



Reductive leaching of zinc, cobalt and manganese from zinc plant residue



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ABSTRACT

Zinc plant residue known as hot filter cake (HFC) contains a significant quantity of zinc oxide (ZnO). In addition, it holds cobalt hydroxide Co(OH)₃, manganese dioxide (MnO₂) and minor amounts of nickel, copper, iron and lead containing species. The process consists of three unit operations: (i) selective leaching of zinc; where the effects of parameters such as acid concentration (0–1.0 M), temperature (40–70 °C), time (15–90 min) and solid to liquid ratio (S/L) (0.01–0.1 g mL⁻¹) are investigated. At this stage, 81.5% of zinc, 2.0% of cobalt and 1.7% of manganese were extracted at the optimum conditions determined. (ii) Reductive leaching of cobalt and manganese; where the leaching residue of step (i) was leached with 1 M sulfuric acid solution in the presence of citric acid (C₆H₈O₇·H₂O) as a reducing agent. The investigated independent leaching parameters were citric acid content (30–60% more than the stoichiometric ratio), S/L ratio (0.02–0.1 g mL⁻¹), temperature (75–95 °C) and time (45–75 min). Response surface methodology (RSM) was used to optimize the parameters. In the optimum conditions, recovery of cobalt, manganese and zinc was 96.43%, 90.26% and 64.12%, respectively. (iii) Sulfide precipitation; at this stage, in order to separate Co(II), Zn(II) and Mn(II), sodium sulfide (Na₂S) 1 M was added to the solution from the reductive leaching, at the optimum conditions investigated. Recovery of zinc, cobalt and manganese was 93.45%, 95.15% and 100%, precipitated at pH = 2, pH = 3 and pH = 8, respectively. Finally, based on this research work, a conceptual flowsheet was developed.

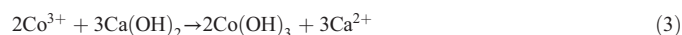
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1. Introduction

In hydrometallurgical processing of zinc, a regular method for elimination of cobalt is precipitation with activated zinc dust in the presence of Cu(II), Sb(III) or As(III) (Böckman and Ostvold, 2000). Cobalt cementation reaction in its simplest form is:



However, this method is not a conventional practice in the plants present in Iran. In zinc production companies in Iran, cobalt is removed in the “Hot purification” stage (Fig. 1). At this stage, potassium permanganate (KMnO₄) is added to the zinc sulfate solution at 80–85 °C and cobalt precipitates as Co(III) compounds on the filter cake. Milk of lime is then added to the solution to keep the pH in the range of 5–5.2. The following reactions occur in the hot purification stage which lead to the formation of Co(OH)₃ (Safarzadeh et al., 2011):



Adding KMnO₄ to the zinc sulfate solution increases the amount of manganese in the hot purification filter cake (HFC). Besides, it complicates the separation of cobalt and manganese. In general, HFC contains 16–24% (w/w) Zn, 0.5–2% Co, 10–16% Mn, 0.1–0.4% Ni, 0.2–0.5% Cd and slight amounts of Cu, Fe and Pb (Safarzadeh et al., 2011; Haghshenas et al., 2007; Moradkhani et al., 2014). Moreover, the presence of manganese and zinc in the filter cake possesses a remarkable commercial value. The amount of HFC generated is about 80–100 kg per ton of the cathodic zinc produced which is quite high. This is due to the fact that in Iran, KMnO₄ is used in the purification stage. This additive removes both Co and Mn as their hydroxides as well as the hydroxides of other metal species.

Growing demand in consumption of cobalt metal and its compounds has led to the primary resources depletion and as a net effect, finding a secondary resource seems to be inevitable. The annual production of HFC in the zinc plants in Iran is ca. 10⁴ tons per year, which makes it a reliable secondary resource of cobalt. However, recovery of valuable metals from HFC has been barely reported in the literature. Safarzadeh et al. (2011) reported that reductive leaching of cobalt and manganese from HFC which contained 0.98% Co, 6.74% Mn, 32.48% Zn, 0.16% Fe, 0.038% Ni and 0.047% Cd, using sulfuric acid and phenol as leaching

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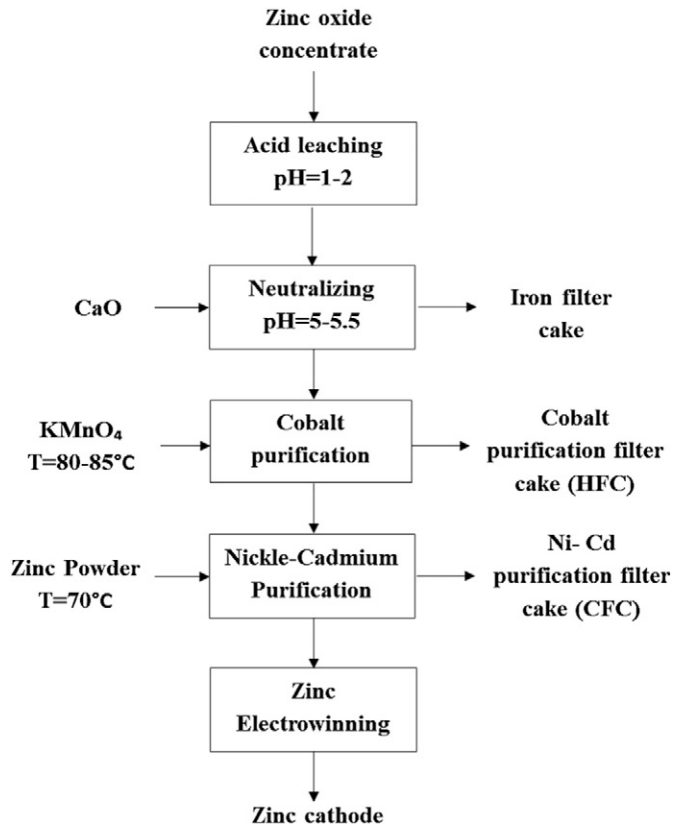
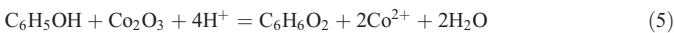
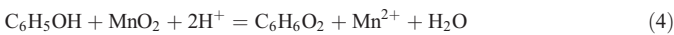


Fig. 1. Zinc cathode production flowsheet in zinc plants in Iran.

and reducing agents, respectively. The following reactions can be proposed for the system investigated by Safarzadeh et al. (2011):



It has been indicated that leaching of the Co(III) compounds is only feasible in the presence of a reducing agent. They also reported 97% cobalt recovery at the optimum condition of 2.0 M H_2SO_4 , 85 °C, phenol dosage of 10%, 600 rpm and 60 min. Moreover, Haghshenas et al. (2007) used H_2O_2 as a reducing agent in a reductive leaching step of manganese and cobalt, existing in HFC, in the presence of sulfuric acid as the leaching agent. The filter cake contained 4.8% Co_3O_4 , 0.17% CdO , 22.9% MnO , 0.07% NiO and 14% ZnO . They separated zinc in 2 min using 30 g L^{-1} H_2SO_4 , 25 °C and liquid to solid ratio of 0.85. The optimum concentration of sulfuric acid to leach cobalt was determined to be 50 g L^{-1} . Meanwhile, addition of 5 g L^{-1} H_2O_2 solution indicated the best influence on the cobalt leaching process which increased its recovery to ca. 1.5 g L^{-1} . Additionally, Moradkhani et al. (2014) suggested a process comprising of four major unit operations to recover and separate cobalt and manganese from HFC containing 1.19% Co, 9.1% Mn, 14.66% Zn, 0.07% Ni, 0.035% Cd and 6.64% Ca. The aforementioned process included: (i) washing zinc using 200 g L^{-1} H_2SO_4 solution, at $T = 25$ °C, and solid to liquid ratio (S/L) = 1/8, with $t = 120$ min, and at $\text{pH} = 1$; (ii) reductive leaching with hydrogen peroxide using 30 g L^{-1} H_2SO_4 solution, 3% v/v H_2O_2 solution, having $S/L = 1/10$, at $T = 25$ °C, and $t = 45$ min; (iii) cadmium cementation by zinc powder with 10 times of stoichiometric quantity of cadmium at $\text{pH} = 3.5$, $T = 25$ °C, and $t = 30$ min and (iv) separation of cobalt from manganese by beta naphthol with 8 times of stoichiometric value, during 30 min, at $T =$

Table 1
Solubility products of some metal sulfides at 25 °C (Jandova et al., 2005).

Sulfides	CuS	ZnS	CoS	NiS	FeS	MnS
Log K_s	-47.70	-25.70	-22.00	-21.00	-18.80	-13.30

25 °C and $\text{pH} = 1.5$. At these conditions, cobalt precipitated up to 99%, while manganese remained in the solution.

Organic acids are under development to serve both as leaching agents and reducing agents. These acids are considered to operate by replacing hydrogen ions and metal cations from the ore matrix and as a result, induce dissolution of metals. They can also sequester metals into soluble metal–ligand complexes by chelation (Tzeferis and Agatzini-Leonardou, 1994; Ma et al., 2013). Among different varieties of organic acids, citric acid offers the greatest potential as chelating agents (Peters, 1999). Furthermore, citric acid is a less expensive and more environmentally friendly reductant (Larba et al., 2013). It has been utilized as a reducing agent to recover manganese and zinc from spent batteries, which are present as MnO_2 and ZnO , respectively, together with inorganic acids such as H_2SO_4 and HCl (Sayilgan et al., 2010). Citric acid has also been used to remove heavy metals from soils, nickel extraction from laterites, copper and zinc extraction from copper–zinc oxidized ores (Tzeferis and Agatzini-Leonardou, 1994; Peters, 1999).

The chemical precipitation of metal hydroxides is the most conventional method for separating metal cations in the leach liquor. However, it faces some deficiencies such as high solubility and lack of functionality in the presence of a chelating agent. On the other hand, sulfide precipitation of metals is a viable alternative (Mishra and Das, 1992). It provides high grade of heavy metal elimination over a wide pH range and possesses several advantages over hydroxide or carbonate precipitation, such as the low solubility and high stability of metal sulfides (Jandova et al., 2005). Moreover, most of the metal ions can be precipitated as sulfides even in the presence of chelating agents (Mishra and Das, 1992). Hence, applying sulfide precipitation for separation of manganese, cobalt and zinc is advantageous. The solubility products of some metal sulfides are presented in Table 1.

New routes of metals recycling are constantly investigated to reduce costs and to prevent the environmental pollution. In the present paper a new flowsheet is developed to extract cobalt, manganese and zinc from HFC generated in zinc purification steps. In order to recover zinc from the residue, selective leaching of zinc with dilute sulfuric acid was performed. To recover cobalt and manganese from the residue, reductive leaching was performed to change the cobalt compound in the cake to a soluble form. In this step, a combination of sulfuric acid and citric acid ($\text{C}_6\text{H}_8\text{O}_7 \cdot \text{H}_2\text{O}$), as a reducing agent, was used as the leaching system. After leaching tests, sodium sulfide (Na_2S) solution was added to the leach liquor to evaluate its effectiveness in the precipitation of cobalt, manganese and zinc with the purpose of their separation from leach liquor.

2. Materials and experimental procedures

2.1. Materials

The filter cake used in the present study was kindly supplied by Zarrin-Rooy Company, Zanjan, Iran. The HFC sample was dried, ground

Table 2
Size distribution of the hot filter cake (HFC).

Mesh size (μm)	Mesh ASTM	Retained (%)
+105	140	3
74–105	200–140	12
38–74	400–200	41
–38	–400	44

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