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Extraction of copper from copper and cadmium residues of zinc hydrometallurgy by oxidation acid leaching and cyclone electrowinning

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ABSTRACT

Copper and cadmium residue (CCR) is a hazardous solid waste generated in the process of zinc hydrometallurgy, and contains large amounts of Cu, Zn, Cd and Pb. Recovery of Cu from this material was investigated in the present study. CCR containing 30–40 wt.% Cu was leached in an oxidizing atmosphere with H_2SO_4 and the optimum leaching conditions were determined as follows: H_2SO_4 concentration of 180 g/L, L:S ratio of 3:1 (mL/g), H_2O_2 excess coefficient of 7.0, leaching temperature of 80 °C, and leaching time of 3 h. The leach solution was then subjected to cyclone electrowinning without purification or concentration, for recovery of Cu. The leaching step showed over 95% extraction of Cu under the optimized conditions. The cyclone electrowinning yielded Cu of > 99.5% purity with current efficiencies exceeding 97%.

1. Introduction

Currently, more than 85% of zinc is produced by hydrometallurgical processes (Lu et al., 2014). Purification of the leach liquor in these processes is carried out by adding zinc powder that removes the more noble impurities such as Cu^{2+}, Cd^{2+} and Co^{2+}. As a result, the excess zinc powder together with compounds of other metals (e.g. copper, cadmium and lead) form a residue known as copper and cadmium residues, CCR (Tang et al., 2014). Fig. 1 shows the process of CCR generation in zinc hydrometallurgy. It is reported that 80–100 kg of CCR is produced in the process of making one tonne of refined zinc (Tang et al., 2014). Due to the large contents of Cu and Cd (Cu 30–40%, Cd 2–10%), CCR has been designated a hazardous solid waste. The environmental concerns and health risks associated with the CCR together with loss of metal values if unused, make the CCR a serious environmental liability. In China, 500,000 t CCR is produced annually most of which is not utilized effectively. Therefore, a sustainable method is highly demanded for recovery of metals from the residues.

Several studies have been conducted on the extraction of valuable metals from CCR (Chen et al., 2014; Kaksonen et al., 2017; Li et al., 2016; Shi, 2012; Tang et al., 2014; Yuan, 2013; Yuan and Shi, 2009; Zeng et al., 2004). A small fraction of CCR is treated in zinc or copper extraction plants; much larger amounts are processed in small smelting facilities. Recovery of copper is currently accomplished through smelting: the material is fed to reverberatory furnaces where Cu reports to matte and other metals enter the slag phase. The yield of Cu is however low in this process and Cd reports to slag, making its recovery difficult.

CCR is characterized by fine particle size, high water content, and high sulfur. Therefore, its processing method should be specifically tailored to avoid generation of secondary pollutants. For this purpose, processing of the material through smelting necessitates additional facilities for dust collection and treatment of flue gas and acid mist. Such facilities are only economically feasible in larger smelters, limiting future prospects of these methods. The hydrometallurgical methods, on the other hand, do not generate dust or off-gas. They also allow recovery of Cu as well as other valuable elements such as Zn, Cd, and In. The traditional and simple leaching-solvent extraction-electrodeposition scheme is not capable of producing high quality Cu due to the complex nature of the leach liquor containing a range of metal cations in different concentrations. Therefore, a cost-effective method with high throughput that is capable of complete recovery of valuable materials from CCR is urgently required.

Taking advantage of the difference in electrodeposition potential of various metals, one can selectively electrowin the target metal from a poly-ionic solution. The purity can be negatively affected by polarization, high concentration of impurity ions, pH value, electrode overpotential and the deposition potentials of different metals. Such effects

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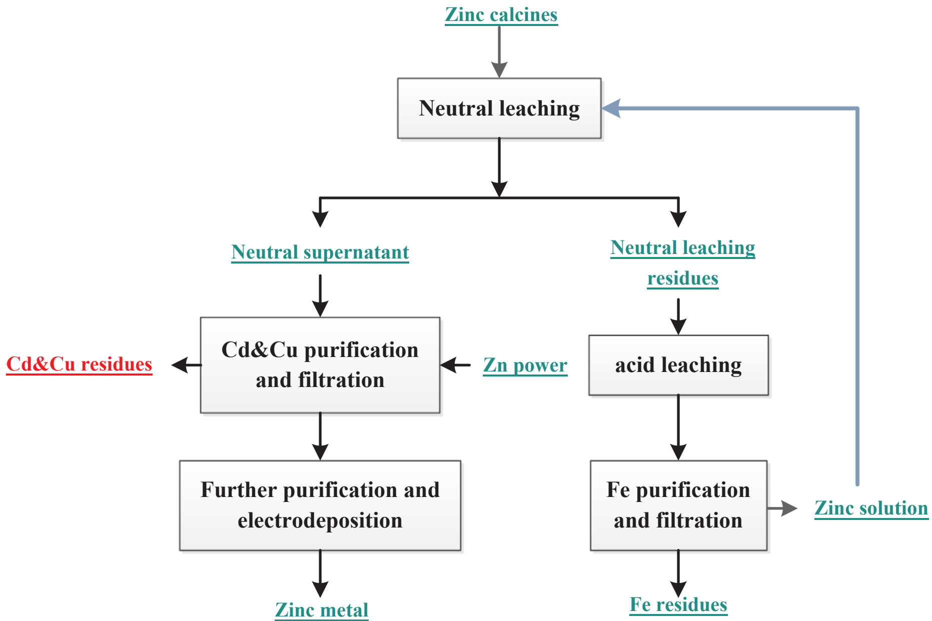

Fig. 1. Flowsheet of Zn extraction and CCR generation.

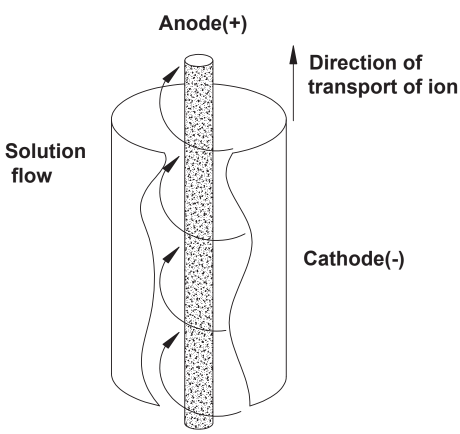

Fig. 2. The principle diagram of cyclone electrowinning.

can be minimized through a strong flow of electrolyte that provides sufficient supply of the target metal species on the cathode with minimum thermodynamic or kinetic preference for the deposition of impurity metals. This has been demonstrated by higher purity of product obtained in cyclone electrowinning than traditional electrodeposition methods (Guo et al., 2010). Some successful cases were proposed, for example, Yang et al. investigated cyclone electrowinning of antimony from antimonic gold concentrate ores and proved that cyclone electrowinning was effective for the treatment of antimonic gold concentrates (Yang et al., 2018), Wang et al. researched efficient electrochemical recovery of dilute selenium by cyclone electrowinning (Wang et al., 2018). Fig. 2 shows a basic diagram of cyclone electrowinning. Compared with the traditional electrodeposition, cathode current density can reach 1000 A/m^2 in this process. The large current density together with strong flow of the solution in the cyclone generates a large number of smaller bubbles with short residence time in the solution, leading to a smaller content of acid mist content in such bubbles than those in conventional electrowinning cells. As a result, the release of acid mist on bursting of bubbles at the surface is significantly reduced in cyclone electrowinning process, leading to a cleaner work environment and reduced need for ventilation and air cleaning.

Considering the characteristics of CCR and the advantages of the cyclone electrowinning in extracting metals from polymetallic solutions, the use of this method for recovery of Cu from CCR is presented in this paper. The process consists of the following steps: atmospheric oxidation acid leaching, cyclone electrowinning of Cu, and recovery of Cd and Zn in Zinc hydrometallurgy process. The advantages of the process are higher leaching efficiency, lower purification requirements on electrolyte, higher cathode current density, and higher metal recovery efficiency.

2. Experimental

2.1. Material

The CCR used in this study was obtained from a zinc extraction plant in Yunnan province of China. The CCR samples were crushed, dried at 105 °C for 24 h and ground to pass a 100 mesh sieve. The sample was mainly composed of copper, lead, zinc and cadmium with smaller amounts of iron and manganese (Table 1). Fig. 3 shows the X-ray diffraction pattern of the material, indicating the presence of cuprite [Cu_2O] and anglesite [$PbSO_4$] as the main crystalline phases.

2.2. Analysis methods

Phase analysis was carried out using a Japan Science X-ray diffractometer with Cu Kα radiation (λ = 1.5406 Å), an operating voltage of 40 kV, and a current of 40 mA. The concentration of Zn^{2+}, Cu^{2+} and Cd^{2+} were determined by Atomic Absorption Spectroscopy.

2.3. Experimental methods and apparatus

Leaching in H_2SO_4 was achieved by dissolving 10 g of CCR in various amounts of solution under controlled conditions of temperature, solid/liquid ratio, oxidizing agent amount, H_2SO_4 concentration, and

Table 1
Chemical composition of CCR.

Element	Cu	Zn	Cd	Fe	Pb	Mn
Content/wt.%	35.4	4.6	3.4	0.4	20.1	0.12