Recovery of Lead form CRT Glass by Pyrogenic Process

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Abstract: *With a large number of abandoned traditional CRT(Cathode Ray Tube) display, a large amount of waste CRT glass pose a great challenge to the harmless disposal and recycle. The traditional methods still exist many problems including the low recovery rate of lead、the high lead content of molten slag. This paper studied the process optimization of precipitation recovery PbS from CRT glass in the molten state. Achieved the optimal addition of* Na_2CO_3*, the optimal reaction temperature, the optimal reaction time and the optimal addition of* Na_2S*. The recovery rate of PbS can reach more than 90%. This method has advantages of high recovery rate, simple process, high utilization ratio of raw materials and low energy consumption. Lay a solid foundation for large-scale industrial production and recycling of waste CRT glass in the future.*

Keywords: *Waste CRT glass; Recovery of lead, Melting precipitation; Process optimization*

1. Introduction

In recent years, with the constant development of electronic imaging technology, the traditional CRT display gave way to flat-screen LCD (Liquid Crystal Display) [1]. According to the research, over 500 thousand tons of waste CRT glass can be disassembled and recycled annually. What's more, it can increase by 25% to 35% each year [2]. The mass disposal of CRT display in China and import of discarded CRT display from other countries pose a great challenge to the harmless disposal and recycle of waste CRT glass.

The lead contained in waste CRT glass is far more than most lead ore. For instance, a 17-inch CRT glass bulb contains about 1.12kg of lead. As lead is one of the most important non-ferrous metallurgy resources, the large amount of waste CRT glass can be a proper material to recycle secondary lead. Meanwhile, the inappropriate disposal of waste CRT glass will greatly threat people's physical health and the environment. If waste CRT glass was improperly deposited or disposed, lead will slowly dissolved in the water soluble acidic environment, which may cause severe pollution [3]. According to the "National hazardous waste list", the waste display cone-glass has been classified into the dangerous wastes.

As reported at home and abroad, in order to recycle lead from waste CRT glass[4-7], there is a representative method that using the wet process to recovery of PbS and preparing sodium silicate. However, there still exists many problems including the low recovery rate of lead、the high lead content of molten slag[8]. So it can hardly be put into mass production[9-10]. It's high time we find an appropriate way to recycle waste CRT glass. To recycle PbS from CRT glass in the molten state has many benefits, including low energy consumption, simple technology and high recovery rate, which is the ideal recycling approach and represents the research trend of the future. A further research to the process optimization of precipitation recovery PbS from CRT glass in the molten state can be of great significance.

2. Experimental

2.1. Experimental Apparatus

Box type resistance furnace: Model XS-6-13, AC 220V, Power 6Kw, Furnace dimensions 250x200x100, Maximum working temperature 1300℃, SCR temperature controller.

Crucible: 300mL high temperature crucible.

Balance: 300g electronic balance, precision 0.01g.

2.2. Experimental Materials

Waste CRT glass powder, from 34-inch Samsung production of colour TV cathode ray tube cone-glass (excluding the neck tube, weld part). The elements of the glass are determined by using the S-4800 field emission scanning electron microscope, test results are shown in TABLE I. Crushed and grinded，over 40 mesh standard sieve, spared.

TABLE I: The Chemical Composition of Waste CRT glass

Components	SiO_2	PbO	K_2O	Na_2O	Al_2O_3	CaO	MgO	BaO	Fe_2O_3	TiO_2	Rest	Whole
Contents (%)	54.20	23.3	7.44	6.49	1.42	3.75	2.60	0.13	0.06	0.01	0.07	100

Na_2CO_3, analytical reagent grade, Na_2CO_3 content 99.0%, removal of lumps, over 40 mesh standard sieve.

Na_2S, analytical reagent grade, $Na_2S\cdot 9H_2O$ content 98.0%, over 20 mesh standard sieve.

2.3. Experimental Design

In the reaction of PbS recovery by melting precipitation, using Na_2S as a precipitating agent, Na_2S can react with the $PbSiO_3$ component in CRT glass to produce Na_2SiO_3 sodium silicate and PbS precipitate. The chemical formula of the reaction is as follows:

$$Na_2S + PbO \bullet mSiO_2 = Na_2O \bullet mSiO_2 + PbS \downarrow \tag{1}$$

The feasibility of this reaction has been verified by experiments. The key to the recovery of PbS is the reaction S^{2-} and Pb^{2+} generate PbS and gravity settling to the bottom of the crucible in melting condition.

According to the law of chemical reaction, the addition of Na_2S, the addition of Na_2CO_3, reaction temperature and reaction time are the key factors to affect the recovery rate of PbS. Under the high temperature melting conditions, heightening reaction temperature can accelerate the reaction rate that S^{2-} and Pb^{2+} generate PbS. When the temperature reaches the reaction temperature, the length of reaction time determines the degree of the formation of PbS reaction and precipitation. When reaches the reaction temperature, the length of reaction time determines the degree of reaction and precipitation. In the experiment, needs to accord the modulus of sodium silicate to adding a certain amount of Na_2CO_3, modulus of sodium silicate is the value of n in $(Na_2O^{+}K_2O)\bullet nSiO_2$. And the addition of Na_2CO_3 can produce carbon dioxide foam expansion in the process of heating, so that the reaction can getting on sufficiently. The addition of Na_2CO_3 and Na_2S can affect the modulus of sodium silicate.

According to the designed experiment proportion, the corresponding quality of Na_2CO_3 and $Na_2S\cdot 9H_2O$ were added into 100g waste CRT glass powder and mixed evenly. The mixture was putted into the crucible compacted and stamped in order to ensure the atmosphere during the reaction. The resistance furnace is preheat to 500℃ and maintain stability, put crucible into the resistance furnace and step heating, heat preservation when reach the reaction temperature. After the reaction completed, separating the PbS precipitation in the bottom of crucible, weighing PbS and calculate the recovery rate. According to previous research results[11], the heating curve is shown in Fig. 1.

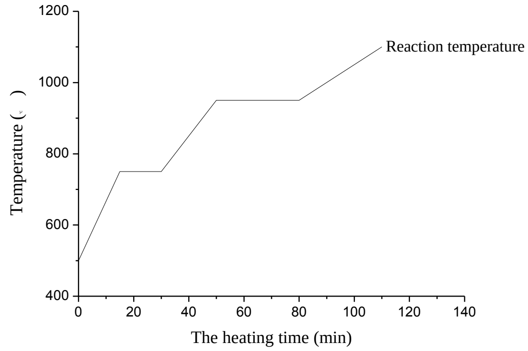

Fig. 1: The heating curves.

The formula of PbS recovery is as fallow:

$$K_{PbS} = \frac{Q_{PbS}}{Q_{CRT}} \times 100\% \quad (2)$$

In the formula: K_{PbS} is the recovery rate of PbS; Q_{PbS} is the recovery quality of PbS, unit is gram; Q_{CRT} is the quality Pb in CRT glass conversion for PbS, unit is gram. According to the content of PbO in Table 1, conversion of PbS to 24.98g.

In the design of orthogonal experiment, amount of Na_2S was set to the theoretical addition, considered the effect of the recovery rate of PbS was determined by addition of Na_2CO_3, reaction temperature and reaction temperature. The theoretical addition of Na_2S is 8.15g, and $Na_2S{\cdot}9H_2O$ is 25.08g.

According to the content of Si, K, Na in CRT glass, and the theoretical addition of Na, choose addition of Na_2CO_3 when the modulus of sodium silicate(n) was 1.5, 1.75, 2, 2.25 and 2.5.Formula is as follows:

$$\frac{M_{SiO_2}}{N_{SiO_2}} - n\left(\frac{M_{Na_2O}}{N_{Na_2O}} + \frac{M_{K_2O}}{N_{K_2O}} + \frac{M_{Na_2S}}{N_{Na_2S}}\right) = n\frac{M_{Na_2CO_3}}{N_{Na_2CO_3}} \quad (3)$$

Nx is the relative atomic mass of each substance, Mx is the quality of the material, and M_{Na2CO3} is the addition of Na_2CO_3 in different modulus of sodium silicate. The addition amount of Na_2CO_3 was 33.21g, 24.10g, 17.27g, 11.96g, 7.71g. Choose experiments reaction temperatures were 1100℃, 1125℃, 1150℃; 1175℃, 1200℃; reaction time were 90min, 105min, 120min, 135min, 150min. Design orthogonal test, calculate the PbS recovery rate, draw curve analysis to get the most suitable amount of Na_2S, and calculate the water glass modulus at this time. Design the orthogonal experiment, calculate the recovery rate of PbS, draw the curve analysis results and get optimal addition of Na_2CO_3, optimal reaction temperature and reaction time.

Use the optimal addition of Na_2CO_3, optimal reaction temperature and reaction time resulted in the orthogonal experiment, and 100g CRT glass powder, configure the experimental samples according to 1, 1.25, 1.5, 2, and 1.75 times theory addition of Na_2S. To calculate the recovery rate, draw the curve to analysis optimal addition of Na_2S , and calculate modulus of sodium silicate at this time.

3. Result and discussion

The results of orthogonal experiment is shown in TABLE II, draw the curve analysis results(Fig. 2).

TABLE II: The results of orthogonal experiment

Sample number	Sample components/g			Reaction time/min	Reaction temperature/℃	Pb/g	Recovery rate/%
	CRT glass powder	$Na_2S•9H_2O$	Na_2CO_3				
1			33.21	90	1100	16.2	0.649
2			33.21	105	1150	17.6	0.705
3			33.21	120	1200	18.2	0.729
4			33.21	135	1125	18	0.721
5			33.21	150	1175	18.1	0.725
6			24.10	90	1200	16.8	0.673
7			24.10	105	1125	17.5	0.700
8			24.10	120	1175	18.1	0.725
9			24.10	135	1100	17.5	0.700
10			24.10	150	1150	18.3	0.735
11			17.27	90	1175	16.6	0.665
12			17.27	105	1100	15.7	0.629
13	100	25.08	17.27	120	1150	17.6	0.705
14			17.27	135	1200	17.8	0.713
15			17.27	150	1125	17.6	0.705
16			11.96	90	1150	15.9	0.637
17			11.96	105	1200	16.7	0.669
18			11.96	120	1125	16.9	0.677
19			11.96	135	1175	17.2	0.689
20			11.96	150	1100	16.8	0.673
21			7.71	90	1125	14.8	0.592
22			7.71	105	1175	16	0.641
23			7.71	120	1100	15.1	0.604
24			7.71	135	1150	16.5	0.661
25			7.71	150	1200	16.6	0.665

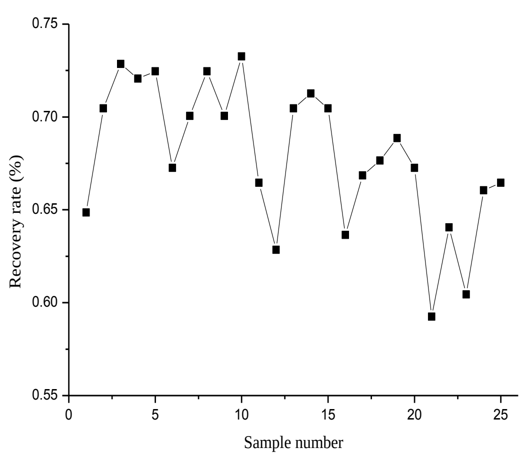

Fig. 2: The results of orthogonal experiment.

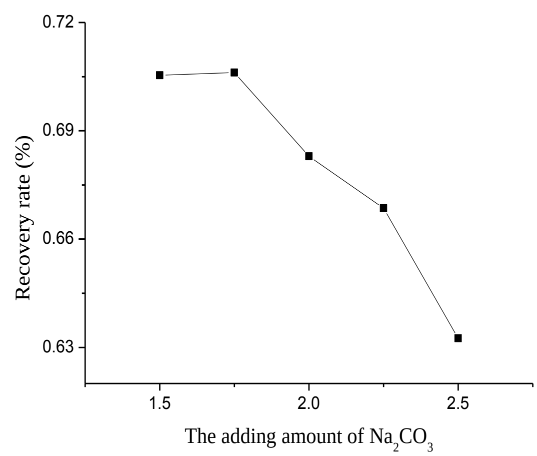

Fig. 3: The relationship between addition of Na_2CO_3 and the recovery rate of PbS.

Fig. 3 shows the recovery rate of PbS increased with the increases of addition of Na_2CO_3, namely decreased with the increases of modulus of sodium silicate. When addition of Na_2CO_3 reaches 24.10g, Na_2CO_3 overdose. Continues to increase addition of Na_2CO_3, the recovery rate of PbS level off, the recovery rate achieve maximum recovery rate region, remaine stable basically. The optimal addition of Na_2CO_3 is 24.10g.

Fig. 4 shows the recovery rate of PbS increased with the increases of reaction temperature in the range of 1100-1150℃, recovery rate is influenced by the reaction temperature greatly. When the reaction temperature reaches 1150℃, continue to increase reaction temperature the recovery rate changed little. When the reaction temperature ≥1150℃, recovery rate reaches the maximum area, and remain stable. The optimal reaction temperature is 1150℃.

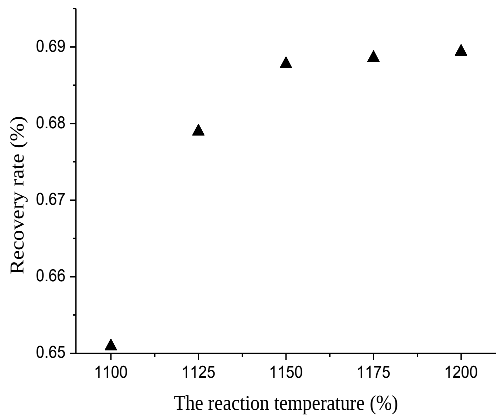

Fig. 4: The relationship between reaction temperature and the recovery rate of PbS.

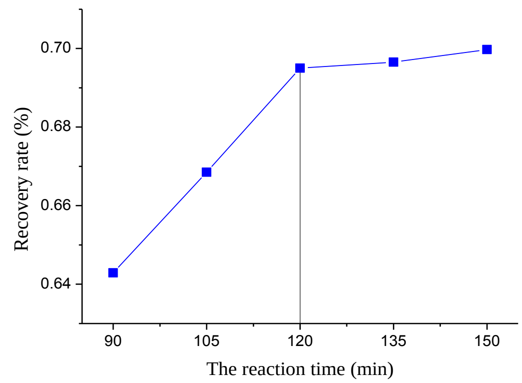

Fig. 5: The relationship between reaction time and the recovery rate of PbS

Fig. 5 shows the recovery rate of PbS increased with the increase of reaction time in the range of 90-120min, recovery rate is influenced by the reaction time greatly. When the reaction time reaches 120min, recovery rate changes slowly in the range of 120-150min. When the reaction time≥120min, recovery rate reaches the maximum area, and remain stable. The optimal reaction time is 120min.

Configures the experimental samples according to the optimal addition of Na_2CO_3, CRT glass 100g, 1, 1.25, 1.5, 2, and 1.75 times theory addition of Na2S, test under the optimal reaction temperature and the optimal reaction time. The experimental results are shown in TABLE 3.

TABLE 3:The results of the addition of Na_2S experiment

Sample number	Sample components/g			Reaction time/min	reaction temperature/℃	Pb/g	recovery rate/%
	CRT glass powder	Na_2CO_3	$Na_2S•9H_2O$				
1			25.08			18.1	0.725
2			31.35			21.4	0.857
3	100	2	37.62	120	1150	22.4	0.897
4			43.89			22.6	0.905
5			50.16			22.7	0.909

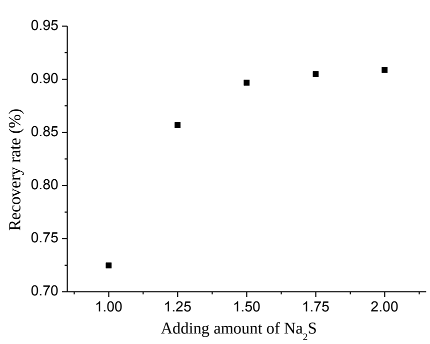

Fig. 6: The data analysis of the addition of Na_2S experiment

Fig. 6 shows the recovery rate of PbS increases from 72.5% to 90.9% in the range of 1-1.5 times of theory addition of Na2S, and the recovery of PbS increased with the increase of addition of Na2S. When the addition of Na2S is higher than 1.5 times theory addition of Na2S, recovery rate tends to be flat. The recovery rate of PbS increased slowly when continues to increase addition of Na2S. Therefore, select 1.5 times theory addition of Na2S as the optimal addition amount.

4. Conclusions

The research shows that waste CRT glass and Na_2S can react in melting condition in high temperature and recovery PbS precipitation. The addition of Na_2S, the addition of Na_2CO_3, reaction temperature and reaction time are the key factors to affect the recovery rate of PbS. The experiment obtains the optimal conditions that recovery of Pb from CRT glass by melting precipitation. The optimal addition of Na_2CO_3 is 24.10g, the optimal reaction temperature is 1150℃, the optimal reaction time is 120 min and the optimal addition amount is 1.5 times theory addition of Na_2S. Besides obtaining the high grade of PbS, glass slag can be further used as raw material for preparing sodium silicate, achieve resource, harmless, reduction of recycling for CRT glass. This method improves the recovery rate of Pb in waste CRT glass greatly. And the method is simple and low energy consumption, and it has very important social significance and very considerable economic value. Laying a solid foundation for large-scale industrial production and recycling of waste CRT glass in the future.

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