Research Progress on Recycling Technology of Lead-containing Glass in Waste Cathode Ray Tubes

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Abstract. With the development of kinescope technology, the quantity of discarded cathode ray tubes (CRTs) glass continues to increase. The waste CRTs glass contains a lot of lead, which could bring about the environmental risk. Based on the research status on the treatment of lead-containing glass in waste CRTs, the technologies of lead separation and recycling were summarized, and their characteristics and developments were analyzed. It was pointed out that the further research and development of new technologies in this field should pay close attention to two aspects, one is the environmental risk in the product realization process of recycling waste CRTs, and another is the satisfiability to economic feasibility and the recycled products from lead-containing Glass in waste CRTs.

1. Introduction

The problems of waste cathode ray tubes (CRTs) have attracted much attention in recent years because of containing a large number of toxic and harmful substances [1]. There are more than 500 million color TV sets in China. In 2010, the number of waste electrical appliances recovered and dismantled in China reached 560000, 80% of which were CRTs monitors [2]. Statistics show that 19.5 million CRTs televisions will be abandoned in China in 2020 [3]. CRTs are generally made of four different types of glass, namely neck glass, funnel, frit, and panel glass, which have different chemical compositions and properties [4]. Especially in the neck, funnel and frit glass, high levels of lead were detected, which could arise a huge environmental risk [5,6]. The envelope of a CRT mainly consists of 65% screen glass, 30% cone glass and 5% neck glass, wherein the lead is mainly concentrated in the cone glass and the neck glass [7]. The content of lead in the lead-containing glass of the CRTs varies depending on the sources. 0 shows the chemical composition of lead-containing glass in the picture tubes of Hitachi color TV sets [8]. Some research has shown that the average weight of each display is about 13 kg, and the lead content is about 2 kg [9]. By 2020, the accumulated amount of lead in waste CRTs in China will reach 430,000 tons [10].

Table 1. Chemical composition of lead-containing glass in waste CRTs

| Oxide | Mass percent % |
|-------|----------------|
| SiO₂  | 53.64          |
| PbO   | 21.13          |
| K₂O   | 8.38           |
| Na₂O  | 7.11           |
| Al₂O₃ | 4.48           |
| CaO   | 3.32           |
Material recovery technology mainly considers that the main component of the waste CRTs is silicon dioxide, the content is above 50% [16], and its properties are similar to those of building materials such as fly ash commonly used in building materials. Therefore, waste CRTs could be used as a substitute material for clay bricks and roof tiles, and research on the properties of building materials made from waste CRTs is often related to the application of waste CRTs material recovery technology [17].

2.1 Concrete building materials. Shi et al. prepared concrete specimens by replacing 25% river sand with CRTs waste glass sand in different particle sizes, and the tests of concrete performance conducted in this study involved slump, apparent density, compressive strength, alkali aggregate reaction and γ ray shielding. The results showed that waste CRTs glass sand was helpful to improve the flow performance and increase the apparent density of concrete, and its slump value and apparent density decreased with the decrease of particle size. In addition, due to the existence of lead, the radiation shielding of concrete was enhanced. Liu et al. studied the feasibility of using waste CRTs glass sand as a substitute for magnetite to produce radiation-proof concrete, and the replacement rate was up to 60%. The results showed that 20%-40% of waste CRTs glass sand could significantly improve the radiation resistance of radiation-proof concrete, while varying degrees decrease in the apparent density, compressive strength and static elastic modulus of the materials were observed.

2.1.1 Glass building materials. Song et al. prepared foam glass by using alkaline leached slag from waste CRTs, and studied the effects, such as foaming temperature, adding amount of foaming agent and adding amount of stabilizing agent, on the properties of the foamed glass. The results showed when the foaming temperature was 800°C, the addition of screen glass was 50% (wt.), the addition of boric acid was 5% and the addition of SiC was 15%, the foam glass would meet the physical properties of type IV foam glass for building. GAO et al. prepared waste CRTs glass into high silica glass powder without heavy metals by using carbon as the reducing agent, which could strengthen glass phase separation. Carbothermic reduction and subsequent glass phase pickling can effectively remove various heavy metal oxides in waste CRTs glass and obtain SiO₂ glass powder with a purity of up to 93%. This porous high-silica glass powder can be used as adsorbent and catalyst carrier.
Due to the sharp decline in the demand for closed loop recycling of waste CRTs, material recovery technology in open loop recycling is more and more important. The material recovery technology without changing the original structure of the material has the characteristics of large processing capacity, low energy consumption and wide application. Radiation-proof concrete and foamed glass are the main research directions, and the research is often focused on the changes of material performance, the feasibility of application, the achievement of environmental protection and the adaptability of the environment. In the future, the optimization of formulation, stability, the development of the field of material application and environmental impact assessment of waste CRTs glass materials are still the focus of attention.

2.2 Lead separation and recovery technology
The development of lead separation and recovery technology for waste CRTs glass is mainly based on two considerations. First, the material recycling method does not completely solve the environmental risks in the recycling process; second, the content of lead in waste CRTs lead-containing glass is much higher than the grade of lead in primary lead ore. The separation and recovery of lead has the dual benefits of economic and environmental protection, therefore, the research and development of lead separation and recovery technology has been an important research field of waste CRTs leaded glass treatment. The development directions of this field are mainly along two paths, namely wet method and fire method.

2.2.1 Wet method. Wet method is the process by which lead in waste CRTs lead-containing glass is extracted by leaching and then converted to high-purity and high-value products. Because of the continuous honeycomb network structure of waste CRTs lead-containing glass, it is extremely difficult to separate and recover lead from it. Therefore, the release of lead in waste CRTs lead-containing glass needs certain pretreatment to destroy the dense network structure. A large number of experiments have shown that mechanical ball grinding contributes to the destruction of the mesh structure of leaded glass in waste CRTs.

Zhuang et al. studied the leaching efficiency of sodium hydroxide on lead in waste CRTs lead-containing glass, and investigated the effects of different additives such as silica and reduced iron powder on mechanical activation. The results show that the reduced iron powder can disperse and reduce the bond energy in the mechanical activation, which can greatly improve the leaching rate of lead. Compared with the sample of metal lead leaching rate of 40.86% without adding any material for mechanical activation, the leaching rate of lead can reach above 85% when the 15% iron powder assisted the ball mill reaction in the sodium hydroxide leaching system of 4mol/L for 3h. Yuan et al. studied the kinetics of leaching reaction of mechanically activated waste CRTs glass in nitric acid leaching system, and investigated the influence of technological parameters such as mechanical ball grinding speed, leaching temperature and initial concentration of nitric acid on the leaching effect of lead in waste CRTs leaded glass. The results show that the mechanical activation pretreatment can obviously improve the reaction activity, and the lead-leaching rate of the waste CRTs in the lead-containing glass is also greatly improved. The apparent activation energy and reaction order of leaching reaction decreased from 109.4kJ/mol and 0.79 to 54.3kJ/mol and 0.51. Although the leaching systems such as strong acid and strong alkali have significant effects on the leaching of lead, the safety and environmental risks are uncertain, which is not conducive to the industrialization.

2.2.2 Fire method. Fire method is to melt lead out of waste CRTs glass at high temperature and recycle it in the form of simple substance lead. Under high temperature, the continuous honeycomb network structure of CRTs leaded glass is easy to be broken, and lead exists in the form of free state in the viscous molten material, which is easy to be separated and recovered by contact reaction with other materials.

Lu et al. added 20% carbon and kept it in the air atmosphere at 950°C for 3 minutes to melt 90.3% lead out of waste CRTs lead-containing glass. Moreover, the dissolution rate of lead reaches
maximum value when C:Na₂CO₃ is 1:3 and the melting temperature reaches 1200°C. Hu [25] et al. designed a high-temperature melting carbon thermal reduction process, which produced glass frits while reducing metal lead, and then hydrolyzed the glass frits to prepare water glass. When the melting temperature is 1200°C and the holding time is 2h, the recovery rate of metal lead can reach above 90%, while the amount of lead in the residue is only about 1%. Narendra Singh [26] et al. pretreated waste CRTs leaded glass particles with 10% carbon powder at 900°C for 30 minutes, and then obtained 93.60% lead after acid leaching. In addition, other smelting processes can also be used to extract lead from waste CRTs leaded glass, such as alkali melting, oxidation smelting, reduction smelting and so on [27].

In terms of wet method and fire method, both have advantages and disadvantages. The wet method has relatively low energy consumption, but the recovery efficiency of lead is relatively low. The fire method has relatively high energy consumption, but the recovery efficiency is relatively high. In the future, how the lead separation process can save energy, reduce energy consumption, protect the environment and high efficiency will be its main research direction, and also the basic condition for realizing its industrialization.

3. Conclusion
Facing with the high amount of waste CRTs, how to realize the reuse of waste CRTs glass with harmless is still widely concerned by researchers in the world. A comprehensive analysis of the technical research results in recent years shows that the recycling methods of waste CRTs glass mainly focus on building materials. The recycling way of waste CRTs leaded glass is mainly embodied in the separation, extraction and recovery of lead in waste CRTs glass. It is still an important research and development direction to achieve energy saving, consumption reduction, high efficiency and environmental protection while ensuring a high recovery rate.

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