合材，灼烧生料掺量为5% 时效果最佳。电解锰渣还可制备高炉矿渣水泥和TiO_2涂层水泥材料。

电解锰渣具有潜在火山灰活性，可与水泥中的C_3S和C_2S（硅酸二钙）反应，改善混凝土性能。另外，电解锰渣中的硫酸盐对一些低活性矿物掺合料的活性有硫酸盐激发作用，可用作混凝土复合掺合料原料和硫酸盐激发剂。利用5%-10%的电解锰渣可制备具有良好的抗压强度、杨氏模量和抗氯离子侵蚀性的C25/C30混凝土[45]。电解锰渣还可用作硫磺混凝土填料，当掺量为30% 时，混凝土的抗压和抗弯强度分别达到63.17 MPa和9.47 MPa，产品具有良好的耐酸碱腐蚀性能和致密性，浸出毒性满足GB 8978-1996规定[46]。然而，由于硫磺的价格高、聚硫橡胶的供应困难和生产成本高，此技术并未实现推广和应用。

限制电解锰渣在水泥中资源化利用的主要原因是高含水率电解锰渣中氨氮和硫酸盐含量较高、脱氨脱硫工艺不成熟、成本较高。掺加未进行脱氨脱硫处理或处理不完全的电解锰渣时，水泥水化形成的强碱性环境（pH值为12-13）会使残留的铵盐以氨气形式逸出，污染环境，危害人体健康。为防止水泥中SO_3超标（≤ 3.5%）导致水泥安定性不良，电解锰渣掺量不宜过高。宁夏某企业投资15亿元建成了两条日产4500 t的水泥熟料生产线，通过煅烧水泥协同处置电解锰渣，综合固废利用率达51%，但投资成本高昂，电解锰渣掺量仅为3%-5%。同时，所生产的水泥在使用时会释放氨气，影响建筑内空气质量，危害人体健康，市场接受程度不高。限制电解锰渣在混凝土中利用的原因是其活性低，缺乏低成本的高效活化技术。重庆秀山某企业利用回转窑煅烧电解锰渣，激发了活性，可用作水泥混合材和混凝土掺合料，但脱硫程度不高，同时由于氨回收系统投资成本高，目前尚未规模化生产。

4.2 墙体材料

墙体材料是建筑工程中必不可少的一类材料，消耗量巨大。传统的墙材主要是粘土烧结砖，其生产过程会消耗大量土地资源和能源，造成环境污染，居住舒适度也较差。随着自然资源的日渐枯竭和国家生态环境保护政策的愈发严厉，在可持续发展背景下，以工业、农业和建筑垃圾废弃物及河道淤泥等废弃物为原料生产墙体材料已成为墙体材料行业发展的趋势。利用电解锰渣可制备免烧砖、烧结砖、蒸压砖和蒸压加气混凝土等墙体材料。

郭盼盼等[47]研究表明以电解锰渣60%、石灰10%、粉煤灰20%和水泥10%为胶凝材料，可以制备28 d抗压强度为7.76 MPa的免烧砖。杨洪友等[48]利用经预处理的电解锰渣和硅矿制备了免烧砖，电解锰渣掺量为80% 时，抗压强度达到11.25 MPa，相关性能满足JC 422-91 和 JC 239-91的规定。蒋小花等[49]发现以电解锰渣、粉煤灰、石灰和水泥为胶凝材料，电解锰渣掺量为50% 时，掺入一定的骨料，免烧砖的28 d抗压强度可达10 MPa以上。王勇[50]利用60% 的电解锰渣制备了抗压强度达到26.6 MPa的蒸压砖，产品浸出毒性和放射性满足相关

标准要求。杜兵等[9]利用 30%-40% 的电解锰渣制备了抗压强度超过 50 MPa 的蒸压砖。余举学等[51]利用 35%-60% 的电解锰渣制备了加气混凝土，发现将其浇筑至空心砌块中，传热系数可降低 40%，且产品环保。潘荣伟等[52]利用 59% 的电解锰渣和 15% 的再生集料制备了强度等级达到 MU15 级的蒸压制品，浸出毒性检测和放射性均满足相关标准要求。王亚光等[53]利用 30%-60% 的电解锰渣制备了非烧结透水砖，劈裂抗拉强度和渗透系数分别可达到 3.53 MPa 和 3.2×10^{-2} cm/s。他们还利用 15% 的电解锰渣制备了免烧透水砖，并利用工业 CT 研究了其孔结构。

上述研究指出利用电解锰渣可制备性能优良的墙体材料，但重金属固化机理、强度形成机理、氨氮脱除机理和耐久性还需进一步研究。某些企业利用电解锰渣生产了透水路面砖、蒸压砖和蒸压加气混凝土。但是，由于未对电解锰渣进行脱氨处理，相关产品在潮湿环境下返霜严重。同时，生产工艺过程未对逸出的氨进行回收，会造成环境污染，影响人体健康。而氨回收装置的设置会增加产品生产成本，同时当地建材市场不足以消耗所生产的产品，这些公司尚未实现真正的产业化生产。

4.3 玻璃陶瓷和陶粒

目前，利用廉价高硅质和高铝质工业固体废弃物制备玻璃陶瓷已成为资源化利用工业固体废弃物的研究热点。从化学组成来看，电解锰渣富含 SiO_2 和 Al_2O_3 等氧化物，可用于制备玻璃陶瓷。钱觉时等[54]发现，无需任何成分调整，电解锰渣研磨后与聚乙烯醇溶液混合，在 1350 ℃下煅烧 1 h，经过成核和结晶，可制备 $CaO-MgO-Al_2O_3-SiO_2$ 系列玻璃陶瓷，结晶活化能仅为 429.00 kJ/mol。宋谋胜等[55]利用电解锰渣、滑石、工业氧化铝和石英合成了性能良好的堇青石/钙长石复相陶瓷，电解锰渣掺量达 25%。王功勋等[56]利用 10% 的电解锰渣和 90% 的废陶瓷磨细粉制备了再生陶瓷砖，实现了两种废弃物的协同利用。胡春燕等[57]利用电解锰渣、废玻璃和高岭土制备了陶瓷砖，发现锰被固化于锰钙辉石晶格中，实现了锰的解毒，电解锰渣掺量达 40%。冉岚等[58]以电解锰渣和废玻璃粉为主要原料制备了陶瓷砖，结果表明掺加 32% 的电解锰渣，900 ℃下可制备性能优良的陶瓷砖。此外，电解锰渣还可制备钙长石/顽辉石多相陶瓷、再生陶瓷砖和多孔陶瓷。

电解锰渣生产陶粒并进行相关产品的开发利用也是目前电解锰渣建材资源化利用的一个研究方向。黄川等[59]利用 42.02% 的电解锰渣、54.63% 的粉煤灰和 3.35% 的木屑，制备了满足 GB/T 17431-2010 要求的 700 级轻骨料。胡超超等[60]以 12% 的垃圾飞灰、43% 的电解锰渣和 45% 的粉煤灰制备了陶粒。结果表明，颗粒强度为 769 N、堆积密度为 687 kg/m^3、1 h 吸水率为 6.44%。向晓东等[61]发明了一种电解硫酸锰渣制备陶粒的方法，利用 50-70 份电解锰渣、20-30 份粘土、10-20 份粉煤灰和 5-15 份赤泥制备了颗粒抗压强度为 5.1 MPa、堆积密度为 546 kg/m^3、1 h 吸水率为 4.12% 的陶粒。

虽然利用电解锰渣制备玻璃陶瓷和陶粒技术可行、产品性能优良，但目前还停留在实验室阶段，未见工业化生产。这是因为相关产品生产成本较高，虽然部分生产工艺简单，但整体而言工艺复杂，氨的脱除和回收工艺不成熟。从产业化角度来看，电解锰渣产渣地并不是玻璃陶瓷和陶粒的主要产地，产业化示范和工业化生产缺乏市场助推力，同时电解锰渣掺量不高，并不能实现电解锰渣的规模化消纳。最后，所制备产品的后续开发

利用尚不明确，未形成经济合理的产业链。

4.4 其他建筑材料

电解锰渣还可制备路基材料和地聚物。张玉良等[62]利用 30% 的电解锰渣、10% 的赤泥、5% 的电石渣、5% 的矿物掺合料、50%-60% 的骨料和 3% 的水泥制备了路基材料，7 d 无侧限抗压强度达到 5.6 MPa，超过了中国标准中公路路基 3-5 MPa 的强度要求。同时，此体系实现了电解锰渣中重金属的固化。黄煜镔等[63]发现 5-10 份电解锰渣、5-10 份流化床燃煤固硫灰渣可替代水泥和石灰固化红粘土制备满足公路施工要求的路基材料。赵荣等[64]发现，水灰比为 0.45、碱激发剂为 10% 时，利用 80% 的电解锰渣、10% 的镁渣和 10% 的粉煤灰，可制备 28 d 抗压和抗折强度分别为 8.89 MPa 和 1.22 MPa 的地聚物。王亚光[65]利用电解锰渣和粉煤灰制备了地聚物，结果表明电解锰渣掺量为 30% 时，抗压和抗折强度分别为 43.46 MPa 和 9.92 MPa，可实现电解锰渣中重金属离子的固化。詹欣源等[66]利用 75% 的垃圾飞灰和 25% 的电解锰渣制备了地聚物，结果表明 NaOH 溶液固含量为 0.50 时，重金属离子固化效果最佳。Han 等[67]发现，河砂与电解锰渣重量比为 0.80、磷酸浓度为 65% 时，经 80 ℃ 固化 2 d，地聚物的抗压强度达到 96.30 MPa，锰的固化效率为 95.40%。

尽管制备路基材料和地聚物为电解锰渣建材资源化利用提供了新的思路，但目前的研究主要集中在强度等宏观性能上，浸出毒性、微观性能、耐久性和固化机理的研究相对较少。同时，由于重金属离子和 NH_4^+-N 的稳定和去除工艺不成熟，产品市场需求不足，使用相关产品可能会造成二次污染，上述研究难以实现工业化

4.5 电解锰渣制备水泥混合材和蒸压加气混凝土可行性分析

综合市场和技术因素，电解锰渣制备水泥混合材可行。从市场容量来看，水泥和混凝土废渣消纳量大，可实现电解锰渣规模化利用，市场前景广阔。但混凝土掺合料主要是发挥粉体的火山灰效应、形态效应、微集料效应和界面效应，作用是改善混凝土的工作性能、耐久性能和抗腐蚀性能，活性要求较高，细度要求也高，有严格的标准（《混凝土用复合掺合料》（JG/T 486-2015））；而水泥混合材只是水泥原材料之一，主要作用是改善水泥的性能、调节水泥标号和增加水泥产量，活性和细度要求相对较低，并无严格的标准要求，只需检测所生产水泥的性能。技术上，混凝土掺合料要求更高，普通 III 型复合掺合料规定：细度（45 μm 筛余）（质量百分比）≤ 30%，流动度比 ≥ 95%，7 d 活性指数 ≥ 65%，28 d 活性指数 ≥ 70%，含水率 ≤ 1.0%，SO_3 含量 ≤ 3.5%，经过简单预处理的电解锰渣并不能达到标准要求，需与高活性矿物掺合料如粉煤灰、矿粉和硅灰等复配，并球磨至相应细度；水泥混合材活性要求低，经简单预处理和配方调整即可利用，同时水泥回转窑窑尾余热可以对电解锰渣进行干燥脱水，降低处置成本。混凝土掺合料主要供应到商品混凝土搅拌站，而混凝土生产过程中为了降低生产成本，需要掺加大量高活性、高性能的复合掺合料，以电解锰渣为主要原料难以生产满足实际生产需求的优质复合掺合料。水泥混合材主要用于生产水泥，活性要求低，电解锰渣经适当预处理即可利用。

综合市场和技术因素，电解锰渣制备蒸压加气混凝土可行。蒸压加气混凝土具有轻质、保温性能好、隔音效果佳、抗渗性能、耐火性能好和易施工等优势，随着装配式建筑的迅猛发展，蒸压加气混凝土市场机遇良好。技术上，蒸压加气混凝土中电解锰渣掺量可达 60%，脱硫脱氨措施得当时，蒸压体系（$5\text{-}8\times10^5$ Pa，175-205 ℃， 10h）可实现电解锰渣中低活性硅、铝、钙的活化，同时还可固化重金属离子。电解锰渣的高含水率、低活性、重金属离子多严重制约其在路基材料、免烧砖等建材产品中的资源化利用。但对于蒸压加气混凝土体系，高含水率和低活性不再是限制性因素，同时蒸压加气混凝土电解锰渣掺量高，可实现电解锰渣的规模化利用。

5 结语

电解锰渣处置不当会造成严重环境污染，破坏周边环境的生物多样性，影响人类健康，其规模化消纳已成为制约电解锰行业发展的难题。建材作为最大宗消纳固废的行业，可有效解决电解锰渣难题。从理化特性来看，电解锰渣的主要氧化物组成为 SiO_2、Al_2O_3、Fe_2O_3和 CaO 等，是良好的建材原材料。目前，电解锰渣在建材中的应用主要集中在制备水泥、混凝土、墙体材料、玻璃陶瓷、陶粒、路基材料和地聚物等。受制于电解锰渣的高硫酸盐含量、高铵盐含量、高含水率、高粘度、低活性、重金属离子多，虽然针对其建材化应用已有一定研究，且取得了不少成果，但未见经济稳定，可推广应用的成功案例。制约电解锰渣建材资源的因素整合起来主要有技术因素、经济因素、市场因素和政策因素。后续，电解锰渣建材资源化应该在减量化和无害化的基础上，从上述四方面入手，具体如下。

（1）技术上，目前针对电解锰渣前端处置的研究主要集中在无害化，尤其是锰和氨氮的固化和脱除，而针对降低其含水率和粘度，提高其活性的研究相对较少，缺乏电解锰渣建材产品的相关标准。后续研究可以在锰矿浸出过程中定向调控电解锰渣颗粒尺寸分布以及颗粒分散强化，降低电解锰渣含水率，实现其源头减量；利用水泥窑中间产物、电石渣等低成本碱性物料对电解锰渣进行改性，在固化锰和脱除氨氮的同时，增加电解锰渣的活性，降低其粘度；利用低温脱氨、高温脱硫工艺，通过还原剂的添加，实现电解锰渣中硫和氨的低成本高效脱除，同时提高电解锰渣的活性。在此基础上，深入研究电解锰渣在建材中的作用机理、耐久性、微观机理和浸出毒性，并结合电解锰渣和相关建材产品的指标要求，制定相关产品标准。

（2）经济上，目前已有的一些电解锰渣建材资源化的产业实践虽然技术上可行，但成本较高，不具有推广价值。电解锰渣制备水泥混合材，生产工艺简单，还可以协同其它工业废渣发挥电解锰渣的活性和硫酸盐激发效果，生产成本低。电解锰渣制备蒸压加气混凝土，其含水率高和粘度大的缺点不再是限制因素，经过蒸压可实现电解锰渣中低活性硅、铝和钙的活化及重金属离子的固化，在市场有保障的基础上，有一定经济性。

（3）市场方面，随着国家基础设施建设进程的不断推进，优质的水泥混合材十分稀缺，以工业废渣生产水泥混合材已成为一大热点。而以电解锰渣为原材料结合其他工业废渣生产的水泥混合材具有良好的市场前景。建筑模式革新和严格的环保政策使得蒸压加气混凝土这种环保墙材市场前景广阔。不过，市场对电解锰渣建材产品的接纳程度还需进一步提高，需加快规模化、高值化综合利用技术和产品的推广应用。

（4）政策上，虽然国家和地方针对电解锰渣处置已经定下了“以渣定产”的基调。但考虑到电解金属锰企业给当地带来的税收和经济价值，相关政策并未得到严格执行。因此，政府应结合当地市场需求，结合自身经济条件、政策优势以及当地整体规划，引进吸收国内外成熟技术，积极孵化相关产业，并予以政策和资金扶持。

结合技术和市场因素，电解锰渣制备水泥混合材和蒸压加气混凝土具有一定的可行性，但需针对性地研究

低成本高效脱硫脱氨技术以及电解锰渣含水率控制技术，制定相应产品和工程应用标准，政府需完善相关产业政策加大环境治理力度。

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我国镍矿尾矿库污染特征分析及防治建议

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摘要：镍矿经过选矿后尾矿排入尾矿库，尾矿中含有重金属元素如镍、铜、砷、镉等，在堆放过程中可能存在地表水、地下水、土壤、环境空气等环境污染问题。本研究介绍了我国镍矿尾矿的产生与贮存现状，对其污染特征进行了详细分析，并针对污染问题提出了相关建议。

关键词：镍矿尾矿库；污染特征；重金属

Pollution characteristics analysis and prevention suggestions of nickel mine tailings pond in China

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Abstract: The tailings are discharged into the tailings pond after beneficiation. The tailings contain heavy metal elements such as nickel, copper, arsenic, and cadmium. During the stacking process, the tailings can make the environmental pollution in the surface water, groundwater, soil, and environment air. This paper introduced the current status of the production and storage of nickel mine tailings in China, analyzed its pollution characteristics in detail, and put forward relevant suggestions for pollution problems.

Keywords: nickel mine tailings pond; pollution characteristics; heavy metals

镍金属具有良好的耐腐、耐磁、延展等特性，主要用于我国国民经济、国防建设和科学发展中，在电镀、电池、航天、划工和冶金领域应用较多[1]。目前，我国已有镍矿矿床（点）339 处，其中大型 14 处，中型 26 处，小型 75 处[2]。镍矿包括硫化镍矿和氧化镍矿，其中硫化镍矿占全国总量的 90%以上，有种类较多的共伴生矿产，综合利用值高。镍矿主要分布在西北、西南和东北，其保有储量在西北占据比例最大，甘肃省储量最多，占全国镍矿总储量的 62%，其次是新疆、云南。

在镍矿的开采、冶炼及运输等过程中，产生大量废弃物，如废石、尾矿及冶炼炉渣等，其中含镍尾矿中的硫化物氧化后与镍化合成溶于水的含镍的磺酸盐，以及重金属如果渗到下游的地下水和河流中时，则会对环境产生污染。本研究重点分析镍矿尾矿库中废水和固体废弃物的污染特征，并提出应对的管控措施，尽可能减少由于尾矿库安全环境问题而造成周边土壤、水源及居民的危害。

1.镍尾矿产生与贮存现状

国内金属矿山采选回收率较低，尤其是矿产资源的伴生元素的开采和选冶。而矿产资源共伴生元素的回收关键在于冶炼、选矿等工艺技术的创新与改进[3]，一些企业只是通过粗加工精矿的方式提取主金属，对其他伴生元素未进行二次回收，因此，有价金属回收利用程度较低。镍尾矿中含有大量镍、钴、铜、铁、镁等有用矿物成分，甚至含有稀贵金属成分，可见这类尾矿资源的回收价值之大。近年来，部分企业开始回收尾矿中的有价元

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素，目前仅有少量尾矿得到回收，大量的尾矿仍然以堆存的方式存在，占用周边林草地。

随着镍矿产品和选矿规模的扩大，镍矿尾矿库数量也逐渐增多。尾矿的堆存不仅占地面积大，重金属环境污染和扬尘问题突出，会对周边土壤和地表水以及周边居民造成了较大的影响。硫化镍矿选矿产出的尾矿量较多，年产 420～450 万 t，1 吨原矿产生尾矿约 560 吨，系数约为 0.56，尾矿粒度较细，常堆存于尾矿库中，近年来也通过添加一定比例的水泥等材料用于井下充填。镍矿选矿主要工艺流程见图 1。

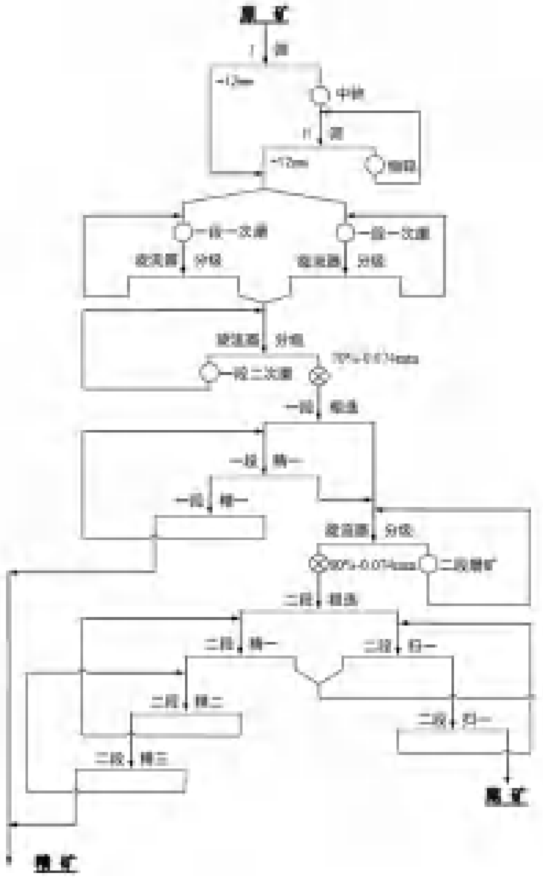

图 1　镍矿选矿主要工艺流程

Fig.1 The main technological process of nickel ore dressing

2.镍矿尾矿库主要污染特征

镍矿尾矿中含有 Ni、Cu、Co 等重金属，某镍矿尾矿矿物成分见表 1。

表 1　镍尾矿矿物成分

Tab.1 Nickel tailings mineral composition

成分（%） 样品	Cu	Ni	Fe	SiO_2	CaO	MgO	Co	S	Al_2O_3
尾矿	0.05~0.48	0.09~0.23	18.07	34.26	5.25	12.15	0.005~0.015	0.22~1.25	9.95

镍矿选矿废水主要来自精矿脱水、尾矿浓密机的溢流水、压滤机过滤水、尾矿澄清水等。选矿废水呈碱性，且含有剩余选矿药剂，须通过添加一定的絮凝沉淀剂处理后才能进行利用或排放，其中的主要污染物质有悬浮物、COD、硫化物、Cu、Zn、Pb、Cd、As、Ni、Co 等，尾矿废水中的主要污染物及浓度见表 2。

表 2　尾矿水中的主要污染物及浓度　（单位：mg/L，pH 值无量纲）

Tab.2 Main pollutants and concentration in tailings water (unit: mg/L, pH value is dimensionless)

pH	SS	COD	S	Cu	Fe

6~12	80~200	60~200	1~20	0.5~2	5~100
Zn	Pb	Cd	As	Ni	Co
0.5~5	0.1~0.5	0.01~0.1	0.1~0.5	0.1~0.5	0.005~0.03

以西北某镍矿公司的尾矿为例，尾矿毒性浸出试验得出，各检测项目浓度均低于《危险废物鉴别标准 浸出毒性鉴别》（GB 5085.3-2007）中浸出毒性鉴别标准值和《污水综合排放标准》（GB 8978-1996）最高允许排放浓度值。尾矿属性为第Ⅰ类一般工业固体废物，浸出毒性试验结果见表 3。

表 3　浸出毒性试验结果（单位：mg/L，pH 值无量纲）
Tab.3 Leaching toxicity test results (unit: mg/L, pH is dimensionless)

元素	浸出浓度	GB5085.3-2007	GB8978-1996	是否达到标准
pH 值	7.6	2-12.5	6~9	/
F	0.55	100	10	达标
Ni	0.023	5	1.0	达标
Cr^{6+}	未检出	5	0.5	达标
Cd	未检出	1	1.5	达标
Pb	未检出	5	1.0	达标
Zn	0.010	100	2.0	达标
Cu	0.024	100	0.5	达标
Co	0.005	/	/	/
As	0.014	5	0.5	达标
S	0.18	/	1.0	/
Hg	未检出	0.1	0.05	达标

镍尾矿中对环境有潜在影响的有害元素为来自于尾矿及尾矿水中的镍、铜、砷、镉等。其中尾矿中潜在污染元素含量为镍 0.09~0.23%、铜 0.05~0.48%、铁 18.07%、硫 4.91%等，尾矿水中潜在污染物含量为镍 0.1~0.5mg/L、铜 0.5~2mg/L、铁 5~100mg/L、硫化物 1~20mg/L、砷 0.1~0.5mg/L、镉 0.01~0.1mg/L 等。因此，镍尾矿及尾矿水中的主要污染因子为 Ni、Cu、As、Cd。

3.镍矿尾矿库潜在环境污染问题

尾矿在选矿过程中通过球磨等方式，粒度接近 200 目，粒径小，比表面积大，在尾矿送至尾矿库时，呈浆体状，形成泥石流的风险极大，严重危及到周边居民人身和财产安全，对周边土壤和水体环境也会造成重大影响。尾矿堆存高度也随着尾矿量的增加而增高，环境风险日益增大。

含重金属尾矿大量的堆置在尾矿库中，正常情况下尾矿库内的选矿废水处理后同雨水全部收集返回选矿厂进行循环使用。新建尾矿库一般设有截洪沟和事故应急池等措施，当发生事故以及遇到极端降雨条件时，尾矿库内废水及雨水可以贮存在尾矿库坝下回水池和尾矿库事故应急池中。然而，由于部分尾矿库建设年代久远，底部防渗措施不到位，尾矿库防渗结构发生破裂，尾矿库内选矿废水、雨水及尾矿会渗漏到下游水体中，具有重大的环境污染风险。

如果库内排水设施（如排水管、排水井、排水斜槽等）不完善或存在安全隐患，运行中则可能出现排水井倾斜或倒塌、排水涵管断裂漏砂、排洪隧洞片帮冒顶等事故，则可能造成尾矿和尾矿废水的泄漏，其中的重金属等因子会造成周边土壤、地表水和地下水的污染。

再者尾矿库对环境空气产生的主要影响是扬尘，主要来自于尾矿库干滩面。如果没有采取防扬尘等处理措施，尾矿库干滩及堆积坝体边坡在遇到大风天气时，会引起大量的扬尘污染。镍矿尾矿库潜在环境影响的主要途径和污染因子见表 4。

表 4　镍矿尾矿库潜在环境影响的主要途径和污染因子
Tab.4 Main ways and pollution factors of potential environmental impact of nickel mine tailings pond

分类	主要途径	污染因子
环境空气	扬尘	TSP、Ni、Cu、As、Cd 等
地表水	地表径流	Ni、Cu、As、Cd 等
地下水	废水泄漏及渗漏	Ni、Cu、As、Cd 等
土壤	地表径流、入渗、大气沉降	Ni、Cu、As、Cd 等

4.建议

1）不断完善规范化管理制度。完善岗位责任制度和机制，配备专业岗位技术人员；制定并持续执行尾矿库年度作业计划、环保投入计划以及应急预案并进行演练。

2）妥善处置渗滤废水。设置渗滤水收集池，并做好防渗措施，收集的渗滤液返回选厂循环利用或排入尾矿库，确保尾矿渗滤水不外排。对废水达标外排的尾矿库，应设置并正常启动废水处理设施及在线监测设施，确保废水达标排放，并保存好监测数据。

3）有效控制扬尘污染。如覆盖、使用抑尘剂、喷雾洒水、绿化植皮等，避免在恶劣天气下，导致尾矿库及周边扬尘污染严重。

4）定期做好隐患排查。应加强坝体、截排洪设施、库内排水设施等的排查与巡视，防止出现尾矿、废水的泄漏问题，维持尾矿库及其周边环境安全。

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建筑空调环境影响评价与减排潜力分析-以深圳市为例

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摘 要：建筑业节能减排是全社会节能减排的重要领域。而国内外关于建筑业节能减排的研究主要集中于建设阶段、使用阶段及建筑废弃物产生处理阶段。本文结合深圳市建筑碳排放特征,选择建筑使用阶段的主要碳排放来源—空调使用过程的环境影响作为研究对象，同时考虑了空调使用过程中因电力消耗和制冷剂释放所产生的间接和直接环境影响来源、分布特征及减排潜力进行量化分析。研究结果表明：（1）深圳市空调使用阶段碳排放当量从 2005 年的 605±32 万吨 CO_2-eq 增长到 2017 年的 1088±64 万吨 CO_2-eq，其中主要为间接排放，达 799±60 万吨 CO_2-eq；（2）在基准情景下，深圳市民用建筑空调碳排放将持续增长，并在 2030 年达到 1723.1 万吨 CO_2-eq；（3）在最优情景下，2018-2030 年间累计减排量可达 6490 万吨 CO_2-eq。本研究结果可从“精准和高效减排”角度为政府部门提供减排工作的重点方向及建议，弥补了当前深圳市居住建筑能耗研究方面基础数据不足的问题，也为构建深圳市空调能耗管理体系提供数据支持。同时也为温室气体减排研究提供新视角。

关键词：空调 能耗 制冷剂 碳排放 深圳市

Environmental impact assessment and CO_2 emission mitigation potential analysis of air conditioners in civil buildings: a case Study of Shenzhen

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Abstract: Energy conservation and emission mitigation is an important field in the construction industry of the whole society, and the research on this field mainly focuses on the construction stage, the use stage, and the construction and demolition waste stage. Based on the characteristics of building CO_2e in Shenzhen city, the study selects the main CO_2e sources in the building use stage - the environmental impact of air conditioners. At the same time, the indirect and direct environmental impacts caused by energy consumption and refrigerants emission during air conditioners' use stage are analyzed quantitatively. The results show that: (1) The CO_2e of using air conditioners increased form 6.05± 0.32 to 10.88±0.64 million metric tons (Mt) between 2005-2017 in Shenzhen. (2) In the business-as-usual scenario (BAU), the CO_2e of air conditioners in civil buildings will grow and peak at 2030 (17.2 Mt) in Shenzhen. (3) In the optimal scenario, the cumulative CO_2e mitigation could reach 64.9 Mt between 2018-2030. The results of this study can provide directions and suggestions for the government to reduce emission from the perspective of "precise and efficient emissions mitigation". They make up for the shortage of basic data in energy consumption research of residential buildings in Shenzhen, and also provides data support for the construction energy management of air conditioners in Shenzhen to develop a new perspective for research on greenhouse gas emissions mitigation.

Key words: air conditioner; energy consumption; refrigerants emission; Shenzhen

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空调已成为建筑业减排所面临的重要挑战之一[1]。据联合国报告称，目前全球建筑物中的空调数量已超过16亿台，其能源消耗量也在近8年内增加了25%。而随着人民生活水平的不断提高以及全球变暖所造成的持续高温天气，空调将持续推升建筑业能耗需求量及温室气体(GHGs)排放量。因而，分析衡量空调使用过程中的环境影响特征及发展趋势，将对建筑业“精准减排”工作有着重大指导意义。

空调使用过程中的环境影响主要来源于能耗和制冷剂释放两方面。现有研究主要侧重于空调能耗统计衡量及节能分析方面。大量研究表明空调为建筑能耗的主要贡献源(约占10%-40%)，同时我国空调能耗水平增速快、差异大，应因地制宜地采取相宜的空调节能方案[2-7]。此外，在相同气候条件和建筑围护结构的情况下，用户行为模式的差别是导致其空调能耗差异的主要因素[8,9]。但目前却少有研究对空调制冷剂的释放影响进行全面深入讨论。

深圳市是我国夏热冬暖地区的典型城市，该地区的户均空调保有量约为全国平均水平的2.5倍[10,11]。但当前深圳市民用建筑空调在能耗统计工作未全面落实、制冷剂释放量未知等问题，并且随着深圳市人口及建筑规模的持续稳定增长，其民用空调用量也会不断增加。因此，本文以深圳市为例，从城市层面对于民用建筑中空调使用过程的环境影响及减排潜力进行量化分析，为全市建筑减排工作确定重点开展方向、提供数据支撑及决策建议，同时也为温室气体减排研究提供新视角。

1 计算方法与数据来源

1.1 研究范围及指标选取

本研究的范围为深圳市民用建筑空调使用过程的环境影响及减排潜力预测，并未考虑工业及农业建筑中的空调设备。其中，由于研究局限性，本文未涵盖所有民用建筑类型，仅选择居住及部分公共建筑(办公、百货商场、宾馆酒店、文化教育、医疗卫生和综合性公共建筑)来进行研究。此外，民用建筑常用的空调类型主要有分体式、窗式及中央空调，但本研究并未其进行细分，均按分体式空调进行计算。

空调使用过程的环境影响主要来源于耗电和制冷剂释放所造成的温室效应及臭氧层破坏等问题，因此本文选取全球变暖潜力值(GWP)作为评价指标。根据碳排放来源，可将空调耗电产生的碳排放归为间接环境影响，而制冷剂释放所产生的碳排放量则属于直接环境影响。此外，由于现空调中使用的制冷剂均为零臭氧消耗潜能值(ODP)类或超低ODP类制冷剂，其对臭氧层破坏较小，所以本研究未将ODP值纳入评价指标中。

1.2 间接环境影响计算方法

1.2.1 空调能耗计算

宏观层面的空调能耗估算研究一般是以制定国家或地区的节能目标为研究目的，当前国内外的宏观研究主要集中在欧洲地区，常用的核算方法有“自上而下”的电力需求-温度回归法和“自下而上”的单位面积法。

其中，电力需求-温度回归法是通过建立电力消耗与气温之间的非线性回归模型，来核算国家或地区的建筑供暖或空调制冷的电力消耗量[12]。而单位面积法是基于单位面积的空调能耗数据，结合宏观层面的建筑面积来衡量国家或地区的建筑空调能耗量[13]。与“自上而下”的电力需求-温度回归法相比，单位面积法可对于不同建

筑特征(如建筑类型、建成年份等)的空调能耗数据进行区分，更有利于识别当前宏观层面空调能耗中所存在的问题，并可为政府部门制定节能减排措施提供数据支撑。

因此本研究采用单位面积法，基于单位面积空调能耗和建筑面积两类参数，“自下而上”地对深圳市民用建筑空调能耗进行计算，计算公式如下：

$$Elec_t = \sum_m A_{m,t} \times W_{m,t} \qquad (1)$$

式中，$Elec_t$代表 t 年时民用建筑空调总能耗，$A_{m,\ t}$为 t 年时 m 类建筑面积，$W_{m,\ t}$为 t 年时 m 类建筑中的单位面积空调能耗。其中，本研究中的 m 包括居住建筑及部分公共建筑类型(办公建筑、百货商场、宾馆酒店、文化教育、医疗卫生和综合性公建)。

1.2.2 间接环境影响计算

间接环境影响可由空调能耗与电力排放因子相乘得出,计算公式如下：

$$CE_{indirec,t} = Elec_t \times q_{E,t} \qquad (2)$$

式中，$CE_{indirec,t}$代表 t 年时民用建筑空调间接碳排放，$q_{E,t}$为 t 年时南方电网排放因子。

1.3 直接环境影响计算方法

1.3.1 制冷剂释放量计算

为应对臭氧层空洞及全球变暖等环境问题，我国正按《蒙特利尔议定书》的要求，逐步淘汰空调行业中 R22 和 R410a 类制冷剂；同时也在逐年加大环保型制冷剂(R32 及 R290)的使用量[14,15]，详见图 1。因此，在计算空调制冷剂释放量时，需将此“更新迭代”过程考虑在内。

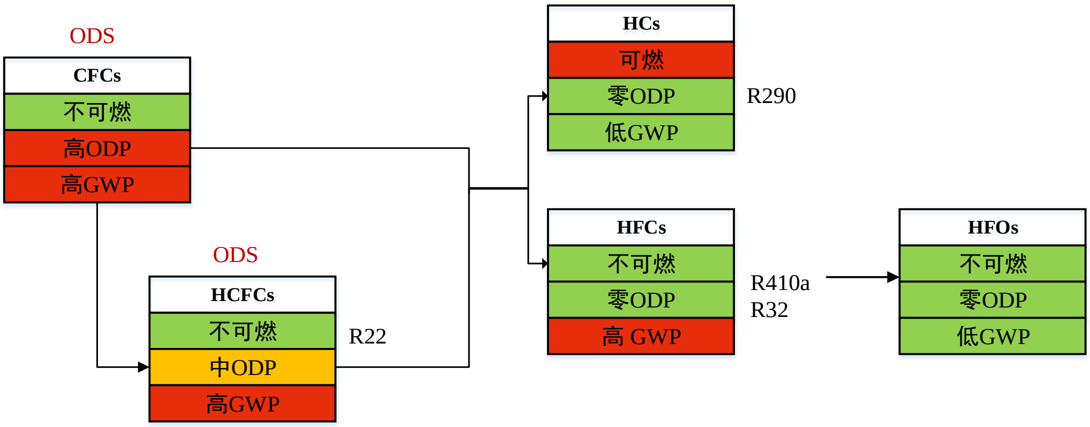


图1 各类型制冷剂特征及其替换进程[16]

Fig.1 Characteristics of different types of refrigerant and their replacement process

动态存量-流量分析方法(Dynamic Flow and Stock Analysis)是基于物质流的原理，将时间跨度内某物质“更新迭代”的变化过程考虑在内，用于量化物质数量的计算方法[17, 18]。而对于空调来讲，其制冷剂替换是一个动态的过程，不同时期生产空调所充注的制冷剂类型也有所区别。基于上述分析，动态存量-流量分析方法则能将精准地将动态替换过程纳入估算中，此计算过程可分为如下三步：

（1）计算每年空调新购量

基于动态存量-流量分析方法的物质守恒原理，空调年新购量可由其存量的年变化量和年淘汰量量之和计算得出，计算公式如下：

$$P_t = \begin{cases} N_t,\ t = 1990 \\ N_t - N_{t-1} + D_t,\ t \geq 1991 \end{cases} \quad (3)$$

式中，P_t代表 t 年时空调新购量，N_t为 t 年时空调年存量，D_t为 t 年时空调年淘汰量。由于深圳市 1990 年前空调存量较少，所以本文假定 1990 年为计算起始年份，即第一批空调均于 1990 年购买。

其中，D_t可根据每年流入量与淘汰概率计算得出，计算公式如下：

$$D_t = \sum_{1990}^{t-1} P_{t_0} \times f_{(t,t_0)} \quad (4)$$

式中，$f_{(t,t_0)}$为 t_0 年购买的空调在 t年被淘汰的概率。本研究假定$f_{(t,t_0)}$符合韦伯分布，即$f_{(t,t_0)} = \frac{k}{\lambda^k}(t - t_0)^{k-1}e^{-\left(\frac{t-t_0}{\lambda}\right)^k}$，其中 k和λ的取值分别为 2.2 和 12.7 [19]。

(2) 计算每年空调制冷剂使用量

在计算空调制冷剂年使用量时，本文不仅将制冷剂动态替换过程纳入计算中，同时也综合考虑了空调型号大小及不同制冷剂的充注量差异，计算公式如下：

$$I_{i,t} = \sum_j P_t \times C_{i,t} \times V_{i,j} \times Prop_j \quad (5)$$

式中，$I_{i,t}$代表 t 年时 i 类制冷剂使用量，$P_{i,t}$为 t 年时 i 类制冷剂的使用比例，$V_{i,j}$为j类型号空调中 i 类制冷剂充注量，$Prop_j$为j类型号空调的权重。

(3) 计算每年空调制冷剂存量

同上，根据物质守恒原理，空调制冷剂年存量可用如下矩阵计算公式表示：

$$S_{i,t} = \sum_{1990}^{t} I_{i,t_0} \times U_{(t,t_0)} \quad (6)$$

式中，$S_{i,t}$代表 t 年时 i 类制冷剂存量，$U_{(t,t_0)}$为可靠度函数,即空调器在$[t_0, t]$年间正常使用而未被淘汰的概率。其中，$U_{(t,t_0)} = e^{-\left(\frac{t-t_0}{\lambda}\right)^k}$。

(4) 计算每年空调制冷剂释放量

$$F_{i,t} = S_{i,t} \times L_t \quad (7)$$

式中，$F_{i,t}$代表 t 年时 i 类制冷剂释放量，L_t为制冷剂年释放率。

1.3.2 直接环境影响计算

同理，直接环境影响也可基于各类制冷剂释放量与各制冷剂的排放因子计算得来，计算公式如下：

$$CE_{direct,t} = \sum_i F_{i,t} \times GWP_i \quad (8)$$

式中， $CE_{direct,t}$为 t 年时民用建筑空调直接碳排放，GWP_i为 i 类制冷剂的排放因子。

1.4 减排潜力预测方法

1.4.1 情景分析法

情景分析法是目前 GHGs 排放及能源消耗研究中常用的预测方法之一。不同于常规的趋势外推法得到的单一预测结果，情景分析法则是通过考虑各种影响因素的不确定性，分析各因素不同政策及发展条件下可能出现的多种结果，其结果呈现较为全面及精准，同时也有利于决策者根据不同情景的预测结果而做出合理决策[20]。因此本文选用情景分析法来，设定基准情景及三种不同节能程度的情景来对深圳市民用建筑空调环境影响未来发展趋势进行预测，为政府相关节能减排政策的制定提供数据参考。

1.4.2 关键影响因素识别

基于上述分析，本文将关键影响因素罗列如下，并依据变化规律将其分为三类：理论不变因素，单一变动因素及多重变动因素(详见图 2)

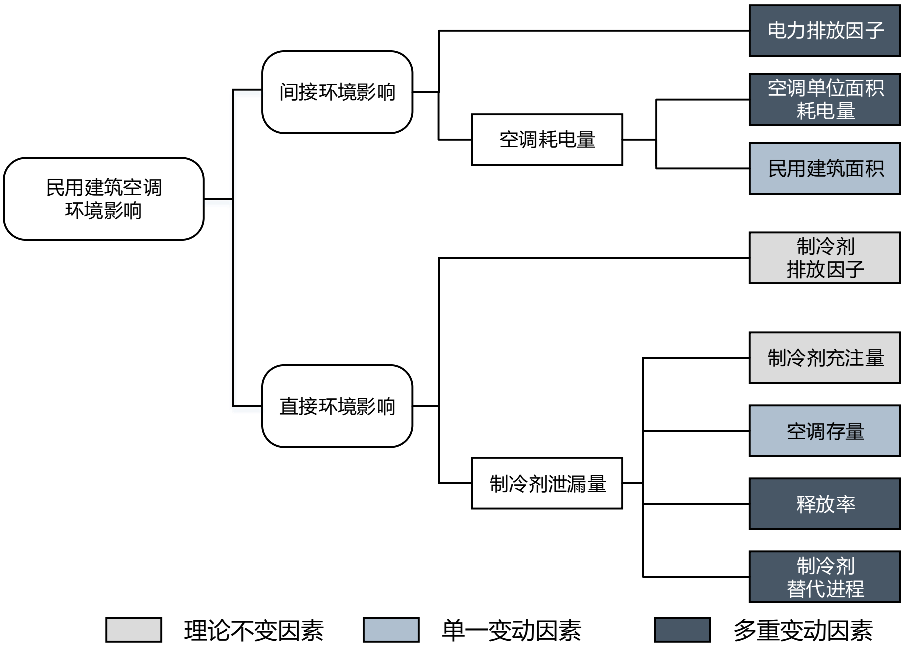


图 2 本文情景分析中的关键影响因素

Fig.2 Key factors in scenario analysis

其中，理论不变因素是指短时间内该类因素不会出现变化;单一变动因素是指该类因素呈现单一变化趋势，本研究采用趋势外推法对其进行简单预测；而多重变动因素是指该类因素会因经济、技术发展及政策变化而呈现不同的变化趋势，并且该类因素可以通过不同政策设定而实现人为可控，也是情景假设中需根据不同政策力度而设置的参数。

1.4.3 情景假设与参数设置

情景假设的核心在于各情景参数的设定，本文以 2017 年为基准，参照深圳市及发达国家相关节能政策力度来对各情景参数进行预测，以模拟各政策力度下的变化趋势。本文共假定 4 种情景：基准情景(未考虑减排措施)、保守减排情景(S1)、中度减排情景(S2)及理想减排情景(S3)，各类情景参数设定及描述如下：

表 1 情景假设参数描述

Table 1 The parameters of Scenario analysis

指标		基准情景	S1	S2	S3
单位面积空调能耗	居住	每年 2.2%-3.2%增速(趋势外推)	每年增长 1 %	每年增长 0.5%	每年增长 0.1%
	公共	每年 1%-1.1%增速(趋势外推)	每年增长 0.5%	每年增长 0.25%	每年增长 0%
电力排放因子		维持不变	每年减少 0.5%	每年减少 1%	每年减少 1.5%
制冷剂替换		详见图 1			
制冷剂释放率		维持 6%不变	2030 年降低至 5% (美国水平)	2030 年降低至 4% (德国水平)	2030 年降低至 2% (日本水平)

注：单位面积空调能耗的 S1、S2、S3 假设情景参考 Santamouris（2016)研究[21]；电力排放因子 S1、S2、S3 情景参考 Khanna 等人(2016)研究[22]；制冷剂替换 S1 参考日本当前替换进程[23]；S2 及 S3 参考能源基金会研究报告[15]；各国空调制冷剂释放率来源于 UNEP（2010)[24]、Koronaki 等(2012)[25]、MOE（2016)[26]。

1.5 数据来源

1.5.1 各类计算参数来源

在能耗计算中，本研究主要用到两类参数：单位面积空调能耗和建筑面积。其中，2017 年居住和公共建筑单位面积空调能耗分别来源于实地调研和《深圳市大型公共建筑能耗监测情况报告(2017 年度)》[27]；历年值则参考《深圳市统计年鉴》中的民用建筑耗电量增长率来对其变化趋势进行估算。

此外，各类建筑面积通过《深圳市统计年鉴》和于深圳市住建局数据估算得到。

在制冷剂释放率计算中，空调存量数据通过《深圳市统计年鉴》估算得到；制冷剂充注量取自 Duan 等(2018)[16]；Xue 等(2017)[23]；Wang 等(2016)[28]学者的研究结果；制冷剂使用比例取自能源基金会研究报告[15]；空调型号权重取自中关村家用空调年度销售报告[29]；释放率取自孙锌(2014)[81]及蒋诗新(2016)[82]的研究结果。

南方电网和各制冷剂排放因子分别来源于国家发改委应对气候变化司[30]和联合国环境署[24]。

1.5.2 实地调研

本研究选择精度较高的电费账单调查法，在 2017 年 1 月至 2018 年 5 月期间，对于深圳市 40 个小区共 511 户住宅的电费账单进程三次集中入户搜集，获取了其 2017 年逐月用电量数据。其次，依据调研结果，本研究分析得出 11-3 月为深圳市非空调开启月份，并选择该时间段作为基础月份，通过月份相减法计算出空调能耗(全年空调能耗量=全年耗电量-基础月份耗电量*12)。

2 结果与讨论

2.1 空调能耗量分析

深圳市民用建筑空调能耗计算结果如图 3 所示。从增长趋势来看，2005-2017 年间，深圳市空调能耗增长了近一倍左右。2017 年时，该数值已达 95.3 亿 kWh(±5 亿 kWh)，约占民用建筑总能耗的 39%，相当于英国同年空调能耗的 1.4 倍(75.8 亿 kWh)[31]。

从建筑类型来看，2017 年深圳市居住建筑的空调能耗总量(45 亿 kWh)与公共建筑(50 亿 kWh)较为接近；但近年来随着人民生活水平的快速提高及常住人口的爆发式增长，导致居住建筑空调能耗的增长速度高于公共建筑。

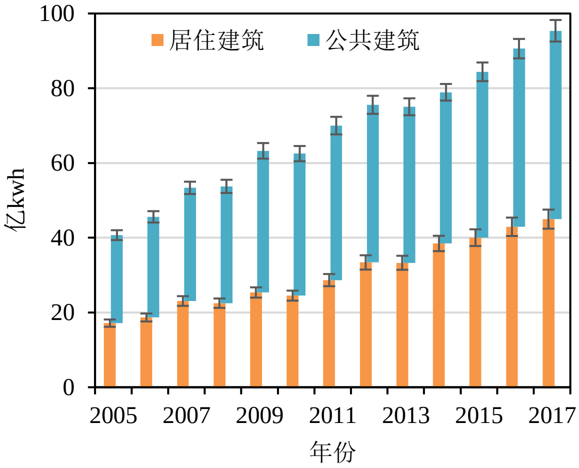


图 3 深圳市民用建筑空调能耗量

Fig.3 The energy consumption of air conditioners in civil buildings in Shenzhen

2.2 空调制冷剂释放量分析

深圳民用建筑空调制冷剂释放量计算结果如图 4 所示。

从增长趋势来看，深圳市空调制冷剂释放量在 2005-2017 年间增加了 1.4 倍左右，2017 年该数值达 1,484.6 吨(±108 吨)，相当于日本同年全国家用冰箱制冷剂释放量的 6.5 倍(248.0 吨)[32]。

从制冷剂类型上来看，R22 释放量呈现先增加后减少的趋势,其排放量峰值出现在 2012 年，此趋势也说明当前 HCFCs 的淘汰工作已初显成效，制冷剂的逐年释放过程对于臭氧层的影响逐渐减少；与之相反，R410a 释放量自 2012 年后迅速增加，并于 2017 年达到 701.4 吨，较接近于同年 R22 的释放量；而现阶段 R32 和 R290 的使用量较少，两者的逐年释放量可忽略不计。

2.3 空调使用过程的环境影响评价

深圳民用建筑空调使用过程的环境影响评价结果如图 5 所示。

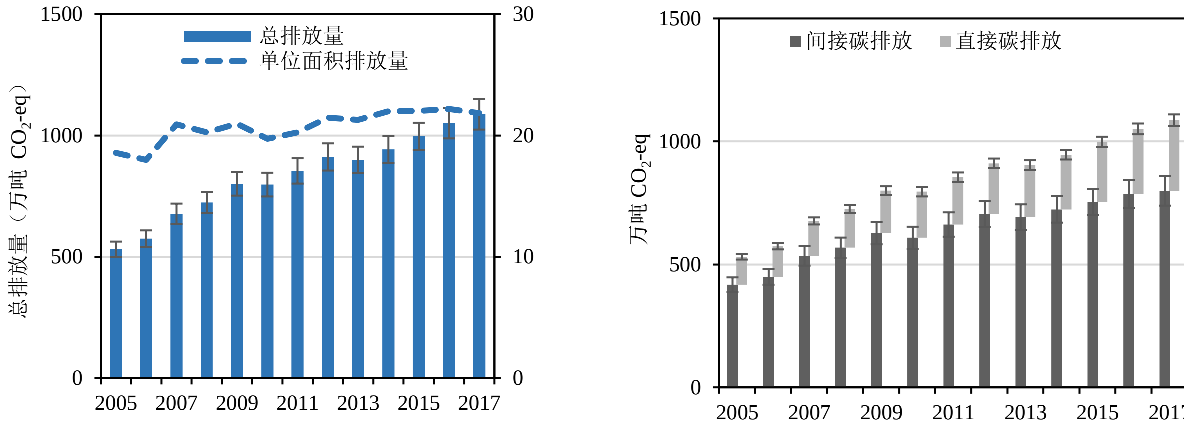
从总量来看，空调使用过程的碳排放呈现持续增长的趋势,其碳排放量在 2005-2017 年间增长了接近一倍，在 2017 年该碳排放量达到 1,087.8 万吨 CO_2-eq(±63.5 万吨 CO_2-eq)，相当于新西兰 2017 年全国碳排放量的 1/3(约 3,000 万 t CO_2-eq)[33]。但其单位面积碳排放量却呈现先增加、再减少、后趋于稳定的波动趋势.2005 年深圳市空调使用过程的单位面积碳排放量为 18.6kg CO_2-eq/m^2，随后出现波动增长并在 2012 年达 21.48kg CO_2-eq/m^2 的峰值，而近五年来该数值稳定在 22kg CO_2-eq/m^2 左右。此结果同时也说明了近年来深圳市对于绿色建筑和节能建筑的大力推行政策，以及整个空调行业对于节能空调的推广措施初见成效。

从碳排放来源来看，空调耗电所产生的间接碳排放为深圳市民用建筑空调碳排放的主要来源。2017 年其间接碳排放量达 799.2 万吨 CO2-eq(±60.2 万吨 CO2-eq)，约占碳排放总量的 73.7%左右；但制冷剂释放产生的间接碳排放也占到 26.3%左右的比例，因此在民用建筑空调节能减排工作中，制冷剂释放造成的环境影响也不可忽略。此外，目前极少有研究涉及到空调使用过程中制冷剂释放所产生的环境影响方面，大量研究均集中在空调使用能耗及空调节电技术研究上，本文结果也进一步说明了直接碳排放量不可忽略，如何通过低

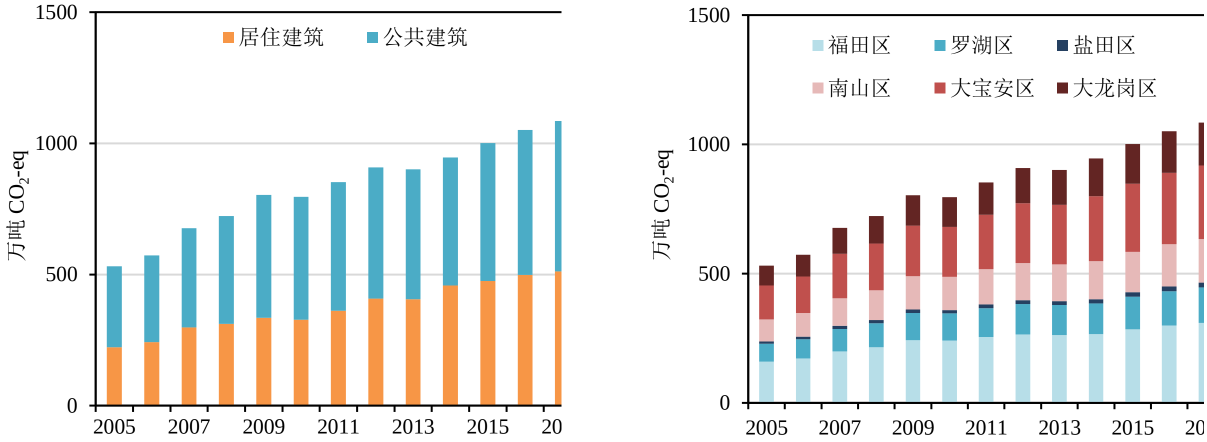
GWP 制冷剂的替换措施及降低制冷剂释放率减少该直接碳排放,也应得到整个建筑部门减排工作的重视。

从建筑类型来看，公共建筑的碳排放量要略高于居住建筑，2017 年两者的空调碳排放量分别为 572.8 万吨 CO2-eq(公共建筑)和 511.8 万吨 CO2-eq(居住建筑)。但从两者的增长速度来看，居住建筑的年增速(约为 10.8%)要高于公共建筑(约为 10.8%)。长期以来，深圳市建筑节能减排工作的重点均以公共建筑为主，但随着近年来深圳市常住人口的爆发式增长及人民生活水平的提高，其居住建筑部门的能耗及 GHGs 所占的比重愈来愈重，因此，相关部门也应加大对居住建筑部门的关注。

从区域分布来看,福田区和大宝安区(包括宝安、龙华及光明)为全市的主要碳排放贡献源(约占 55%)，2017 年两者的碳排放量分别为 308.9 万吨 CO2-eq 和 284.7 万吨 CO2-eq；而同年，其他区域的碳排放量分别为：南山区(168.8 万吨 CO2-eq)>大龙岗区(包括龙岗、坪山及大鹏)(165.8 万吨 CO2-eq)>罗湖区(137.55 万吨 CO2-eq)>盐田区(168.82 万吨 CO2-eq)。因此，相关部门在进行建筑节能减排工作规划时，应重点关注福田区及大宝安区的空调环境影响。



(a) 增长趋势　　　　(b) 来源分布



(c) 建筑类型分布　　　　(d) 区域分布

图 5 深圳民用建筑空调使用过程的环境影响计算结果

Fig.5 The environmental impact of air conditioners in civil buildings in Shenzhe

2.4 减排潜力预估

深圳市民用建筑空调使用过程的减排潜力预测结果如图 6-7 所示。

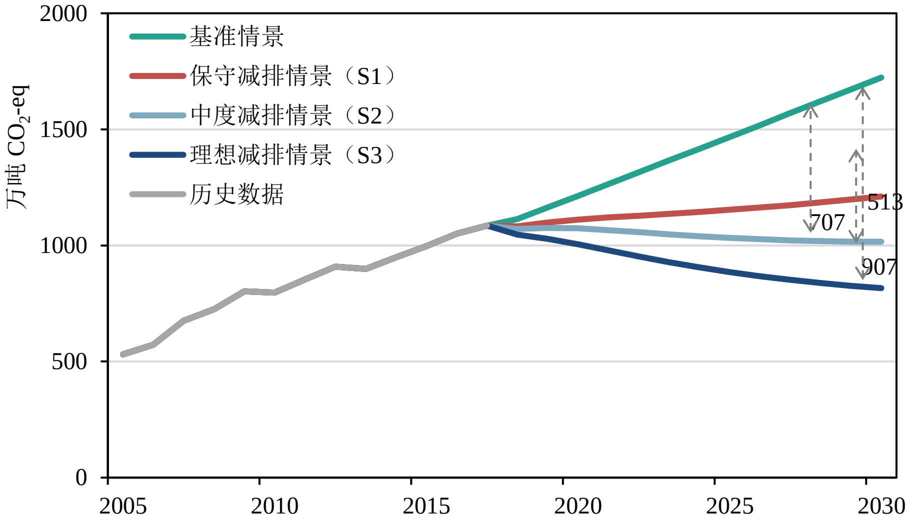
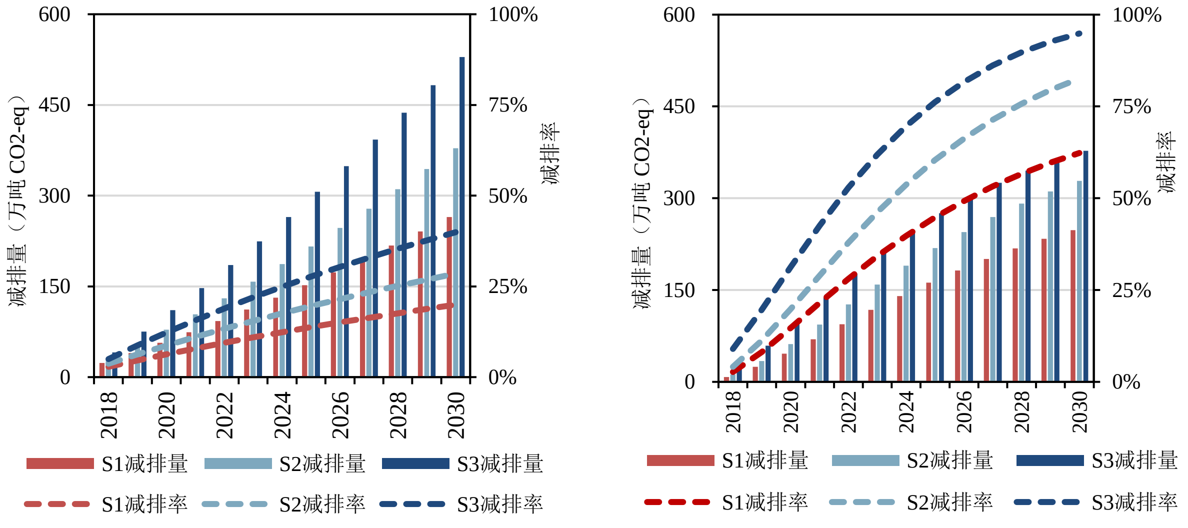


图 6 深圳市民用建筑空调环境影响预测值

Fig.6 The forecasting environmental impact of air conditioners in civil buildings in Shenzhen

基准情景下，深圳市民用建筑空调碳排放将持续增长，并在 2030 年达到 1,723.1 万吨 CO_2-eq；情景 S1 下，深圳市民用建筑空调碳排放增长速度将趋于平缓，2030 年其碳排放量为 1,210.6 万吨 CO_2-eq，相比于 2017 年仅增加了 122.8 万吨 CO_2-eq，并有望在 2030 年左右达到碳排放量峰值；情景 S2 及 S3 下，深圳市民用建筑空调碳排放将呈现逐渐下降的趋势，2030 年两种情景的碳排放量分别为 1,016.2 和 816.4 万吨 CO2-eq，相比于 2017 年分别减少了 71.6 和 271.4 万吨 CO2-eq。



(a) 间接环境影响减排潜力

(b) 直接环境影响减排潜力

图 7. 深圳市民用建筑空调减排潜力

Fig.7 The carbon mitigation potential of air conditioners in civil buildings in Shenzhen

从减排潜力来看，三种减排情景的减排潜力及效果较为乐观。与基准情景相比，S1、S2 和 S3 在 2018-2030 年间的累计减排量可达为 3,517.4、4,856.7 和 6,489.7 万吨 CO2-eq。从不同碳排放来源来看，三种情景的直接碳排放和间接碳排放的累计减排量相近；S1、S2 和 S3 直接碳排放的累计减排量分别为 1,744.5、2,340.9 和 2,944.9 万吨 CO_2-eq，其间接碳排放的累计减排量则分别为 1,722.9、2,515.9 和 3,545.8 万吨 CO_2-eq。但从减排率上来看，直接排放的减排率远高于间接排放；S1、S2 和 S3 直接碳排放的累计减排率分别为 38.3%、12.6%和 64.7%，其间接碳排放的累计减排率则分别 12.7%、18.1%和 25.6%。这意味着不同程度的碳减排方案与技术经济措施有可能控制深圳市民用建筑空调系统的碳排放增长速度，此外，不难发现，在三种减排情景下，直接排放的累计减排潜力不可忽略，推进制冷剂加速替代进程和降低制冷剂释放率等措施必不可需。

3 结论与建议

(1)空调为深圳市民用建筑能耗的主要来源，2017 年全市民用建筑空调能耗量已达 96 亿 kWh(± 5 亿 kWh)，约占民用建筑总能耗的 39%。

(2)深圳市民用建筑空调使用过程中的环境影响不容小视。自 2005 年来，深圳市民用建筑空调所带来的环境影响已增长了一倍左右，2017 年其碳排放量高达 1,088 万吨 CO_2-eq(±64 万吨 CO_2-eq)，约为新西兰同年全国碳排放量的 1/3。

(3)空调能耗和制冷剂释放产生的碳排放比例约为 3:1，因此制冷剂的逐年释放不可忽略。

(4)空调使用过程的减排潜力较为可观。情景分析结果表明，按当前的发展模式和增长速度,深圳市空调的碳排放当量将会持续增长并在 2030 年达到 1,723 万吨 CO_2-eq；而不同力度的减排措施可产生显著的减排效果；在最优模式下，其累计减排量可达 6,490 万吨 CO_2-eq(2018-2030 年)—约为挪威 2017 年全国碳排放量的两倍。

(5)为实现深圳市空调的低碳可持续发展，政府应加大对环保型空调的补贴，从而推进低能耗、低 GWP 制冷剂及高密封性空调的保有率，从源头上实现空调减排。此外，相关部门也应进一步提高能耗监测平台的接入率，并加大相关激励制度及宣传力度。同时，需进一步推进可再生能源的发电比例，优化电力能源结构，以降低电力排放因子。

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形貌调控在废旧半导体灯具回收预处理中的应用

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摘要：废旧半导体灯具在城市矿山中的地位不可忽视，其成分包含少量单位纯度极高的金、银、铜等贵金属，铕、铈、钇、钆等稀土元素金属，以及铝、玻璃和塑料。废旧半导体灯具作为典型电子废弃物，其回收技术的瓶颈之一在于其破碎料呈片状与丝状，导致了分选过程中流场干扰造成的富集困难。本文采用形态调控技术，以废旧 LED 塑包铝球泡灯为实验原料，球化破碎料颗粒的三维形貌，通过对物料外形的改性实现其比重差异的强化。通过探究处理时间、驱动转速、温度等设备参数对颗粒改性的影响，研究调控后物料颗粒风选分离与富集效率。以废旧半导体灯具入手，为电子废弃物预处理技术开发提供研究基础。

关键词：粒度分布；电子废弃物；物理分选；资源化

Application of shape control in recycling pretreatment of used semiconductor lamps

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Abstract: The status of waste semiconductor lamps and lanterns in urban mines cannot be ignored. Their components include a small amount of precious metals such as gold, silver and copper with extremely high unit purity, rare earth metals such as europium, cerium, yttrium and gadolinium, as well as aluminum, glass and plastic. As a typical electronic waste, used semiconductor lamps and lanterns, one of the bottlenecks of their recycling technology is that the crushed material is in the form of flakes and filaments, which leads to the difficulty of enrichment caused by flow field interference in the sorting process. In this paper, the shape control technology is adopted, the waste LED plastic clad aluminum bulb is used as the experimental material, the three-dimensional morphology of the spheroidized crushed material particles, and the difference in specific gravity is strengthened by modifying the shape of the material. By exploring the effects of processing time, driving speed, temperature and other equipment parameters on particle modification, the air separation and enrichment efficiency of the material particles after regulation is studied. Start with waste semiconductor lamps and lanterns to provide a research basis for the development of electronic waste pretreatment technology.

Key words: size distribution, waste electric and electronic equipment, mechanical separation, resource

半导体照明（Semiconductor Lighting）是新型照明技术，其基本器件发光二极管（Light Emitting Diode）是可将电能转化为光能的固态半导体器件。LED 照明产品具有节能、环保、寿命长等优点，但由于驱动电源老化等原因，该照明产品平均寿命仅为 5-7 年，这导致 LED 发光照明产品将在未来几十年内大规模出现在废物流中，增加电子废弃物处理负荷[1-5]。在废旧 LED 的发光模块中，含有金、银、铜等贵金属，以及作为荧光粉以获取白光的铕、铈、钇和钆等稀土元素金属[6-8]，有价组分的含量相对原矿来说更具提取价值。

LED 灯具回收技术的研究在实验室采用破碎[9,10]、分选[11,12]和湿法回收[13,14]进行研究。以 LED 塑包铝球泡灯为例，其粉碎料中含有大粒径的铝片与塑料，微粒级的稀贵金属，细长形的铜丝。采用现有电选技术可实现较好的金属、非金属分离[15,16]，但实施成本高，且处理量小。采用金属与非金属的密度差异对电子废弃物破碎料中的铝、铜和塑料实施分离具有低成本、大处理量的潜在优势，典型分选技术有风力分选[17,18]、跳汰分选[19,20]、重介质分选[21]等。但在此类重力分选的介质流场中，片状颗粒在不同时空受流场力的面积，即有效面积，存在巨大不确定性[22-27]。接触面积的大小决定了在流场中同等质量的颗粒受力情况的不同，颗粒在流场中的运行速度与轨迹将不可预判。

机械分选过程中不同的分选方式有不同的粒径范围，邱等[28]人研究发现 0.6-1.2mm 是高压静电分选的最佳粒径，而且不同形状的金属颗粒在电场中的运动行为不同。其中球形金属颗粒的轨迹和落点最远，其次是柱状颗粒和片状颗粒[29-31]。而张等[32-35]人通过对非球形颗粒在均匀流场中绕流运动进行数值计算，结果表明颗粒绕流曳力系数随球形度增大而减小，球形颗粒绕流曳力系数最小，同时等粒径颗粒，球形度越小其分离效率越低。因此颗粒整形可以使分选变得更加容易。谭等[36]通过对石屑颗粒整形研究发现，整形之后石屑的性能得到了很大改善，颗粒粒形得到改善，颗粒级配较好；由于大颗粒的破碎和大量小颗粒的生成，其堆积密度和紧密密度提高、空隙率降低；泥块含量、压碎值、棱角性降低[37-40]。针对以上电子废弃物特有瓶颈问题，考虑通过改变其颗粒外形优化分选效率。铜、铝均具有较佳的延展性，在外力作用下易于变形，若对丝状铜与片状铝进行外力强化改变或优化其外形，使其变形为质量集中的团状或块状将强化其质量优势，在重力分选中拥有更高分选效率，弱化外形带来的分选劣势。

本文介绍一种机械外场力强化方法对 LED 破碎料进行机械力强化，将其不利于分选的形貌通过调控趋于均一化。通过调控后外形前后比较、粒径分布和风选效率分析，研究形貌调控对废旧半导体灯具回收预处理的影响。

1．材料与方法

1.1 颗粒特征

本文采用的 LED 球泡灯由佛山市蜀南电子有限公司生产制造，由电源驱动、灯珠、灯珠基板、灯杯、PC 灯罩和灯头组成，功率 5W，直径 60mm 高 110mm，30g。LED 球泡灯中塑料占总质量的 45.50%，铝占 32.12%，铜占 2.53%。组件间的连接方式有粘结、螺丝连接、焊锡固定和卡扣连接。本实验采用剪切式破碎机对 LED 灯具进行剪切式整体破碎，获得铝由片状形式存在，铜为丝状，塑料为块状，粉状混合物。块状塑料与片状铝片多集中在大粒级破碎料中，铜丝集中与小粒级破碎料中。发光模块中的金、银、铜、镓、铟等贵金属，铕、铈、钇和钆等稀土元素金属在破碎后均集中于小粒径粉末中。

2.2 实验方法

选用 100 个 LED 球泡灯进行剪切破碎，收集破碎物料并移至形貌调控装置进行机械物理强化。本文采用机

械外场力强化技术对破碎料实施机械-物理形态调控，将铜丝、铝片通过外力作为改变原有外形以及形貌。形态调控过程中耦合温场强化，使片状的塑料颗粒在软化温度下进入获取可塑性，同期实现片状到块状的调控。依次称取 300g 破碎物料作为单次形貌调控实验的处理量，选择电动机转速为 500r/min、1000r/min、1500r/min，分别在室温、77℃、117℃的条件下处理 3min、5min、10min。物料取出后采用 5 目、6 目、8 目、12 目、16 目、24 目、30 目筛网进行筛分确定粒径分布。通过风选分选粒级相同的铜、铝和塑料，并对得到的风上产物和风下产物采用电感耦合等离子体（ICP-OES）进行定量测试其成分含量，比较形貌调控前后物料分选效率。

通过采用形貌调控技术，减小破碎物料的长径比，增加其球形度，使其达到较佳的分选粒径是实验的首要目标。为了减少大颗粒物料的损失，限制调控过程中因碰撞、磨损产生的微粒量是形貌调控技术的另一关键。

2. 实验结果

2.1 颗粒外形变化

形貌调控处理前后铝片与铜丝形貌发生了显著变化，图 1 展示了形貌调控前后变化，铝片通过调控变成了形貌规则、大小相近的类球形颗粒，铜丝也从细长形变成了集中的铜丝线团。形貌调控前后，颗粒平均长径比减小，球形度提高，颗粒表面粗糙度降低。

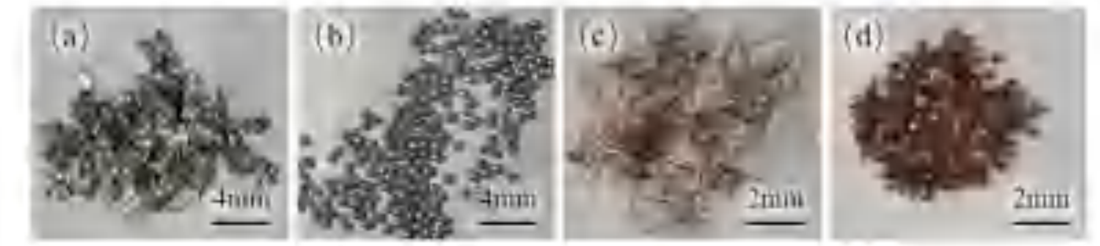

图 1 形貌调控前后对比

Fig 1 Contrast before and after shape control

2.2 粒级变化

形貌变化技术使调控前扁平和细长的大粒径颗粒变成了调控后类球且体积集中的小粒径颗粒，前后粒度分布发生显著变化。相同转速、温度条件下，未整形、5min、10min 的处理时长的粒级分布如图 2 所示，无论是 5min、10min，3.3-4mm 粒径的大颗粒在处理后大量减少，使得 1-2.4mm 粒径的颗粒增加，这是因为调控过程中的碰撞与挤压产生微粒。在 5min 和 10min 的处理时间下，皆产生<0.55mm 颗粒，并且 10min 产生颗粒多于 5min。但是在中等粒径范围内，10min 产生的颗粒少于 5min 产生的，可见增加处理时间将增加微粒产生的量。图 2 数据显示，不论是在室温、77℃、117℃，3.3-4mm 粒径的大颗粒在发生调控后都急剧减少，进入小粒级。这是由于调控过程中的碰撞与磨损，微粒的产生无法避免。在室温和 117℃环境下实施形貌调控时，粒径<0.55mm 颗粒增加明显。但是，当在 77℃环境下实施形貌调控时，<0.55mm 粒径颗粒总量相对较小，1-1.4mm 粒径颗粒明显较多，其余粒径 0.55-0.7mm 和 0.7-1mm 与室温和 117℃条件下的总量趋于相同。因此，通过控制处理时长、温度，在改变颗粒长径比的同时，可以显著减少颗粒形貌调控中大粒径颗粒的质量损耗，减少微粒的产生。

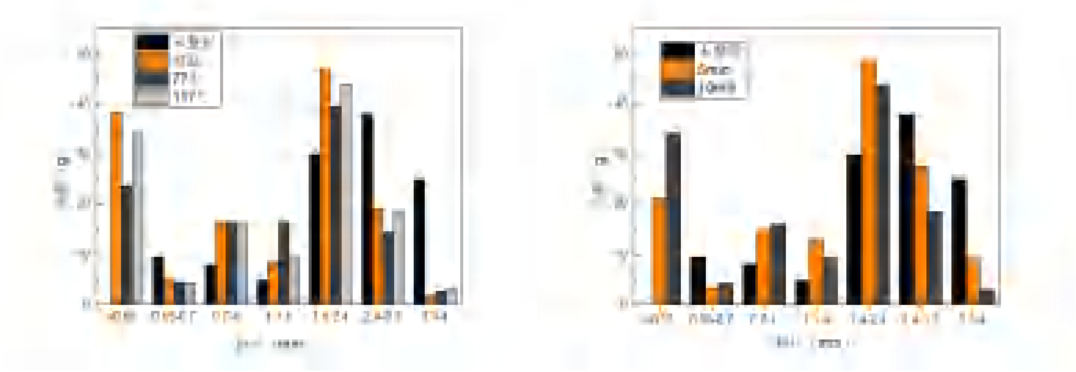

图 2 形貌调控前后粒度分布

Fig 2 Particle size distribution before and after shape control

为了进一步验证形貌调控对机械物理分选效率的影响，此次试验采用风选的方式分离处理之后的物料，首先将形貌调控后的物料筛分为四组分别进行风选分离。风选分离的效果通过金属分离效率来确定，

$$\text{金属分离效率}p=\frac{m_1}{m_{\text{总}}} \tag{1}$$

其中，m_1表示风下金属质量，$m_{\text{总}}$表示该粒径范围内物料的总质量。

图 3 所示为经过形貌调控后物料的分离效率与处理时间的关系，未经处理的物料颗粒无法进行有效分离，粒径在 0.7-1.4mm 范围内的颗粒分选效率为 0，并且 1.4-2.4mm 粒径范围内的分离效率为 7%。但经过形貌调控处理之后物料的分选效率有了显著提高，并且随着处理时间的增加分选效率也在逐渐增加，但是增加速率在减小。为了进一步量化形貌调控对机械回收效果的影响，通过计算中等粒径颗粒的回收率与产物纯度同形貌调控处理前进行对比，得到对比图如图 3，从图中可以明显看出，中等颗粒的回收率由 18.94%上升到了 81.85%，同时取 2.4-3.3mm 粒径分析得到未处理时分选产物纯度为 76.75%，经过处理之后的产物纯度增加至 100%，有效的提高了机械分选的分离性能。经过形貌调控处理再分选不仅提高了金属的分离效率，而且经风选分离之后风下产物的纯度得到明显提高。未经过形貌调控处理直接风选的物料在 1.4-2.4mm、2.4-3.3mm 粒径范围内风下产物的纯度分别为 30.4%、76.8%，而 0.7-1.0mm、1.0-1.4mm 粒径范围内的颗粒，风选未能将其分离，风选之后只得到风上产物。但是经过形貌调控处理之后，除在常温条件下形貌调控的 1.4-2.4mm 粒径范围内的颗粒风下产物的纯度为 79.9%以外，其他不同条件处理之后风下产物的纯度均为 100%。

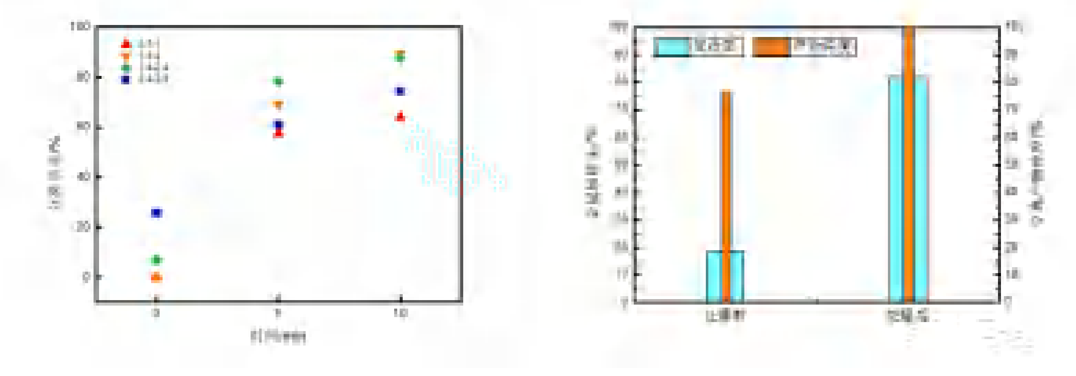

图 3 风选分选效率

Fig 3 Air separation efficiency

表 1 形貌调控前后分选对比

Table 1 Separation comparison before and after shape control

项目	目数	6-8 目		8-12 目		12-16 目		16-24 目	
		风上	风下	风上	风下	风上	风下	风上	风下
整形前	金属(%)	11.85	4.59	12.89	1.19				
	非金属(%)	27.13	1.39	25.05	2.73	1.64		0.33	
整形后	金属(%)	2.15	6.26	2.49	18.18	0.31	2.68	1.75	3.10
	非金属(%)	6.00		18.81		5.43		11.54	

3. 讨论

通过破碎物料颗粒的形貌调控，使块状的物料颗粒更加趋近球形，同时还可以使片状和丝状的物料接近类球形。本实验通过对废旧 LED 破碎物料进行形貌调控，结果表明在初始阶段片状铝颗粒尖锐的棱角受到冲击变得圆滑；随着形貌调控处理的进行，片状颗粒不断受到撞击而蜷曲成球形，铜丝也在压缩摩擦中逐渐成球；不同颗粒在成球后继续受到冲击，其球形度得到进一步提高。在经过不同的处理条件处理之后，3.3-4mm 粒径范围内的颗粒占比均下降，同时也产生了大量的粒径小于 0.55mm 的颗粒，这是因为在整个设备内部颗粒会发生剧烈的摩擦与碰撞，这个过程中塑料尖锐的边缘会被磨损，产生大量粉末。

在经过形貌调控处理之后，一是物料的形貌发生变化，破碎后片状铝颗粒变成了类球形，丝状的铜线也蜷曲成为铜线团颗粒；二是不同粒径的物料质量发生变化，最大粒径的物料质量减少；三是由于各个颗粒的形貌更加接近，并通过筛分之后同粒径同组分的质量接近，而且形态调控之后的颗粒在重力分选的介质中的有效面积差距较小，因此球形颗粒的运动状态也更稳定，所以破碎物料在经过形貌调控处理后金属的分离效率提高。

其中随着转速的增加，金属的分离效率逐步增加；在不同的处理时间下，处理时间越长最终金属的分离效率也越高；与随着时间、转速增加金属分离效率也同时增加不同，随着温度的增加金属的分离效率并没有持续增加，从室温增加至 77℃时，金属的分离效率有所增加，然而当温度增加至 117℃时，不同粒径范围内的金属分离效率均出现不同程度降低，经过分析形貌调控的结果，发现由于温度过高导致部分塑料融化并相互粘连并包裹金属颗粒形成无法分离的团状物，造成在 117℃时金属的分离效率相较于 77℃有所降低。

4、总结

对 LED 球泡灯破碎物料进行形貌调控预处理使物料颗粒球形度增加，后续风选效率显著增加且风下分离产物纯度得到明显提高。通过对比形貌调控处理前后物料颗粒的形貌，证明形貌调控可以改变颗粒的形貌。进一步颗粒形貌的改变使其在分选分离中获得更好的分选效果，分离效率和分下产物纯度都得到提高。而当前电子废弃物机械物理分选由于破碎物料的形貌不规则导致分选效率不高，但是本实验中通过在机械分选之前进行形貌调控预处理，最终提高了金属的分离效率与纯度，因此形貌调控预处理同样可以应用于其他电子废弃物的机械物理分选过程中。

形貌调控的优势在于可以处理粒径较大的破碎物料，使其在破碎过程中能够无需破碎更小的级别，节约能源；同时通过形貌调控可以使破碎物料形貌更加规则，提高最终分选效率和物料纯度。但是不足之处在于尽管能够处理粒径较大的物料，但是在处理过程中将产生部分粒径小于 0.5mm 粉末难以处理，温度控制不均匀还会导致局部过热融化塑料使其相互粘连并粘附其他组分。不仅如此形貌调控处理过程中会有部分物料卷曲包裹其他组分物料的情况，但是具体物料卷曲会包裹多少材料，我们将会在接下来的实验中做进一步的研究。

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我国动力电池回收与梯次利用研究

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摘要：2019 年我国动力电池回收与梯次利用产业整体发展态势良好，国家层次先后出台政策标准，积极引导产业健康发展；地方省市开展回收利用试点，推动区域内规范回收利用。相关责任主体主动上传溯源数据，申请回收服务网点，探索退役电池在储能、基站备电和低速电动车领域的应用和示范。未来国家将进一步加强对回收服务网点、上下游产业链合作以及梯次利用产品认证等方面的管理。建议进一步针对产业现存的不规范、不完善、不成熟等问题，加强市场监督、政策管理、技术研发和合作交流。

关键词：动力电池；回收；梯次利用

Research on Recycling and Echelon Use of EV Batteries in China

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Abstract: In 2019, the overall development trend of EV batteries recycling and echelon use industry in China is developing well. The country has successively issued policies and standards, and actively guided the healthy development of the industry. Several provinces and cities have launched recycling pilots to promote standardized recycling activities. Relevant responsible parties proactively upload traceability data, apply for recycling service outlets, and explore the application and demonstration of retired batteries in the fields of energy storage, base station backup and low-speed electric vehicles. In future, China will strengthen the management of recycling service outlets, cooperation between upstream and downstream industry chains, and certification of echelon use products. In order to solve the current problems of irregularity, imperfection, and immaturity during industry development, it is recommended to strengthen market supervision, policy management, technological research and development, cooperation and exchanges in the regional and international level.

Key words: EV batteries, Recycling, Echelon use

一、2019 年动力电池产业概况

1、我国新能源汽车产销量情况

近年来，中国新能源汽车（仅包括纯电动汽车和插电式混合动力汽车两类）产销量情况如图 1 所示，新能源汽车产销量基本平衡，2018、2019 年产销量均在 120~127 万辆。自 2016 年开始，纯电动汽车占比在 75%~85%之间波动。根据中国汽车工业协会最新数据，受疫情影响，2020 年 1-4 月，纯电动汽车产销均完成 15.5 万辆，同比分别下降 46.9%和 44.6%；插电式混合动力汽车产销分别完成 5.1 万辆和 4.9 万辆，同比分别下降 37.6%和

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39.8%。

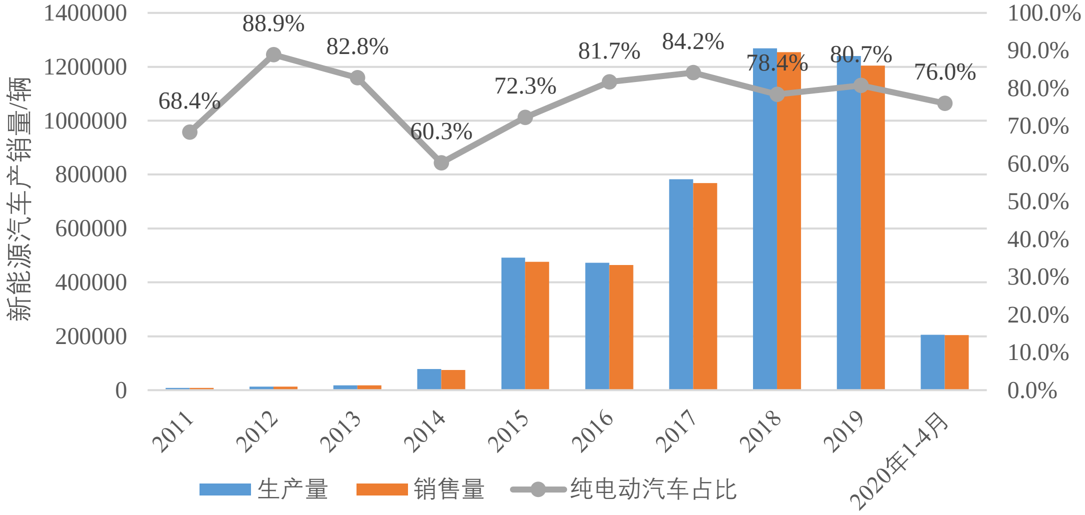

图 1 我国新能源汽车产销量情况

2、我国动力电池类型及装机量情况

中国动力电池（包括磷酸铁锂电池/三元电池和其他电池）装车辆数据如下图所示，装车量逐年上升，从 2015 年的 15.72 GWh 增长到 2019 年总装车辆为 62.6GWh。从 2016 年开始，三元电池占比逐年上升，从 2016 年的 22.7%增长到 2019 年的 64.7%。2019 年 1-12 月，我国动力电池装车量累计 62.2GWh，同比累计增长 9.2%。其中三元电池装车量累计 40.5GWh，占总装车量 65.2%，同比累计增长 22.5%；磷酸铁锂电池装车量累计 20.2GWh，占总装车量 32.5%，同比累计下降 9.0%。2019 年我国动力电池企业装车量排名为：宁德时代、比亚迪、国轩高科、力神电池、亿纬锂能、中航锂电、时代上汽、孚能科技、比克电池、欣旺。

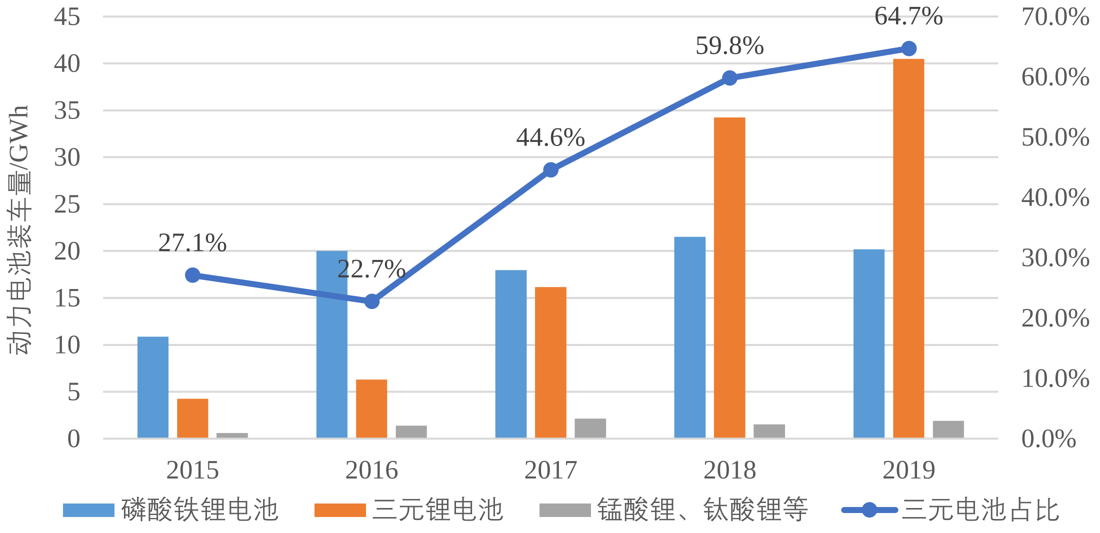

图 2 主要动力电池类型及其装车量情况

3、动力电池回收利用政策

（1）国家层面回收利用政策梳理

2018 年以来，国内动力电池回收利用政策不断更新发布，涉及动力电池管理办法、试点方案、溯源管理、管理平台建设、规范条件、网点建设与运营等各方面。政策梳理见表 1。

表 1 动力电池回收与梯次利用政策汇总（2018-2020）

	签发日期	政策文件名称
1	2018 年 1 月 26 日	新能源汽车动力蓄电池回收利用管理暂行办法
2	2018 年 2 月 22 日	新能源汽车动力蓄电池回收利用试点实施方案
3	2018 年 7 月 2 日	新能源汽车动力蓄电池回收利用溯源管理暂行规定
4	2018 年 7 月 23 日	关于做好新能源汽车动力蓄电池回收利用试点工作的通知
5	2018 年 8 月	新能源汽车国家检测与动力蓄电池回收利用综合管理平台
6	2018 年 9 月 3 日	符合《新能源汽车废旧动力蓄电池综合利用行业规范条件》企业名单（第一批）
7	2019 年 10 月 31 日	新能源汽车动力蓄电池回收服务网点建设和运营指南
8	2019 年 12 月 2 月	关于进一步做好新能源汽车动力蓄电池回收利用溯源管理工作的通知
9	2019 年 12 月 16 日	《新能源汽车废旧动力蓄电池综合利用行业规范条件（2019 年本）》；《新能源汽车废旧动力蓄电池综合利用行业规范公告管理暂行办法（2019 年本）》
10	2020 年 3 月 23 日	2020 年工业节能与综合利用工作要点

（2）地方层面回收利用政策梳理

2018 年 7 月 23 日，工业和信息化部、科技部、生态环境部、交通运输部、商务部、市场监管总局、能源局联合发布《关于做好新能源汽车动力蓄电池回收利用试点工作的通知》（工信部联节〔2018〕134 号），确定京津冀地区、山西省、上海市、江苏省、浙江省、安徽省、江西省、河南省、湖北省、湖南省、广东省、广西壮族自治区、四川省、甘肃省、青海省、宁波市、厦门市及中国铁塔股份有限公司为试点地区和企业[1]。各试点地区纷纷出台适应当地产业现状的回收利用试点实施方案，部分地方政策梳理如下：

2018 年 8 月 31 日，**广东省**印发《广东省新能源汽车动力蓄电池回收利用试点实施方案》的通知（粤经信节

能函〔2018〕169 号）[2]。2018 年 11 月 13 日，公布广东省新能源汽车动力蓄电池回收利用试点企业名单（第一批）的通知（粤工信节能函〔2018〕244 号）[3]。

2018 年 12 月 18 日，**京津冀**三地工信部门联合发布《京津冀地区新能源汽车动力蓄电池回收利用试点实施方案》[4]。2019 年 6 月 14 日，京津冀三地工信部门发布《关于京津冀地区新能源汽车动力电池回收利用试点示范项目的公示》[5]。

2019 年 3 月 6 日，**四川省**印发《四川省新能源汽车动力蓄电池回收利用试点工作方案》的通知[6]。

2019 年 3 月 29 日，**宁波市**印发《宁波市新能源汽车动力蓄电池回收利用试点实施方案》的通知[7]。

2019 年 4 月 2 日，**湖南省**印发《湖南省新能源汽车动力蓄电池回收利用试点实施方案》的通知，并确定了试点单位名单、工作任务及目标[8]。2020 年 4 月 29 日，湖南省工业和信息化厅组织召开新能源汽车动力蓄电池回收利用政策培训暨试点工作推进视频会议。

2019 年 4 月 29 日，**厦门市**新能源汽车动力蓄电池回收利用试点工作领导小组办公室（代）发布关于印发《厦门市新能源汽车动力蓄电池回收利用试点实施方案》的通知（厦电池回收办〔2019〕1 号）[9]。

2020 年 2 月 17 日，**福建省**印发《福建省开展新能源汽车动力蓄电池回收利用体系建设实施方案（2020-2022 年）》的通知（闽工信法规〔2020〕32 号）[10]。

4、动力电池回收利用国家标准体系

构建动力蓄电池回收利用全生命周期国家标准体系，计划车用动力电池回收利用相关标准 22 项，其中 7 项标准已发布实施，主要涉及产品规格尺寸、编码规则、余能检测、拆卸要求、拆解规范、材料回收要求以及包装运输规范等内容。标准体系梳理见表 2。

表 2 动力电池回收利用国家标准体系

序	类别	部分	内容
1	通用要求	第 1 部分	拆解指导手册编制规范（立项中）
2		第 2 部分	术语和定义
3		第 3 部分	退役技术条件
4		第 4 部分	分类技术规范
5		第 5 部分	企业安全生产通用要求
6		第 6 部分	绿色工厂评价规范
7	规格尺寸		电动汽车用动力蓄电池产品规格尺寸（GB/T 34013-2017）
8	编码规则		汽车动力蓄电池编码规则（GB/T 34014-2017）
9	梯次利用 GB/T 34015	第 1 部分	余能检测（GB/T 34015-2017）
10		第 2 部分	拆卸要求（GB/T 34015.2-2020）

11		第 3 部分	梯次利用要求（已报批）
12		第 4 部分	梯次利用产品标识（公示中）
13		第 5 部分	可梯次利用设计指南
14		第 6 部分	剩余寿命评估规范
15	再生利用 GB/T 33598	第 1 部分	拆解规范（GB/T 33598-2017）
16		第 2 部分	材料回收要求（GB/T 33598.2-2020）
17		第 3 部分	放电技术规范（起草中）
18		第 4 部分	回收处理报告编制规范
19	管理规范 GB/T 38698	第 1 部分	包装运输规范（GB/T 38698.1-2020）
20		第 2 部分	回收服务网点建设规范
21		第 3 部分	装卸搬运规范
22		第 4 部分	存储规范

二、动力电池回收利用管理

1、国家溯源管理平台建设情况

新能源汽车国家监测与动力蓄电池回收利用溯源综合管理平台（https://www.evmam-tbrat.com/），简称“国家溯源平台”，是工业和信息化部依据《新能源汽车动力蓄电池回收利用溯源管理暂行规定》委托北京理工大学电动车辆国家工程实验室而建立，其主要功能是将动力蓄电池生产、销售、使用、报废、回收、利用等全过程进行信息采集，同时对各环节主体履行回收利用责任情况实施监测，从而实现动力电池的来源可查、去向可追、节点可控。2018 年 7 月 31 日，国家溯源平台启动会召开，标志着国家溯源平台正式运营。国家溯源平台包含车载管理模块和回收利用管理模块以及地方溯源履责监管模块三个部分，涵盖新能源汽车监测和动力蓄电池溯源功能，为我国动力蓄电池回收利用溯源信息采集与管理的官方平台，可实现对各环节主体履行回收利用溯源责任情况实施监测。

根据中国汽车技术研究中心有限公司报告，截至 2020 年 4 月，共有 790 余家产业链上下游企业完成国家溯源平台注册。其中，车载管理模块已有 330 家国内新能源汽车生产企业完成注册，注册率 95%；注册企业合计产量占总产量的 99.9%；12 家新能源汽车进口企业完成注册，注册率 71%。回收利用管理模块已有 269 家报废机动车回收拆解企业完成注册，注册率 37%；86 家梯次利用企业完成注册，其中 19 家企业已上传溯源信息；95 家再生利用企业完成注册，其中有 15 家企业已上传溯源信息。

截至 2020 年 3 月，11 家回收拆解企业、17 家梯次利用企业以及 15 家再生利用企业共上传 94 万余溯源数据。11 家回收拆解企业上传 811 个车辆报废环节数据信息，包括 401 个车辆数据以及 410 余个报废电池包信息。17 家梯次利用企业上传 15.95 万个单体/模组/包级的梯次产品生产销售信息，其中，梯次利用模块产品主要应用于基站备电（占 49%）、低速电动（占 32%）、储能（占 19%）等领域。15 家再生利用企业共上传 1.1 万吨废旧

动力蓄电池的回收入库信息，上传 9100 余吨电池回收资源信息，其中，3.1%为磷酸铁锂电池，96.9%为三元电池。

2、动力电池回收网点建设情况

根据工业和信息化部 2019 年 10 月 31 日出台的《新能源汽车动力蓄电池回收服务网点建设和运营指南》（工业和信息化部公告 2019 年 第 46 号），新能源汽车生产企业应在本企业新能源汽车销售的行政区域（至少地级）内建立收集型回收服务网点，在本企业新能源汽车保有量达到 8000 辆或收集型回收服务网点的贮存、安全保障等能力不能满足废旧动力蓄电池回收要求的行政区域（至少地级）内建立集中贮存型回收服务网点。梯次利用企业应在本企业梯次利用电池使用的行政区域（至少地级）内建立收集型回收服务网点，可与新能源汽车生产企业共建、共用回收服务网点。收集型回收服务网点的贮存场地面积应不低于 10 平方米，废旧动力蓄电池贮存量应不超过 5 吨；集中贮存型回收服务网点废旧动力蓄电池的贮存能力应不低于 30 吨，贮存场地面积、消防安全设施等应与贮存能力相匹配。

据中国电池联盟统计[11]，截至 2020 年 2 月，全国共计 130 家企业申报了 11229 个回收服务网点，平均每家车企申报 86 个回收网点。其中，部分网点为多家车企提供回收服务，共计有 7634 个回收服务网点。目前，国内回收服务网点申报以汽车企业为主，约有 123 家车企进行了申报，其中有 4 家车企的申报数量超过 500 个，4 家车企申报总量达到 2668 个，占比约为 35%。国内回收网点申报数量超过 300 个的省级行政区有广东、浙江、江苏、山东、河南、四川、河北、湖北等 8 个地区。广东省回收服务网点数量最多，达 777 个。

回收服务网点建设渠道方面，目前主要有 4S 店、电池企业、材料或电池回收企业、汽车拆解厂、其他渠道等 5 种建设渠道。其中，4S 店仍是当下主要的设置方式，占比约 98.8%。4S 店回收服务网点有 7542 个；材料或电池回收网点有 57 个，占比约 0.75%；汽车拆解厂网点有 23 个，占比约 0.3%；其他渠道网点有 8 个，占比约 0.1%；电池企业网点有 4 个，占比约 0.05%。

回收网络布局方面，逐渐呈现多元化发展趋势，包括分散式分布、集中式分布和合作共建等方式，但依托自有销售渠道建设仍是主流。分散式分布的特点是同一省市会布置多个回收网点，如上海大众（762 个回收网点）及浙江豪情（761 个回收网点）。集中式网点分布的主要特点是在同一省市通常只布局 1-2 个回收网点，比较典型的企业有比亚迪（11 个回收网点）、安徽江淮（13 个回收网点）等。与第三方合作共建回收网点模式的分布特点与自有渠道网点建设集中式分布类似，但是回收网点是第三方回收企业，如赛德美通过与材料回收企业、汽车报废企业合作共建回收服务网点，目前已与 63 家企业展开合作，其中材料回收企业 30 家，汽车拆解厂 25 家。

三、动力电池梯次利用建设与示范应用

1、 梯次利用相关专利情况

根据 2019 年专利公开与申请统计情况，2019 年申请“梯次利用”主题相关专利共计 102 项，其中，发明专利 81 项，实用新型专利 20 项，发明授权专利 1 项，外观设计专利 0 项。申请的专利中国家电网有限公司最多，申请 12 项；中国电力科学研究院有限公司次之，申请 5 项。

2019 年公开“梯次利用”主题相关专利共计 148 项，其中，发明专利 94 项，实用新型专利 39 项，发明授权专利 14 项，外观设计专利 1 项。公开的所有专利中国家电网有限公司最多，申请 15 项；中国电力科学研究院有限公司次之，申请 10 项。94 项发明专利中主要涉及退役电池的筛选、评估、配组和检测方法；14 项发明授权专利（其中 11 项为 2016 年申请）中主要涉及电池的检测（或测试、评估）及电池控制（或监管、管理）方法。

2、梯次利用企业建设要求

根据工业和信息化部发布的《新能源汽车废旧动力蓄电池综合利用行业规范条件及公告管理暂行办法》（2019 年），梯次利用企业布局和项目选址应符合国家政策和所在地区相关要求，布局应与本企业废旧动力蓄电池回收规模相适应；场地要求为：具备土地证或土地租用合同不少于 15 年，作业场地满足硬化、防渗漏、耐腐蚀要求，面积与企业综合利用相适应。梯次利用企业应申请厂商代码、规范编码标识、具备信息化溯源能力、建立梯次产品回收体系、规范上传溯源信息。梯次利用企业应采用节能、节水、环保、清洁、高效、智能的新技术和新工艺，淘汰能耗高、污染重的技术及工艺；应具备废旧电池主要性能指标以及安全性的检测技术及装备，具备机械化或自动化拆解设备以及无损化拆分工艺，应具有梯次产品质量、安全等性能检验技术设备和工艺。

资源综合利用及能耗方面，遵循先梯次利用后再生利用的原则，生产过程中产生的零部件、材料（如石墨、橡胶等）及不可利用残余物均应合理回收和规范处理，并做好跟踪管理。鼓励梯次利用电池在基站备电、储能、充换电等领域应用，规范回收报废梯次产品并移交至再生利用企业；梯次利用企业应建立用能考核制度，配备必要的能源计量器具，加强各环节的能耗管控，降低综合能耗。此外，在环境保护要求，产品质量和职业教育，安全生产、人身健康和社会责任等方面，对梯次利用企业规范要求进行详细解读。

3、动力电池梯次利用示范应用项目

目前，我国梯次利用产业正处于由示范工程向商业化转变的过渡阶段。在通信基站备电、电网储能、低速车等领域，梯次利用已开始实用化。基站备电场景应用主要是将梯次利用电池应用在通信基站备用电源系统，在停止供电的情况下为基站用电设备供电。电网储能场景应用主要是实现发电侧储能的负荷调节、提高新能源消纳等，输配电储能的电能质量提高、线路损耗降低等，以及用户侧分布储能的削峰填谷、负荷转移等。低速车场景主要是在微型电动车、电动自行车等低速车上，替代原用的铅酸电池，减轻装载电池重量，提升电池循环使用寿命等，主要使用领域包括外卖、物流、环卫等[12]。梯次利用电池典型应用案例如下：

（1） 电网储能领域

国家电网在北京大兴建设了 100kWh 梯次利用锰酸锂电池储能系统示范，在张北建设了 1MWh 梯次利用磷酸铁锂电池储能系统示范。北京匠芯研发了梯次利用光储能系统，并正在建设基于大数据的动力蓄电池包（组）

评估系统。北京普莱德与北汽等合作实施了储能电站项目、集装箱式储能项目等，累计梯次利用量约 75MWh[13]。

2019 年 3 月上旬，江苏南京江北储能电站动工，共利用“旧电池”总容量为 7.5 万千瓦时，其中包含磷酸铁锂电池 4.5 万千瓦时，铅酸电池 3 万千瓦时。此外，该站还建设了锂电池储能电站，容量达 19.36 万千瓦时，梯次利用和锂电规模均为国内之最[14]。

2019 年 8 月 6 日，由深圳市比克动力电池有限公司、南方电网综合能源服务公司合作建设的 7.27MWh 梯次电池用户侧储能系统，在深圳比克工业园区正式投入运营，项目实际占地约 600 平米，通过 10kV 高压并网方式集成了 4.23MWh 三元电池和 3.04MWh 磷酸铁锂电池两种储能系统[15]。

（2） 通信基站备电领域

中国铁塔在 2018 年已停止采购铅酸电池，统一采购梯次利用的锂电池。2018 年底，中国铁塔在全国 31 个省市 12 万个基站中使用梯次锂电池 1.5GWh，替代铅酸电池约 4.5 万吨；2019 年，中国铁塔基站备用电源新增使用磷酸铁锂电池约 5GWh，替换铅酸电池约 15 万吨；到 2020 年 3 月，中国铁塔公司在 38 万基站累计使用梯次利用电池 5.5GWh，在沈阳等 10 余个城市投入运营 300 余个换电网点。此外，深圳比亚迪、国轩高科等企业利用退役动力蓄电池，生产用于备电领域的梯次利用电池产品。

（3） 低速车场景

中天鸿锂在外卖快递用电动车、城市物流车、观光车辆、 环卫车辆等领域积极开展“以租代售”梯次利用新型商业模式，通过出租而非出售的方式，向客户收取部分押金，定期收取租金，改善梯次利用后电池的回收。此外，无锡格林美与顺丰公司探索将梯次利用电池用于城市物流车辆。

四、动力电池回收与梯次利用发展趋势

1、开展回收服务网点评估。进一步强化政策落实，将基于《新能源汽车动力蓄电池回收服务网点建设和运营指南》（工业和信息化部公告 2019 年 第 46 号），编制《网点规范性评估手册》，指导开展回收服务网点建设的合规性评估工作。并将评估结果及时反馈企业，不符合要求的及时进行整改，将评估结果反馈工信部门，便于及时了解企业合规性和整改情况，并实现动态管理（新增和取缔网点）。

2、强化回收利用体系建设。为促进动力蓄电池回收体系的规范、集约、高效建设，提升废旧动力蓄电池回收利用效率，将探索成立充分联合新能源汽车生产企业/梯次利用企业、综合利用企业以及回收服务网点等相关责任主体的生产者责任组织（PRO），进一步推动动力蓄电池回收利用体系建立，并研制《动力电池回收利用实施方案》。

3、优化梯次利用管理制度。据有关部门报告透露，未来将进一步优化动力电池梯次利用管理制度，借鉴再制造产品认定及机动车零部件再制造管理的模式，结合梯次利用行业发展实际和市场监督管理总局的认证职能，出台《梯次利用管理办法》。拟建立梯次产品自愿认证制度，以市场为主导，规范引导梯次产品的生产、使用、认证及回收。目前《梯次利用管理办法》已完成各部委意见征求工作。

五、问题及建议

1、存在的问题

（1）管理制度缺乏强制约束力

国家和地方已出台的政策措施均属行政性文件，虽明确了回收利用主体责任，但尚无法律约束力，对不法行为缺乏强制性处罚措施。市场存在一些“作坊式”回收企业，普遍不具备相关的技术能力和设备，通过低成本运作挤占市场资源。

（2）梯次利用行业缺乏引导

梯次利用仍处于探索阶段，退役电池的残值评估、自动化拆解、快速分选重组等共性技术储备不足，梯次产品的质量、安全缺乏保障。另一方面，部分企业为追逐短期利益，开发充电宝等小型化梯次产品，导致产品应用领域分散，产品报废后再回收难度增大。

（3）梯次利用技术有待突破

动力蓄电池有 130 多种规格，种类多、连接性及互换性差，行业还存在产品合格率低、一致性差等问题。电池及汽车生产企业正在提供拆卸、拆解等技术信息支持，但在通信协议、历史数据等关键资源分享方面还没有形成机制。目前梯次利用还存在效率偏低，电池剩余寿命及一致性评估等技术还不成熟。

（4）回收体系建设不完善

目前动力电池回收体系主要依托汽车生产企业现有销售网络建设，存在一定的安全风险，且操作人员的专业性不足。动力电池回收体系覆盖率待提升，回收量不足，缺乏规模效应，总体回收成本较高，回收利用企业效益不明显。上下游企业的合作还有待加强，回收体系的资源配置有待优化。

2、产业发展建议

（1）完善回收利用管理政策，加快制定相关标准

一方面要加强监督管理合力，完善配套政策支撑体系。通过加强立法，制定技术规范，采取生产者责任延伸和押金制度等推动电池的回收利用，并通过许可证加强对电池生产企业和废旧电池资源回收利用企业的监管。另一方面，要采取多样化激励措施，探索可持续商业模式。

（2）加强企业准入与梯次利用产品管理，规范市场秩序

研究制定梯次利用企业准入与梯次利用电池产品管理制度，制定奖惩措施，适时开展梯次利用电池产品认定和标识工作，发布梯次利用企业及产品名单，营造规范回收、生产和销售的有序市场秩序。

（3）强化关键技术开发与物联网技术应用

以企业为主体，加强产学研合作，推动动力蓄电池生态设计、退役判定及检测、梯次利用电池残余价值评估、电池自动化拆解及材料分选等共性技术攻关和关键设备研发。融合物联网、大数据等新兴技术，提高动力蓄电池回收利用的质量和效率。

（4）加强上下游产业链和区域间合作，发挥第三方平台作用

加强产业链上下游合作，探索动力电池回收利用创新模式，依托产业联盟等第三方服务机构组建商业服务平台，整合和优化上下游资源，提高回收率、降低回收成本。依托巴塞尔公约亚太区域中心等区域性平台，加强全方位的国际交流合作，促进关键技术、优势资源以及先进理念的引进和输出。

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我国快递包装物质流分析及生命周期评价研究[21]

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摘要：采用实地调研方法，对国内多个城市进行抽样调查，获取快递包装物单件重量数据；通过物质流分析，估算 2019 年我国全年快递包装废弃物产生量，并运用生命周期评价法对快递包装废弃物生产与废弃阶段对环境造成的影响进行计算分析。结果显示，2019 年全国共产生 1173.55 万吨的快递包装废弃物材料，其中瓦楞纸 1031 万吨，塑料包装约 75 万吨，胶带和填充物约 30 万吨。其中约有 637.76 万吨废弃物进入回收利用体系，得到约 542.01 万吨的再生产品，总体的回收利用率 46%左右。环境影响方面，快递包装废弃物生产阶段所造成的环境影响是最大的。其次是再生阶段，再生产量替代生产所造成的环境效益。填埋环境影响要普遍高于焚烧影响。最终处置方面绝大部分影响类别方面为负面环境影响，即环境效益。基于研究结果，可以有针对性地进行改进措施，如由于纸类包装材料占比较高，优先开展纸类包装的各方面优化活动，能够产生更明显的环境效益，相关研究结果可为我国快递包装的有效管理提供一定的参考。

关键词：快递包装物、物质流分析、生命周期评价、环境影响

Material flow analysis and life cycle assessment of China's express package products

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Abstracts: The field research method was adopted to carry out sampling survey in many domestic cities to obtain the weight data of express packages. Based on material flow analysis, the annual output of express packaging waste in China in 2019 was estimated, and the impact of the production and disposal stage of express packaging waste on the environment was calculated and analyzed by using life cycle assessment method. The results show that in 2019, China produced 11.735,500 tons of express packaging waste materials, including 10.31 million tons of corrugated paper, 750,000 tons of plastic packaging, and 300,000 tons of tape and filler. About 6,377,600 tons of waste went into the recycling system, and about 5,420,100 tons of recycled products were obtained, with an overall recycling rate of about 46%. In terms of environmental impact, the production stage of express packaging waste has the greatest environmental impact. The second is the regeneration stage, the environmental benefits caused by the replacement of production by the regeneration yield. The environmental impact of landfill is generally higher than that of incineration. Most of the impacts in the final disposal fall into the category of negative environmental impacts, i.e., environmental benefits. Based on the research results, targeted improvement measures can be taken. For example, due to the high proportion of paper packaging materials, paper packaging optimization activities in all aspects should be given priority to produce more obvious environmental benefits. Relevant research results can provide certain reference for the effective management of express packaging in China.

Key words: express packaging, material flow analysis, life cycle assessment, environmental impact

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近年来随着经济社会发展，快递业由于人们需求的逐年增大，迎来了高速的发展。在 2014-2018 年，我国快递业务量连续跨越 100 亿、200 亿、300 亿、400 亿、500 亿的台阶，并在 2019 年达到 600 多亿。但伴随大幅增长的快递量一同而来的是巨量的快递包装废弃物，它的数量伴随快递业务量的持续增长而增长，同样带来的，还有快递包装物相关的一系列问题。在我国，许多学者关注到了有关快递包装废物的问题，并进行了各方面的研究：王代兵等 [1]通过文献调研，结合过往五年的物流发展，对快递包装几个特点进行了详细研究，列举其产生原因并依此从国家、物流、消费者三方面制定解决措施。路永华 [2]采用问卷调查的形式，辅以实地访谈调查，对快递包装当前现状进行调研，并进一步就如何针对上述因素减少快递包装垃圾产生作出指导性建议。姚瑶等[3]则对快递包装回收体制的发展情况进行了详细的调查，主要集中在消费者对使用的快递包装的了解与回收态度。并针对受访者的回馈，对快递包装回收体制的建立给出政策上的建议。周丽俭等 [4]将研究目标放在我国快递包装废弃物再利用方面，将快递包装回收环节存在的问题具体罗列，并作出针对性建议。王昕雨等 [5]选择作为目前快递业消费主体之一的大学生进行调研，根据大学生问卷回馈的问题提出适配循环经济下快递包装回收的策略。李宇铭等 [6]研究发现我国快递包装废弃物治理目前面临的三个难关：立法效果不佳、快递包装废弃物处理技术欠缺、快递包装废弃物回收利用意识薄弱。因此通过对美、日、德、韩四国的治理经验介绍及经验总结，对比借鉴之下提出符合我国发展情况的政策建议。张浩等 [7]通过文献资料分析和国外实地考察，梳理了快递包装物回收处理的整体复合系统架构，对不同国家快递包装回收系统实际操作过程中的成功经验和经典做法进行整理分析。对比我国目前回收系统各环节存在的不足之处提出完善建议，强调了系统的整体优化。韩育霖 [8]结合国内外研究现状，对快递包装材料的法律相关知识制度进行整理，包含法律体系、相关体制与机制建设等。之后结合当前的快递包装材料机制提出相关的法律方面构想，用立法促进快递包装材料回收的技术转化及用法律手段促进发展绿色包装的推广及应用。

就目前来说，对于快递包装物本身产生，流向及环境影响方面的研究还较为稀少，因此本研究关注当前快递行业附属的快递包装废弃物产生问题，探究全国范围内快递包装废弃物产生情况，调研并建立模型计算分析，并选用环境影响因子分析快递包装废弃物可能对环境造成的影响，用以填补我国当前领域上的空白并为之后更细化的研究提供可选参考数据。

1、材料与方法

1.1 研究方法及框架介绍

1.1.1 研究方法

（1）物质流分析

物质流分析最早起源于国外，基本思想的出现可以追溯到十九世纪六十年代，由Udo deHaes第一次明确提出物质流的概念。物质流分析（Material Flow Analysis）运用系统思想对经济活动中物质流动评估的分析方法，是产业生态学中一种重要的研究方法，遵循物质守恒定律，将经济与环境联系在一起。随着发展，物质流分析也越来越多被用于分析有害物质的流动过程及污染减排措施的科学实用性、原材料的循环利用效率以及废弃物管理成效等。

（2）生命周期评价

生命周期评价（Life Cycle Assessment)，关于它的研究已有近五十年的发展历史。它最早的起源可以追溯到二十世纪七十年代初，美国展开的一系列对包装品的分析和评价，在当时被称为资源与环境状况分析（REPA)。生命周期评价作为产品环境特征分析和决策的工具，被广泛地运用于技术科学、自然科学、和国际关系学等领域，它可以被认为是一种全新的 21 世纪最具潜力的适应可持续发展战略要求的环境管理工具。生命周期评价（LCA）是对一个产品系统整个生命周期中的输入、输出以及潜在环境影响进行整理与评估，起始于生命周期清单分析，作为一种环境管理的工具，被称作“从摇篮到坟墓”的分析。ISO 将其定义为汇总和评估一个产品(或服务)体系在其整个生命周期内的所有投入和产出对环境造成的和潜在的影响的方法。[9]ISO14040(生命周期评价—原则和框架)将一个完整的生命周期环境分析工作分为四个基本阶段：范围与目标确定、列表分析、影响评价和结果解释。

1.1.2 生命周期框架

（1）研究目标和范围

本研究采用生命周期评价法对快递包装废弃物从生产到废弃过程中造成的环境影响进行估算，旨在分析并量化快递包装物使用可能对环境造成的影响，令其更为直观地展示，并希望可以通过该研究为相关研究提供一个可供参考的快递包装物环境影响评估模型。选定研究年份为 2019 年，范围为中国全国范围，快递包装废弃物包研究范围分为纸类与塑料类，纸类包括快递瓦楞纸箱、快递结单及纸档袋，塑料类包含快递塑料袋、气泡袋、编织袋及塑料泡沫箱等。

（2）生命周期方法

本次研究中主要采用 SimaPro 软件对相关过程的环境影响进行评估，所需快递包装废弃物相关影响因子也由此软件获取。SimaPro（System for Integrated environmental Assessment of products）分析软件是由荷兰 Leiden 大学环境科学中心在 1990 年完成推出的综合型 LCA 软件，在国际上普遍使用，使用群体广泛分布在超过五十个国家。本研究中，将重点 CML 评价方法对快递包装生命周期过程产生的环境影响进行分析，具体环境应县种类包括：非生物资源消耗潜值（ADP)、酸化潜值（AP)、富营养化潜值（EP)、全球变暖潜值（GWP 100)、臭氧层消耗潜值（ODP)、人类潜在毒性潜值(HTP)、淡水生态毒性潜值(FAETP)、海洋生态

毒性潜值(MAETP)、陆地生态毒性潜值(TETP)以及光化学氧化毒性潜值（PCOP）这十类影响类别。

1.2 数据来源

应用物质流分析方法对快递包装废弃物的回收和处置过程进行分析，并对不同种类的快递包装废弃物总质量进行估算。由于研究局限，本次研究省略了快递包装废弃物的运输及存储环节的消耗及影响，特此说明。针对以上框架设计和关注环节，总结得到其中涉及的主要参数并列出计算方法，如表 1 所示。

表 1 快递包装废弃物物质流分析计算方法

Table 1 Material flow analysis and calculation method of express package wastes

参数	公式	公式解释
快递包装废弃物数量	$Q_s = Q_t \times X_s$	Qs 代表不同种类快递包装废弃物 s 的数量；Qt 代表总快递数；Xs 代表 s 种类快递包装废弃物在总快递数中的占比。
快递包装废弃物重量	$M_s = AM_s \times Q_s$	Ms 指的是 s 种类快递包装废弃物的总重量；AMs 指的是 s 种类快递包装废弃物的单件平均重量。
快递包装废弃物质量占比	$P_s = M_s/M_t \times 100\%$	Ps 代表 s 种类快递包装废弃物总重量在整体快递包装废弃物重量中的占比；Mt 为快递包装废弃物整体重量。
快递包装废弃物回收利用及损失重量	$HM_s = M_s \times HP_s$ $SM_s = M_s - HM_s$	HMs 指的是 s 种类快递包装废弃物的回收利用重量；HPs 代表 s 种类快递包装废弃物的回收利用百分比；SMs 指的是 s 种类快递包装废弃物的损失重量。
快递包装废物回收利用产出量	$C_s = HM_s \times CP_s$	Cs 指的是 s 种类快递包装废弃物的再生利用产出量；CPs 代表 s 种类快递包装废弃物的再生利用率。
快递包装废弃物填埋及焚烧重量	$TM_s = SM_s \times T$ $FM_s = SM_s \times F$	TMs 和 FMs 指的是 s 种类快递包装废弃物填埋和焚烧的重量；T 和 F 代表城市固体废弃物的填埋比和焚烧比。
快递包装废弃物焚烧热能	$R_s = FM_s \times RZ_s \times G$	Rs 指的是 s 种类快递包装废弃物焚烧所能产生的热能总量；RZs 代表 s 种类快递包装材料的焚烧热值；G 指的是焚烧时化学能转化为热能的效率比值。

根据国家资料的统计，获得 2019 年全国范围内的快递量总计为 635.2 亿件。其次通过对城市内各个快递收发货点的实地调研（对不同快递驿站一段时间内的快递流量进行统计，计算不同包装类型占比），结合相关研究报告、文献资料，得出不同种类的快递包装物在总快递包装物量中的占比情况。在快递包装废弃物不同组成材料类型的重量占比研究上，选择在快递驿站进行调研各类包装材料重量，调研点位有北京、武汉、西安、深圳等多个城市。其中瓦楞纸箱、塑料袋等根据尺寸或颜色再进行细分，胶带考虑不同尺寸包装所需长度，获得相应重量区间，并取其平均值，作为快递包装材料的单件平均重量。获得所需参数后，根据表 1 公式，计算可得 2019 年各类包装废弃物使用数量、数量占比及其总重量和重量占比，如表 2 所示。

表 2 2019 各类包装废弃物使用数量及重量

Table 2 The quantity and weight of various packaging wastes in 2019

材料种类	瓦楞纸箱	塑料袋	气泡袋	结单	纸信封
数量占比(%)	54.0%	43.0%	4.0%	100.0%	5.0%
总数（亿件）	343.0	273.1	25.4	635.2	31.8
总重（万吨）	1031.26	67.12	1.39	20.65	14.94
重量占比(%)	87.88%	5.72%	0.12%	1.76%	1.27%
材料种类	编织袋	塑料泡沫箱	胶带	填充物	总计
数量占比(%)	2.8%	0.7%	-	-	-
总数（亿件）	17.8	4.4	-	-	-
总重（万吨）	6.85	1.38	10.11	19.85	1173.55
重量占比(%)	0.58%	0.12%	0.86%	1.69%	100.00%

注：部分包装为“瓦楞纸箱加塑料袋”，经调研占比约为 9.5%，在数量占比计算时同时加入瓦楞纸箱及塑料袋部分；结单数量即为快递总数量；胶带及填充物由于其依附于快递外包装，不以件数记，故在数量统计部分略过；“-”代表略过。

表 3 包装材料回收情况[10]、[11]、[12]

Table 3 Recovery of packaging materials

材料	去向	比例
瓦楞纸箱	回收利用	60%
	处理处置	40%
纸质信封	回收利用	48%
	处理处置	52%
塑料袋、编织袋及气泡袋	回收利用	2%
	处理处置	98%
塑料泡沫箱	回收利用	30%
	处理处置	70%
胶带及填充物	处理处置	100%

物质流分析中的各个废弃物回收利用率及再制造过程中的再生利用率等来源于文献资料和相关报告，如表 3 所示；再生利用率方面，参考相关文献数据，考虑快递包装箱胶带等的不可利用情况的影响，设定瓦楞纸箱、纸信封及结单共享废纸的再生利用率 85%[13]，塑料袋、气泡袋、泡沫塑料及编织袋共享废塑料的再生利用率 80%[14]。由于快递包装废弃物除部分回收，剩余部分进入了生活垃圾处理体系，其处理方式和所占比例参照全国生活垃圾处理情况。通过查询国家统计局-国家数据里的数据，得到我国生活垃圾处理情况，根据 2010 年至 2018 年填埋和焚烧比例变化规律进行预测，2019 年的填埋与焚烧百分比为 57%与 43%；焚烧热能方面，考虑到化学能与热能间的转换，焚烧炉一锅炉系统的热效率一般为 78%左右，故取 78%作为锅炉效率系数并加入计算[15]。

环境影响因子主要从 ELCD 及 Ecoinvent3 数据库中选取数据，采用 CML 2 baseline 2000 V2.05 / the Netherlands, 1997 方法，获得不同阶段不同影响类别的对应影响因子系数，详细情况如表 4。评价过程代

表总值，即相应物质的重量，则由物质流分析部分提供。需要说明的是，由于缺少符合我国国情的本国生命周期环境影响因子，这里选用的是欧盟标准下的影响因子。

表 4 影响因子表[16]

Table 4 Impact factor table

影响类别	单位	纸生产	纸填埋	纸焚烧	塑生产	塑填埋	塑焚烧
ADP	kg Sb eq	1.31E-02	-5.29E-04	-1.40E-04	2.92E-02	-5.29E-04	1.28E-02
AP	kg SO2 eq	6.60E-03	-3.77E-04	-1.35E-04	1.51E-02	-2.33E-04	1.33E-02
EP	kg PO4 eq	2.71E-03	-6.53E-04	-4.63E-05	1.06E-02	-4.64E-04	5.17E-04
GWP 100	kg CO2 eq	1.85E+00	-8.30E-01	-3.67E-02	2.23E+00	-6.97E-02	-8.96E-01
ODP	kg CFC-11 eq	-2.09E-07	-2.78E-09	-7.87E-10	3.21E-07	-2.78E-09	1.97E-07
HTP	kg 1,4-DB eq	7.09E-01	-1.22E-02	6.54E-02	1.97E+00	-1.19E-02	1.48E-01
FAETP	kg 1,4-DB eq	6.02E-01	-1.74E-04	3.03E-04	1.61E+00	-3.44E-04	6.20E-03
MAETP	kg 1,4-DB eq	2.52E+03	-6.37E-01	3.26E-01	3.86E+03	-7.93E-01	4.95E+01
TETP	kg 1,4-DB eq	1.30E-02	-3.14E-05	-3.91E-05	1.09E-02	-5.18E-05	1.83E-03
PCOP	kg C2H4 eq	2.73E-04	-1.93E-04	-4.66E-06	6.51E-04	-1.98E-05	6.62E-04

2、结果与分析

2.1 物质流分析

我国快递包装废弃物物质流情况如图 1 所示。瓦楞纸箱及塑料袋的使用在快递行业中的数量占比达到 54%和 43%（包含同时使用纸箱和塑料袋的 9.5%）；从重量上来说，瓦楞纸箱就占据了快递包装废弃物总重量的 88.7%，比重位列第二的塑料袋占比 4.6%，两者总计贡献超过百分之九十。2019 年全国共产生 1173.55 万吨的快递包装废弃物材料，其中瓦楞纸 1031 万吨，塑料包装约 75 万吨，胶带和填充物约 30 万吨。其中约有 637.76 万吨废弃物进入回收利用体系，得到约 542.01 万吨的再生产品，总体的回收利用率 46%左右。

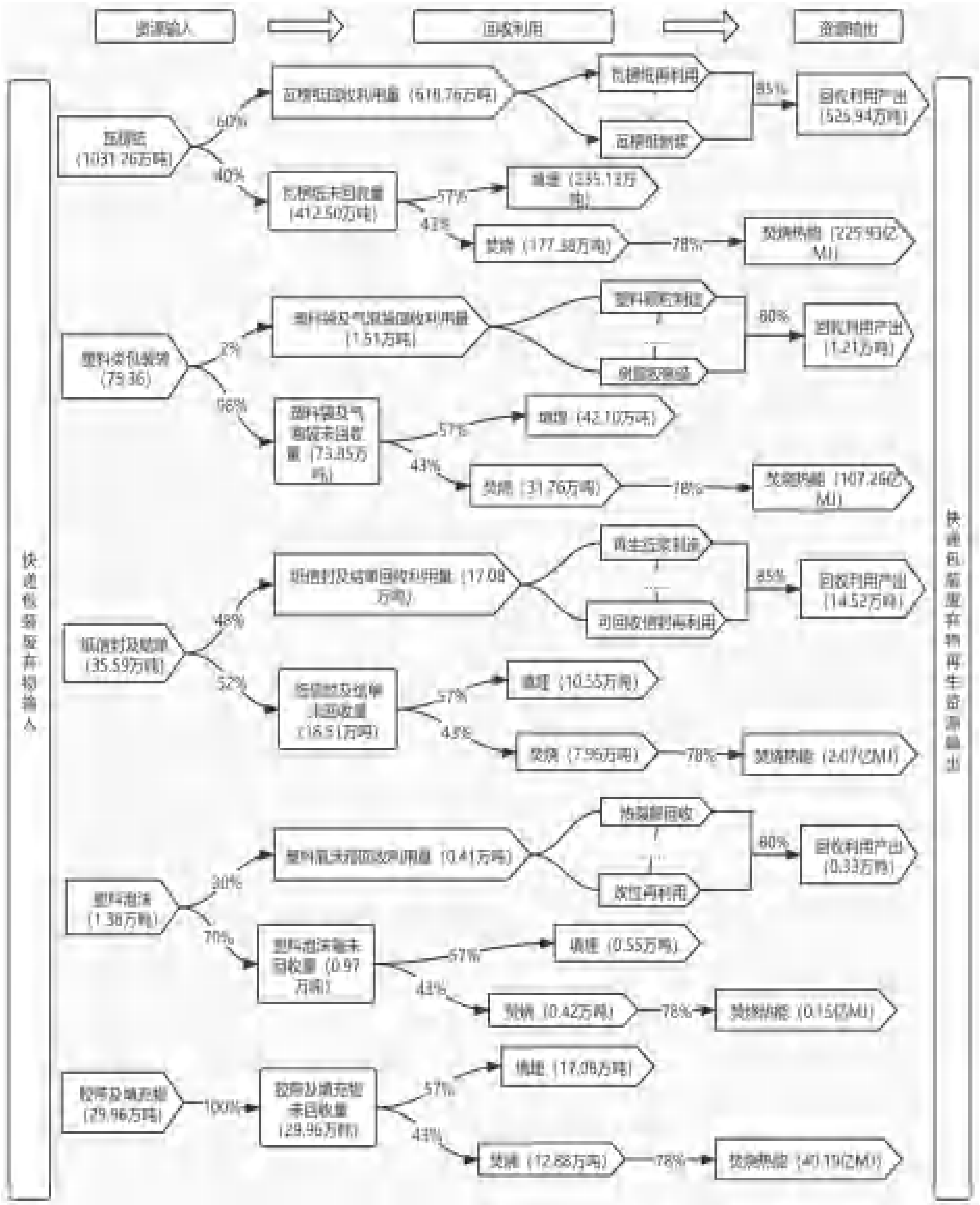

图 1 全国快递包装废弃物物质流（2019 年）

Figure 1 Material flow of Express packaging Waste in China (2019)

城市快递瓦楞纸废弃物回收利用率大致为 60%，剩余 40%则作伴随城市生活垃圾统一进行填埋、焚烧处理。收集的瓦楞纸箱通过回收再造，可用于生产新的瓦楞纸箱或是制成纸浆用于生产其它纸制品产出。2019 年共产生废弃瓦楞纸箱 1031.26 万吨，其中进入回收体系的约有 618.76 万吨，再生各类纸制品产出 525.94 万吨；未回收的 412.50 万吨中，有 177.38 万吨被焚烧，可产生焚烧热能 225.93 亿 MJ（根据“城市生活垃圾的焚烧与热值”[17]提供的瓦楞纸箱热值 16.33MJ/kg 进行计算）。

塑料袋及气泡袋仅有近 2%进入回收利用系统，剩余 98%则进入了城市生活垃圾处理系统。收集的废弃塑料袋可回收用于生产再生塑料，重新作为塑料袋或其它塑料产品使用。废弃快递塑料袋 2019 年产生量约为 75.36 万吨，其中进入回收体系的只有 1.51 万吨，也意味着产出大约 1.21 万吨再生塑料制品；剩余的 73.85 万吨中，其中共有 31.76 万吨被焚烧，，可产生焚烧热能 107.26 亿 MJ（使用 HDPE 与 LDPE 的热值 43.3MJ/kg 进行计算）。

其他包装废物物质流分析数据如图 1 所示。总体上，当前除瓦楞纸箱回收再生率较高外，其他材料基本都进入城市生活垃圾处理系统进行处置，再生利用体系仍需进一步改善。

2.2 生命周期环境影响分析

将快递包装材料按照大类分为纸类、塑料类。废旧瓦楞纸、废弃纸信封及结单归作纸类，塑料袋、气泡袋、编织袋、塑料泡沫、胶带及填充物归为塑料类，两者都分为生产、再生生产、填埋以及焚烧过程。在影响因子的选择上，根据纸类多数为硬质纸，及塑料种类多为 PE、PP 等，选取相应的生产、填埋及焚烧数值进行计算。物质流部分提供的各类快递包装废弃物各个流程总质量数据统计如表 5 所示

$$\text{生产环节：}\boldsymbol{ES_{a,b} = Sx_{a,b} \times SN_b}$$

$$\text{再生生产环节：}\boldsymbol{EZ_{a,b} = -Sx_{a,b} \times ZN_b}$$

$$\text{填埋环节：}\boldsymbol{ET_{a,b} = Tx_{a,b} \times TN_b}$$

$$\text{焚烧环节：}\boldsymbol{EF_{a,b} = Fx_{a,b} \times FN_b}$$

E 为环境影响评价特征化值；ES,EZ,ET 和 EF 分别代表生产，再生，填埋及焚烧过程中产生的环境影响评价特征化值；a 为影响类别（如 ADP）；b 为评价产物类别（纸类及塑料类）；x 为影响因子系数；N 为评价过程代表总值。其中在计算过程中，回收利用后再生生产产生的产品可以看作清洁生产的产品（省去原材料消耗），因此产生的环境影响数值可以用纸类与塑料类的生产影响因子乘以总量后再取负值估算而得。

表 5 2019 年包装材料处理流向（万吨）

Table 5 Direction of Packaging Material treatment in 2019 (tons)

2019 年	初始生产	再生生产	填埋	焚烧
纸类	1066.85	540.47	245.68	185.34
塑料类	106.70	1.54	59.73	45.06

2.2.1 纸类包装环境影响

纸类快递包装废弃物环境影响计算结果如表 6 所示。从生产、再生等各阶段影响值的对比上可以看到，从非生物资源消耗潜值到光化学氧化毒性潜值，纸类快递包装废弃物生产阶段所造成的环境影响是最大的。其次是再生阶段，再生产量替代生产所造成的反向环境影响处于次一量级。填埋与焚烧产生的环境影响体量则再低一个层次，其中填埋环境影响要普遍高于焚烧影响。再看其各阶段结合后的总环境影响值，可以看到除臭氧层消耗潜值（ODP）以外皆为正值，这代表着纸类快递包装物从生产到回收处置过程中，除 ODP 方面为环境带来了正面影响，也可以成为环境效益，相当于减少了 1100 kg CFC-11 eq 的排放外，其它影响类被方面所产生的均为负面环境影响。以酸化潜值举例来说，2019 年全国纸类快递包装废弃物生产处置在酸化潜值方面造成的影响相当于增加了 3.35 万吨 SO_2 eq 的额外排放。

表 6 纸类快递包装废弃物生命周期环境影响

Table 6 Life cycle environmental impact of paper express packaging waste

影响类别	单位	生产(纸)	再生(纸)	填埋(纸）	焚烧(纸)	环境影响值
ADP	kg Sb eq	1.40E+08	-7.08E+07	-1.30E+06	-2.59E+05	6.74E+07
AP	kg S02 eq	7.04E+07	-3.57E+07	-9.25E+05	-2.50E+05	3.35E+07
EP	kg P04--- eq	2.89E+07	-1.47E+07	-1.60E+06	-8.59E+04	1.26E+07
GWP 100	kg C02 eq	1.98E+10	-1.00E+10	-2.04E+09	-6.81E+07	7.64E+09
ODP	kg CFC-11 eq	-2.23E+03	1.13E+03	-6.83E+00	-1.46E+00	-1.11E+03
HTP	kg 1,4-DB eq	7.56E+09	-3.83E+09	-3.00E+07	1.21E+08	3.82E+09
FAETP	kg 1,4-DB eq	6.42E+09	-3.25E+09	-4.28E+05	5.62E+05	3.17E+09
MAETP	kg 1,4-DB eq	2.69E+13	-1.36E+13	-1.56E+09	6.04E+08	1.33E+13
TETP	kg 1,4-DB eq	1.38E+08	-7.01E+07	-7.72E+04	-7.25E+04	6.81E+07
PCOP	kg C2H4 eq	2.92E+06	-1.48E+06	-4.74E+05	-8.63E+03	9.56E+05

2.2.2 塑料类包装环境影响

塑料类快递包装废弃物各阶段环境影响值见表 7。塑料类快递包装废弃物各阶段环境影响值量级规律与纸类类似，不同之处在于塑料类焚烧的环境影响值在部分影响类别中，例如酸化潜值，要高于再生及填埋产生的环境影响值。在总环境影响值方面，与纸类不同的是塑料类快递包装废弃物所产生的环境影响在十类中均为正数，意味着全部对环境造成负面影响。分析对比纸类及塑料类不同环节影响差异，可以看出在生产环节中，纸类生产所造成的环境影响值占据主导地位，其约为塑料生产影响的 3-8 倍，全球变暖潜值影响中，纸类生产达到塑料生产的 8.3 倍。这与包装材料中纸类包装材料使用量大相关联，但由于纸类包装材料使用量为塑料类包装材料的 10 倍左右，相较于其在环境影响方面的差别，可以看出塑料包装材料虽然重量占比较小，但环境影响较大，应该引起更高的关注，减少塑料类包装材料的使用。在填埋环节，纸类包装材料影响一般为塑料类包装材料的 3-6 倍，但在全球环境变暖潜值上，纸类包装材料释放二氧化碳达到塑料类的 49 倍，若考虑减少碳排放，在处理方式上，纸类应该尽量选择其他处理方式。在焚烧处理环节，塑料类包装材

料多产生的负面的环境影响，而纸类包装材料在部分影响类别上能带来正向的环境效益，在同样是产生负面影响的类别上，塑料类包装材料也远高于纸类包装材料。因此，在处理快递包装废弃物环节上，应尽量减少塑料类包装材料的焚烧处理量。

表 7 塑料类快递包装废弃物生命周期环境影响

Table 7 Environmental impact of plastic express packaging waste life cycle

影响类别	单位	生产	再生	填埋	焚烧	环境影响值
ADP	kg Sb eq	3.11E+07	-4.49E+05	-3.16E+05	5.79E+06	3.61E+07
AP	kg SO2 eq	1.61E+07	-2.33E+05	-1.39E+05	5.99E+06	2.18E+07
EP	kg PO4--- eq	1.13E+07	-1.63E+05	-2.77E+05	2.33E+05	1.11E+07
GWP 100	kg CO2 eq	2.38E+09	-3.44E+07	-4.16E+07	-4.04E+08	1.90E+09
ODP	kg CFC-11 eq	3.43E+02	-4.95E+00	-1.66E+00	8.86E+01	4.25E+02
HTP	kg 1,4-DB eq	2.10E+09	-3.03E+07	-7.12E+06	6.66E+07	2.13E+09
FAETP	kg 1,4-DB eq	1.72E+09	-2.48E+07	-2.05E+05	2.79E+06	1.70E+09
MAETP	kg 1,4-DB eq	4.12E+12	-5.95E+10	-4.74E+08	2.23E+10	4.08E+12
TETP	kg 1,4-DB eq	1.16E+07	-1.68E+05	-3.10E+04	8.23E+05	1.22E+07
PCOP	kg C2H4 eq	6.95E+05	-1.00E+04	-1.18E+04	2.98E+05	9.71E+05

2.2.3 总体环境影响分析

将纸类及塑料类快递包装废弃物环境影响值综合分析，如表 8 所示。在所选的环境影响因素中，快递包装从生产到废弃后处理处置过程中，仅臭氧层消耗潜值的最终值是负数，说明 2019 年内全国范围下的快递包装废弃物生命周期评价中，在整个过程中带来正环境效益的仅有臭氧层消耗潜值一块，其余影响类别均产生负面环境影响。以全球变暖潜值为例，整个过程会带来相当于 954 万吨 CO2 eq 的额外排放环境影响，而臭氧层消耗潜值方面，2019 年全年全过程可减少 682 kg CFC-11 eq 的排放。

表 8 快递包装废弃物生命周期环境影响（2019 年全国）

Table 8 Life Cycle environmental impact of Express packaging Waste (nationwide in 2019)

影响类别	单位	纸类影响值	塑料类影响值	总环境影响值
ADP	kg Sb eq	6.74E+07	3.61E+07	1.04E+08
AP	kg SO_2 eq	3.35E+07	2.18E+07	5.53E+07
EP	kg PO_4--- eq	1.26E+07	1.11E+07	2.37E+07
GWP 100	kg CO_2 eq	7.64E+09	1.90E+09	9.54E+09
ODP	kg CFC-11 eq	-1.11E+03	4.25E+02	-6.82E+02
HTP	kg 1,4-DB eq	3.82E+09	2.13E+09	5.95E+09
FAETP	kg 1,4-DB eq	3.17E+09	1.70E+09	4.87E+09
MAETP	kg 1,4-DB eq	1.33E+13	4.08E+12	1.73E+13
TETP	kg 1,4-DB eq	6.81E+07	1.22E+07	8.04E+07
PCOP	kg C_2H_4 eq	9.56E+05	9.71E+05	1.93E+06

针对不同的环境影响类别，各个过程的影响大小也有较大差异，通过分析可以针对性地研究和制定合适的回收处理措施。这里列举较为令人关注的非生物资源消耗潜值、全球变暖潜值及人类潜在毒性潜值作为代

表进行分析。非生物资源消耗潜值、全球变暖潜值、人类潜在毒性潜值最后为正数，带来环境负面影响。相比于纸类及塑料类快递包装废物填埋或焚烧处理过程中产生的环境影响，它们的生产及再生所占环境影响比例更高，在全球变暖潜值中的纸类填埋同样占比可观。同时，由于纸类和塑料类的再生，替代了原材料生产，一般对环境产生正面效益。由于纸类包装材料占比较高，重视纸类包装的生态设计和回收利用环节，能够更明显的产生减排效果。鼓励更节约、更易于回收的纸类产品研发，以获得更大比例的纸回收利用量，更节能、高效的再生纸类产出率，这些都可以有效地降低以上影响潜值，从而减少人类活动对环境造成的影响。

3、结论

通过调研计算，得出我国 2019 年快递包装废弃物使用及处置情况：快递包装物使用中，以瓦楞纸箱及常见塑料袋为主，使用数量占所有快递包装的 54%及 43%，剩余 3%由编织袋、文件袋等组成；快递包装物使用质量则主要由瓦楞纸箱占据，达到了总量的 87.8%。2019 年全国共产生 1173.55 万吨的快递包装废弃物材料，其中瓦楞纸约 1031 万吨，塑料包装约 75 万吨，胶带和填充物约 30 万吨。其中约有 637.76 万吨废弃物进入回收利用体系，得到约 542.01 万吨的再生产品，总体的回收利用率 46%左右。

通过简易的物质流流程图，可以较为清晰地展现出不同种类快递包装物从生产到回收的物质量，可被使用于快递包装使用统计、回收分析与绿色化发展规划等一系列相关工作。将物质流分析结果用于分析我国全年快递包装物对环境所能产生的影响，生命周期评价结果如下：从生产、再生等各阶段影响值的对比上反映，快递包装废弃物生产阶段所造成的环境影响是最大的，其次是再生阶段。大部分环境影响类别上，填埋与焚烧产生的环境影响体量则再低一个层次，且填埋环境影响要普遍高于焚烧影响（由于再生率，部分塑料类再生影响绝对值小于填埋与焚烧且部分焚烧影响值高过填埋）。各阶段结合后的总环境影响值中，除纸类 ODP 方面为环境带来了正面影响外，其它影响类别方面所产生的均为负面环境影响。

整体上，由于纸类包装材料占比较高，优先开展纸类包装的减量化设计和回收利用活动，能够产生更明显的环境影响优化效果。此外，政府与企业联手推行更节约、更易于回收的纸类产品研发，以获得更大比例的纸回收利用量，更节能、高效的再生纸类产出率等等，都可以更快地减少快递包装废弃物在我国环境问题上的负面影响，为我国绿水青山的可持续发展尽一份力。

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澳门废弃铅酸电池产生特性及管理现状研究

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摘要：基于铅酸电池的进出口总量和电池寿命分布等关键参数，应用市场供给 A 模型，本研究估算了澳门 2006-2030 年的废铅酸电池产生特性，讨论了铅酸电池中铅资源的可回收性和资源价值，最后分析了澳门当前的管理现状。结果表明，澳门铅酸电池的废弃量未来呈上升趋势，预计将于 2024 年后趋于稳定和饱和状态。2017 年铅酸电池的废弃量达到了 7.6 万只，预计 2030 年废弃量将达到 9.1 万只，所蕴含二次铅资源量为 466.1 吨，预计 2018-2030 年累积的铅资源含量将达到 0.6 万吨。当前澳门政府已经推行废弃电池的回收计划，但尚未将铅酸电池的纳入管理范畴，大量铅酸电池仍然未进入政府监管之下，仍存在较大的环境和健康风险。研究结果有望为澳门废弃铅酸电池的有效管理和循环利用提供基础数据和科学依据。

关键词：铅酸电池；市场供给 A 模型；废弃量；资源价值

RESEARCH ON THE GENERATION CHARACTERISTICS AND MANAGEMENT STATUS OF WASTE LEAD ACID BATTERY IN MACAU

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Abstract: Based on the import and export data of lead-acid battery and its life distribution, this paper estimates the generation amount of waste lead-acid battery in Macau using the market supply model A, analyzes the recyclability and resource value, and finally discusses the current management status of waste lead-acid battery. The results show that the waste lead-acid batteries reached 76 thousand units in Macau in 2017, and will reach 91 thousand units with about 466.1 tons of lead resources in 2030. It is estimated that the accumulated lead resources from 2018 to 2030 will reach 0.6 million tons. On the whole, the waste lead-acid battery is on the rise in Macau, and finally tends to be stable after 2024. At present, the Macau government has implemented a recycling plan for waste batteries, but this plan still do not include the lead-acid batteries, which makes that the recycling of lead-acid batteries is still not under government's recycling management policy. The research is expected to provide some basic data and scientific basis for the effective management and recycling of waste lead-acid batteries in Macau.

Keywords: Lead-acid battery (LABs)；market supply model A；Waste quantity；Resource value

引 言

近年来，随着电子信息产业的高速发展，推动了电池消费量的逐年递增。然而，电池的高消费也导致了大量废弃电池的产生。铅酸电池(LABs)作为一种成熟的电池系统，具有价格低廉、原材料易获得、操作安全性高、回收技术成熟和可移植性强等优势，被广泛应用于汽车，电力备用系统和固定电源，占据着电池市场很大的份额[1][2]。2013 年中国电池的产量市值高达 330 亿美元，其中最大销量为铅酸电池，约占 57.7%[3]。

一般来说，废弃铅酸电池包含两种潜在的价值：资源价值和剩余功能价值。铅酸电池的回收处理可以回收大部分的铅。一方面，从循环经济的角度上看，铅酸电池仍旧是世界上产量较高的电池，每年都会消耗大量的铅资源，是重要的城市矿产，是维持许多行业可持续发展的关键资源[4]。在一些发达国家或地区，再生铅产量远高于一次铅产量。废弃铅酸电池作为再生铅的主要来源，约占再生铅产

量的 85%以上。例如，二次铅生产占美国铅的总产量的 80%以上，欧洲占 90%，二次铅的全球平均水平已达到铅的总产量的 60-66%。而中国的二次铅产量仅为 29.3%，远低于世界平均水平综合利用率低[5]。另一方面，废弃铅酸电池的污染成分主要为铅和废酸液[6]。由于缺乏完整的回收体系，大部分的铅酸电池会流入一些二手回收商贩，以传统手工和简单拆解等落后的技术进行处理，加上拆解后的处理处置措施不规范，不仅会造成资源浪费，更造成环境的污染[7]。与此同时，过量的铅会对人体神经系统，消化系统和呼吸系统造成严重的破坏[3]。因此，废弃铅酸电池的管理和处理处置已成为一个重要的问题。

澳门，中国特别行政区，是目前粤港澳大湾区的核心城市，其著名的博彩旅游业和轻工业使澳门成为全球最发达、富裕的地区之一。但澳门在迅速发展的同时，环境问题和资源短缺问题接踵而来，如何提高资源利用率和废弃物的循环利用变得尤为重要[8]。自 2011 年起，澳门机动车保有量已超过 20 万，这些车辆消耗着大量的铅和含铅产品，尤其是铅酸电池。目前，澳门大量的铅酸电池进入报废阶段，急需采取有效的管理措施对废弃铅酸电池进行回收处理及综合利用。

虽然，澳门环保局于 2016 年推出“废弃电池回收计划”，并已经回收累超过 5 吨废弃电池[9]，但由于澳门地区对废弃铅酸电池管理和处理处置仍处于起步阶段，尚未有针对澳门铅酸电池废弃量评估等相关研究的开展。基于此，本文主要估算澳门铅酸电池的废弃总量，并探索铅资源的可回收性和资源价值，最后解析当前澳门政府对铅酸电池的管理政策，并提出建议。本研究的结果有望为澳门地区的废弃铅酸电池的管理及政策的制定提供科学依据。

1 材料与方法

1.1 预测模型选取

研究表明，废弃铅酸电池的废弃量估算可以参考电子废物估算模型，并根据电池的自身的特点及数据收集的工作获得合适的模型[10]。目前，国际上共有7种具有代表性且较为常用的电子废物产生量的估算模型，即市场供给模型、时间梯度模型、卡内基·梅隆模型、斯坦福模型等5种模型以及2种近似模型 [11]，这些模型都有其自身理论依据。

铅酸电池的更新换代速度比较稳定，其平均使用寿命变化幅度也较小，适用于市场供给模型和市场供给A模型。因为模型涉及的参数较易获得，既能估算废弃量产生量的发展趋势，也能基本预测废弃产生量。其中市场供给模型是假定销售出去的产品在达到平均寿命后全部做报废处理，而实际使用过程与其并不相符。因此，本研究中考虑产品的平均使用寿命，并根据其最长和最短使用寿命的范围做正态分布，再利用市场供给A模型估算和预测铅酸电池的报废量[12]。

市场供给A模型是对市场供给模型估算方法的改进，将产品的平均寿命采用分布值的形式，假定产品的寿命围绕平均寿命呈正态分布，就可以赋予每个寿命期产品一个比例，市场供给A模型的估算公式为：

$$Q_W = \sum_i S_i P_i \qquad （1）$$

式中：Q_W为x年份的废弃电池废物的产生量，S_i为从x年算起i年前的电子产品销售量，P_i为寿命为i年的电子产品的百分比，i为电子产品的实际寿命。

1.2 数据来源

澳门地区没有铅酸电池的生产企业，其铅酸电池保有量全部依赖于进口，而进口途径又分为铅酸电池的直接进口和汽车进口时所含有的铅酸电池。因此，本研究中将铅酸电池废弃量的估算分为两个部分，一是直接进口铅酸电池的报废量；二是新注册汽车中铅酸电池的报废量。这两类铅酸电池的进口数据分别来自澳门统计暨普查局的外贸数据库和统计年鉴。

铅酸电池的直接净进口是供启动活塞式引擎用（《澳门协调制度》编码：850710）及启动活塞式引

擎用的除外（《澳门协调制度》编码：850720）的算术和，以上两者还包括含汞或不含汞的铅酸电池，但其中含汞的铅酸电池的占比极低，尤其是近十年含汞铅酸电池的进口量为零，因此，在计算过程中不单列项。

1.2.1 直接净进口量

澳门统计暨普查局缺少 2005 年之前的铅酸电池进出口量的数据。如表 1 所示，研究的铅酸电池的进口量的时间为 2005 年-2018 年之间。

表 1　2005-2018 年澳门铅酸电池进出口量及净进口量（万只）

Table 1 Import and export volume of lead acid batteries in Macau from 2005 to 2018

年份	2005	2006	2007	2008	2009	2010	2011
进口总量	3.6	5.7	11	3.7	3.2	4.5	4.4
出口总量	0	0	3.9	2.9×10^{-2}	0.1	0.2	0.1
净进口量	3.6	5.7	7.1	3.6	3	4.3	4.3
年份	2012	2013	2014	2015	2016	2017	2018
进口总量	4.9	5.4	6.4	7.9	7.4	6.6	7.3
出口总量	0.1	0.7	0.4	0.4	0.1	0	1.7×10^{-2}
净进口量	4.8	4.7	5.9	7.5	7.3	6.6	7.2

备注：2009 年铅酸电池进口总量，出口总量和净进口量分别为 31573，1113 和 30460 只；2014 年铅酸电池进口总量，出口总量和净进口量分别为 63689，4264 和 59425 只。

1.2.2 新注册车辆中铅酸电池的量

进口汽车中包含的铅酸电池的数据通过澳门统计年鉴中每年新注册车辆的数量进行统计，避免了直接利用车辆净进口量时数据的滞后性。首先，通过澳门《统计年鉴》收集澳门地区 2000-2017 年的新注册汽车量（不包括其中的电力驱动），其中包括轻型汽车、重型汽车、工业机器车、轻型电单车、重型电单车等。最终，通过计算得出新注册车辆中所含的铅酸电池的量，如表 2 为 2000-2018 年新注册车辆中所含的铅酸电池的量。

表 2　2000-2018 年澳门新注册车辆中铅酸电池的量（万只）

Table 2 Lead acid batteries volume of newly registered vehicles in Macau from 2000 to 2018

年份	2000	2001	2002	2003	2004	2005	2006	2007	2008	2009
新注册车辆中铅酸电池的量	0.7	0.9	1.0	1.2	1.5	1.7	1.8	2.2	2	1.6
年份	2010	2011	2012	2013	2014	2015	2016	2017	2018	
新注册车辆中铅酸电池的量	1.6	1.8	1.8	1.9	2	2	1.4	1.7	1.8	

1.3 参数的确定

1.3.1 使用寿命及平均重量的确定

铅酸电池的使用寿命一般与放电深度，温度和浓酸浓度等因素有关。通文献调研，资料查询和实地调研等方法，计算得澳门地区铅酸电池的平均使用寿命为 3 年，且服从正态分布，铅酸电池的使用寿命在其平均年限的±2 年的区间内波动，即使用寿命在 1-5 年的范围。本文选取铅酸电池的平均值 x=3 为 μ 值，代入公式（2）。

$$\sigma=\sqrt{\frac{\sum_{i=1}^{n}(x_i-\mu)^2}{n}} \tag{2}$$

解上式得：$\sigma=\sqrt{2}$，$\sigma^2=2$，铅酸电池使用寿命服从正态分布（3,2），经标准化后，通过查正态分布表可得铅酸电池的寿命分布比例见表 3。

表 3 澳门铅酸电池寿命分布比例

Table 3 Life distribution ratio of lead acid battery in Macau

铅酸电池寿命/年	1	2	3	4	5	6 及以上
比例/%	7.93	16.27	25.8	25.8	16.27	7.93

为了深度解析废弃铅酸电池的铅含量，将外贸数据库中铅酸电池的每年的进口重量除以进口数量，获得每只铅酸电池的重量约为 8kg。

1.3.2 拟合模型的选取

基于 2005 年至 2017 年铅酸电池的销售数据，采用 Origin 9.0 软件对已有数据进行 Nonlinear (Logistic)模型拟合，获取参数值。基于表 1 中澳门铅酸电池直接净进口量进行非线性拟合，对 2000-2004 年和 2019-2028 年澳门铅酸电池直接净进口量的表观消费量进行预测，数据拟合方程式为

$$y=\frac{A_1-A_2}{1+(x/x_0)^P}+A_2 \quad R^2=0.86658 \tag{3}$$

式中，A_1 的值为 36271.3；A_2 的值为 72807.1；X_0 的值为 2 013.2；p 值为 1972.5。

基于表 2 中澳门新注册车辆中铅酸电池的量，采用 Origin 9.0 软件对现有数据进行 Nonlinear (Logistic)模型拟合，获取参数值。为了最大程度保证数据的准确性，将 2007 年和 2016 年的数据（与拟合方程偏差较大）进行隐藏。数据拟合方程为

$$\mathrm{y}=\frac{A_1-A_2}{1+(x/x_0)^P}+A_2 \quad R^2=0.8681 \tag{4}$$

式中，A_1 的值为 7720.4；A_2 的值为 18152.4；X_0 的值为 2003.1；p 值为 2409.3。

2. 澳门铅酸电池废弃量及可回收铅资源量的预测

2.1 表观消费量

表 4 为 2000-2017 年澳门铅酸电池的两种主要来源途径中估算表观消费量（产量+净进口量）。从数据上看，澳门铅酸电池的表观消费量大幅度变化趋势。2000 年-2007 年呈大幅度上升趋势，而 2008 年之后会的变化趋势为先下降在增加，到达 2015 年后又呈下降趋势。

表 4 2000-2035 年澳门铅酸电池表观消费量（万只）

Table 4 Apparent consumption volume of lead acid batteries in Macau from 2000 to 2035

年份	2000	2001	2002	2003	2004	2005	2006	2007	2008
总量	4.4	4.5	4.6	4.8	5.2	5.3	7.5	9.3	5.6
年份	2009	2010	2011	2012	2013	2014	2015	2016	2017
总量	4.6	5.8	6.0	6.6	6.6	8.0	9.5	8.7	8.3

图 1 描述了 2018-2030 年内澳门铅酸电池表观消费的变化趋势。根据公示（4）估算，澳门 2018-2030 的新注册汽车中铅酸电池的预测值为 1.8 万只，且以达到饱和状态[图 1（a）]。因此，澳门铅酸电池的表观消费量的增加主要是由于直接净进口量引起。从预测结果可知[图 1（b）]，澳门铅酸电池的预测表观消费量呈缓慢增长趋势，至 2025 年时将达到最高点 9.1 万只，且在之后的几年呈稳定的趋势。

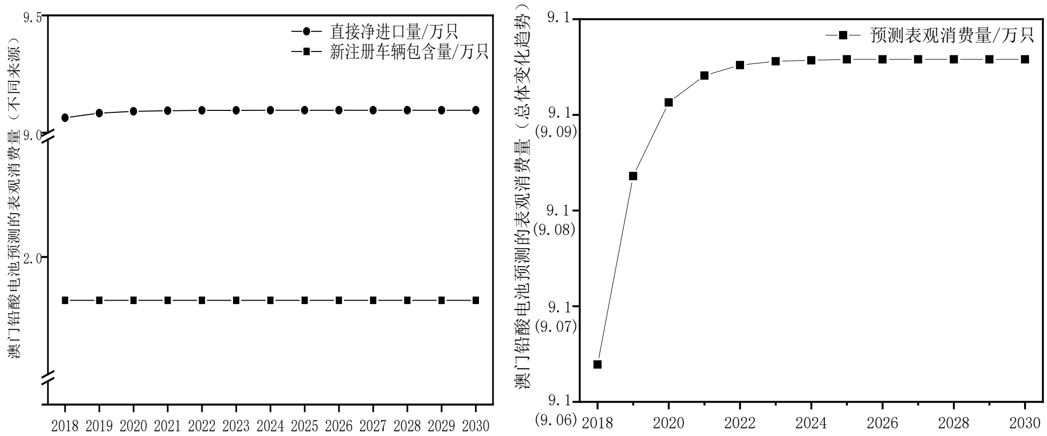

图 1　2018-2030 年澳门铅酸电池预测的表观消费量（a）不同来源贡献量（b）总体变化趋势

Fig. 1 Apparent consumption volume of lead acid batteries in Macau from 2018 to 2030 (a) Contribution from different sources (b) Overall change trend

2.2 废弃量的估算及预测

通过上表中澳门铅酸电池预测的表观消费量以及表 3 中铅酸电池的使用寿命，代入公式（1）进行计算。可得到 2006 年至 2017 年的澳门铅酸电池的废弃量估算值，以及 2018 年至 2030 年铅酸电池的废弃量与测量。同时，在此基础上，利用铅酸电池的废弃量与平均重量的乘积，获得废弃铅酸电池的总重量。结果如图 2 所示。

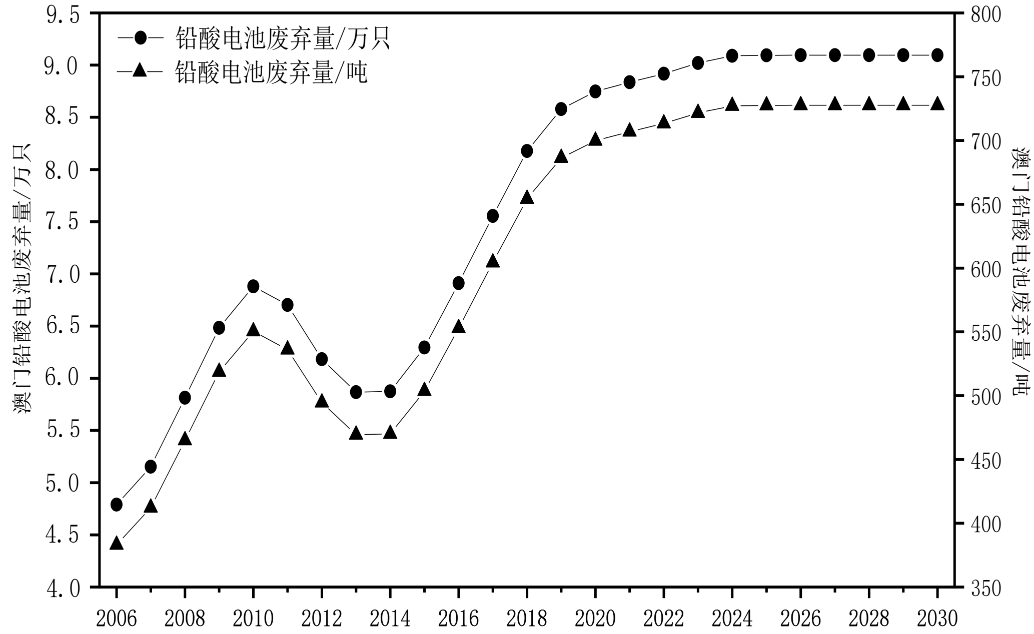

图 2

2006-2030 年澳门铅酸电池废弃量预测

Fig. 2 Generation prediction of waste lead acid battery in Macau from 2006 to 2030

估算结果表明，2010 年铅酸电池的废弃量为 6.9 万只，废弃的总重量为 550.5 吨，之后会出现短暂的下降趋势，2013 年澳门铅酸电池的废弃量减少至 5.9 万只（废弃的总重量：469.4 吨）。废弃铅酸电池 2014-2024 年会先呈快速增长趋势，2025 年后呈缓慢增长。预测 2028 年达澳门废弃铅酸电池的数量将达到 9.1 万只，且废弃重量高达 727.7 吨，趋于稳定状态。考虑到铅酸电池的可回收性和其对环境可能产生的风险，本研究还会对铅酸电池中的主要成分铅的产生量及危险性进行分析，为后续相关管理政策的制定提供参考。

2.3 废弃铅酸电池的废料成分，可回收铅资源量及不定性分析

2.3.1 废弃铅酸电池的废料成分以及可回收铅资源量的估算

废弃铅酸电池主要由四个部分组成，包括电解质（H_2SO_4溶液）、有机物（聚丙烯、聚乙烯、PVC、甲酸酯等）、金属铅（栅极、连接件）和铅膏。其中铅膏主要是极板上活性物质经过充放电使用后形成的料浆状物质，其中含有大量硫酸盐以及不同价态的铅氧化物，因此，废弃铅膏的回收利用是废铅酸蓄电池回用的难点[13]。通过文献调研，得到典型的废铅酸电池各组分比例，如表 5。

表 5 典型的废铅酸电池各组分比例（%）[14]

Table 5 Typical composition ratio of waste lead acid batteries (%) [14]

电池组分	金属铅	铅膏	有机物	电解质	其他材料
废铅酸电池	28-30	48-50	7-8	12-13	0.3-1

其中栅极和连接件中的铅含量为 92%～95%[15]、铅膏中铅含量为 72.3%[16]。

2.3.2 废弃铅酸电池的可回收铅资源量的估算

在估算废弃铅酸电池中铅资源量的过程中，各组分及其铅含量如下所示：栅极和连接件（30%）、铅膏（50%）、栅极和连接件中铅含量（93%）、铅膏中铅含量（72.3%）。结果如表 11 所示。

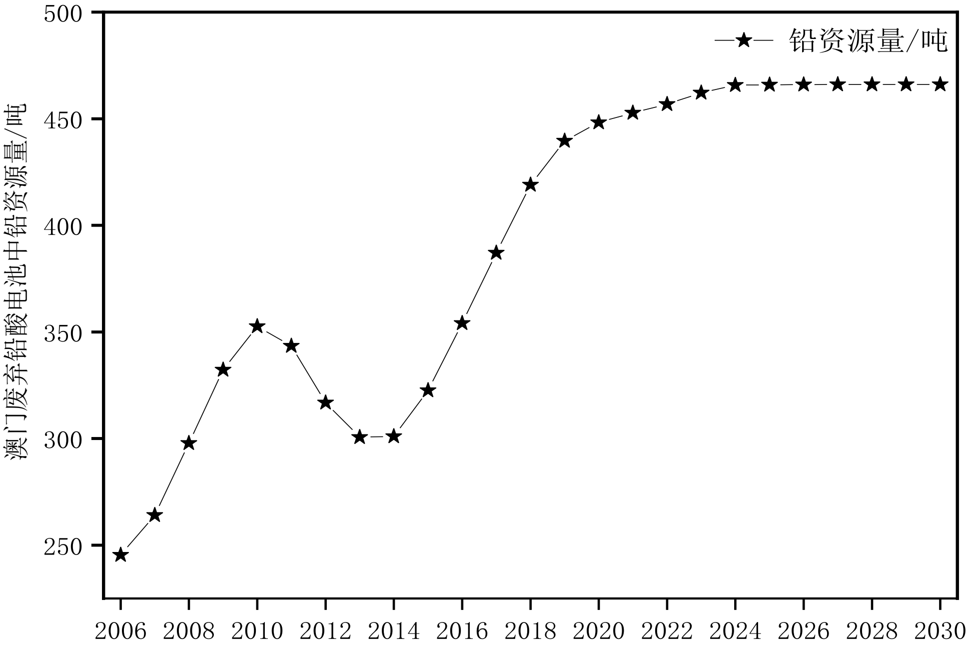

图 3　2006-2030 年澳门废弃铅酸电池中铅资源量估算

Fig. 3 Lead resources estimation of waste lead-acid batteries in Macau from 2006 to 2030

如图 3 所示，从总体上看，澳门废弃铅酸电池中的铅资源量呈明显的上升趋势，且至 2026 年铅资源量的增加速度逐渐放缓，且趋于稳定。2006-2017 年澳门废铅酸电池中可回收铅的总量累计高达 0.4 万吨，至 2030 年废弃铅酸电池中铅资源将达到 466.1 吨。2018-2030 年累积的铅资源含量将达到 0.6 万吨。铅资源作为重要的城市矿产资源，如果能采取恰当的方式回收，不仅能缓解资源稀缺的问题，同时，也能避免破坏环境，甚至能为城市的可持续发展创造经济效益。因此，澳门急需采取有效的管理措施对废弃铅酸电池进行回收处理及综合利用。

2.3.3 不确定性分析

本研究对于铅酸电池废弃量的估算及预测仍然存在一些不确定性，主要包括以下几点：①随着技术的不断更新，铅酸电池的性能和使用寿命将进一步改善。然而市场供给 A 模型中的寿命比例是固定不变，除此以外，铅酸电池的使用寿命回音电池品牌，型号和使用方式等因素存在差异；②2018-2027 年表观消费量是通过往年的消费量的变化趋势拟合估算得出，，估算的结果可能不能反应实际的复杂情况；③电动汽车的高速发展会冲击传统汽车市场需求，本研究对于铅酸电池消费量的增减可能存在误差，这取决于电动汽车的发展速率。

3. 澳门地区管理现状以及建议

3.1 管理现状

澳门地区的废弃铅酸电池产生量逐年递增，对于澳门废弃铅酸电池的管理制度和循环利用带来巨大的压力。目前澳门的废弃铅酸电池的管理仍然处于起步阶段，并没有建立专门的废弃铅酸电池管理政策的法律体系。随着澳门政府对环境保护的重视，澳门环保局于 2016 年推出“废弃电池收集计划”，设置超过 1100 个收集点，分布于商业大厦，学校，商户，及公共垃圾房等，主要收集一次性电池（包括筒型及纽扣电池）和充电池（锂离子、锂聚合物、镍氢和镍镉）。

当前，澳门铅酸电池的回收并不纳入政府的“废弃电池收集计划”中。根据调研结果显示，铅酸电池与其他电池不同，不可放置于上述的收集点，要送往危险废物处理站，预处理厂或者流动回收点。以澳门报废汽车产生的铅酸电池为例，澳门报废后的汽车中铅酸电池的流向主要为：①澳门交通事务局将报废后的汽车统一交给财政局进行拍卖，拍卖后的车辆不可以留在澳门拆卸，废弃铅酸电池可能随着车辆流入其他地区；②由私人车行收购二手车，车辆进行铅酸电池拆卸后，并进行出售；③普通修车行拆卸下的废旧铅酸电池部分会交给澳门清洁专营公司（C.S.R）运送到澳门特殊及危险废物处理站处置。针对政府部门，非盈利性机构，学校以及车行等场所，环保局将会提供免费上门回收服务，但前提必须达到足够数量的废弃铅酸电池。对于家庭产生的废弃铅酸电池（量少），只能由居民送往要送往危险废物处理站，预处理厂或者流动回收点进行回收。环保局收集到的废弃电池会委托正规企业（政府委托）进行预处理，并按照《巴塞尔公约》相关越境转移程序将废弃铅酸电池运往日本作后续再生资源回收处理[9]。

澳门废弃铅酸电池回收的最大的问题是无法控制其流向，在二手回收商贩中，单个铅酸电池的售价在 100 至 200 澳门币之间，而政府的回收计划是无偿回收，这在很大程度上导致废弃铅酸电池无法流入正规回收企业。

3.2 建议

如何解决当前废弃铅酸电池的回收管理和处理处置问题，能有效控制澳门铅酸电池引起的环境问题，也是澳门政策制定者和管理者当前重要的任务之一。基于研究结果，建议以下几方面开展相关的管理研究工作：

（1）对废弃铅酸电池进行规范化管理，引进先进的管理制度。加强废弃铅酸电池进出口管理，建立生产者责任延伸制度，是进口者承担生产者的回收责任，明确销售者，维修机构、售后服务机构和回收经营者回收废弃铅蓄电池的责任。

（2）根据澳门当地的铅酸电池使用状况，建议针对澳门进口的铅酸电池或者其他电子产品进行编码标注，并通过实名制购买等方式，建立追溯系统，推动铅酸电池最大程度流向正规回收企业，有助于政府对废弃铅酸电池的监管。

（3）政策的管理者需要对澳门地区铅酸电池回收市场进行整治，对于处理渠道不规范的回收点加以取缔，对于较为规范的回收点进行适当的整改并登记。将回收点每年的处理量处理渠道进行上报存档。

（4）编制废弃铅酸电池的环境监管和污染控制技术指南。对回收运输、拆解处理和循环利用等过程的环境监管和污染控制提出相关的管理规定和制度要求。

（5）将铅酸电池纳入澳门政府推出“废弃电池收集计划”中，完善铅酸电池的回收途径，建立专门的铅酸电池回收设施。同时大力开展宣传与教育活动，促进居民和企业将废弃铅酸电池交由政府部门进行回收处理。

（6）开展粤港澳大湾区的协同治理。基于资源配置效率最佳的环境污染问题的解决路径，可研究政府间合作模式，探索在粤港澳大湾区的已有设施进行处理和利用的可能性，解决澳门废弃铅酸电池的回收和处理处置问题。

4. 结论

本文对澳门的废弃铅酸电池的废弃量进行估算和分析。研究结果表明，澳门废弃铅酸电池呈逐年增长的趋势（2024 后趋于稳定状态）。从资源的角度上看，废弃铅酸电池中蕴含丰富的二次铅资源，对废弃的铅酸电池的有序回收和再生利用，既能节约资源也能创造经济效益。但由于澳门地区对废弃铅酸电池管理和处理处置仍处于起步阶段，因此，仍需要重视澳门铅酸电池的回收利用，尽早实现废

弃铅酸电池的资源再生和循环利用。

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我国中小城市生活垃圾分类的困境与破解——以江西省吉安市为例

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[摘要]生活垃圾源头分类，最大限度地实现垃圾资源循环利用，对改善人们的居住环境，有效解决资源紧缺和能源枯竭，推动我国生态文明建设具有重要意义。随着我国中小城市的快速发展，“垃圾围城”问题越来越突出，中小城市实行生活垃圾分类符合国家政策和现实需求。通过梳理国内外中小城市——日本沼津、浙江绍兴、江苏句容等地生活垃圾分类的成功经验，总结江西省吉安市生活垃圾分类的现状和存在的困境，建议吉安市生活垃圾分类采用“一三三”模式，以推进吉安市生活垃圾分类顺利实施，实现吉安城市可持续发展。

[关键词]垃圾分类，中小城市，困境，模式

1.背景

随着城镇化进程的不断推进，我国中小城市的数量不断增加，中小城市的综合承载力、人口吸纳能力和资源集聚能力稳步增强，中小城市在国民经济发展中的地位不断提升。截至2018年底，我国中小城市已达2809个，总人口达11.81亿，占全国总人口的84.66%；经济总量达76.43万亿元，占全国经济总量的84.89%[1]。中小城市经济的快速发展，导致城市生活垃圾产量与日俱增，“垃圾围城”在中小城市中越来越突出，持续的垃圾增长不仅带来严重的环境问题，而且对经济、社会发展带来沉重的负担。2016年12月，习近平在中央财经领导小组第十四次会议上强调，“普遍推行垃圾分类制度，关系13亿多人生活环境改善，关系垃圾能不能减量化、资源化、无害化处理[2]。”2019年7月1日，《上海垃圾分类管理条例》正式实施，标志着我国垃圾分类进入“强制时代”。同年，住房和城乡建设部等9部门联合下发的《关于在全国地级及以上城市全面开展生活垃圾分类工作的通知》明确提出：自2019年起在全国地级及以上城市全面启动生活垃圾分类工作[3]，这意味着我国中小城市实行生活垃圾分类势在必行。

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2.1生活垃圾分类是中小城市发展循环经济的必由之路

在马克思看来，“所谓的废料，几乎在每一种产业中都起着重要的作用[5]。”“所谓的生产废料再转化为同一个产业部门或另一个产业部门的新的生产要素；这是这样一个过程，通过这个过程，这种所谓的排泄物就再回到生产从而消费（生产消费或个人消费）的循环中[6]。”马克思关于“物质循环使用”的观点蕴含着“循环经济”的思想。20世纪60年代，美国经济学家K 波尔丁提出“宇宙飞船理论”，循环经济走入大众视野。中小城市的快速发展必然需要大量的资源与能源，在资源和能源有限的条件下，发展循环经济是中小城市发展的最佳选择。“垃圾混置是垃圾，垃圾分类是资源。”生活垃圾分类是实施垃圾减量化、资源化、无害化循环利用的重要举措。生活垃圾中的厨余垃圾可以堆肥后用于城市绿化，干垃圾用于燃烧发电，塑料瓶可以粉碎之后再利用，甚至就连公认的有害垃圾废旧电池、废旧电子产品也具有回收利用的价值。因此生活垃圾分类是实现中小城市发展循环经济的必由之路。

2.2生活垃圾分类是城市可持续发展的助推器

1987年，世界环境与发展委员会在《我们共同的未来》报告中首次将可持续发展定义为是既满足当代人的需求，又不对后代人满足其需求的能力构成危害的发展[7]。可持续发展具体是指经济、社会、资源和环境保护的共同协调发展，这些内容和体系是相互联系的，实现经济、自然资源和环境协调发展，使子孙后代能够在资源满足的前提下持续发展下去。随着土地资源紧缺、能源枯竭等问题的日益加重，由生活垃圾引发的一系列问题很大程度上阻碍着人民的日常生活、生产和社会经济的可持续发展，如一次性塑料引发的“白色污染”、垃圾填埋造成土壤污染、垃圾焚烧的二噁英造成空气污染等。生活垃圾分类是处理垃圾公害的最佳解决解决方法，是城市可持续发展的助力器，正如习近平对垃圾分类工作作出重要指示时强调“培养垃圾分类的好习惯，全社会人人动手，一起来为改善生活环境作努力，一起来为绿色发展、可持续发展作贡献[8]。”

2.3生活垃圾分类是我国生态文明建设的重要举措

党的十八大报告指出，面对资源约束趋紧、环境污染严重、生态系统退化的严峻形势，必须树立尊重自然、顺应自然、保护自然的生态文明理念，把生态文明建设放在突出地位，融入经济建设、政治建设、文化建设、社会建设各方面和全过程，努力建设美丽中国，实现中华民族永续发展[9]。党的十九大报告提出生态文明建设的重要目标是满足人们日益增长的优美生态环境需要。城市生活垃圾管理水平，是优美生态环境建设的重要方面，是衡量城市生态文明建设的重要指标。生活垃圾分类看似小事，实则关乎到生态文明建设的大局，是社会文明水平的一个重要体现。通过生活垃圾分类，实现生活垃圾减量化、资源化、无害化处理，不仅关系到广大人民群众生活环境改善，而且关系到资源节约利用，能有效解决能源紧张、环境污染等问题。中小城市实行生活垃圾分类正是遵从自然规律、使物质得以循环利用，推动我国生态文明建设的重要举措。

3.国内外中小城市生活垃圾分类的成功经验

3.1日本沼津

日本沼津市是日本垃圾分类的发源地，早在上世纪90年代日本垃圾处理方式开始转型时，“沼津模式”就被越来越多的日本地方行政体采用。经过多年实践，它形成了政府引导、市场激励和民众参与的垃圾分类多元主体协作模式[10]。①政府引导。首先制定严格的法律法规，比如《再生资源利用

促进法》、《促进建立循环社会基本法》、《废弃物处理法》、《关于包装容器分类回收与促进再商品化的法律》、《家电回收法》、《食品循环法》、《建设循环法》等，经过近三十年的发展，沼津市形成了完善的垃圾分类法律体系。其次政府积极倡导“ZeroWaste”的社会风尚，将循环经济的“3R”原则落实到位。减量化(reduce)——引导居民尽可能少地制造垃圾，避免铺张浪费，节约资源；再使用(reuse)原则——建立“再利用”中转站，延长废旧物品的使用周期；再循环(recycle)原则——引导企业在生产经营过程中减少垃圾产生，多使用可再生资源。②市场激励。首先是政府鼓励各种垃圾回收利用的技术开发，并给与相应补贴。其次，政府将垃圾资源化处理所获利润还给市民，增加了居民垃圾分类的获得感和认同感[9]。③民众参与。沼津市市民经历过“垃圾围城”的事件，参与垃圾分类的积极性高，加上居民自治会广泛的宣传教育，久而久之，沼津市形成了一种垃圾分类社区文化，每个居民不仅自觉进行垃圾分类，当有新居民搬进来时，原来的居民会主动指导新人进行垃圾分类［11］。

3.2浙江绍兴

2015年，浙江省绍兴市开始积极推进生活垃圾分类工作。通过五年努力，基本形成了“部门协同、涵盖全域、考核推进”的源头减量体系，以“部门牵头、属地负责、镇（街）村（居）落实”的垃圾分类投放体系，以“环卫为主、结合第三方”的垃圾分类收运体系，以“焚烧和餐厨垃圾处置设施为主”的垃圾分类处置体系，取得了良好的环境、经济和社会效益。绍兴市垃圾分类处置流程如图1所示，该市垃圾分类采用“四分法”，垃圾分类前端，居民采用垃圾袋“一户一卡、一户一码”实名制定点定时投放生活垃圾，中端处置由环卫集团集中分类、集中收集、集中运输，政府通过招投标与相关企业签订委托协议，鼓励企业参与垃圾末端处置，其中厨余垃圾由宁波开诚生态技术有限公司通过厌氧堆肥集中处理，可回收物由绍兴市物资再生利用有限图1绍兴市垃圾分类处置流程公司负责收运并资源化处理，有害垃圾由绍兴市上虞众联环保有限公司进行无害化处理，其他垃圾由浙江春晖环保能源有限公司进行焚烧发电处置[12]。通过“前端—中端—末端相互衔接，将“循环经济”和“可持续发展”理念融入垃圾分类的全过程，最终实现绍兴市生活垃圾的减量化、资源化、无害化处理，形成了“政府主导、居民参与、企业加盟”的“绍兴模式”。

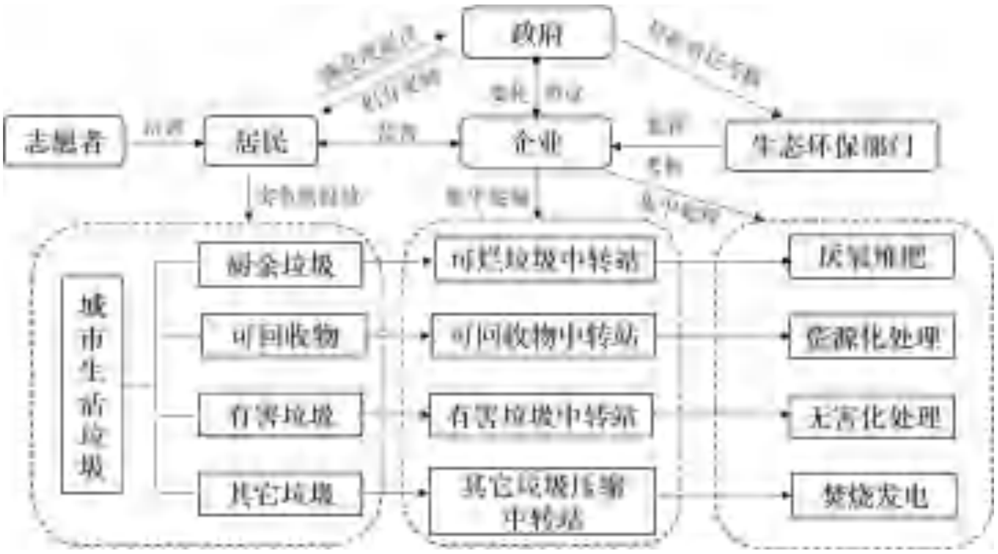

图 1 绍兴市垃圾分类处置流程

3.3江苏句容

2017年，随着《句容市城乡生活垃圾分类和治理实施意见》、《句容市城市建筑垃圾管理办法》等政府相继出台，句容市作为江苏省的县级市，因地制宜地推进生活垃圾分类工作。句容市生活垃圾分类实行“三分法”——可回收物、有害垃圾、其他垃圾，其中可回收物细分为金属、玻璃、纸张、塑料、织物等五类。通过居民初分、站内收集、分类清运、集中处置等四个环节实现生活垃圾的减量化、资源化、无害化。依托互联网技术，每户居民注册专属二维码，领取专属垃圾袋，可回收物由居民用专属垃圾袋打包，贴上二维码，放置蓝色智能垃圾桶或者智能兑换回收服务站称重兑换积分，积分可以换取盐、酱油、洗衣粉等生活用品。有害垃圾投放到红色垃圾桶，由有害垃圾暂存点集中收集，委托第三方有资质的公司进行无害化处理。其他垃圾物特别是餐厨垃圾由市城管局统一收运管理，对绿化垃圾粉碎处理后，用于公园绿地裸露土地覆盖或肥料等，经过近两年的实践探索，逐步形成了“政府推动、全民参与、互联网助力、城乡统筹、因地制宜”的垃圾分类体系（见表1）。

表 1 句容市生活垃圾分类的治理体系

序号	名称	具体内容
1	政府文件	《句容市城乡生活垃圾分类和治理实施意见》、《句容市城市建筑垃圾管理办法》等
2	原则	政府推动、全民参与、城乡统筹、因地制宜
3	分类方法	“三分”法（可回收物、有害垃圾、其他垃圾）
4	环节	居民初分、站内收集、分类清运、集中处置
5	技术依托	互联网

4.吉安市城市生活垃圾分类现状和困境

吉安市位于江西省中部，是设区的地级市，市区常住人口约35万，年清运生活垃圾量约为12775t，为未细分的混合垃圾。生活垃圾的收集和运输采用政府购买服务的方式，委托深圳龙吉顺实业发展有限公司和长沙玉诚环境景观工程有限公司进行集中收集和运输。生活垃圾集中运往井开区生活垃圾焚烧厂焚烧发电，以实现末端资源化、无公害化处理。2017年，《吉安市城市市容和环境卫生管理条例》第三十条规定：单位和个人应当按照规定的时间、地点等要求，将生活垃圾分类投放到指定的垃圾容器或者收集场所。这是吉安市首次提出生活垃圾分类投放概念。2018年12月，《吉安市生活垃圾分类工作方案（2018-2020年）》实施，将生活垃圾分为四大类即可回收物、有害垃圾、厨余垃圾、其他垃圾，同时明确了垃圾分类目标和进度。2019年9月，《吉安市中心城区2019年生活垃圾分类工作试点实施方案》选取11个垃圾分类示范点试行垃圾分类工作。然而，由于“循环经济”的理念不足、生活垃圾分类未推行市场化、社会力量调动不充分、法律法规缺乏强有力的惩罚措施等原因，吉安市生活垃圾分类仍存在着困境，主要表现在：

4.1生活垃圾分类法律法规体系不健全

实现垃圾减量化、资源化和无害化需要一整套完整的体系配合，尤其是健全的法律法规体系。正如黑格尔所言：“法律规定得愈明确，其条文就愈容易切实地执行[13]。”吉安市关于生活垃圾分类的地方法规和政府文件但不足以形成完整的法律体系，导致执行力不够，不能满足生活垃圾分类的现实需求。同时现有法律法规对政府、企业、公众在生活垃圾分类中缺乏明确的责任规定。首先，对政府的职责规定不明晰，政府不愿担责，导致生活垃圾分类工作缺乏主导力；其次，对企业参加生活垃圾分类的责任不明确，生活垃圾分类产业链难以构建；第三，对公众往往采取激励性规定鼓励其参与生活垃圾分类，缺乏具体的惩罚措施，生活垃圾分类源头分类难以实现。

4.2生活垃圾管理方式落后

吉安市生活垃圾管理方式落后成为制约垃圾分类的重要瓶颈。目前，吉安市生活垃圾管理仍由城管局、环卫处、生态环境局等多部门分头管理，实行的是市、区、街道三级管理体制[13]，尚未按照社会化、市场化、产业化方向，吸引社会资本积极参与垃圾分类。垃圾处理费用资金来源单一，基本依靠政府全额拨款。垃圾处理方面的专业人才、专业技术缺乏，尤其在生活垃圾分类更为突出。随着城市生活垃圾产生量的不断增加，资金利用和承受能力越来越差，不仅难以支撑垃圾分类回收配套体系的建立，而且也难以引进先进的人才和技术对生活垃圾实行末端资源化、无害化处理，久而久之，形成“越没钱越不分类，越不分类越没钱”的恶性循环。

4.3生活垃圾分类践行度和参与率不高

生活垃圾分类投放的主体是公众，公众积极参与和践行生活垃圾分类投放是生活垃圾分类持续往前推进的关键一步。吉安市生活垃圾分类宣传以信息提供为主、自上而下的宣传教育方式为主，采用发放宣传册、张贴海报或电子屏滚动播放等方式，效果不太理想。居民虽然认同生活垃圾分类的重要性，但对分类方法、分类流程却一知半解，加上长期形成的生活习惯，造成很多居民不会分类或者不愿意分类。在周围居民都不进行生活垃圾分类或者乱丢乱放生活垃圾的情况下，有生活垃圾分类想法的居民因“从众心理”，慢慢放弃生活垃圾分类。硬件上生活垃圾投放、收集、运输、回收处置相关配套设施、设备跟进较慢，很多住宅小区尚未配备可回收物、有害垃圾、厨余垃圾、其他垃圾的垃圾桶，即使居民在家进行了初次分类，后续仍是混和收运，严重挫伤了居民参生活与垃圾分类的积极性。加之不进行生活垃圾分类通常不会遭受处罚和道德谴责，生活垃圾分类的践行度进一步减弱。

5.吉安市生活垃圾分类的建议和对策

相比大城市而言，吉安市的生活垃圾分类刚刚起步，基本不存在“不破不立”的囧境，加上人口较少，生活垃圾产生量较小，政府各部门之间便于协调等有利条件，通过借鉴日本沼津、浙江绍兴、江苏句容等地生活垃圾分类的成功经验，建议吉安市生活垃圾分类采用“一三三”模式即树立“循环经济”一个理念，推动三方——政府、企业、公众——协同，形成生活垃圾分类多元主体协同机制，以系统思维方式构建垃圾分类回收体系，推行垃圾分类三端——前端、中端、末端——无缝衔接，从而推进吉安市生活垃圾分类的顺利实施，实现吉安市的可持续发展。

5.1以“循环经济”理念为引导，制定生活垃圾分类地方性法律法规和开展宣传教育

（1）树立“循环经济”理念的中心地位，制定完善的垃圾分类法律体系。

日本在垃圾分类处理上取得成功的主要原因之一就是制定了垃圾分类回收利用的一系列法律法

规[15]，而在这一系列法律法规中处处体现出“循环经济”的理念。1993年，《环境基本法》以可持续社会为目的，将环境政策的重点转移到国内的环境污染防止。2000年，《循环型社会形成推进基本法》确立了循环型社会的基本原则，将循环经济的理念融入其中，明确提出了减少废弃物的产生（Reduce）、再使用（Reuse）和再资源化（Recycle）的“3R”原则。为了实现循环型社会的理念，抑制垃圾的产生，日本为每一个类别的产品都制定了循环法如《容器包装循环法》、《家电循环法》、《建设循环法》、《食品循环法》、《汽车/机动车循环法》、《小型家电循环法》等，顺利解决了垃圾分类中资源回收利用存在的问题。环境基本计划，循环型社会形成推进基本计划，以及各种产品的循环法案，每五年（环境基本计划六年）进行一次修正。这一系列法律法规形成完善的垃圾回收利用“3R”政策框架（见图2）[16]。上文中提到的“沼津图2日本“3R”的政策框架模式”成功的前提也是得益于全面的垃圾分类法律体系。因此，吉安市应树立“循环经济”理念，因地制宜地建立垃圾分类管理体系和综合性环境规划，以法律法规的形式规定垃圾回收的种类和环境标准[17],具体而言，就是制定相应的综合性法律、专项法律法规、地方性法规规章和政府文件，实现彼此协调、衔接和补充，完善垃圾分类回收循环利用的法律体系。

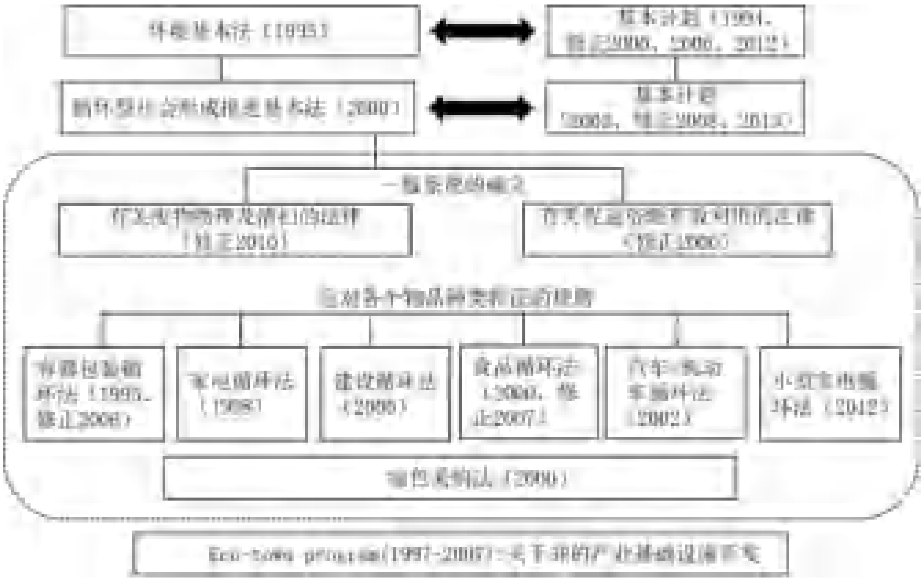

图 2 日本“3R”的政策框架

（2）“循环经济”理念融入到生活垃圾分类宣传教育

公民是垃圾分类回收投放的主体，他们的认知程度决定着垃圾分类回收投放的成败。为了促进公民积极参与垃圾分类，转变其认知观念，对公民进行系统而细致的循环经济特别是垃圾分类方面的教育显得尤为重要。吉安市在垃圾分类中要取得成功，就必须改变传统的自上而下的“行政命令式”的宣传教育方式，将“循环经济”理念融入到垃圾分类的宣传教育活动中。首先生活垃圾分类宣传教育常态化。生活垃圾分类看似小事，实则是利国利民的大事。宣传教育需要长期坚持，切忌“一阵风”。譬如在日本，每年10月是“再循环推进月”，全国和各个地方均会进行广泛的普及教育活动，除此之外，地方政府环境管理部门还定期给居民授课，内容就是与循环经济相关的各类知识[18]。如此坚持了几十年，“循环经济”的理念深入人心，日本的垃圾分类才能成为全世界典范。其次生活垃圾分类宣传教育形式细微化。“润物细无声”的宣传教育可提高生活垃圾分类的可执行性。具体而言，主要是将“循环经济”理念特别是垃圾分类方法体现在日常细微生活中。譬如商品包装上印刷包装回收的

正确步骤，让公民随时随地学习垃圾分类知识；全国垃圾分类小程序有效解决公民垃圾分类分不清的难题；垃圾分类游园活动以游戏的方式普及垃圾分类知识；建立垃圾分类科普基地，增加垃圾分类普及的有效性和丰富性等。第三垃圾分类宣传教育要从学校教育抓起。编制《垃圾分类知识读本》、垃圾分类宣讲进校园、开展垃圾分类志愿者活动等，使垃圾分类逐渐成为一种根深蒂固的文化并得以传承[14]，这样“循环经济”理念才能内化为全体公民的日常生活习惯，垃圾分类回收投放才能真正落到实处。

5.2推行三方——政府、企业、公众——协同，形成生活垃圾分类多元主体协同机制

根据贝塔朗菲的一般系统理论，生活垃圾分类回收系统中的居民、政府、企业通过物质流和价值流的相互作用、相互联系形成一个完整、有机协调的整体，任何一个主体的行为都会影响到其他主体[19]。因此，垃圾分类需要政府、企业和公众各负其责、各负其责。首先，政府应当在法规政策的顶层设计、宣传教育、激励惩罚措施等方面发挥主导组织作用。除制定完善的垃圾分类法律体系和保证宣传教育的常态化和细微化，这在前文已经论述，还应出台内容明确细致、操作性强的垃圾分类实施细则，以解决公众“难分清”、“分不清”的实际问题。采取激励措施鼓励公众、企业积极参与到垃圾分类之中，如日本沼津政府以补贴形式鼓励企业进行各种垃圾回收利用技术的研发，江苏句容公众将可回收垃圾换取积分，积分换取生活用品等。对未实施垃圾分类的个人实施罚款的处罚规定，可以进一步约束公众行为。其次，企业发挥市场和技术优势。分类后的生活垃圾主要依托企业进行资源化、无害化处理，企业通过公开竞标，以承包经营、租赁经营、特许经营、政府购买服务等方式参与到垃圾分类，实现垃圾分类的市场化和专业化。充分利用互联网技术，在智能垃圾分类回收箱、信息化大数据平台等方面下功夫，打造“互联网+垃圾分类”的创新模式。在垃圾处理环节上，企业应积极突破技术瓶颈，不断创新垃圾焚烧生态化技术、餐厨垃圾处理技术等。第三，公众发挥主体参与和监督作用。良好的垃圾分类有赖于居民的积极参与[10]。垃圾分类的宣传教育、激励措施都可以提高公众参与垃圾分类的积极性和主动性。公众对垃圾分类相关政策执行情况进行监督，能有效促进垃圾分类的开展。如此以来，形成政府发挥主导组织作用、企业发挥市场和技术优势、公众发挥主体参与和监督作用的垃圾分类多元主体协同机制，政府、居民、企业在垃圾分类项目上充分合作与互动[15]，能保证三方在垃圾分类、回收、利用过程中发挥最大社会合力。

5.3构建垃圾分类回收体系，实现垃圾分类三端——前端、中端、末端——无缝衔接。

生活垃圾分类是一个系统工程，按照物质的流向进行划分，整个垃圾分类的流程可分为前端分类、中端回收、末端处置三个阶段。前端主要以社区分类为主，吉安市居民按照可回收物、有害垃圾、厨余垃圾和其他垃圾将生活垃圾分类投放，由环卫部门负责分类收运；中端以政企结合的形式实现生活垃圾的二次分选即精细分类，有使用价值的生活垃圾规范化修理进入二手交易市场，不能直接使用的生活垃圾分拣后运送至后端处置市场；末端主要以市场运作的方式，将可回收物图3生活垃圾分类流程和有害垃圾由相关资质的企业进行资源化利用或无害化处置，湿垃圾和丧失利用价值的干垃圾进行堆肥、填埋和焚烧处置（见图3）。

“一个良好的垃圾分类体系是有效的垃圾管理的基础和先决条件”[20]。从生活垃圾分类流程可知，生活垃圾分类涉及分类投放（前端）、收集运输（中端）、处理（末端）等多个环节，这些环节环环相扣，又相互影响。末端的处置方式决定了前端的分类方式，前端的分类结果又影响着末端的处

置效果[21]。因此，吉安市生活垃圾应当将居民生活垃圾分类行为，企业收集运输生活垃圾行为，企业生活垃圾处理行为等整合为一个垃圾分类回收体系。注重前端、中端、末端之间的协同配合，形成叠加效应，而不是“互相打架”。完善生活垃圾分类配套设施，包括生活垃圾收集容器、生活垃圾分类运输车、智能废品回收垃圾箱等，切忌出现“前端分完类、中端混装运、末端一锅烩”的局面。在此基础上，鼓励有条件的企业参与生活垃圾分类事业，提高生活垃圾分类自动化水平，逐步建立标准化、规范化的中端分拣流程，促进回收、运输、分拣、利用各环节协作配套。末端以龙头企业培育为抓手，打造形成“企业成群、产业成链、要素成市、功能凸显”的垃圾分类和资源化利用市场，最终实现垃圾分类三端——前端、中端、末端——无缝衔接，畅通垃圾分类回收渠道。

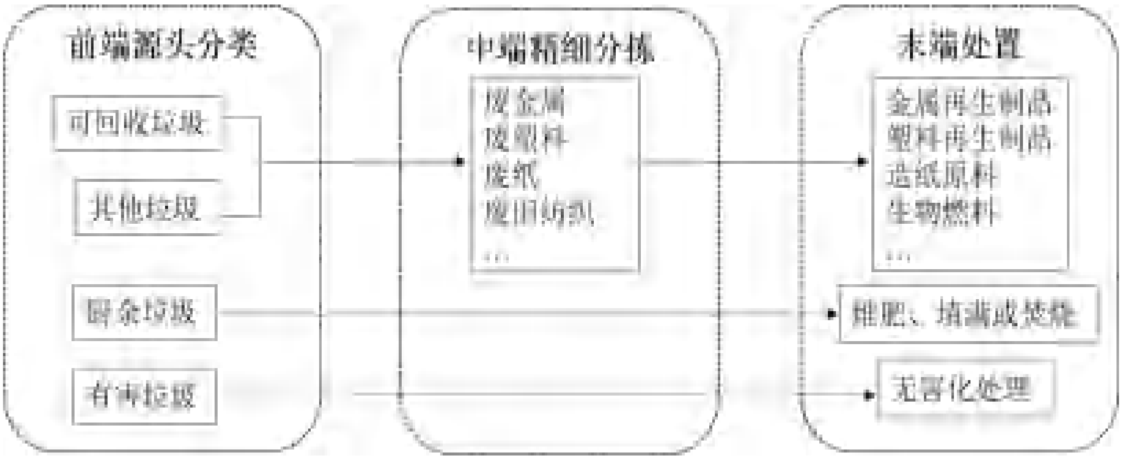

图 3 生活垃圾分类流程

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回收钒钛磁铁矿尾矿制备轻质泡沫陶瓷

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Recyclingofvanadium-titaniummagnetitetailingstopreparelightweightfoamceramics

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摘要：钒钛磁铁矿尾矿（VTMT）是一种常见的工业固体废弃物，大量尾矿堆积对生态环境和经济发展均造成巨大危害，因此实现钒钛磁铁矿尾矿综合利用是非常重要的。试验以攀西钒钛磁铁尾矿为主要原料通过高温烧结法制备轻质泡沫陶瓷。试验研究尾矿含量、发泡剂添加量和烧结温度对材料性能及微观形貌的影响，并深入探究高温状态下泡沫陶瓷的发泡机理。结果表明：以钒钛磁铁矿尾矿、长石、石英、高岭土为主要原料，质量比为 55:20:20:5，可制备出性能最优的泡沫陶瓷。通过优化发泡剂用量可有效改变样品内部气孔结构，进而提高材料性能。当 SiC 含量超过 0.15wt.%时，样品中的缺陷孔数量急剧增加。SiC 最优添加量为 0.10wt.%。随着烧结温度的升高，样品体积密度降低，吸水率增大。样品最优烧结温度为 1130°C。最终，最优泡沫陶瓷的体积密度为 0.78g/cm^3，吸水率为 14.3%。

关键词：钒钛磁铁矿尾矿；泡沫陶瓷；SiC；环境管理

Abstract: Vanadium-titanium magnetite tailings (VTMT) are a common industrial waste in China, which are harmful to the environment and economic development, so the efficient utilization of this industrial waste is urgently needed. In this study, VTMT were used as the main raw material to prepare lightweight foamed ceramics by high-temperature sintering method. The effects of VTMT content, SiC content, and sintering temperature on the properties and microstructure of foam ceramics were investigated. Furthermore, the foaming mechanism was further explained. Results show that the optimum foam ceramics were formed with 55 wt.% VTMT, 20 wt.% feldspar, 20 wt.% quartz, and 5 wt.% kaolin. By optimizing the content of SiC, the stomatal structure of the sample can be changed effectively, and the material performance can be improved. When the SiC content exceeded 0.15 wt.%, the number of defective holes in the sample increased sharply. The optimum additive amount of SiC was 0.10 wt.%. With the increase of sintering temperature, the sample bulk density decreased, and water absorption increased. The optimum sintering temperature was 1130 °C. Finally, the optimal bulk density of the sample was 0.78 g/cm^3, and the water absorption was 14.3%.

Keywords: Vanadium-titanium magnetite tailings; Foam ceramics; SiC; Environmental management

资源与环境是人类发展的永恒主题，清洁生产与固废资源综合利用受到越来越多人的关注[1-3]。目前，国内外铁尾矿具有储量大，种类多，成分复杂，综合利用率低的特点。我国的铁尾矿堆存量高达 26.14 亿 t，但综合利用率仅为 11.3%左右[4]。四川攀西地区是我国最大的钒钛磁铁矿开采矿区，在选取铁精矿的过程中将产生大量的钒钛磁铁矿尾矿（VTMT）。目前，攀西地区约有 5.7 亿吨 VTMT 堆积在当地尾矿库中，这将对陆地生态系统构成持续威胁，并给当地居民健康带来风险[5]。此外，每吨铁尾矿的储存和维护费用约为 0.73-1.18 美元，攀西地区逐年增加的尾矿堆存量将给当地企业与政府带来巨大的经济负担[6]。因此，迫切需要一种有效的回收技术来解决这类工业固体废物堆存问题，并最终建立一套完整的废物管理流程。

3. 尾矿中主要化学成分与陶瓷粉料相似，因此可利用尾矿代替部分或全部的陶瓷粉，并通过配方优化制备泡沫陶瓷。Xi[7]等以 20wt.%攀枝花提钛尾矿为原料，在 780℃下烧制泡沫陶瓷，配方中 SiO_2 含量为 60.3wt.%，Al_2O_3 含量为 17.2wt.%。Liu[8]等以 40wt.%的铅锌矿尾矿为主要原料制备无机多孔陶瓷。试样体积密度为 0.93g/cm^3，抗弯强度为 11.9MPa。利用尾矿制备泡沫陶瓷既能实现尾矿资源的减量化，又能避免二次污染物的产生。

4. 目前，相关领域还存在一些空白[9,10]。第一，在保证材料性能的前提下，应最大限度地利用固体废物。第二，样品的发泡机理尚未充分研究。最重要的是，利用钒钛磁铁矿尾矿制备泡沫陶瓷的相关研究较少。

本研究的目的是实现钒钛磁铁矿尾矿的增值化利用。通过高温烧结成功制备性能优良的泡沫陶瓷。试验研究了尾矿含量、SiC 含量和烧成温度对材料体积密度、吸水率和显微结构的影响。另外，试验深入探究了泡沫陶瓷高温发泡机理。

1.实验

1.1 原材料

5. 以攀钢钒钛磁铁矿尾矿为主要原料。长石和高岭土产于中国山西。石英、碳化硅（SiC）、磷酸钠（Na_3PO_4）、硼砂（$Na_2B_4O_7$）购买于国药化学试剂有限公司。为提高陶瓷浆料的流动性和分散性，钒钛磁铁矿尾矿在 105℃烘箱中烘干 24h 后粉碎并通过 180 目筛网。表 1 为主要原材料粒度分布表。由表可见，长石、粘土、石英和 VTMT 的粒径中位数分别为 25.7μm、6.56μm、6.04μm 和 11.7μm，满足配方的要求。

6. 表 1 原材料的粒度分布

Table1Sizedistributiondateforrawmaterials

原材料	$D_V(10)$/μm	$D_V(50)$/μm	$D_V(90)$/μm
长石	3.26	25.7	7.89
黏土	1.50	6.56	17.7
石英	3.30	6.04	10.2
VTMT	1.65	11.7	77.2

原料的化学成分和 XRD 如表 2 和图 1 所示。由表可见，VTMT 中主要化学成分为 SiO_2 及碱金属、碱土金属氧化物，如 MgO、CaO、Na_2O、K_2O。VTMT 中主要的晶相包括二氧化硅（SiO_2）、钾长石（$KAlSi_3O_8$）、钠长石（$NaAlSi_3O_8$）、透辉石（$CaMgSi_2O_6$）、钛铁矿（$FeTiO_3$）和碳酸钙（$CaCO_3$）。长石中主要的晶相为 $KAlSi_3O_8$ 和 $NaAlSi_3O_8$。粘土主要的晶相为高岭石（$Al_2Si_2O_5(OH)_4$）和硅酸铝（Al_2SiO_5）。

表 2 原材料主要化学成分(wt%)

Table2 Chemicalcompositionsofrawmaterials(wt.%)

原料	SiO_2	Al_2O_3	CaO	MgO	K_2O	Na_2O	FeO	Fe_2O_3	TiO_2	Others
VTMT	37.59	9.27	11.48	7.83	0.97	1.75	7.74	7.70	9.70	5.97
长石	60.74	17.86	1.93	0.92	9.08	4.98	-	-	-	4.49
黏土	51.15	44.77	0.23	0.13	-	-	-	-	-	3.72
石英	99.01	-	-	-	-	-	-	-	-	0.99

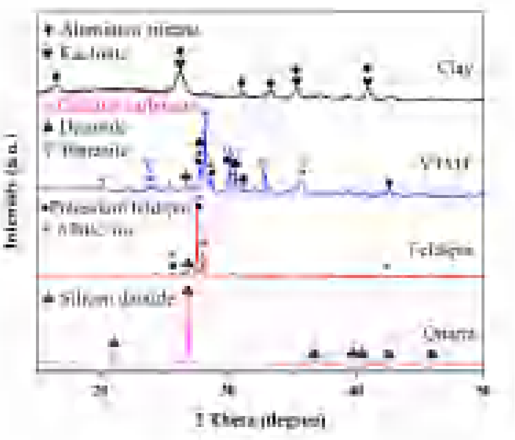

图 1 原料的 XRD 图

Fig.1.XRDofrawmaterials

1.2.实验流程

1.2.1.配方设计

为保证液相和气相在合适的温度范围内产生，需要在前期进行配方设计。表 3 为不同样品的原料组成。根据相关文献[11,12]，为减少能源消耗，配方的化学成分点应位于最低共熔点附近，同时 SiC 能正常反应。因此，利用 FactSage7.3 设计高温下的作用体系。图 2 为 SiO_2-Al_2O_3-CaO-Na_2O 伪三元相图。由图可见，伪三元相图中最低共熔点为 1130℃。为了最大限度地利用 VTMT 并降低能源消耗，试验的实际烧结温度初步设为 1130℃。

表 3 主要原料组成（wt.%）

Table3Mainrawmaterialscompositionsofsamples(wt.%).

样品	VTMT	石英	长石	黏土
1	50	25	20	5
2	55	20	20	5
3	60	15	20	5
4	65	10	20	5
5	70	5	20	5
6	75	0	20	5

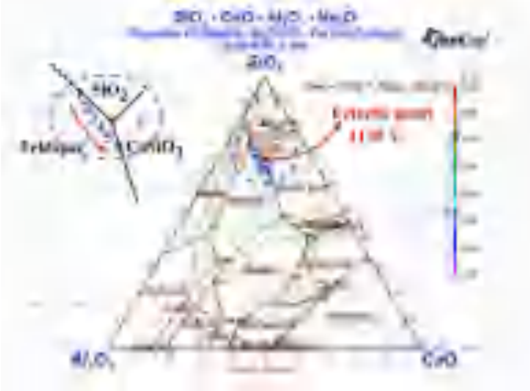

图 2SiO_2-CaO-Al_2O_3-Na_2O 伪四元相图

Fig.2.PhasediagramofSiO$_2$-CaO-Al$_2$O$_3$-Na$_2$O

1.2.2.样品制备

将钒钛磁铁矿尾矿放入密封式液压压紧制样机中，粉磨时间为60s。根据 SiO_2-Al_2O_3-CaO-Na_2O 伪三元相图配料，VTMT和石英的添加量分别设为50-75wt.%和0-20wt.%。长石作为助熔剂，掺量20wt.%，高岭土掺量 5wt.%。上述原料的总质量为 100wt.%。SiC 添加量设为 0.00-0.20wt.%，并添加 3wt.%的 Na_3PO_4 和 3wt.%$Na_2B_4O_7$。随后将所有原料放入球磨机中球磨 2h，其中原料与玛瑙球与水的质量比为1:2:0.6。将陶瓷浆料放入 105℃烘箱中烘干 5h，将块状粉料进一步破碎并通过 40 目筛。称取 20g 陶瓷粉料进行压片处理（4MPa，30s），样品直径为30mm，厚度为13mm。最后将样品置于马弗炉中，以10°C/min 升温到 1000℃；再以 3°C/min 升温到最终温度（1090-1150℃）并保温 40min。保温结束后，样品随炉降温。

1.3.性能测试及表征

采用 X 射线衍射（XRD,PANalyticalBV.Corp.,TheNetherlands）分析原料及样品中的矿物组成和晶体结构。利用扫描电子显微镜（SEM,ULTRAPLUS）观察样品的微观结构。采用国家标准测定样品体积密度 ρ_b 和吸水率 W。分别对公式中的 3 个数据进行测定，测试定流程如下。首先样品在 105°C 的烘箱中干燥 24h，干燥后称取样品的干质量为 m_1。其次将样品放入沸水，煮沸时间设为 2h，并用电子天平测量试样在水中的重量 m_2。第三步，取出样品，用湿布擦去样品表面水分，称取样品的湿重 m_3。ρ_{ing} 为水的密度。公式如下：

$$\rho_b = \frac{m_1}{m_3 - m_2} \times \rho_{ing} \quad (1)$$

$$W = \frac{m_3 - m_1}{m_1} \times 100\% \quad (2)$$

2.结果和讨论

2.1VTMT 含量

图 3 为不同 VTMT 含量下样品体积密度和吸水率变化曲线。由图可见，随着尾矿含量增加，样品的吸水率从 9.39%上升到 25.69%，随后急剧下降，这与样品内部的缺陷孔数量有关。另一方面，样品的体积密度由 0.82g/cm^3 缓慢下降到 0.78g/cm^3，然后上升。

样品的吸水率应保持较低值，通过对比分析，样品 A1，A2 和 A6 的相关性能较好。为了降低建筑物的承重压力，泡沫陶瓷的体积密度越低越好，因此可选取配方 A1 和 A2。实验应尽可能的提高VTMT 整体利用率，综合分析，最优样品配方为 A2。

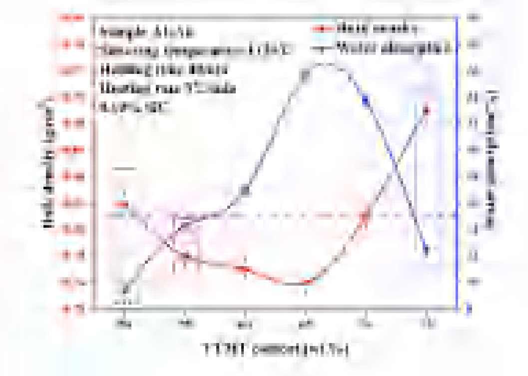

图 3VTMT 含量对样品体积密度及吸水率影响

Fig.3.TheeffectofdifferentVTMTcontentonbulkdensityandwaterabsorption

图 4 为不同配方的样品图。由图可见，当 VTMT 含量为 50wt.%和 55wt.%时，样品中气孔分布相对均匀。随着尾矿含量的增加，样品内部气孔逐渐融合，在白色区域内缺陷孔数量逐渐增加。主要原因为相同条件下，高温液相中碱和碱土离子（K+、Ca+、Na+、Mg+）的含量越多，熔体粘度相应越低，气泡生长越充分。在红色区域内气孔由下到上逐渐增大。主要原因为当其他条件保持相对不变的情况下，随着熔体粘度的增加，气泡上升速度进一步加快，气泡合并的可能性增大。这种现象满足 Stroks 定律[13]。计算公式如下:

$$V = \frac{2(\rho_1 - \rho_2)gr^2}{9\eta} \quad (3)$$

式中：V 是气泡上升速度，ρ_1 是高温液体密度，ρ_2 是气泡内气体密度，g 是重力加速度，r 是气孔半径，η 是有效粘度。

图 4 不同尾矿含量样品图

Fig.4.SampleswithdifferentVTMTcontent

2.3SiC 含量

图 5 为不同 SiC 含量下样品体积密度变化曲线。由图可见，随着 SiC 含量的增加，样品体积密度逐渐减小。当 SiC 添加量为 0.10wt.%时，样品的体积密度为 0.78g/cm^3。对样品进行对比可见，随着 SiC 含量的增加，样品内部气孔孔径逐渐增大，气孔的均匀性变差。试验结果表明 SiC 效果明显，但过量的 SiC 会严重破坏材料内部结构。

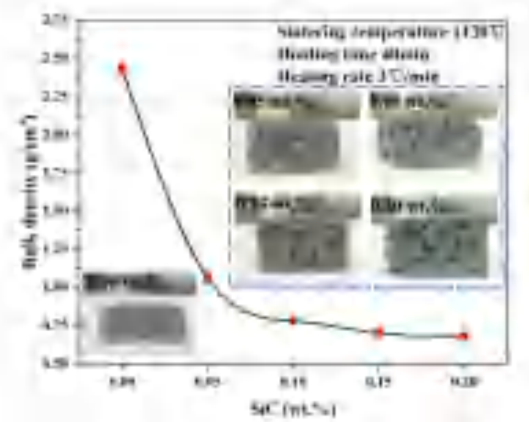

图 5 发泡剂含量对样品 A2 体积密度影响

Fig.5.TheeffectofdifferentSiCcontentonthebulkdensityofsamplesA2

图 6 为样品内部微观形貌图。由图可见，随着 SiC 含量的增加，样品内部气孔逐渐增大。如图 6（a）所示，样品内部存在少量微孔，原因为高温下少量 $CaCO_3$ 分解。如图 6（c）所示，当 SiC 添加量为 0.10wt.%，样品内部气孔分布均匀，孔壁厚度范围为 87.33-143.13μm。进一步观察可见，样品内部具有类似泡沫的三维互联网络结构，这种内部结构有助于提高材料性能。如图 6（d）所示，当发泡剂添加量为 0.15wt.%时，材料内部气泡发生破裂、熔融、逸出，大量缺陷孔的产生将严重影响材料性能。因此最优样品的 SiC 添加量为 0.10wt.%。

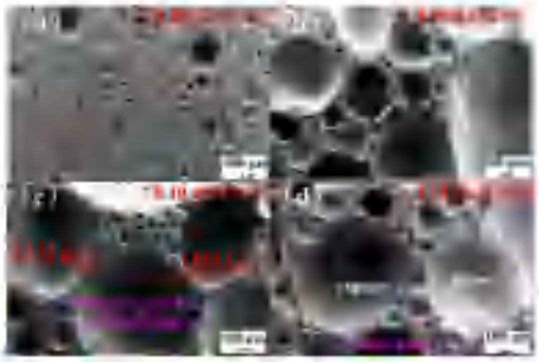

图 6 不同 SiC 含量样品的微观结构（a）0.00wt.%，(b)0.05wt.%，(c)0.10wt.%，(d)0.15wt.%

Fig.6.MicrostructureofsampleswithdifferentSiCcontentfor(a)0.00wt.%,(b)0.05wt.%,(c)0.10wt.%,(d)0.15wt.%

2.3 烧结温度

烧结温度是影响材料性能和改变材料内部结构的重要因素之一。图 7 为不同烧结温度下材料体积密度变化曲线。由图可见，随着烧结温度的升高，泡沫陶瓷的体积密度从 1.47g/cm³ 急剧下降到 0.71g/cm³。当温度为 1090℃时，样品内部气孔较小。结合 SiO_2-Al_2O_3-CaO-Na_2O 伪三元相图可知，温度较低时样品内部产生的液相量不足，气体主将通过孔间间隙逸出。当烧结温度为 1130℃时，材料内部气孔分布均匀，气孔呈现圆形或椭圆形。这是因为高温状态下材料内部产生适量的液相，熔体内部气-液平衡，气泡能够均匀的向四周生长。当烧结温度过高，材料内部出现大量缺陷孔，不利于材料的应用。因此最优样品的烧结温度为 1130℃。

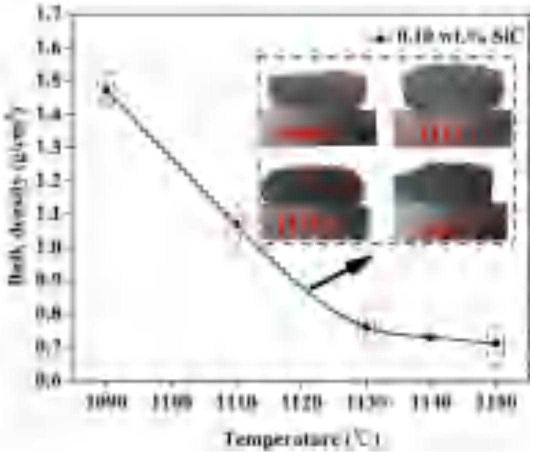

图 7 烧结温度对样品体积密度影响

Fig.7.Bulkdensityoffoamceramicspreparedatdifferentsinteringtemperatures

图 8 为不同温度下样品 XRD 图。泡沫陶瓷主要晶相包括氧化铁（Fe_2O_3）、透辉石（$CaMgSi_2O_6$）、铁板钛矿（Fe_2TiO_5）、钙长石（$CaAl_2Si_2O_8$）和氧化硅（SiO_2）。由图可见，随着温度的升高，氧化硅的峰值强度逐渐降低，主要原因为高温状态下氧化硅参与新相的生成。

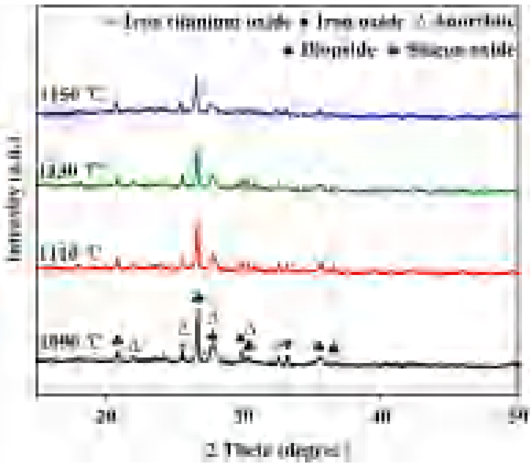

图 8 不同温度下样品 XRD 图

Fig.8.XRDofsamplespreparedatdifferenttemperatures

2.4 发泡机理

泡沫陶瓷在高温烧结过程中，发泡机理如图 9 所示。由图 9（a）可见，随着温度的升高，样品内部气泡逐渐增多，合适的温度有利于气泡在熔体内均匀分布。温度过高时，泡沫陶瓷内部将会产生大量的缺陷孔。此外，这种现象将通过样品的高度变化进一步体现。如图 9（b）所示，温度过高时，样品内气泡逸出速率增加，样品发生塌陷，b6 的高度急剧下降。图 9（c）为 SiC 的发泡机理图。由图可见，在低温条件下，SiC 氧化反应首先生成致密的 SiO_2 保护膜。随着温度的升高，碱性熔体或碱性盐会破坏 SiO_2 保护层，保护层表面生成更多的硅酸盐液相。随后氧气进入速率率显著增加，熔体内将产生更多气体。随炉内冷却，气泡将被留在样品内部。

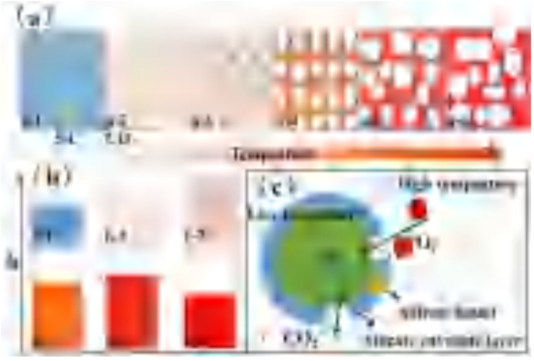

图 9 泡沫陶瓷发泡机理（a）气泡变化,（b）样品高度变化,（c）SiC 反应机理

Fig.9.Foamingmechanism(a)Bubbleschange,(b)Sampleheightvariation,(c)SiCreactionprocess

7. 总结

（1）该研究强调了利用攀西钒钛磁铁矿尾矿制备泡沫陶瓷材料的可行性，为钒钛磁铁矿尾矿综合利用提供一条可行的工艺路线，从长远来看，该方案可为其他固体废物资源的综合利用提供参考。主要结论如下：

（2）以 VTMT、长石、石英、高岭土为主要原料，质量比为 55:20:20:5，该配方可制备出性能最优的泡沫陶瓷，样品体积密度为 0.78g/cm^3，吸水率为 14.3%。

（3）SiC 是合适的高温发泡剂。随着 SiC 含量的增加，样品的体积密度逐渐减小，平均气孔尺寸逐渐增大。当 SiC 含量超过 0.15wt.%时，样品中的缺陷孔数量开始增加。最优样品的 SiC 添加量为 0.10wt.%。

（4）随着烧结温度的升高，样品体积密度降低，吸水率增大。当烧结温度过低时，样品内部气孔较小；当烧结温度过高时，样品内部将产生大量缺陷孔。最优样品的烧结温度为 1130℃。

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重庆“城市矿产”基地效益评价与对策研究

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摘要:“城市矿产”是具有固定形状、有序物理结构等鲜明产品特征，在人为活动条件下产生的再生资源。开展“城市矿产”示范基地建设不仅是缓解资源瓶颈约束的有效途径、减轻环境污染的重要措施，也是发展循环经济的重要内容和培育新的经济增长点的客观要求。为了推进“城市矿产”示范基地的验收工作，本文立足我国西部开发战略规划及“城市矿产”基地发展的现状，以重庆“城市矿产”基地为研究对象，解析物质流特征，评估发现重庆“城市矿产”基地2017年的建设总体处于“较好”水平；在此基础上，提出了重庆“城市矿产”基地建设提升的具体建议及对策。

关键词：城市矿产；城市矿产基地；循环经济；效益评价；重庆

1前言

全球经济增长带来了资源大规模的消费，1970年全球材料消耗271亿吨，2011年增加到790亿吨，2017年变为920亿吨，并将在2060年达到年消耗量1670亿吨[1,2]。资源短缺与环境污染已成为21世纪的重大挑战之一和影响联合国可持续发展目标2030实现的核心指标。“城市矿产”是具有固定形状、有序物理结构等鲜明产品特征，人为活动条件下产生的再生资源[3]。以城市废物资源化为核心的“城市矿产”示范基地建设，是我国缓解资源环境压力，促进循环经济大规模发展的重要内容。开发城市矿产对于我国面临的资源瓶颈有显著帮助，并可以减轻自然矿产开采带来的环境污染，促进社会经济的可持续发展[4,5]。

为了推进“城市矿产”示范基地的验收工作及可持续性，本文选择重庆，评估“城市矿产”基地的运行现状，对”城市矿产”基地的产业链、资源优化整合及有关政策的制定提供经验保障，对推动中西部“城市矿产”资源的合理开发具有重要意义，也对其他“城市矿产”基地验收具有一定的借鉴价值。

2数据及研究方法

2.1 数据来源与处理

为了对重庆“城市矿产”基地的建设和运营现状做出科学客观的评价，在重庆“城市矿产”基地经济发展局、园区管委会及环保分局的协助下，作者对基地的建设情况、管理情况、经济发展、环境保护、资源利用等进行了系统调研。调研获取的数据，定量指标以园区管委会、重庆市永川区环保局、重庆城市矿产基地2015—2017年统计数据为主，部分数据通过企业走访调研及项目公示网站所得，并参考所在地历年相关调查问卷数据。资源产量、消费量、再生量参考《中国有色金属工业年鉴》、《中国钢铁统计年鉴》、《中国钢铁工业年鉴》；资源消费结构参考《再生资源产业年度报告》、《有色金属行业年度报告》；再生资源能源环境效益系数参考《再生有色金属产业发展推进计划》、《废钢铁产业“十三五”发展规划建议》等。

重庆“城市矿产”基地位于重庆永川南部，地处渝川黔三省市交界，紧临长江黄金水道，区位优势明显，

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水陆运输发达，基础设施完善。2007年被重庆市确定为第一批循环经济试点园区（渝办发〔2007〕329号），也是第二批获准创建的国家“城市矿产”示范基地。

2.2 研究方法

物质流分析（MaterialFlowAnalysis，简称MFA）方法已成为揭示城市代谢、工业生产过程的核心工具，本研究将利用该方法描绘资源材料在重庆“城市矿产”基地流动过程，为分析问题奠定基础[6]。层次分析法（AnalyticHierarchyProcess，简称AHP）它是指将与决策相关的要素分解为目标、标准、方案等，采用定性和定量的分析方法[7]。

重庆“城市矿产”基地评价指标体系的设置，需要考虑到科学性、系统性、动态性和可操作性原则。将循环经济评价体系、可持续发展评价体系作为采选的基本范围。根据层次结构和具体指标的设置，将本文的评价体系构成列于表1。

表1重庆“城市矿产”基地建设运营评价体系

总指标	一级指标	二级指标	单位
重庆“城市矿产”基地建设运营评价体系	经济运行B1	工业增加值年均增长率C1	%
		人均工业增加值C2	万元/人
	生态网络B2	生态工业链数量C3	条
		企业生态关联度C4	%
	资源利用B3	工业用水重复利用率C5	%
		工业固体废物利用率C6	%
		企业排污排放达标率C7	%
		危害废弃物无害化处理率C8	%
	环境保护B4	企业清洁生产审核事项实施率C9	%
		企业环保违法事件数量C10	件
		环境空气质量优良率C11	%
		基地绿化覆盖率C12	%
	科技支撑B5	科技投入经费占GDP比重C13	%
		高新技术产业产值比重C14	%
	政策管理B6	生态环境管理制度的指定与实施C15	
		生态工业信息平台完善度C16	%
		企业环境管理标准化认证率C17	%
	社会发展B7	从业人员对生活配套设施的满意程度C18	%
		公众对环境的满意度C19	%

3. 研究结果及讨论

3.1重庆“城市矿产”基地特征解析

重庆“城市矿产”基地主要发展纸制品、“城市矿产”两大主导产业，配套发展冶炼压延及热电产业。以热电联产为动力，以废旧纸回收利用为造纸提供原料，以“城市矿产”回收再生利用为冶炼压延及废旧塑料综合利用提供原料，引入上下游关联产业，实现园内循环、共生及固废“零排放”目标，建成围绕回收、分拣、交易、加工、产成品为一体化综合循环利用工业园区（图1）。目前，依托纸及纸制品产业引入了理文造纸有限公司建成100万t/年牛皮箱板纸生产线和18万t竹木浆生产线。依托“城市矿产”产业引入了30万t新格再生铝、尧富10万t再生锌、交运6万辆报废汽车、其纬、顺得、顺贸再生塑料等资源综合循环利用企业。依托热电联产引入了200万t东方希望水泥粉磨站及20万t嘉韵粉煤灰利用项目，配套引入了中明环保、鼎达物流等关联企业，已基本建成废纸、废旧塑料、废旧金属、热电灰渣综合循环利用模式。基地年处理废纸140万t，废旧塑料3万t（其中理文废纸依附包装胶带类约15万t），废旧金属及压延40万t，热电灰渣100万t规模。再生塑料类项目承接重庆市九龙坡区塑料产业整体转移，再生资源循环利用已辐射周边及云、贵、川等地区。

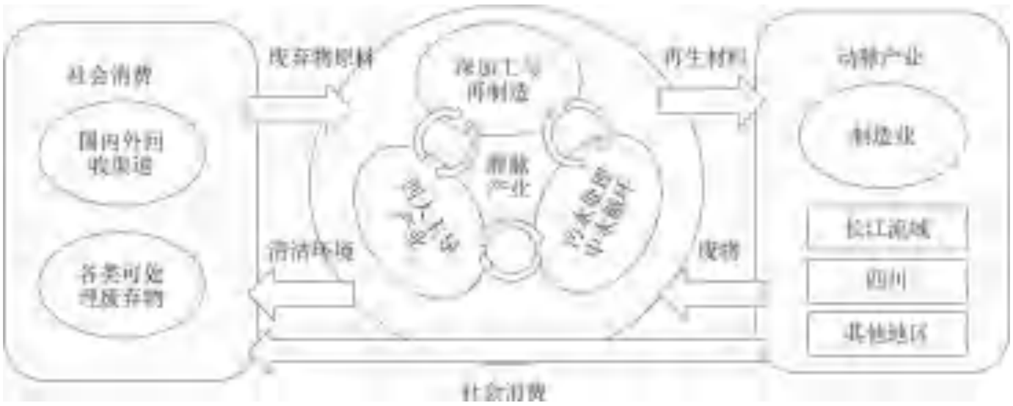

图1重庆“城市矿产”基地运行特征

3.2 物质流分析

再生资源通过再生资源回收网络进入基地，由分拣集散中心对再生资源进行分类，然后由不同的拆解项目或者再生项目进行加工再利用，最后重新回到资源市场（见图2，图中wt表示万吨）。通过物质流动示意图可见，基地在协同处理各种废弃物的同时将再生资源回收网络、分拣集散中心等纳入基地的循环系统，每年能处理废旧资源50万t，在解决废弃物资源化利用途径的同时解决了城市再生资源的回收问题。

图2重庆“城市矿产”基地中物质流特征

3.3重庆“城市矿产”基地综合效益评价

(1) 建立综合评价矩阵

设定评价对象的因素集$X=\{X_1，X_2…，X_n\}$，设定评价对象评判集$V=\{V_1,V_2,…,V_n\}$，然后依据X和 V的关系建立模糊评判矩阵，$R=(r_{ij})_{n\times m}(i=1,…,n;j=1,2,…,m)$，其中$r_{ij}(0\le r_{ij}\le 1)$表示因素$x_i$与等级$y_j$的隶属度。根据隶属度原则，评定各一级指标和整个总指标层在“A”，“B”，“C”，“D”和“F”五个标准，其中A代表很好，B代表较好，C代表一般，D代表及格，F代表不及格。

(2) 权重的计算

为了客观合理的确定一级指标与二级指标之间的相关性和权重程度，本文选择了园区管委会、重庆市永川区环保局、重庆“城市矿产”基地相关负责人对基地的7个一级指标的权重判定，得到本文最终的两两判断比值构成的矩阵（见表2）

表3重庆“城市矿产”基地评价一级指标两两判断矩阵

一级指标	B1	B2	B3	B4	B5	B6	B7

B1	1	1/3	1/3	1/3	1	3	3
B2	3	1	1	1	2	3	3
B3	3	1	1	1	2	3	3
B4	3	1	1	1	3	3	3
B5	1	1/2	1/2	1/3	1	2	2
B6	1/3	1/3	1/3	1/3	1/2	1	1
B7	1/3	1/3	1/3	1/3	1/2	1	1

根据前文层次分析法权重计算公式，得到各一级指标对总指标的权重量（见表3）

表3一级指标相对总指标权重

B/A	B1	B2	B3	B4	B5	B6	B7
权重	0.106	0.219	0.219	0.239	0.106	0.060	0.060

根据一致性检验，计算出该矩阵一致性比例结果为0.024，符合要求，权重有效。根据求得的权重，权重占比由高到低分别为环境保护、生态网络、资源利用、经济运行、科技创新、政策管理和社会发展，与基地发展相吻合。

(3) 综合效益评价结果

基于层次分析法建立的评价体系，以及模糊评价矩阵建立的关于“城市矿产”基地的评价标准分级，将获取的重庆“城市矿产”基地2015—2017年期间的评价指标数值列于表4。

表4重庆“城市矿产”基地2015—2017评价指标结果

一级指标	二级指标	单位	指标数值		
			2015	2016	2017
经济运行B1	工业增加值年均增长率C1	%	16.10	17.23	18.07
	人均工业增加值C2	万元/人	24.64	28.02	31.55
生态网络B2	生态工业链数量C3	条	8	9	9
	企业生态关联度C4	%	24.89	24.89	25.89
资源利用B3	工业用水重复利用率C5	%	81.44	83.96	86.21
	工业固体废物利用率C6	%	88.21	90.17	92.01
	企业排污排放达标率C7	%	100	100	100
	危害废弃物无害化处理率C8	%	100	100	100
环境保护B4	企业清洁生产审核事项实施率C9	%	98	100	100
	企业环保违法事件数量C10	件	0	0	0
	环境空气质量优良率C11	%	92.01	93.43	96.68
	基地绿化覆盖率C12	%	23.71	25.12	27.14
科技支撑B5	科技投入经费占GDP比重C13	%	2.10	2.18	2.28
	高新技术产业产值比重C14	%	28.14	30.96	33.12
政策管理B6	生态环境管理制度的指定与实施C15	%	99	99	99
	生态工业信息平台完善度C16	%	96	99	99
	企业环境管理标准化认证率C17	%	32.75	35.25	38.05
社会发展B7	从业人员对生活配套设施的满意程度C18	%	92	95	97
	公众对环境的满意度C19	%	93	95	98

从表4中看出，工业增加值年均增长率的幅度为16.10%—18.07%；人均工业增加值的幅度为24.64—31.55。通过对比可以看出，工业增加值年均增长率在三年间稳定增长。人均工业增加值，2015年“C”占比较高，2016年“B”占比高，2017年“A”水平占比高，说明经济运行在这三年间有较好的发展趋势。同时，基地的良性发展可提高再生资源利用率，缓解资源瓶颈压力，减轻环境污染给经济带来的社会影响，有效增加社会资源供给，同时能创造大量的就业机会，预计可解决8000人的就业问题。

生态网络方面，基地围绕产业构筑的生态工业链发展良好，但基地企业生态关联度还有待进一步提高。生态供应链熟练2015年“C”水平将提升到2017年“B”水平，生态关联度从2015年24.89%小幅提升到2017年25.89。综合分析生态网络在这三年间平缓发展，水平提升有限。

环境效益评估包含两方面的内容，一是资源利用，二是环境保护。通过对比可以看出，虽然工业用水重复利用率和工业固体废物利用率的增长幅度比较缓慢，但是从一般往很好的范围良性发展。排污标准和无害化处理均能达到100%且没有环保违法事件的发生。

科技支撑方面，由于基地主要以静脉产业为主，高新科技产业发展较为缓慢，科技投入经费占GDP比重指标从“D”提升到“C”，高新技术产业产值比重又“D”提升到“B”，综合分析，指标总体较好，应加大科技研发经费和力度的投入和高新技术产业的融合。

在政策管理和社会发展方面，这三年已经有了长足的进步，这与基地开展平台化建设和国家政策扶持息息相关，由于环境保护和生态开展顺利，工作人员和生活人员对基地的满意度也在不断提高。

4结论及建议

根据评价体系对重庆“城市矿产”基地效益的评价分析，基地应该在以下4个方面，不断完善和加强建设运营水平和效益水平。

⑴ 加强设备和技术的研发力度和研发经费：基地主要以静脉产业为主，高新科技产业发展较为缓慢，未来将会面临更难以拆解或者加工利用的废弃资源，如何在保证环境保护和经济效益的前提下，最大程度的利用废弃资源，需要技术装备的提升，且并不仅仅依靠进口装备和技术。因此，增加研发经费、提高自主研发水平势在必行。

⑵ 加强基地企业生态关联度：目前重庆“城市矿产”基地企业生态关联度并不高，可以从两个方面来进行提高。一是通过延补产品上下游的产品链，二是加强基地内部各企业之间相互利用副产品、废弃物。

⑶ 完善相关标准和评价指标体系：完善相关标准和评价指标体系，这是“城市矿产”基地良性发展的基础，随着基地的规模化，批复标准、验收标准、监督标准需要进一步完善。同时，完善评价指标体系也是基地进一步增强科技创新能力的迫切需要，基地不能仅仅满足于回收、加工利用、资源循环这些基本的功能，科技的创新能使循环经济得到更好的发展。

⑷ 加快基地配套设施建设及信息平台建设，加强员工培训，提高从业人员生产技能素质：目前基地的从业人员大多数是当地务农人员转业或是满足工作基本要求的人员，素质水平一般，对循环经济的理解较差，基地需要往高新产业园区的道路前进，必须加快信息平台建设、引进一流人才并通过培训提高从业人员素质。

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城市建筑水泥流量-存量分析及环境影响评估

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摘要：我国城镇化进程持续深入推进，大规模城市更新建造活动消耗了大量水泥等建筑材料。本文以深圳市为例，采用自下而上的物质流分析方法估算了自特区建设以来（1979-2018年）城市房屋建筑中的水泥存量和流量，并分析了其产生的综合环境影响（以碳排放当量为度量指标）研究结果表明：1979-2018年间，深圳市建筑水泥历史累积消耗约为8,120万吨，年均消耗超过200万吨，水泥累计流出量（废弃量）约为总流入量的25%-29%；截至2018年，深圳市建筑水泥存量超过6,000万吨，人均水泥存量达到4.7吨左右。相应地，全部所消耗的水泥材料在生产阶段的碳排放累计接近7,000万吨CO_2eq，其中仅有9%的碳排放量可被既有建筑所“自然”吸附，但仍有至少约11%的碳排放量可通过混凝土再生骨料进行“逆向”吸附封存。

关键词：城市建筑；水泥；流量存量；碳排放；固碳

Analysis of Cement Flow and Stock of Urban Buildings and its Environmental Impact Assessment

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Abstract: Accompanied with China's steady urbanization process, large-scale urban renewal and construction activities have consumed a lot of cement and other building materials. Taking Shenzhen as an example, this paper employs the bottom-up material flow analysis method to estimate the cement stock and flow in urban civil buildings since the establishment of the special zone (1979-2018), and analyzes its environmental impact (measured by carbon emission equivalent).The research results show that the cumulative consumption of cement in buildings in Shenzhen city is approximately 81.2 million metric tons (Mt) from 1979 to 2018, with an average annual consumption of over 2 Mt. The cumulative outflow (waste) of cement accounts for 25% - 29% of the total inflow. By 2018, the cement stock in urban buildings was more than 60 Mt, with a per capita cement stock of 4.7 tones. Consequently, the total carbon emission of cement consumed in the production stage is close to 70 Mt in 2018, of which 9% were directly

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absorbed by the existing buildings, and another 11% can be carbonated by recycled concrete aggregate if subject proper condition.

Key words: Urban buildings; Cement; Flow and stock; Carbon emission; Carbon sequestration

自改革开放以来，我国城市化率已从1980年的19.4%增长至2018年的59.6%，城市化水平不断提高[1].城市是建筑的集聚地，城市对建筑空间和品质的需求促进了建筑业的继续发展，建筑密度和强度持续提升，消耗了大量资源.目前我国城市化进程仍处于加速发展阶段，未来城市规模将会进一步扩张，城市增量建设和存量优化建设在持续耗用大量资源能源的同时，也将排放大量的废弃物与污染物，引致相应的环境问题.关注建筑系统与城市环境间的物质流动，深入研究建筑代谢的过程与机制，不仅能够知悉建筑资源、能源的具体演变趋势，还能明确建筑代谢产生的相关环境影响，为城市可持续发展奠定基础[2].物质流分析是产业生态学领域的主要方法之一，同时也被广泛应用于与建筑物质代谢相关的研究，它可以系统地分析特定系统在不同时空范围内的物质流动与贮存[2].目前国内外已有较多利用物质流分析方法对建筑存量、流量进行分析的研究.Ortlepp等人基于动态的材料强度系数，运用自下而上的物质流法对德国住宅建筑材料存量和流量进行了核算[3];Müller等人应用物质流法研究了荷兰住宅建筑的存量与流量，并预测了2003-2100年间住宅建筑的资源需求和废物排放[4]；Zhang等人对我国基础设施中的物质存量进行了自下而上的估算分析，并进一步评估了存量物质所带来的环境影响[5].Tanikawa等人分别选择了日本和英国的一个城市，借助GIS工具对所选城市的建筑材料库存进行了量化分析[6];Huang等人估算了北京、天津、上海城市基础设施的主要建筑材料，并对三个城市的材料存量进行了历史演变分析[7].通过物质流分析可以有效揭示城市建筑物质流通，促进资源管理与环境保护。

水泥是主要的建筑材料之一，在建筑业中具有重要的应用价值[8].从水泥的全寿命周期来看，其生产阶段会伴随大量的资源能源消耗与温室气体（碳）排放[9]；而在其使用与废弃阶段，水泥材料又具有一定的固碳功能，是城市非生态系统的重要碳汇[10].深入了解特定时空下水泥的新陈代谢具有一定的社会环境意义.目前已有研究专门从水泥角度出发，通过关注水泥存流量的历史演变情况，为后续资源管理与环境评估奠定基础.Cao等人采用自上而下的动态物质流法估算了我国1920-2013年中各年的水泥存量，并通过描述水泥库存的历史发展预估了未来水泥的需求趋势[11]；为了更好地进行基础设施规划管理以及了解其碳汇贡献，Amit等人建立了美国水泥库存模型并估算了20世纪美国在用水泥的积累量[12].上述研究都是从国家层面对水泥进行的研究，而宏观尺度的研究往往忽略了地区或城市尺度水泥的历史使用情况与其引起的资源环境问题.因此本研究以我国高度城市化的深圳市为例，对深圳市40年来的建筑水泥流量与存量进行了估算，并综合分析了水泥带来的相关环境影响，为城市建筑可持续发展提供数据参考.

1 研究区域及对象选择

深圳于1979年撤县建市，随后城市发展逐步加快，现为我国四大一线城市之一。截至2018年，深圳市建成区面积达927.96平方千米，城镇人口突破1,300万.全市房屋建筑供给不断增强，1979-2018年间建筑竣工总面积超过3亿平方米，平均每年竣工796万平方米.水泥的使用部门可分为城市房屋建筑、基础设施和农业设施，而建筑承载的水泥量远超过其余两个部门[11].因此，本研究以城市民用建筑为研究对象，将建筑分为住宅建筑和非住宅建筑两个类别来衡量深圳市1979-2018年间的建筑水泥量，其中非住宅建筑包括了公共、商业、工业及其他类型的房屋建筑。

2 研究方法

2.1 水泥存量流量分析

2.1.1研究方法

基于不同的计算角度，物质流分析法又可进一步分为自下而上和自上而下两种方法[13].自上而下地进行物质核算则需要量化系统边界处进行的物质交换，明确系统内部累积的物质总量.此种核算方法往往基于宏观的经济社会数据，对统计数据的依赖度较高，所以一般用于国家层面的物质流动研究.自下而上法则要求从系统内部的微观层面出发，通过获取标准单位的物质含量与标准单位数量来得到物质的存流量，明晰系统内部物质代谢机制.自下而上法需要更为详实的底层数据，往往用于区域、城市尺度的物质存量、流量核算.由于缺乏深圳市水泥内外销等宏观统计数据，本研究采用自下而上的动态物质流法进行深圳市建筑水泥存流量估算，研究框架如图1所示。

图1建筑水泥流量-存量研究框架

Fig.1Researchframeworkofcementflowandstockofurbanbuildings

2.1.2材料估算模型

公式（1）给出了材料估算总思路，建筑部门每年在用水泥存量值取决于上一年份的水泥存量与同期水泥净流量，水泥净流量等于水泥流入量与流出量的差值，流入量指的是构成新建建筑实体而进入城市建筑系统的水泥材料量，流出量指随着建筑被拆除而流出存量系统的水泥量.t年份的水泥流入、流出量分别等于当年新建建筑面积、拆除建筑面积与水泥强度系数的乘积，相关数据来源见表1.根据深圳市的实际发展情况，假定1979年以前深圳市既有建筑面积为零，则1979年的建筑水泥存量应等于该年份的水泥净流量，即$CS_{1979}=CS^{in}_{1979}-CS^{out}_{1979}$.

$$CS_t=CS_{t-1}+CS^{in}_t-CS^{out}_t \quad (1)$$

$$CS^{in}_t=CM_t*MI \quad (2)$$

$$CS^{out}_t=DA_t*MI \quad (3)$$

CS-建筑水泥存量；CM-建筑新建面积；DA-建筑拆除面积；MI-水泥强度系数

2.1.3建筑拆除面积

建筑拆除和建筑寿命密切相关，建筑寿命分布通常由不同的生存函数近似给出.常见的生存函数有韦伯、正态、伽马以及对数正态分布函数[4,11-12,14].本研究基于正态分布函数和韦伯分布函数分别求算建筑的年拆除面积值，每年的新建面积可直接从市统计年鉴获取.关系式（4）中，$CM_{t'}$为t'年的新增建筑面积，$DA_{t',t}$指的是t'年进入城市系统的建筑在t年份被拆除的面积.

$$DA_{t',t}=CM_{t'}*D(t)-CM_{t'}*D(t-1)=CM_{t'}*S(t-1)-CM_{t'}*S(t) \quad (4)$$

$$D(t)=\frac{1}{\sigma\sqrt{2\pi}}*e^{-\frac{(t-t_0-\mu)^2}{2\sigma^2}} \quad (5)$$

$$S(t)=e^{-\left(\frac{t-t_0+c}{\lambda}\right)^k} \quad (6)$$

公式（5）为正态分布函数，其中$D(t)$指建筑在t年份的拆除率，是一个累积概率；t_0为计算基期，这里为1979年；μ为建筑平均寿命值；σ为标准差，一般取平均寿命的30％[15-16].建筑平均寿命采用调研数据，研究通过实地调查获取了深圳市380个住宅、非住宅建筑单元的使用寿命，其中住宅建筑使用寿命平均值为22.4年，非住宅类建筑平均寿命为24.4年[17].

公式（6）为韦伯分布函数，$S(t)$代表建筑的存活概率；其中λ和c为比例参数，k为形状参数.Cai及其同事基于最小二乘法拟合出了参数λ、c和k的值，最后估算出我国建筑平均寿命为23.2年[18].Cai等人给出的平均寿命与深圳市建筑寿命的调研数据相差不大，差值在1-2年之间，这与深圳市建筑实际情况较为相符，故韦伯分布函数的参数λ、c、k分别取80.3、54.5、11.

2.1.4水泥强度系数

材料使用强度系数是计算材料流量、存量的关键参数，不同时期的水泥消耗强度由于技术、经济和管理等因素而存

在一定的差异.本研究参考了Huang等人所给出的水泥强度系数，该系列值是基于各省水泥使用强度计算出的全国水平的平均值[15].由于现代建筑的进一步发展需要一定时间，建筑材料的投入使用强度在相当长的时间内不会发生较大变化，故可以假定2011-2018年的水泥强度系数与紧邻时间段1990-2010年的水泥使用强度相同（见表1）。

表 1 水泥流量-存量分析主要数据来源

Tab. 1 Main data sources of cement flow and stock analysis

	数据来源	数据详情
年新建面积	深圳市统计年鉴 （2019 年）	房屋竣工建筑面积 （含住宅、工业、商业建筑等各类房屋建筑）
年新建面积（住宅）		住宅竣工建筑面积
人口		城市历年常住人口
年拆除面积	模型计算	见公式（4）
水泥强度系数	文献总结	见参考文献[17]

2.2 水泥碳核算

水泥的上游生产过程会排放大量二氧化碳，而在其使用与废弃阶段也会吸收部分二氧化碳.本章节拟对水泥生产所排放的二氧化碳以及使用与废弃阶段建筑水泥所吸收的二氧化碳进行核算分析，如图2所示.

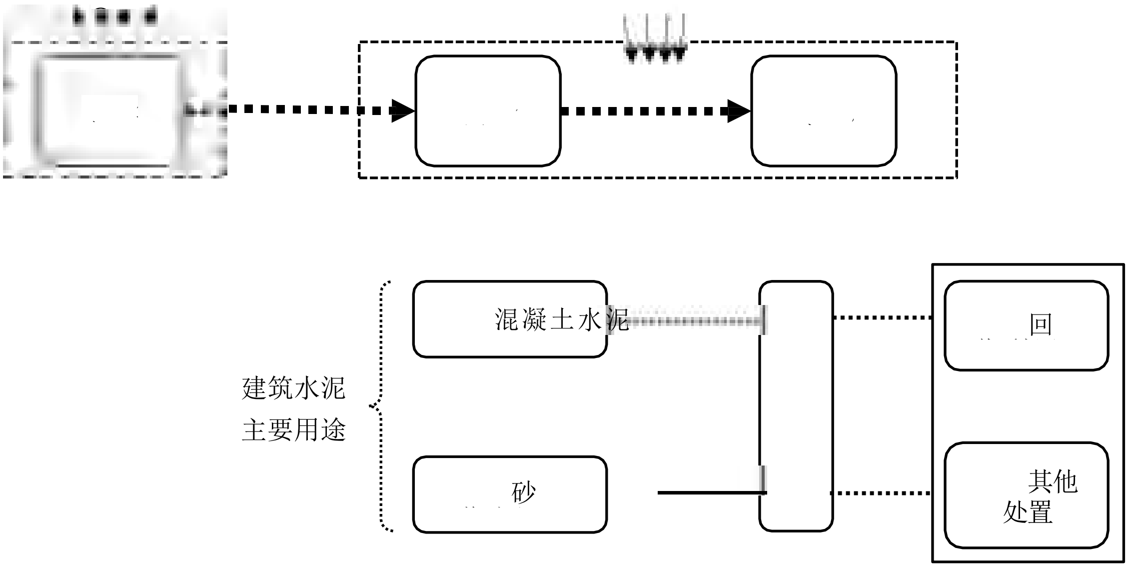

图 2 建筑水泥碳核算分析

Fig. 2 Carbon accounting analysis of building cement

2.2.1水泥生产碳排放分析

水泥生产阶段的碳排放主要来自于生料制备、熟料煅烧和水泥粉磨三个阶段.根据是否为直接碳源，一般将水泥生产过程的碳排放分为直接排放和间接排放，前者来自水泥原料煅烧及燃料燃烧，后者来自电力消耗.为避免电力生产部门重复计算电力生产排放的二氧化碳，本文将不考虑水泥生产中的间接排放部分.据统计，2012年新型干法水泥占我国水泥总产量的98.8%[19]，合理假定深圳市2013至2018年建筑所用水泥皆为新型干法工艺所产水泥，而2013年以前为新型干法与立窑混合水泥.新型干法水泥生产的直接碳排放因子为840.33 kg/t，立窑水泥的直接碳排放因子为857.40kg/t[20].在计算水泥制备造成的二氧化碳排放时，2013年以前的碳排放因子取新型干法水泥和立窑水泥碳排放因子的平均值，2013年以后则采用新型干法水泥的碳排放因子.水泥生产的直接碳排放量（E_{CO2}）可由式（7）得到，包含了水泥生产量（Q）及水泥生产的直接碳排放因子（EF）。

$$E_{CO_2}=Q*EF$$

2.2.2水泥固碳及碳汇分析

水泥行业是我国碳排放的主要来源之一[21]，而目前关于水泥的研究正从另一个维度深入.水泥的生产是一个高碳排过程，但越来越多的研究也表明水泥其实也是碳汇系统中的重要一员。Xi等基于量化模型算出在1930-2013年间全球约有45亿吨二氧化碳被水泥封存，这相当于同期水泥生产排碳量的43%[22].水泥的固碳过程始于水泥的水化，并持续发生在水泥使用、拆除及回收处理阶段[23].目前水泥碳汇的生命周期评价框架已基本形成，主要从水泥的四个去向（混凝土水泥、砂浆水泥、水泥窑灰及建筑过程损失的水泥）来测算水泥的固碳量[24].而建筑用水泥主要储藏在混凝土和砂浆中，建筑拆除时水泥便随着混凝土、砂浆废弃物流出城市建筑系统.砂浆水泥在建筑使用阶段就已完成碳化，所以建筑拆除时的砂浆废弃物一般已不具有碳捕捉能力[24].废弃混凝土便成为水泥在拆除及处理阶段的主要碳汇源.拆除后的混凝土废弃物主要处理方式包括作为再生材料进行回收利用、进行露天堆放与填埋处置[25]。

徐东旭对沈阳地区的既有建筑进行了调查统计，并对不同类型建筑的碳汇量进行了核算，最终给出了各类型建筑的年碳汇系数[25].本文拟采用该文献提供的系数值对深圳市既有建筑的碳吸附量进行核算，具体见公式（8）.对于回收处理的混凝土废弃物，课题组在前期研究成果提出了其碳封存潜力的计算简式，式中含有混凝土产废量、回收率和固碳率三个参数，可用来估算废弃混凝土在回收处理阶段的固碳量；本研究中，通过整理相关文献，总结出了混凝土再生骨料的最佳碳化条件，在该条件下每千克再生混凝土骨料将吸碳0.12千克[26].与一些国家相比，我国废弃混凝土作为再生骨料回收时的回收利用率较低，仅为5%[27]，而深圳市建筑拆除废弃物中混凝土的循环利用率可达40%[28].采用单位面积产废量法计算建筑拆除混凝土的产生量，其中建筑拆除面积采用基于正态分布函数的求算值，混凝土产废量指标来自于Wu等人的研究[28].通过公式（9）和（10）可计算得出混凝土再生骨料所吸收的二氧化碳量。

$$S_{CO_2}=CA_t*C \tag{8}$$

S_{CO_2}-碳汇量；CA-既有建筑面积；C-建筑碳汇系数

$$CA_t=CA_{t-1}+CM_t-DA_t$$

$$G=DA*CW \tag{9}$$

G-混凝土产废量；CW-混凝土产废率

$$S_{CO_2}=G*R*S \tag{10}$$

R-回收利用率；S-固碳率

2.3 不确定性分析

考虑到部分参数带来的不确定性，运用crystalball软件进行了蒙特卡洛模拟，以修正对结果影响较大的关键参数，提高结果的精确度.由于估算模型中的参数来源于相关文献，鉴于文献所提供参数的准确度，本文拟对水泥强度系数、混凝土产废率及建筑碳汇系数进行不确定性分析.水泥强度系数和混凝土产废率服从对称三角分布，上下限值采用不同建筑类型的参数的最小与最大值，最可能值则采用平均值[29].对不同类型建筑的碳汇系数[25]进行了函数拟合，发现住宅建筑的碳汇系数服从对数正态分布，而非住宅建筑服从逻辑分布.综合考虑上述参数的不确定性，在crystalball

软件进行了10,000次试验后，得到了含有误差区间的相关结果值.

3　　结果与分析

3.1水泥存量-流量分析

由图3可知，1979-2003年间，深圳市建筑水泥年流入量呈现出波动递增趋势，2003年以后建筑水泥消耗起伏较大.进一步分析，深圳市建筑水泥流入量在1990年骤降后又继续维持原增长趋势，并在2003年达到峰值562万吨；2004-2007年间水泥流入急剧下降，其主要原因是“十五”期间国家及深圳市政府颁布了系列规定，加大了对土地供应的管控力度，使房屋建设热度有所下降[30].1979-2018年期间深圳市建筑

部门累计消耗水泥量超过8,100万吨，平均每年消耗水泥203万吨，其中住宅建筑的水泥累计消耗占总使用量的41%，非住宅建筑消耗的水泥总量占59%.此外，从建筑水泥流入量的百分比堆积图（图3）中可以看出不同时期各类建筑水泥投入力度有所差异，1990-2010年住宅和非住宅建筑年水泥流入量相当；而1979-1989年和2011-2015年两个时期段非住宅建筑水泥流入量占比明显偏大.其因1979-1989年为深圳市改革开放初期，以发展工业为主来带动国民经济发展，工业建设活动得到加强[31]，而“十二五”期间，为提高城市公共服务和社会治理水平，深圳市加大了重大民生工程的建设力度[32].

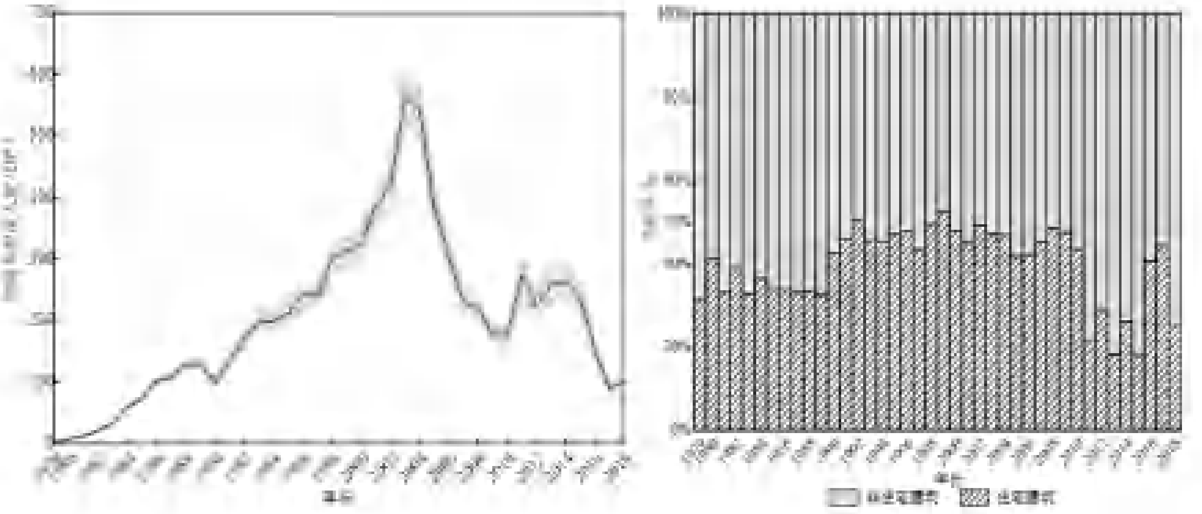

图 3 深圳市房屋建筑年水泥消耗量（流入量）分析：左图，总量及误差分析；右图，按建筑类别占比

Fig.3 Analysis of annual cement consumption (inflow) of buildings in Shenzhen: total amount and error analysis(left); proportion by building type(right)

由不同寿命分布函数计算的建筑拆除面积具有一定差异，导致建筑部门年水泥流出量也有所不同.图4显示，1979-2018年水泥年流出量呈指数上涨趋势，2017年前基于韦伯分布函数的计算值一直是大于基于正态分布函数的计算值，两者间的差值先增大后减小，最大差值为21万吨；至2017年，基于正态函数的求算值与基于韦伯函数的求算值大致相等，都为205万吨；研究时段内，深圳市建筑水泥历年流出总量超过2,000万吨，约为建筑水泥总消耗量的25%-29%.

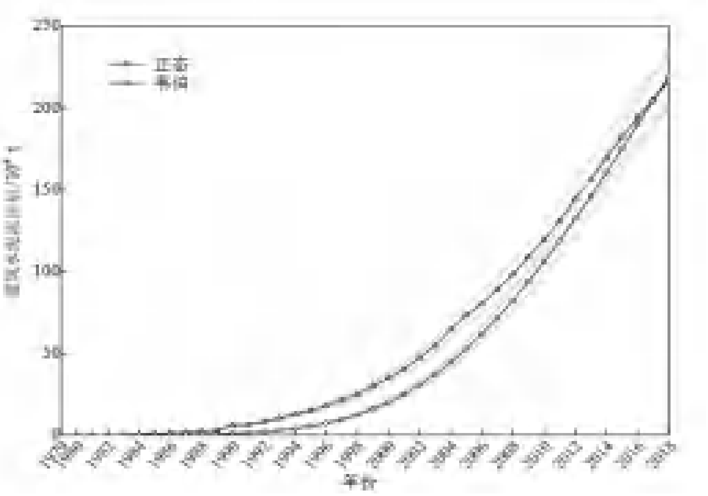

图4深圳市房屋建筑年水泥流出量估算

Fig.4AnnualcementoutflowestimationofbuildingsinShenzhen

水泥年净流量的累加序列即是水泥年存量的历史序列值，深圳市建筑水泥在用量的历史演变情况如图5所示.总体来看，深圳市的建筑水泥存量呈现出持续攀升的态势，2000-2005年间存量快速增长，年增长达400多万吨，主要原因是期间深圳市迎来了基本建设高峰，基础设施配套建筑的建设力度得到加强[33]；2005年以后水泥存量整体增长趋势放缓，于2015年达到高峰，峰值接近6,500万吨；2015-2018年间水泥存量略有下降趋势，基于水泥存量历史发展模式的稳定性，可预推未来几年水泥存量将会继续保持下降趋势.另外，深圳市非住宅建筑的年水泥在用量一直都是高于住宅建筑的.主要原因是因深圳市二、三产业的蓬勃发展导致了对非住宅建筑的较高需求，且相比于住宅建筑，同一时期非住宅建筑的水泥使用强度往往更高.从图6可以看出，与城市建筑水泥存量演变情况相比，人均水泥存量在研究时段内呈现出不同的变化趋势.1979-1990年间人均水泥存量快速增长，从1979年的不足100kg/人到1990年人均水泥存量超过5吨.此后人均水泥存量便保持在4-6吨左右，这与长期呈增长态势的深圳市总人口及建筑水泥存量有所差异，从侧面反映出逐步发展起来的深圳市对人口的强大吸引力。

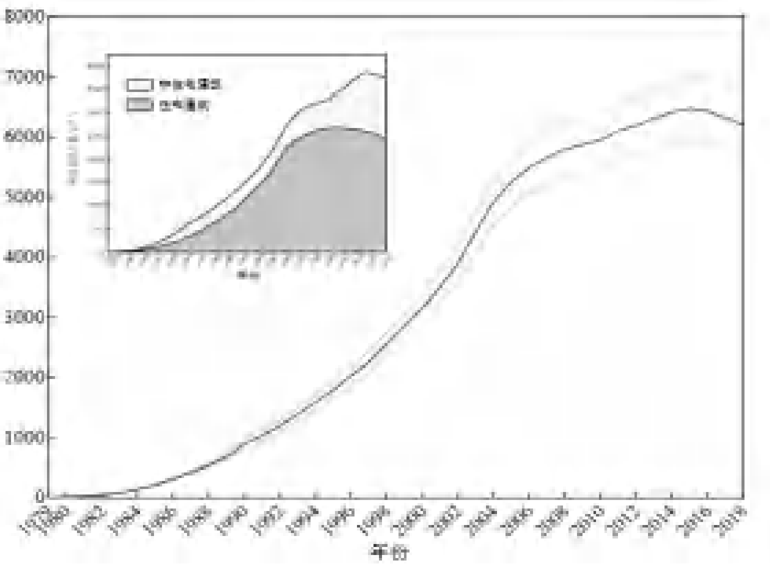

图5深圳市房屋建筑水泥存量分析
Fig.5CementstockanalysisofbuildingsinShenzhen

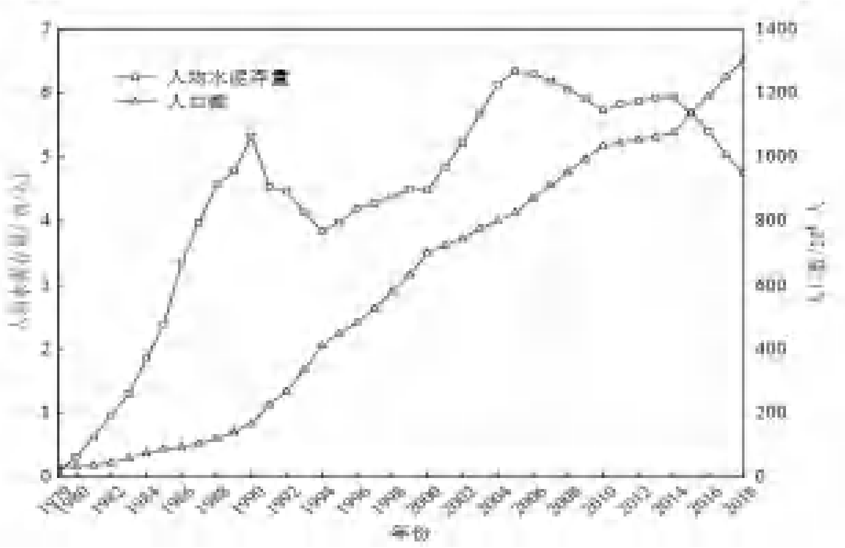

图6深圳市常住人口及人均建筑水泥存量演化特征
Fig.6EvolutioncharacteristicsofpopulationandpercapitabuildingcementstockinShenzhen

3.2碳排放与碳汇效应分析

1979-2018年内深圳市建筑水泥累计消耗约8,120万吨，生产这些水泥需要向环境直接排放6,884万吨CO2eq.从图7中可以看出，年度碳排放量变化趋势与水泥年消耗量相似.同一时间段内，深圳市建筑自然碳吸附量由1979年的不足200吨增长到2018年的32万吨，建筑碳汇量累计达到650万吨CO2eq，约占水泥生产所造成的碳排放总量的9%.

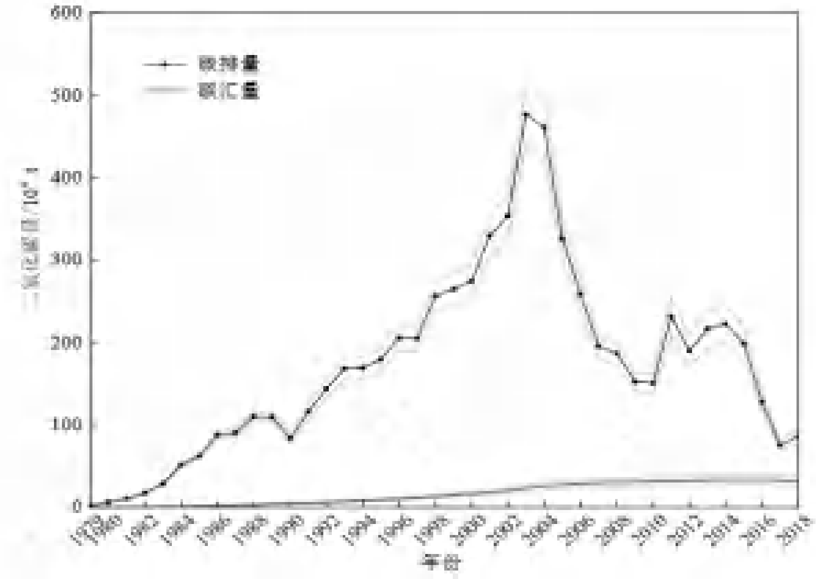

图7水泥生产碳排放及建筑碳吸附统计

Fig.7Statisticsofcarbonemissionincementproductionandcarbonadsorptioninbuildings

另外，1979-2018年间深圳市建筑拆除所产生的混凝土量累计达7,506万吨，年均产废量约为188万吨.对2019-2035年内的混凝土产废量进行估算，仅考虑1979-2018年间竣工建筑拆除所产生的废弃混凝土量，暂不考虑未来时段新增建筑的拆除影响.如图8所示，2018年后，深圳市房屋建筑混凝土产废量持续攀升，到2026年达到最大值1,065万吨，是2018年混凝土产废量的1.3倍，随后呈下降趋势，至2035年为779万吨.若对回收处理阶段的混凝土再生骨料的碳吸附条件进行人工调控，2019-2035年间将实现至少788万吨CO2eq的固定（图9），是1979-2018年间建筑部门累计消耗水泥生产时直接碳排量的11%，这能很大程度弥补水泥制备所造成的环境负效益.

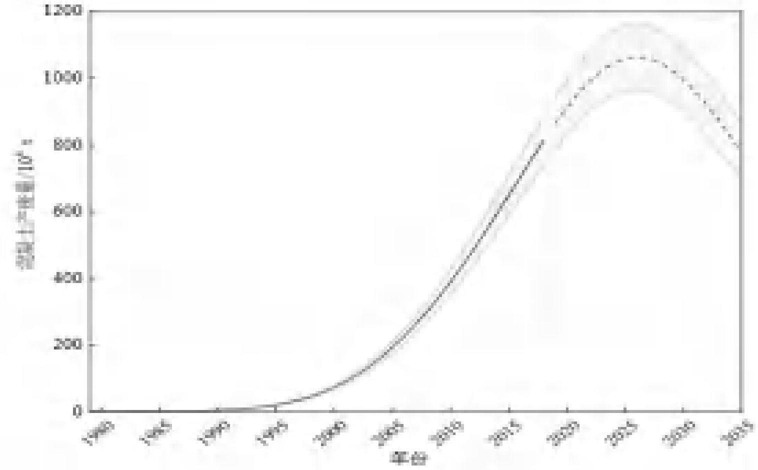

图8深圳市房屋建筑废弃混凝土产生量估算

Fig.8EstimationofwasteconcreteproductionofbuildingsinShenzhen

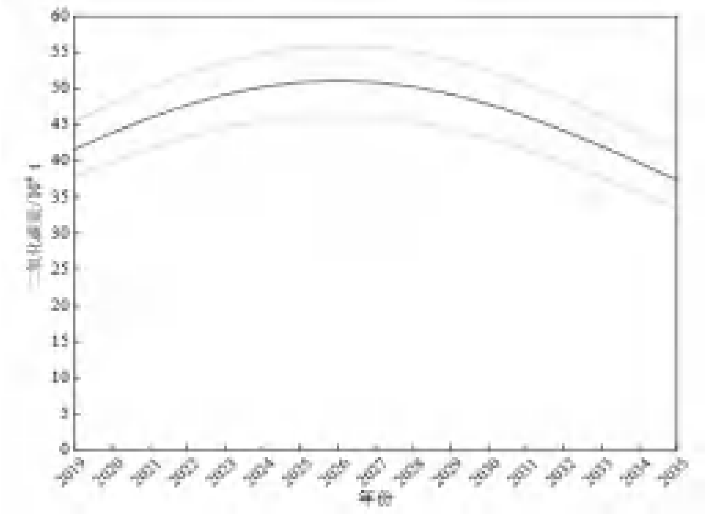

图9混凝土再生骨料碳吸附潜值估算

Fig.9Estimationofcarbonadsorptionpotentialofrecycledconcreteaggregate

4 结论

本论文研究结论如下：

1. 1979-2018年间，深圳市建筑部门累计消耗水泥约8,120万吨，其中非住宅建筑水泥消耗总量是住宅建筑水泥消耗总量的1.4倍，其间接反映了深圳住宅与非住宅建筑的规模增长与城市发展水平的提升.
2. 基于不同寿命分布函数估算出的深圳市建筑水泥流出量存在微小差异，过去40年，深圳市建筑水泥累计流出量约为建筑水泥总消耗量的25%-29%，大量水泥仍处于使用阶段.
3. 截至2018年，深圳市建筑中储存了6,200万吨左右的水泥.未来城市既有建筑的拆除与新建建筑的建设将持续伴随着“旧”水泥的流出与“新”水泥的流入，建筑水泥的“新陈代谢”将会带来资源需求与资源管理挑战.
4. 从水泥的环境影响评估来看，1979-2018年深圳市建筑所消耗水泥在生产时会直接排放6,884万吨CO2eq，而同一时期城市既有建筑能够主动吸收650万吨CO2eq.但实际上，另至少约780万吨CO2eq能够被特定碳化条件下的混凝土再生骨料所吸收.政府及行业相关方应该致力于水泥碳汇能力的提升，其对实现城市建筑低碳绿色发展具有重要意义。

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从垃圾分类探讨乌鲁木齐“无废城市”建设

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摘　要：建立“无废城市”体制是生态文明制度建设的重要内容，“无废城市”的建设，对推进固体废物源头减量和资源化利用，减少填埋量具有重要的意义。生活垃圾是固体废物的主要成分，垃圾分类对生活垃圾的减量化具有重要的意义，也在相当程度上决定“无废城市”建设的成败。本文从垃圾分类出发，结合乌鲁木齐市生活垃圾处理现状，分析实施生活垃圾分类带来的生态、经济、社会效益，同时提出如何通过垃圾分类将乌鲁木齐打造成“无废城市”的几点建议。

关键词：乌鲁木齐；无废城市；垃圾分类

【Abstract】The establishment of "zero waste city" system is an important part of the construction of ecological civilization system. The construction of "zero waste city" is of great significance to promote the reduction of solid waste sources and the utilization of resources, and reduce the amount of landfill. Domestic waste is the main component of solid waste. Waste classification is of great significance to the reduction of domestic waste, and also to a certain extent determines the success or failure of "zero waste city" construction. This paper analyzes the ecological, economic and social benefits brought by the implementation of domestic garbage classification from the perspective of waste classification, combined with the current situation of domestic waste treatment in Urumqi, and puts forward some suggestions on how to build Urumqi into a "zero waste city" through garbage classification.

【key words】Urumqi；zero waste city；garbage classification

“无废城市”是一种新的城市发展模式，也是一种先进的城市管理理念。建设“无废城市”体制是生态文明建设重要内容，根据《“无废城市”建设试点工作方案》的要求，要践行绿色生活方式，推动生活垃圾源头减量和资源化利用。国务院于2018年无废城市建设要求持续推进固体废物源头减量化和资源化利用，减少废弃物填埋量，从而将固体废弃物对城市的影响降到最低。无废城市并不是不产生固体废弃物，也并不要求所有的固体废弃物均得到资源化利用，　而是一种以实现固体废弃物源头减量和充分资源化利用，　最终达到处置安全的城市管理理念。生活垃圾作为固体废弃物最主要的一部分，其减量化、资源化与“无废城市”的建设息息相关。垃圾分类对生活垃圾源头减量与控制具有重要作用，因此，推进垃圾分类是建设“无废城市”的重中之重。

1、乌鲁木齐市生活垃圾处理现状

1.1 乌鲁木齐生活垃圾处置方式

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乌鲁木齐生活垃圾均采用卫生填埋的方式进行处置。乌鲁木齐市终端处理设施场地有三处，分别为市固体废弃物处置中心（大浦沟固体废弃物综合处理场）、米东区城市生活垃圾填埋场、达坂城区垃圾填埋场。其中大浦沟固体废弃物综合处理场 2003 年投入使用，总库存为 3000 万 m^3,预期服务年限 30 年，为乌鲁木齐市最大的垃圾填埋场，平均每日生活垃圾量约为 2080 吨，承载着全市 93%的生活垃圾填埋工作。随着人们生活水平的提高，垃圾产生量的日益增加，2016 年运行了 13 年的大浦沟填埋场关停。米东区城市生活垃圾填埋场 2009 年投入使用，有效容积约 109 万 m^3,日均处置生活垃圾 400 余吨。2016 年米东区城市生活垃圾填埋场也关停。2016 年 2 月开始建设米东区固废综合处理场，同年 7 月投入使用，平均每日生活垃圾量为 3500 吨，预计服务年限为 30 年。

1.2 乌鲁木齐市生活垃圾填埋量

乌鲁木齐市辖七区一县，面积 14216.3km²,建成区面积 436km²,常住人口 350.58 万人，城镇人口 261.57 万人，城镇化率 74.61%。乌鲁木齐市生活垃圾均采用卫生填埋的方式进行处理，图 1 为 2005—2019 年乌鲁木齐市生活垃圾清运量。由图 1 可知，自 2005 年以来，除 2007 年生活垃圾清运量有所下降，乌鲁木齐市生活垃圾清运量呈现持续增长势头，年增长率为 8.5%。连续增长的生活垃圾清运量将占用更多的土地资源，使土地严重侵蚀，同时对乌鲁木齐的发展带来一定的困扰。

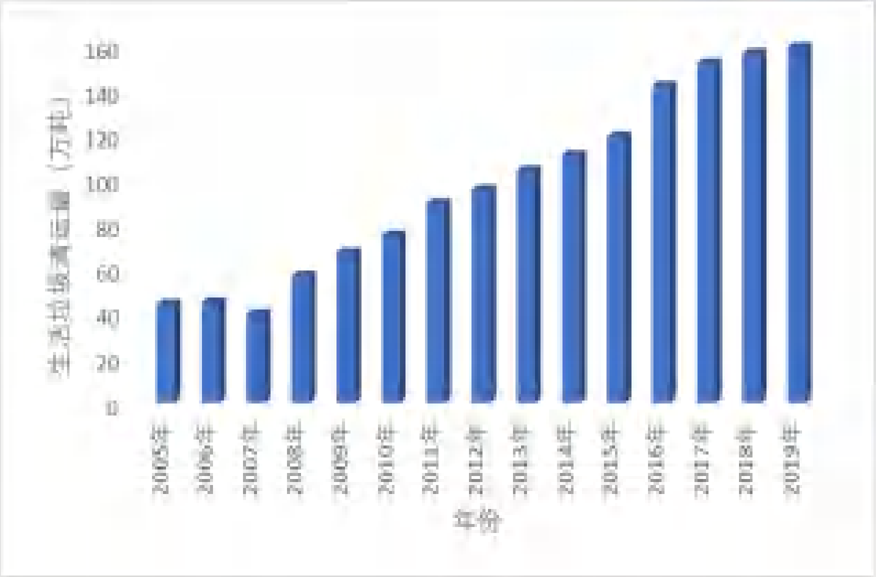

图 1　乌鲁木齐市 2005-2019 年生活垃圾清运量

1.2 乌鲁木齐市生活垃圾成分分析

通过对调查区生活垃圾进行采样分析，得生活垃圾各组分含量如图 2 所示：

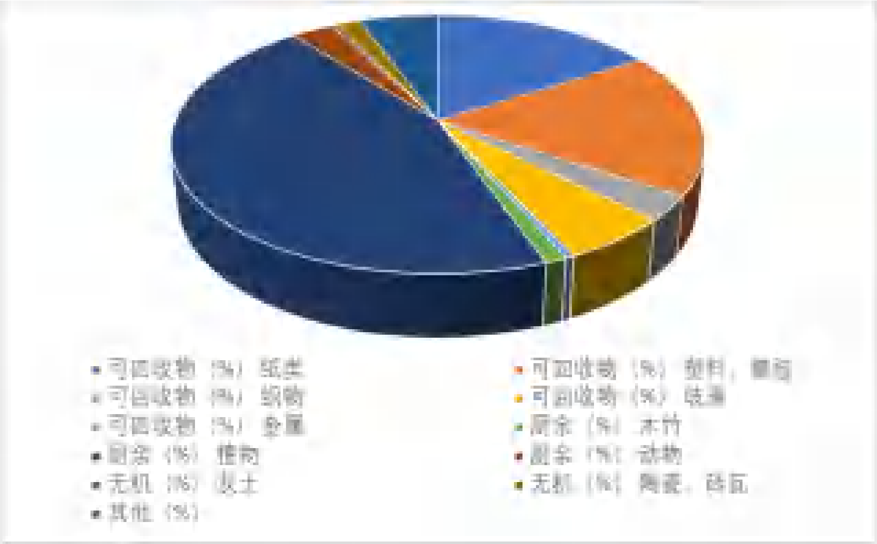

图 2　乌鲁木齐生活垃圾组分分布图

对研究区生活垃圾进行采样分析，可知乌鲁木齐市生活垃圾中易降解有机碳含量 64.24%，不易降解有机碳含量 18.11%，无机物含量 17.65%。其中易降解有机碳中厨余垃圾为主要成分，其含量高于纸类、织物、灰渣、竹木之和。可计算得出乌鲁木齐市生活垃圾中可降解有机碳含量为 8.8%（湿基，新鲜城市生活垃圾）。相比其他城市，乌鲁木齐市有机碳含量相对较低。例如；上海崇明区中生活垃圾有机碳含量为 15.65%[1]；拉萨市生活垃圾中有机碳含量为 10.57%[2-3]；成都市生活垃圾有机碳含量为 9.75%[4]；北京市生活垃圾有机碳含量为 9.85%[5]

2、乌鲁木齐市生活垃圾分类

乌鲁木齐市作为全国 46 个垃圾分类试点城市，从 2013 年逐步启动生活垃圾分类试点工作，采用以试点先行、以点带面、建章立制等方式，抓住分类收集、分类投放、分类运输、分类处理四个环节，展开垃圾分类工作。

2.1 建立垃圾分类规章制度

按照《国务院办公厅转发国家发改委、住房城乡建设部生活垃圾分类制度实施方案的通知》。乌鲁木齐市已出台《乌鲁木齐市生活垃圾分类实施方案》、《生活垃圾分类示范点建设标准》等相关文件。对乌鲁木齐市生活垃圾分类的主要任务、奖罚办法进行了具体的明确 。2020 年 6 月 30 日，《乌鲁木齐市生活垃圾分类管理办法》将正式施行。《办法》对乌鲁木齐市对乌鲁木齐市的生活垃圾分类投放、收集、运输、处置、源头减量、资源化利用及其监督管理等活动，做出了明确的规定。《办法》中还明确了法律责任。

2.2 建立垃圾分类试点小区

2013 年乌鲁木齐市开始逐步建立 34 个垃圾分类试点小区，在居民小区内配备智能垃圾分类房、垃圾分类桶等分类设施设备，2019 年在原有试点小区的基础上，进一步继续扩大试点小区

范围，在巩固垃圾分类成果的基础上，新增生活垃圾分类居民小区不少于 220 个，至少 4 个街道建成生活垃圾分类示范片区。

2.3 开展垃圾分类建设项目

乌鲁木齐市主要主要有两个分类项目，总投资 7.06 亿，一是乌鲁木齐市 2019-2020 年度生活垃圾分类项目，主要是完善乌鲁木齐市生活垃圾分类设施设及垃圾分类转运。二是乌鲁木齐市生活垃圾分类转运处置项目，其中包括购置生活垃圾分类设施设备，建设厨余垃圾暂存区、垃圾转运站等，主要是为保证生活垃圾分类后的转运与处置。

2.4 开展宣传教育工作

乌鲁木齐市就垃圾分类对市区党政机关、企事业单位、中小学及幼儿园、社区等单位举办分类培训活动，同时通过多种途径向公众展示和推送生活垃圾分类相关知识，在全市掀起“垃圾分类引导低碳生活新时尚”的热潮。

3、为什么把乌鲁木齐打造成“无废城市”

乌鲁木齐环境问题日益突出，“无废城市”的建设具有紧迫性和必要性。根据现有生活垃圾清运量增长趋势预测，至 2030 年乌鲁木齐生活垃圾产量将达到 256 万 t，生活垃圾的填埋不仅浪费大量的土地，后期垃圾渗滤液及填埋气体的无害化处理也需要投入大量的资金人力。如果不能合理有效的平衡生活垃圾产生和利用之间的关系，就需要面对环境污染和资源浪费的双重问题，因此，通过垃圾分类将乌鲁木齐打造成“无废城市”是当前形势必然要求。

垃圾分类是一种可持续的经济发展和生态保护模式，具有社会、经济、生态三方面的效益。首先，环境效益明显，通过生活垃圾分类，可去掉可回收物、不易降解的物质，生活垃圾可以减量 60%，可以从源头上实现生活垃圾减量化。垃圾分类可以将有害垃圾分离，从而避免由于填埋或者焚烧引起的环境污染。其次，经济效益显著，垃圾分类可以实现资源再循环，对塑料、金属等可回收物进行循环再利用，对果皮蔬菜等厨余垃圾进行堆肥处理，作为土壤有机肥料，对其他热值较高的垃圾进行焚烧处理，其产生的热量可用于发电等。通过垃圾分类可以构建循环产业链，将不同产业、不同领域的产业链接起来，如将生活垃圾—厌氧发酵—沼气净化—新能源汽车燃料—有机肥—有机食品，形成循环链接和产业集群，应加强产业管理，促进“无废城市”建设和相关产业的健康发展。同时，垃圾分类将是一个新兴行业，将是一个新的经济增长点。最后，社会效益突出，实施垃圾分类顺应绿色发展的时代特点，是实践五大发展理念的有效尝试，通过垃圾分类可以促进乌鲁木齐市经济发展，有利于改善当地居民生活环境，有利于提高乌鲁木齐市城市形象，促进当地国名经济和社会发展。

4、如何通过垃圾分类将乌鲁木齐打造成“无废城市”

4.1 引导居民形成良好的分类习惯

“无废城市”的建设任务十分艰巨，垃圾分类是其中重要一环，其关键点是居民垃圾分类意识的养成，居民是垃圾分类的主要参与者，在前期的垃圾分类工作中，全民动员参与分类意识明显不足，从源头上解决垃圾分类的难题，其中分类投放是重中之重，市民分类的意识相对于一线城市及西方国家仍有很大的差距。提高居民的参与意识，让居民了解垃圾分类的必要性和好处，让居民自愿参与到生活垃圾分类当中。

4.2 完善相关法规法律

乌鲁木齐市作为垃圾分类试点城市，长期以来存在重项目建设、轻行业管理的问题，尤其在生活垃圾立法相对滞后，从 2013 年展开试点项目建设直到目前才形成有关法规文本申报立法。

4.3 加强垃圾分类宣传工作

垃圾分类宣传工作是垃圾分类工作顺利展开的前提，目前，乌鲁木齐市生活垃圾分类宣传活动集中在试点小区，形式较为单一、影响力相对较为局限，未实现全面覆盖。政府层面、公众媒体在垃圾分类的宣传在深度、广度及频次上需要进一步的加强。

4.4 垃圾分类收运能力需要进一步提高

垃圾源头分类是垃圾分类第一步，垃圾分类收运是垃圾能够资源化、无害化处理的保证。乌鲁木齐市采用的是“四分法”进行垃圾分类，在对乌鲁木齐市进行的垃圾成分调查中，可以得到厨余垃圾是居民生活垃圾中最主要成分，但乌鲁木齐市现有的厨余垃圾收运车辆偏少，另外再生资源回收企业存在散而乱、分布不均的现状，并在回收物处置和利用企业还未成规模。

4.5 建立城市生活垃圾分类及资源利用数据监控平台

建立一套城市生活垃圾分类及资源利用数据监控平台，能够全面、综合、及时的反应乌鲁木齐市生活垃圾分类及资源利用状况，同时依靠大数据系统来实现收集、运输、转移、利用、处置等环节的全过程监管。

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