Model experiments using slag during CdO recovery

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Abstract— **A new method of production of cadmium from shredded cadmium-containing batteries using electroslag remelting was proposed, investigated theoretically and experimentally.**

The reduction of cadmium from cadmium oxide with carbon occurs in electroslag remelting equipment in a liquid slag bath. The resulting molten cadmium is collected in a crucible under a layer of molten flux. The intensity of the reduction process is affected by the liquid flux movement. This movement is caused by thermal convection and also by the electrical current interacting with the magnetic field. The work explores the possibility of intensifying the process using the external magnetic field. Magnetic fields are induced by different configurations of permanent magnet systems located outside the bath.

Keywords— Metallurgical applications, Numerical and experimental methods.

I. INTRODUCTION

The development of the technology for recycling and repossession of the exhausted small batteries and storage batteries is a vital problem worldwide, nevertheless, the process keeps going on and new methods of solving the problem appear. The project proposes a new method for recycling cadmium-containing storage batteries and small batteries. The method implies electroslag remelting of preliminary grinded cadmium-containing storage batteries and small batteries.

II. PRESENTATION AF THE PROBLEM

The collecting and recycling of the exhausted batteries and accumulators is very urgent nowadays. The repossession of these wastes is one of the most challenging problems of the secondary raw materials recycling. In fact, almost all batteries contain toxic substances in the form of various metals and chemical compounds, which, when the battery bodies are destroyed, contaminate the surroundings. Lead, nickel, cadmium, mercury, silver oxide, cobalt and lithium are used in the production of the batteries. Nickel-cadmium batteries used in cell phones are the most significant potential sources of cadmium; of large danger are also mercury and lithium batteries as mercury and lithium contaminants to the environment.

The battery recycling is a process aimed to reduce and operate the materials from which the batteries are made of. During this process, the metals are extracted from the batteries, which are then recycled to new products. The goal of this process is the preservation of electricity and raw materials. Recycling of such products contributes to the preservation of the environment for healthy life of human beings.

The project proposes a method for recycling cadmium-containing storage batteries and small batteries. The method implies electroslag remelting of preliminary grinded cadmium-containing storage batteries and small batteries. The cadmium contained in the storage batteries is powder-like cadmium/cadmium oxide. The reduction of cadmium by carbon from cadmium oxide during electroslag remelting ensures a maximum extraction of cadmium from secondary waste.

The reduced cadmium and the cadmium contained in the metal scrap in the crucible are liquid under the layer of melted flux which prevents the evaporation of cadmium and cadmium oxide. The temperature regime of electroslag remelting will ensure the melting of cadmium and the reduction of cadmium oxide by carbon, without bringing cadmium and cadmium oxide to boiling during the reduction. The cadmium from the crucible will be cast into molds from under the flux layer which is molten on the surface in the crucible, which ensures ecological safety of the technological process.

When investigating the electroslag remelting of the cadmium-containing scrap, it is planned to select a composition of the fluxes acting in the process, with the following criteria: the density in molten state should be lower than the density of cadmium oxide and cadmium, the flux melting point should be lower that the melting point of cadmium oxide and cadmium. The flux components must not interact with cadmium oxide and cadmium. A study of the chemical composition of flux and metallic cadmium and their morphology is planned at all stages of electroslag remelting.

We are also investigating the influence of temperature regimes[2] of electroslag remelting on the quality and quantity of the final product (cadmium).

An advantage of this technology is that when applied it can easily replace the traditional grinding systems with compact and high-performance units. Moreover, the new method is characterized by the low power consumption and is perfect for grinding solid materials, but in this case, the full period of recycling of waste batteries remains incomplete.

The method used in the project for the recycling of cadmium-containing storage batteries and small batteries is devoid of the drawbacks of previous projects and ensures the recycling completeness. The preliminary grinding of the cadmium-containing storage batteries and small batteries prior to electroslag remelting will contribute to the maximal reduction of cadmium by carbon from cadmium oxide:

$$2CdO + C \rightarrow t°C \rightarrow 2Cd + CO_2$$

The reduction reaction occurs at a temperature exceeding 500 °C.

Electroslag remelting will be performed by a graphite electrode.

Some characteristics of cadmium are important for choosing material of liquid slag in the remelting bath:

Melting temperature of Cd: 321.1°C.

Boiling temperature of Cd: 766.8°C.
Density of Cd at the melting temperature: 7.996 g/см^3.

For such big temperature diapason of liquid Cd it was easy to choose the slag with melting and boiling temperatures lower than those of cadmium and density smaller than that of Cd. These characteristics corresponding for $ZnCl_2$:

Melting temperature of $ZnCl_2$: 290°C.
Boiling temperature of $ZnCl_2$: 756°C.
Density of $ZnCl_2$ at the melting temperature: 2.54 g/см^3.

The boiling temperature of $ZnCl_2$ is 10.8ºC lower than that of Cd. This is very important from the ecological point of view. When the temperature in the remelting process of cadmium containing waste is raised above the working temperature 600^{0}C and reaches the vaporization temperature of $ZnCl_2$ (756ºC), first starts evaporate covering floes $ZnCl_2$, and only after covering floes is fully vaporized and temperature raised by 10.8ºC, starts the evaporation of Cd. So, the ecologically safe conversion and extraction of Cd from cadmium containing waste is performed.

III. Conclusions

The experimental device for electroslag remelting has been developed and produced (Fig. 1).

In a series of experiments a possibility to obtain cadmium from scrap of batteries containing cadmium was shown. The scrap was poured with liquid zinc chloride and brought their temperature to the temperature of cadmium reduction from cadmium oxide. The carbon was added to crap and carbon electrodes were used in the electroslag installation.

In first experiments, the difference was not observed between cases with and without the external magnetic field applied.

In the course of investigations, model experiments on the reduction of Cd by carbon C from cadmium oxide CdO under a ZnCl2 flux layer were carried out.

The experimental conditions were the following:
1. the reduction of Cd under the flux was performed in a muffle furnace at 500 0C during one hour;
2. the amount of CdO was 128 g;
3. the amount of carbon C was 24 g (powder-like fraction);
4. cadmium oxide CdO and carbon C were being stirred for 5 minutes in a closed 2-litre plastic container;
5. after stirring, the mixture of CdO and C was poured into a metallic mold made of stainless steel;
6. in the mold, 0.5 kg of zinc chloride ZnCl2 was put over the surface of the CdO and C mixture;
7. the mold was placed into the muffle furnace heated up to 123 °C and was kept heating at the heating rate 12.5 °C/min.

Upon the reduction in the muffle furnace and analysis and visual observation of the samples using the optical microscope, the following conclusions have been drawn.

The hygroscopicity of zinc chloride ZnCl2 was of significant impact on the obtained results. The mold heating in the presence of moisture in the zinc chloride leads to its partial hydrolysis in two stages.

Stage 1: ZnCl2 + H2O ↔ Zn(OH)Cl + HCl
Stage 2: Zn(OH)Cl + H2O ↔ Zn(OH)2 + HCl
↓t°
ZnO + H2O

When heating zinc chloride ZnCl2, in the flux there are Zn(OH)Cl, Zn(OH)2, and ZnO.

When exposed to cold and humid air, a reaction takes place:

2Zn(OH)Cl + 3ZnO + 4H2O → Zn5(OH)8Cl2·H2O

is simoncolleite which was found in the samples as the main crystalline phase after leaching by H2O.

Therefore, with reference to the results of the XRD analysis, it is not possible to definitely conclude on the form of Cd (either Cd or CdO) in the analyzed sample.

Preparation of powder samples for investigation.

The obtained after the reduction reaction samples were milled in the agate mortar, washed in distilled water for 15 min and rinsed by distilled water twice to remove ZnCl2. The obtained black powder contains unreacted CdO, reduced Cd, insoluble in water Zn5(OH)8Cl2·H2O, prepared for light microscopy. The investigated black powder was placed on a white surface covered with a sticky layer. By pressing it to the surface, the material under investigation is maximally covered. The excess powder is removed. Using another surface with a sticky layer, non-sticky particles of the powder material are removed. This procedure is repeated several times. In this way, a sample with a monolayer of the material under study and with the cleared outer surface of the metal particles is prepared for optical microscopy. By choosing the polarized light lighting mode, glowing is achieved (reflection of metallic spherical particles; the spherical reflective particles most likely are metallic Cd).

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