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Reductive leaching of cobalt from zinc plant purification residues

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ABSTRACT

The leaching kinetics of the cobalt present in zinc plant purification residues (cobalt filtercakes) was investigated in the presence of the aromatic reducing agent — phenol — without any pretreatments. As such, the effects of particle size (−75+53 to −180+150 μm), reaction temperature (25 to 85 °C), phenol dosage (2 to15%) and sulfuric acid concentration (0.5 to 2.0 M) on the dissolution rate of cobalt and manganese were investigated. The experimental data conformed well to the shrinking core model, and the dissolution rate of cobalt was found to be controlled by diffusion through the product layer. Due to the low percentage of cobalt (<1%) in the filtercake, SEM and XRD studies did not show any cobalt-containing phases. It was demonstrated that sulfuric acid with phenol addition can effectively dissolve cobalt and manganese present in the filtercake. The activation energy of the reaction was calculated as 22.92 kJ/mol. The order of the reaction with respect to H_2SO_4 concentration, particle size, and phenol dosage was found to be 0.61, −1.88 and 0.70, respectively. The optimum conditions for the leaching of cobalt and manganese were found to be as 2.0 M H_2SO_4, 85 °C, −75+53 μm, and 10% phenol at the stirring speed of 600 rpm, which correspond to more than 97% cobalt and ~100% manganese recoveries. The rate of cobalt leaching based on shrinking core model can be expressed by a semi-empirical equation as:

$$1-\frac{2}{3}X-(1-X)^{2/3}=k_0.[\mathrm{H_2SO_4}]^{0.61}\cdot r_0^{-188}.[\mathrm{phenol\%}]^{0.70}.exp\left(\frac{-22.92}{RT}\right)\cdot t.$$

1. Introduction

Cobalt is one of the least abundant industrial metals as compared to copper and nickel, but is being widely used in many applications such as turbine blades for aircraft engines, hard facing alloys, magnets and superalloys because of some unique properties such as ferromagnetism, varying crystal structure with temperature, and wear and corrosion resistance properties (Safarzadeh et al., 2009a; Wang, 2006). On average, 70% of the world's total cobalt production is obtained through hydrometallurgical routes (L-SX-EW) (Pradhan et al., 2001).

With ever-increasing demand for cobalt, primary resources are exhausting and hence the intermediate and secondary resources have come to the forefront. Different types of cobalt resources are listed in Table 1.

Cobalt is present in zinc concentrates in low concentrations (0.001–0.005 wt.%). During certain stages of hydrometallurgical zinc production, cobalt is concentrated up to commercially important values (0.5–2%). Cobalt is detrimental to zinc electrowinning. It plates onto the zinc cathodes, lowers the hydrogen overpotential and catalyzes the production of hydrogen, and even a small amount (~1 mg/L) depreciates the rate of zinc production drastically (Bøckman and Østvold, 2000). Cobalt filtercake, which mainly consists of cobalt, manganese and zinc, is produced during the purification of zinc sulfate electrolyte, and is considered a good resource of cobalt (Stanojević et al., 2000).

Few papers have been published on the recovery of cobalt from zinc plant purification residues. Stanojević et al. (2000) investigated the possibility of enriching the waste sludge produced from electrolytic zinc and cadmium production. The method employed for recovering cobalt was based on selective leaching of accompanying metals from filtercake by sulfuric acid, with small amounts of cobalt dissolution. From the fresh cobalt purification filtercake (0.6–1% Co, 2–6% Cd, 40–55% Zn, 0.1–0.6% Ni, and 0.1–0.7% Cu), cobalt was concentrated to 2.2–12%.

Wang and Zhou (2002) have discussed a hydrometallurgical process for the recovery of cobalt from zinc plant purification residues

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Table 1
Classification of cobalt resources.

Primary	Intermediate	Secondary
Arsenical ores, sulfide ores, nickel laterite ores (Kapusta, 2006), heterogenite (CoOOH), deep sea nodules (Han and Fuerstenau, 1980; Das et al., 1986).	By-products of copper (considerable quantities of cobalt are contained in slag stockpiles produced from copper-smelting operations), nickel and zinc (beta cake) extractions (Hawkins, 1998), mixed sulfide and hydroxide products from laterite process (Kapusta, 2006).	Used superalloys, alloys, catalysts, magnets, cemented carbides, and spent ammonia cracker catalyst (Co-60), (Sadanandam et al., 2008).

(9.43% Zn, 1.40% Fe, 0.68% Co, 0.28% Mn, 0.26% Cu, 0.040% Cd, and 0.0059% Ni). The process included six major unit operations, i.e., washing, roasting and leaching, precipitation of iron and manganese, separation of zinc and cadmium (anion exchange), separation of nickel by selective extraction of cobalt and precipitation of cobalt. The leach liquor contained copper, iron, manganese, zinc, cadmium, nickel and cobalt. The leaching tests were carried out using water at 95 °C to obtain a leach solution containing about 20 g/L of cobalt. After subsequent removal of other impurities through ion exchange, precipitation and solvent extraction, cobalt was stripped from solvent extraction solution, and then precipitated and calcined to cobalt oxide.

Reductive leaching of cobalt from sea nodules has been also considered by a number of investigators (Han and Fuerstenau, 1980; Zhang et al., 2001a,b; Hsiaohong et al., 1992). Han and Fuerstenau (1980) extracted nearly 100% cobalt from manganese nodules using dilute H_2SO_4 and 0.2% SO_2 as reducing agent at ambient temperature. Also they reported the dissolution rates of cobalt, manganese, and nickel to be much faster under reducing conditions in comparison to the normal acid leaching.

Zhang et al. (2001a) reported 95.8–99.2% cobalt extraction using different poly-hydroxyl phenols as reducing agents in the dilute sulfuric acid from manganese nodules (0.43% Cu, 0.65% Ni, 0.33% Co, 21.09% Mn, 13.37% Fe, 0.15% Zn, 0.038% Mo, 1.54% TiO_2, 3.30% Al_2O_3, 11.59% SiO_2, 2.24% CaO, and 1.97% MgO).

Zhang et al. (2001b) reported the application of aniline (an organic reducing agent) for the acid leaching of manganese nodules of the same composition as their previous work. At the dosage of 0.3 g aniline/g nodule, the extraction of Mn, Cu, Ni and Co from manganese nodule was over 97%. Also, the leached pulp was filtered easily using all the mentioned aromatic amines.

The selection of appropriate reducing agent is critical for the acid leaching. Inorganic reagents such as coal lignite (Zhang et al., 2001a) (high reagent consumption, coal/MnO_2 1:1), SO_2 gas (not easy to handle and to regenerate), H_2O_2 (Zhang et al., 2001a) (needs very careful handling because of its explosive nature), cellulose (Veglio and Toro, 1994) (high consumption), sucrose and glucose (Zhang et al., 2001a; Das et al., 1986) (high reagent consumption, slow leaching rate and regeneration issues), $NaBH_4$ and O_2 have been reported to be problematic in terms of filtration of pulp and higher reagent consumption. However, the use of aniline (Zhang et al., 2001b, 2002) as reducing reagent seems to be advantageous considering lower reagent consumptions and easy regeneration by electrochemical means, especially phenol type organic acids that have a reduction–oxidation couple (Zhang et al., 2001a).

Mwema et al. (2002) have reported the application of ferrous ions, copper powder, and sodium metabisulfite ($Na_2S_2O_5$) as the reducing agents for the leaching of trivalent cobalt oxide at Shituru plant (Congo). Consumption of these reagents averaged 0.8 (metric) ton of sodium metabisulfite and 1.2 ton of copper powder per ton of dissolved cobalt, representing approximately 47% of the total operating cost per ton of cobalt metal produced.

It is realized that the sea nodules are one of the major sources of cobalt, and hence significant amount of research has been carried out for the extraction of cobalt from sea nodules. The average percentage of cobalt in the nodules is less than 1%, which is approximately of the same order as in cobalt filtercakes. The consumption of reducing agent for the treatment of filtercake was dealt with respect to sea nodules based on similar cobalt percentage present in the source.

The abovementioned discussions hold true for manganese as well, since manganese is also reductively leached from sea nodules and also cobalt filtercake. In order to obtain a high leaching recovery of manganese in acidic solution, reducing agents are required. Different reductants such as ferrous sulfate ($FeSO_4$) (Das et al., 1982), sulfur dioxide (SO_2) (Naik et al., 2000), and organic alcohols (Momade and Momade, 1999; Trifoni et al., 2001) have been used for the leaching of manganese from secondary sources and low grade manganese ores.

Majority of investigators have studied the reductive leaching of manganese using organic reductants, including glucose and sucrose (Veglio and Toro, 1994; Sahoo et al., 2001), oxalic acid (Sahoo et al., 2001; Sayılgan et al., 2010), lactose (Ismail et al., 2004), glycerin, citric acid, tartaric acid, formic acid, tri-ethanolamine, and thiosulfate (Zhang and Cheng, 2007).

The electrolytic production of zinc in Iran has been discussed elsewhere (Safarzadeh et al., 2009b). In the stage so called as "hot purification", cobalt is removed at 80–85 °C by adding potassium permanganate ($KMnO_4$) to the zinc sulfate solution. Milk lime is added to the solution concurrently to maintain a pH of 5–5.2. Manganese present in the feed and also manganese added as potassium permanganate precipitate as MnO_2. According to the E_h–pH diagram for the Co–H_2O system (Fig. 1), cobalt can precipitate either as $Co(OH)_3$ or CoOOH. Therefore by adding potassium permanganate, the following reactions can occur in the solution:

$$MnO_4^- + 3Co^{2+} + 4H_2O = MnO_2 + 3CoOOH + 5H^+ \tag{1}$$

$$MnO_4^- + 3Co^{2+} + 7H_2O = MnO_2 + 3Co(OH)_3 + 5H^+. \tag{2}$$

It should be noted that the permanganate purification is not a common practice in zinc operations, and therefore this process is an alternative to activated zinc dust cementation or alpha nitroso beta naphtol purification strategies. Generally when cobalt is precipitated using permanganate, it does not start precipitating significantly until all the manganese has precipitated. The consensus seems to be as the cobalt is oxidized it adsorbs onto the freshly precipitated MnO_2.The main drawback is the absence of manganese in the zinc electrolyte, which its presence is considered beneficial for zinc electrowinning, as

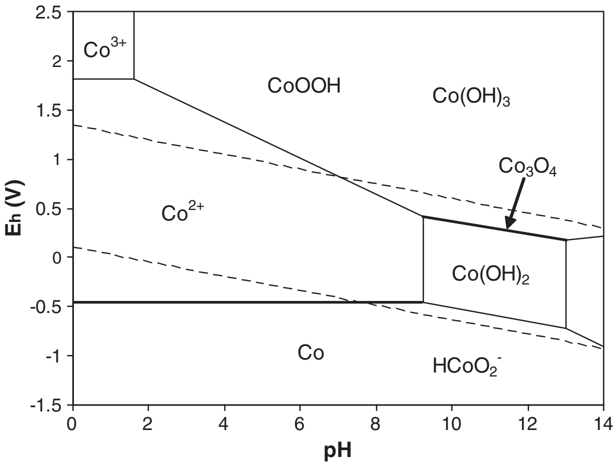

Fig. 1. E_h–pH diagram for cobalt at 85 °C and $a_{Co^{2+}}(aq) = 1$ (drawn using the STABCAL software).