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# Sequential stepwise recovery of selected metals from flue dusts of secondary copper smelting

Li Qiang [a], Isabel S.S. Pinto [b], Zhao Youcai [a,*]

[a] The State Key Laboratory of Pollution Control and Resource Reuse, Tongji University, Shanghai 200092, China
[b] REQUIMTE, Faculty of Engineering, University of Porto, Rua Dr.Roberto Frias, 4200-465 Porto, Portugal

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ABSTRACT

A novel and clean process was developed to convert flue dusts of secondary copper smelters into value-added products. The process consists of three main steps: NaOH leaching, two-stage combined electrolysis, and deep purification of recycle solution. Initially, 80–92% Zn and Pb were dissolved in 5 M NaOH at 80 °C, whereas Cu was concentrated in the residue. Yates' algorithm was used to determine the main effects and interactions of the leaching factors. The leach solution was then electrolyzed at 100–250 A/m$^2$ and high purity Pb (>97%) was separated from the alkaline solution. Subsequently, a pulsed current was introduced to obtain ultrafine zinc powders (~30 μm) with the best performance occurred at $T_{on}$ (current-on) = 15 ms, and $T_{off}$ (current-off) = 10 ms. Finally, Cl and Al were precipitated by evaporation-condensation and CaO addition, respectively. The combination of alkaline media and pulse current enables the green route without distilled water washing and surfactant addition, thus minimizing effluent emissions. This environmentally friendly method has promise to treat other industrial wastes due to its low cost and simple design.



## 1. Introduction

Metallurgical industries generate vast quantities of different types of wastes such as electric arc furnace (EAF) dust, basic oxygen furnace (BOF) sludge, jarosite residue and flue dust of secondary copper smelting (Dvorak and Jandova, 2006; Ju et al., 2011). On the basis of rough statistics, no less than one million tons of these wastes have been produced in China per year (Li et al., 2011). These wastes could be used to recover metallic values or they may be disposed of. However, the disposal of such material is now becoming expensive due to increasingly stringent environmental regulations. Furthermore, the chemical nature of these dust/ash particles is such that these are classified as hazardous waste under the US Environmental Protection Agency classification. In view of the above, there has been an increasing interest in developing processes for the recovery of metals from these wastes.

Usually, pyrometallurgical and hydrometallurgical processes are employed for treating such residues. The pyrometallurgical processes face the problems of generation of worthless residues and costly equipment investment as well as quite high energy consumption (Pinto and Soares, 2012, 2013). Thus, much more attention has been paid to hydrometallurgical processes. For example, Dutra et al. (2006) extracted the zinc present in EAF dust with different alkaline leaching techniques. Oustadakis and coauthors developed a process of $H_2SO_4$ leaching, solvent extraction and electrowinning to recover zinc from EAF dust (Oustadakis et al., 2010; Tsakiridis et al., 2010). Langova et al. (2007) examined the sulfuric acid leaching of EAF dust and studied the influence of acid concentration, temperature, time, and liquid/solid ratio. Zinc extraction reached almost 100% and iron extraction exceeded 90% in 3 M $H_2SO_4$ at 80 °C and liquid/solid ratio of 5 after 6 h. Furthermore, they found that a good selectivity with regard to zinc was achieved with 0.1–0.3 M $H_2SO_4$ at 80 °C. Ju et al. (2011) proposed a clean hydrometallurgical route to recover zinc, silver, lead, copper, cadmium and iron from hazardous jarosite residues produced by zinc hydrometallurgy, whereas Trung et al. (2011) concentrated on the zinc leaching from fine-grain BOF sludge in acid medium. However, there is still not enough information about how to process wastes from the secondary Cu industry.

The flue dusts used in this work were obtained from the city of Fuyang, which is situated in Zhejiang, a developed southeastern province in China; it is one of the biggest national centers for secondary Cu industries. The composition of the dusts varies

* Corresponding author. Fax: +86 21 65982684.
E-mail addresses: zhaoyoucai@tongji.edu.cn, 2011marklee@tongji.edu.cn (Zhao Youcai).

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considerably, and it is dependent not only on the waste used, but also on the operating conditions. However, some general trends have been noted. For example, most of these dusts are rich in Zn, Cu, Cl, Pb, and Al. It is advisable to leach the dusts with caustic soda, because the chlorides will not be tolerated in the acid electrolyte, as even a very small amount can cause severe corrosion problems and thereby damage the electrolysis (Gupta et al., 1989; Guresin and Topkaya, 1998). Moreover, the washing section for removing Cl produces secondary pollutants and complicates the process. During caustic soda process, however, the chloride concentration increased over 25 g/L without any trouble being observed (Frenay et al., 1986). In particular no chlorine evolution was noted in the electrolysis cells, and formation of hypochlorite would be expected from the following reaction:

$$Cl^- + H_2O \rightarrow HClO + H^+ + 2e^-. \quad (1)$$

In addition, most of copper (>90%) is left in the residue when using this alkaline leach reagent. Furthermore, in the alkaline zinc electrowinning process hydrogen evolution on the cathode surface is even more impeded than the one in acidic electrowinning. Current efficiencies (CE) of 97–99% can thus be reached when high current densities are applied (Gurmen and Emre, 2003; St-Pierre and Piron, 1990). This behavior promotes the generation of more profitable products with a lower energy cost.

On the basis of the above analysis, a hydrometallurgical route is presented in this work, as shown in Fig. 1, for the metal recovery from the flue dusts of secondary copper smelters. In the alkaline zinc electrowinning, $Na_2S$ has been used to remove Pb from the leach solution, and this approach can recover lead selectively and quantitatively (Zhao and Stanforth, 2001). However, it is time consuming to separate Pb from alkaline solution, and $Na_2S$ is a toxic agent. Therefore, the present research focuses on the lead recovery from the alkaline media by low current densities electrolysis. In the conventional process, surfactants are widely applied to control the size and morphology of zinc powders (Ghavami and Rafiei, 2006); however the accumulation of these additives could damage the recycle solution quality and increase effluent emissions. Hence, other potential methods are clearly needed to produce ultrafine zinc powders with uniform size. In this work, pulse electrolysis is employed to obtain zinc powder due to its variety of mass transport situations and electrocrystallization conditions. However, the majority of studies on pulse electrolysis have focused on its potential advantages in the electroplating industry (Chandrasekar et al., 2010; Saber et al., 2003; Youssef et al., 2008). Information is lacking regarding its use in powder production.

This work describes a novel and efficient method to extract Pb from an alkaline leaching solution of the sample. Attempt was also made to produce uniform and fine zinc powders with pulse current. Subsequently, we reported the techniques for removing Cl and Al from the resultant alkaline electrolyte.

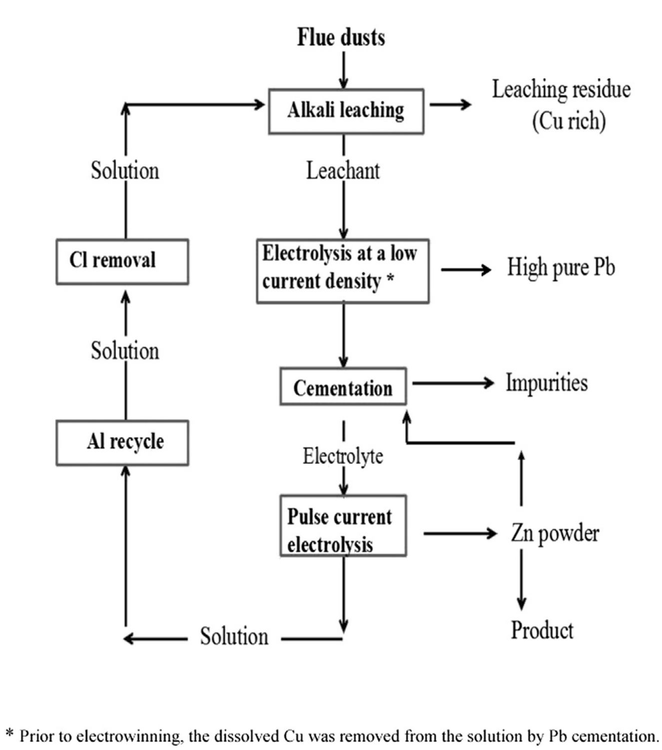


**Fig. 1.** General scheme for treating flue dusts from secondary copper smelters in this process.

## 2. Material and methods

### 2.1. Characterization of the flue dusts

The sample was dried and homogenized before the leaching experiments, and its chemical composition is listed in Table 1. The chemical analysis was determined by ICP-OES (AGILENT 720ES) and Ion Chromatography (ICS-1000). It demonstrates that the major elements present in the sample are zinc, copper, lead, aluminum and chlorine. An XRD (BRUKER D8 ADVANCE) analysis of the as-received dust is displayed in Fig. 2. It shows that most of metal elements are in combination with oxygen, but there can also be chloride.

### 2.2. Computer chemical simulations

Chemical speciation calculations were carried out using the MINEQL+ software (version 4.5) (Schecher and McAvoy, 2003), and the species distribution of metals at different pH values were determined. Metal speciation analysis with MINEQL+ generates chemical equilibrium concentrations of all species being considered in the model by the program reactions, based on component stability constants (Martell and Smith, 2004) and total molar metal concentrations. For computer simulations, total molar metal concentrations were calculated considering a solid to liquid (S/L) ratio of 100 g/L and assuming that the total amount of metals in the dust were in solution. The simulations allow predicting the optimum pH range to solubilize the target metals.

### 2.3. Procedure

The proposed process consists of three main stages, including NaOH leaching, two-stage combined electrolysis, and deep purification of recycle solution. With this method, the stepwise extraction of Cu, Pb, Zn and Al was achieved. Moreover, ICP-OES, XRD, SEM-EDS (PHILIPS XL30), IC, particle size analyses (Malvern 3000), and electrochemical methods were used in this study.

#### 2.3.1. Leaching

The leaching processes were carried out at 30–90 °C under atmospheric pressure. Specific amounts of flue dust samples were

**Table 1**
Chemical analysis of the main elements present in the dust.

| Element | Zn | Cu | Pb | Al | Cl |
|---|---|---|---|---|---|
| Weight (%) | 40.21 | 7.53 | 6.62 | 2.58 | 8.47 |