



# A novel separation process for detoxifying cadmium-containing residues from zinc purification plants



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## ABSTRACT

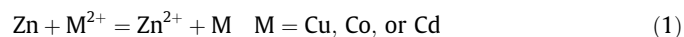
A novel separation process for detoxifying cadmium-containing residues arising from zinc hydrometallurgical processes has been developed. The solution of sulfuric acid and ammonium citrate ((NH<sub>4</sub>)<sub>3</sub>C<sub>6</sub>H<sub>5</sub>O<sub>7</sub>) is used as the lixiviant to partially extract copper and other metals from the residue at room temperature. Copper in the leachate is recovered by solvent extraction (SX) with LIX 973. Cobalt in the raffinate from the copper SX process is recovered by precipitation with  $\alpha$ -nitroso- $\beta$ -naphthol. Zinc remaining in the solution, at high concentrations, is further separated from cadmium by solvent extraction with P204 (di(2-ethylhexyl)phosphoric acid, D2EHPA). The results show that around 50% of the copper and virtually all the zinc, cadmium and cobalt in the residue can be leached under the experimental conditions used here. Virtually all dissolved copper and cobalt can be recovered in the subsequent solvent extraction and precipitation processes. The presence of (NH<sub>4</sub>)<sub>3</sub>C<sub>6</sub>H<sub>5</sub>O<sub>7</sub> could significantly facilitate the extraction of zinc by D2EHPA. More than 97% of the dissolved zinc can be recovered through a two-stage counter current solvent extraction process. After separating copper, cobalt and zinc, cadmium can easily be recovered from the solution either by cementation with zinc powder or by electrowinning, while the purified solution can be recycled back to the leaching process.

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## 1. Introduction

It is estimated that over 95% of the world's zinc is produced from sphalerite (ZnS). Mined zinc ores typically containing 5–15% zinc. They are usually crushed, ground and concentrated by gravity, magnetic separation or flotation to obtain zinc concentrates that typically contain about 55–60% zinc with other impurity metals such as copper, lead, iron and occasionally cobalt, silver, and cadmium (Habashi, 1997). The occurrence of these metals in zinc ores is increasing with continued development of the zinc mining industry. Hydrometallurgical methods are now the main routes for recovering metallic zinc from zinc concentrates (Wang and Feng, 2012). In the traditional roast-leach-electrowin (RLE) process, the zinc concentrate is first roasted or sintered to convert ZnS into zinc oxides and sulfur dioxide. The latter is subsequently converted to sulfuric acid, which is a commercial by-product. Most associated sulfide minerals in the feed zinc concentrate will also be converted into different oxide forms depending on operational conditions. In subsequent leaching stages, sulfuric acid solutions, at varying acidity, are used to leach the calcine and to dissolve zinc. During these

leaching operations iron precipitates and lead and silver remain undissolved; other metals such as copper, cobalt and cadmium dissolve to varying degrees. The leachate must be purified to eliminate the impurity metals before electrowinning to obtain a high-purity zinc product at high current efficiency (Habashi, 1997). In the zinc pressure leaching process, the direct leaching of zinc concentrates with H<sub>2</sub>SO<sub>4</sub> and oxygen is conducted in autoclaves (normally at approx. 150 °C and 1.4 MPa) (Jankola, 1995; Ozberk et al., 1995; Parker, 1981). Zinc and other metals including Cu, Co, and Cd are leached into the H<sub>2</sub>SO<sub>4</sub> solution which, again, must be purified before heading to electrowinning. The most common purification technique adopted in zinc plants is to add zinc dust to the leachate to precipitate most impurity metals by cementation.



The solid residue from the cementation process usually contains Cu, Co, Zn, and Cd at varying concentrations. Obviously, if not detoxified, this residue represents a hazard to the environment due to the toxicity of the heavy metals that it contains, particularly Cd. It is estimated that about 10 tons of the Cd-containing residue will be produced during the production of one kiloton of zinc metal in zinc hydrometallurgical processes. In China, the largest zinc producer and consumer in the world, about 5 million tons of zinc

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metal was produced in 2012, more than 70% of which was produced through hydrometallurgical processes (Kang, 2012). Consequently the amount of the Cd-containing residue thus produced would also be significant.

Various processes for disposing of the Cd-containing residue from zinc processing have been developed. The residue can be directly fed to a copper smelter if the copper grade in the residue is high enough and if the cadmium content is below acceptable levels. In most cases, the residue has to be disposed of locally, ideally in an economic and efficient way. Loredo et al. (1995) proposed a hydrometallurgical process for recovering valuable metals from Cd-containing residue. The residue was first oxidatively leached with water to partially dissolve zinc and most of the cadmium. After liquid/solid separation, the solution was sent to a SX circuit to separate zinc and cadmium. The solid residue from the pressure leach was then leached with strong acid solution to dissolve the remaining Zn. Zinc was recovered from this leachate through solvent extraction and the resulting residue then went through an oxidative acid leaching process to recover Cu. This residue, now devoid of most zinc and copper, contained cobalt and nickel which were concentrated more than threefold with respect to their initial contents and could either be sold or processed on-site for the recovery of cobalt and nickel. The method developed by Li et al. (2008) used similar concepts to treat the Cd-containing residue. Two stages of leaching, namely acid leaching and oxidative leaching, were applied to extract zinc, cadmium and copper into solution, respectively. Rather than by solvent extraction, the recovery of Cd from the first-stage leachate was realized by Zn cementation. Wang and Zhang (2004) proposed to use an oxygenated  $(\text{NH}_4)_2\text{CO}_3\text{-NH}_3\cdot\text{H}_2\text{O}$  solution to leach the copper from the cadmium-containing residue. Copper dissolved in the ammonia solution was recovered by solvent extraction with carboxylic acid. The residue after copper removal, could be acid leached to dissolve zinc and cadmium. The separation of zinc and cadmium from the resulting leachate was realized by solvent extraction or cementation. The main drawback of these multi-stage leaching techniques is the involvement of tedious liquid–solid separation operations and, sometimes, large neutralization demands. Lu et al. (1999) proposed a one-stage leaching technique to treat cadmium-containing residue. The residue was first oxidatively leached with strong acid with virtually all valuable metals such as copper, cobalt, zinc and cadmium dissolved into the leachate. After liquid/solid separation, the liquid solution first passed through a copper SX circuit (copper was extracted by Acorga M5640) and the raffinate was then fed to a zinc SX circuit to recover zinc (by D2EHPA). Lu et al. reported that while the overall recovery of copper, zinc and cadmium was reasonable, the extraction of copper from the strong acid solution by M5640 was inefficient and the separation of zinc and cadmium through the proposed SX system was also difficult to control, resulting in incomplete separation.

Given these limitations, a novel hydrometallurgical process for the recovery of valuable metals from cadmium-containing residue arising from zinc electrolyte purification processes has been developed in this research. In this process, a mixture of  $\text{H}_2\text{SO}_4$  and  $(\text{NH}_4)_3\text{C}_6\text{H}_5\text{O}_7$  is used to extract some of the copper and other metals from the residue. Copper in the leachate is recovered by solvent extraction with LIX 973. Cobalt in the raffinate from the copper SX process is recovered by precipitation with  $\alpha$ -nitroso- $\beta$ -naphthol. Zinc, remaining in the solution, is separated from cadmium by solvent extraction with P204 (DEHPA). Cadmium can then be easily recovered from the raffinate from the zinc SX circuit, either by cementation with zinc powder or by electrowinning, while the purified solution containing  $\text{H}_2\text{SO}_4$  and  $(\text{NH}_4)_3\text{C}_6\text{H}_5\text{O}_7$  can be recycled back to the leaching process. The feasibility of recovering valuable metals and detoxifying the Cd-containing residue through these combined processes has been examined

and a novel process flowsheet has been developed based on the experimental results.

## 2. Experimental

### 2.1. Materials

The cadmium-containing residue used in the research was produced at the Bayannaer Zijin Zinc Smelting Co.'s (Inner Mongolia, China) zinc processing plant. The residue was first dried in an oven at 80 °C for 24 h and then ground to P80 = 75  $\mu\text{m}$ . The main metals in the residue are copper and zinc with some cadmium and cobalt (Table 1). X-ray Diffraction (XRD) analysis of the dried residue is shown in Fig. 1, which demonstrates that while zinc, cadmium, and cobalt occur mainly in their oxidized form (oxides and/or sulfate), copper occurs both as metallic copper and cuprous oxide.

For solvent extraction experiments, LIX973NS-LV was kindly provided by Cognis Chemicals Trade Co. (Shanghai, China) and P204 (di(2-ethylhexyl)phosphoric acid, D2EHPA) by Shanghai Qi Ming Biological Technology Company. The diluent, #260 kerosene, was produced by Puyang Oil Refinery (Henan, China). All chemicals and reagents were of analytical grade and the double-distilled water was used to prepare solutions.

### 2.2. Experimental procedure

#### 2.2.1. Leaching of the cadmium-containing residue

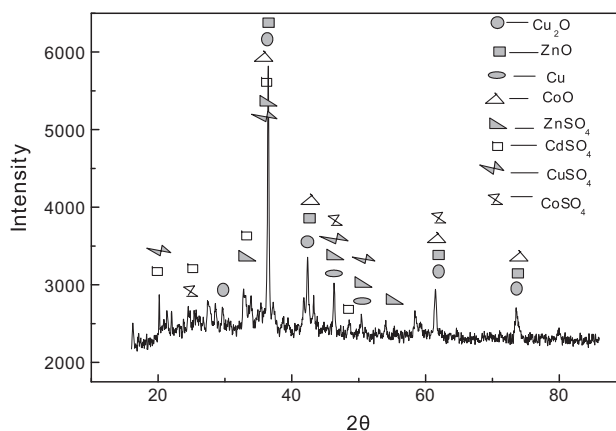
Leaching tests were carried out in a 1L Pyrex™ glass beaker at room temperature ( $20 \pm 2$  °C). Mixing was provided by an agitator with four 2 cm diameter stainless steel impellers powered by a variable-speed electric motor. The agitation speed was maintained at 450 RPM. The leaching slurries were vacuum-filtered and washed three times with distilled water. Both the filtrate and the washing solution were analyzed for metal concentration. The leaching residue was dried at 80 °C for 24 h before analysis for metal concentrations.

#### 2.2.2. Solvent extraction experiments

The solvent extraction and stripping experiments were carried out batch-wise by contacting organic and aqueous solutions in a

**Table 1**  
Chemical composition of the industrial cadmium-containing residue.

Element	Cu	Zn	Cd	Co
wt%	24.6	29.1	2.62	0.39



**Fig. 1.** XRD analysis result of the Cd-containing residue.

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