



Recovery of lead from smelting fly ash of waste lead-acid battery by leaching and electrowinning



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ABSTRACT

Fly ash that was enriched with lead (Pb), formed as an intermediate in waste lead-acid battery (WLAB) smelting, was recycled by the hydro-electrometallurgy. Characterization of fly ash thereof indicated that the Pb was in the forms of PbSO₄ (anglesite) and Pb₂OSO₄ (lanarkite). Nitric acid and sodium hydroxide were firstly used to study the leaching of the fly ash sample, which was affected by leachant dosage and solid-to-liquid ratio (S/L). At an S/L of 60 g L⁻¹, the leachability of Pb was 43% and 67% in 2 M acidic and basic solutions, respectively, based on an average 70 wt% of Pb in the original fly ash. Anglesite was completely soluble in NaOH and lanarkite was mildly soluble in HNO₃. Pb was recovered from the pregnant leach solution within an electrolytic cell constructed with graphite or RuO₂/IrO₂-coated titanium (Ti-DSA) anodes and a stainless steel cathode. Properties of anodes deposited with lead dioxides were analyzed by cyclic voltammetry. The optimized parameters of electrowinning were 2 M NaOH leachant, a current density of 0.75 A dm⁻² and an electrolytic process duration of 120 min, which yielded a Pb removal of higher than 99% and a specific energy consumption of 0.57 W h g⁻¹. This process constitutes an eco-friendly and economic alternative to the presently utilized secondary pyrometallurgy for treating lead-containing fly ash.

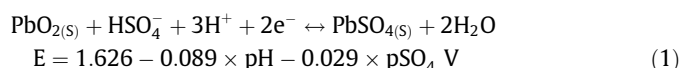
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1. Introduction

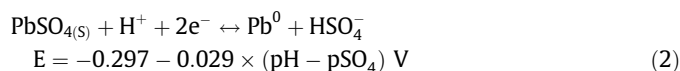
Pulverized fly ash from smelting furnaces is a hazardous waste because it normally is composed of toxic heavy metals, such as Pb, Cu, Cd, Hg, and Zn. In Taiwan, the pyrometallurgical recycling of Pb metal from waste lead-acid batteries (WLABs) has created significant amounts of fly ash as a municipal solid waste over many years. The Environmental Protection Administration of Taiwan (EPA) has reported that about 66,000 tons of spent lead-acid batteries were generated in 2014. The WLAB plant in this case study has a capacity of 500 tons of batteries per month. It adopts the pyrometallurgical carbothermic process with carbon to reduce the lead paste from waste batteries at high temperature, producing 12 tons of fly ash per month.

Electricity is generated from lead-acid batteries as follows (Blanpain et al., 2014).

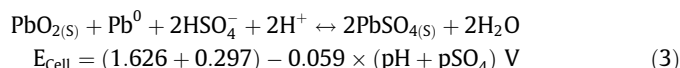
At the positive electrode:



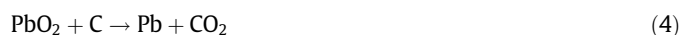
At the negative electrode:



The full reaction proceeds from left to right during discharge:



As a result, the WLAB is composed of mostly electrodes of metallic Pb and PbO₂ with H₂SO₄ as the electrolyte; PbSO₄ is deposited on the electrodes during the charge-discharge cycles of working batteries. The chemical issue to be addressed in the recovery of Pb from waste batteries by the pyrometallurgical method is the removal of sulfur (Ma and Qiu, 2015). The following reactions generally proceed during the thermal process in a smelter. Metallic lead is formed by either the reduction of lead dioxide with carbon or the reaction of PbS with PbO (Stevenson, 2004).



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Therefore, the potential components of fly ash from smelting are Pb, PbS, PbSO₄ and oxysulfates, such as PbO·PbSO₄ (lanarkite) and (PbO)₂·PbSO₄ (Batonneau et al., 2004), which have been characterized as PM₁₀ and PM_{2.5} (Uzu et al., 2011). A majority of the fly ash is disposed of in landfills, but this method of disposal has recently been prohibited by EPA because heavy metals in the fly ash potentially has been leaching into groundwater and drinking water supplies (Gwenzi and Mupatsi, 2016). The secondary smelter recycling of fly ash with moderate Pb enrichment is conducted, but the volatilizing of PbS and the emission of SO₂ gas raise health-related challenges. Pyrometallurgy, such as smelting systems, still dominate the recovery of both primary and secondary lead globally. Pb that is unintentionally released into aquatic systems accumulates in the food chain with a half-life of more than two decades (Cai et al., 2009; Meadows-Oliver, 2012). Hydrometallurgy is more eco-friendly than the pyrometallurgical disposal of fly ash or its disposal in landfills because it emits nothing, is cost-effective, and saves energy (Kinoshita et al., 2003; Sayilgan et al., 2009; Akcil et al., 2015). Several reagents, such as sulfuric acid, nitric acid, hydrochloric acid, hydrofluoric acid, acetic acid, citric acid, sodium hydroxide and ammonia (Zhu et al., 2013; Kuboňová et al., 2013; Tang and Steenari, 2016), are utilized to dissolve metals from solid waste. Aqueous Pb leaching can be followed by electrolysis, chemical precipitation, solvent extraction, and ion-exchange to recover the metal (Angelidis et al., 1995; Orhan et al., 2002), depending on the dissolved species and concentration.

The electrowinning is a relatively efficient route for separating and purifying Cu, Zn, Ni, and Ag from wastewaters (Antunano et al., 2013; Ma et al., 2014). To the best of the authors' knowledge, the feasibility of combining leaching and electrochemistry to dispose of fly ash has rarely been discussed (Tao et al., 2014). To solve the problem that is raised by the conventional landfilling of pyrometallurgical byproducts, hydro-electrometallurgy was used to recycle lead from real fly ash from WLABs smelting. The steps were as follows; (1) Pb from waste fly ash was dissolved in acidic and alkaline chemicals, and (2) the pregnant leach solution were electrolytically recovered as metallic Pb on the cathode and lead dioxide on the anode. Experimental parameters included the concentration of leachants (NaOH and HNO₃), the material of the electrode and the current density. Graphite or RuO₂/IrO₂-coated titanium was selected as the anode, because they are highly stable and insoluble. The voltammetric results were presented here to elucidate the variation among the properties of the various used electrodes.

2. Materials and method

2.1. Chemicals

All reagents were of analytical grade, and used without further purification. Leachants for dissolution of lead from the fly ash of WLAB were sodium hydroxide (NaOH, Merck KGaA, Germany) and nitric acid (HNO₃, 70%, BASF SE, Germany). The voltammetry of lead was conducted in acidic electrolyte using lead nitrate (Pb(NO₃)₂, Kanto Chemical Co. INC., Japan) and HNO₃, and in alkaline electrolyte using lead sulfate (PbSO₄, 99%, SHOWA, Japan) and

NaOH. The waters for all chemicals were doubly deionized using a laboratory-grade RO-ultrapure water system (resistance >18.3 MΩ).

2.2. Fly ash sample and analytical methods

Fly ash samples of secondary lead smelting was provided by CUST Ltd. Co. Taiwan, a resource disposal and recycling plant for WLAB. The as-received fly ash was freeze-dried for 72 h and sieved through a 0.5 mm mesh to ensure uniformity and stored at room temperature in amber glass bottles that had been pre-rinsed with *n*-hexane. A scanning electron microscopy (SEM, JEOL JSM-6700F, Japan), equipped with an energy dispersive spectroscopy (EDS, Oxford INCA 400, UK) was used for the micro-morphology and semi-quantification of the sample. X-ray powder diffractometer (XRD, Rigaku RX III, Japan) was applied to characterize the structural phase of fly ash. Toxicity characteristic leaching procedure (TCLP) method (US EPA SW-846 3rd Ed, Method 1311) was conducted to assess the heavy metal toxicity of fly ash using acetic acid leachant at pH 3.57. Concentrations of Pb and other metals in solutions were measured by an inductively coupled-plasma emission spectrometer (ICP-OES, JY 2000-2, HORIDA) whose acceptable calibrations should have R² values higher than 0.99.

2.3. Experimental procedure

Nitric acid and sodium hydroxide were utilized in examining the leachability of the fly ash samples. (For minimizing the corrosion of electrodes and the production of chlorine gas during the following electrolytic process, nitric acid was selected as the acidic leachant instead of a cheaper hydrochloric acid.) The parameters that most strongly affected the leaching yield of Pb (%) were the ratio of solid to liquid (S/L, 12, 30, 60, 120, and 180 g L⁻¹) and the concentration of the leachants (0.6, 1, and 2 M). The ambient temperature was maintained (~27 ± 3 °C) using a water bath. A batch experiment was carried out by adding a known amount of fly ash into 500 mL of leachant; the mixture was mechanically stirred at 450 rpm. At given intervals, 5 mL solution was withdrawn and filtered through a 0.22 μm filter (ADVANTEC Ltd., JAPAN), and the Pb concentration in filtrates was analyzed using ICP-OES.

After the fly ash had undergone the leaching test, the supernatants of the leachants were transferred to an electrolytic cell, which was made of polymethylmethacrylate (acrylic) (10 × 6 × 12 cm³, in LWH, total reaction solution = 0.3 L) Two electrodes of dimensions 100 × 2 × 100 mm³ (LWH), RuO₂/IrO₂-coated titanium, a dimensionally stable anode (Ti-DSA), or graphite plates as anodes and a plate of stainless steel 316 as the cathode, were connected to a DC power supply. In all cases, the effective surface area was 100 cm², and the distance between anode and cathode was 56 mm. The temperature of the electrolyte was kept at 27 ± 3 °C using a water bath. Electrolytic variables included the current density (0.75, 1.5 and 3 A dm⁻²), the species of the leachants and their concentrations. At fixed intervals, the soluble Pb in the samples was analyzed by ICP, and the difference between the Pb concentrations before and after electrolysis was used to obtain the removal efficiency of Pb in the electrolytic (electrowinning) process.

Cyclic voltammetry (CV) was conducted within a three-electrode system using a potentiostat (CHI611C, CH Instrument, Inc., USA) to characterize the anode materials. A silver chloride electrode (Ag/AgCl, BAS Inc., Japan) was used as a reference electrode, which was in contact with the working electrode, graphite or Ti-DSA, in solution. The stainless steel mesh (super-corrosion-resistant 316, 0.0045" in wire diameter) served as the counter electrode, which was kept 2 cm from the working electrode. The submerged area of each of the working and the counter electrodes in

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