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Optimization of cobalt removal from an aqueous sulfate zinc leach solution for zinc electrowinning

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ABSTRACT

The removal of cobalt from zinc sulfate leach solutions by copper and arsenic activated cementation on zinc powder prior to zinc electrowinning was studied by considering the thermodynamics and kinetics of the cementation process. Arsenic increases the thermodynamic driving force for cobalt cementation in a zinc sulfate solution with the cementing of the cobalt ions as cobalt arsenide at more positive potentials compared to cobalt metal plating. The influence of temperature, the size and quantity of the zinc powder used, and the recirculation of cobalt precipitate on the kinetics of cobalt removal were investigated using batch cementation experiments. It was shown that the rate of cobalt cementation can be enhanced significantly by using finer zinc powder and by recirculating some of the cobalt precipitate such that similar or improved cobalt removal may be achieved at lower operating temperatures or with less zinc added. It was found that the cobalt is cemented by the zinc at an initially high rate with an activation energy of 43 kJ/mol, followed by a slower temperature insensitive stage.

1. Introduction

Zinc is typically produced by roasting zinc sulfide concentrates to zinc oxide, which is then leached with sulphuric acid, followed by purification of the leach solution by cementation with zinc and finally electrowinning the zinc from the purified acidic zinc sulfate solution (Sinclair, 2005). The leach process typically consists of a neutral leach to leach mainly zinc and then allowing the pH to increase to achieve some purification of the leach solution by co-precipitation of the impurities with iron recycled from a subsequent more aggressive weak acid leach stage (Raghavan et al., 1999). This leach solution is however not suitable for zinc electrowinning as it typically still contains unacceptable levels of copper, cadmium, nickel and cobalt. Apart from contaminating the zinc product, and typically more importantly, these metals will also, with the exception of cadmium, catalyse the hydrogen reduction reaction, and so reduce the current and energy efficiencies achievable for zinc electrowinning (Fugleberg et al., 1976; Dreher et al., 2001; Lawson and Nhan, 1981; Raghavan et al., 1999; Xiong and Richie, 1988; Yang et al., 2006).

The metal impurities are typically removed from solution by cementing on zinc powder produced in house from the electroplated zinc product (Fugleberg et al., 1980). If an excess of zinc is used the equilibrium levels of the impurities achievable are well below those typically accepted for electrowinning, as illustrated in Fig. 1.

However, only copper and cadmium cement acceptably fast in acidic aqueous zinc sulfate solutions. The cementation of cobalt and nickel is strongly inhibited in the presence of dissolved zinc, unless the zinc is activated by activators such as copper and arsenic or antimony, using a high stoichiometric excess of zinc dust and increasing the temperature of the solution (Boyanov et al., 2004; Nelson et al., 2000; Oghai et al., 1998; Van der Pas and Dreisinger, 1996; Yang et al., 2006; Yamashita et al., 1989; Zeng et al., 2006). Arsenic improves the driving force for copper cementation slightly and very significantly for cobalt cementation by forming, respectively, Cu_3As and CoAs (Fugleberg et al., 1976; Tozawa et al., 1992; Yamashita et al., 1997a, 1997b), as illustrated in Fig. 2.

The more positive potentials at which cobalt can be plated in the presence of arsenic could contribute to its activating effect as the adsorption of inhibiting cationic species like $Zn(OH)^+$ should be less likely at these potentials. Furthermore, the precipitation of basic cobalt sulfate at higher pH values, illustrated in Fig. 3, and which easily re-dissolves when the local pH decreases or the zinc metal is totally consumed (Bøckman and Østvold, 2000), should be less likely.

The zinc consumed in the purification processes is typically many times the stoichiometric quantity required for the precipitation of the impurities (Raghavan et al., 1999; Sinclair, 2005) and represents a significant fraction of the electrowinning capacity as well as of production cost, mainly in terms of the energy consumed. The choice of the size of the zinc particles used is typically a trade-off between the higher cementation rates achieved with finer zinc due to the higher surface area per mass, and the potential re-dissolution of the plated metals or other precipitates when the zinc particles are completely consumed.

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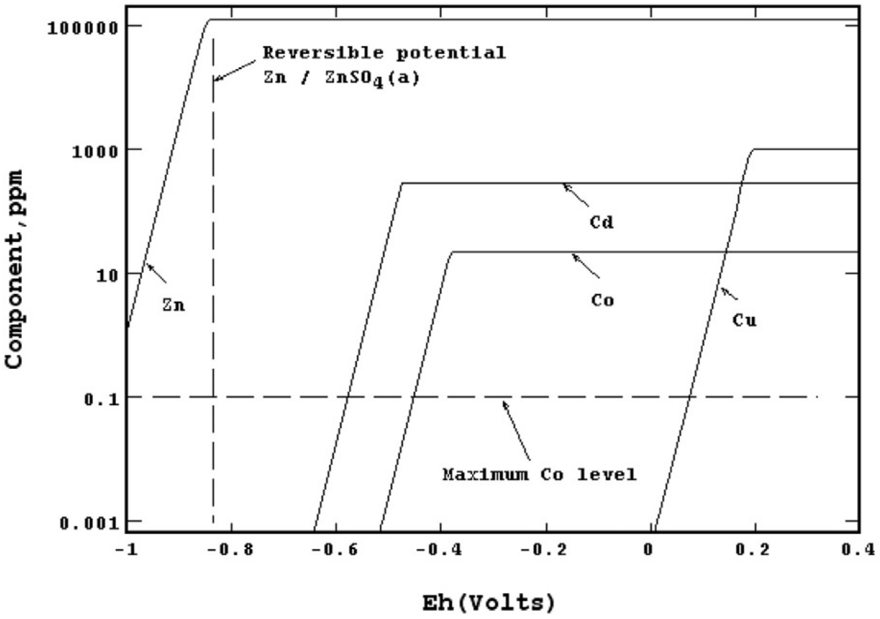

Fig. 1. Calculated equilibrium concentrations of some metal impurities without arsenic in zinc sulfate solutions as a function of electrochemical potential (solution 3, Table 1). Temperature: 25 °C. Constructed with Stabcal using data from the NBS database.

The reactivity of the activated zinc surfaces is determined by the ability of the zinc particle to sustain a potential negative enough to plate cobalt, as well as by the rather undefined role of activating species such as copper and cadmium, and may outlast the residence time of a single pass through the backmix reactor train typically used for this purpose. The work by Fugleberg et al. (1976), Näsi (2004) and Singh (1996)) indicates that some benefit may be gained by the recycling of cobalt precipitate backwards in the reactor train to enhance the kinetics of precipitation and also reduce the overall zinc consumption.

Arsenic on cobalt seed enhances cobalt cementation in a number of ways. Arsenic metal and arsenic in copper arsenide and in cobalt arsenide on the cobalt seed provide an additional reaction surface area with low cobalt deposition overpotential (Fugleberg and Rastas, 1976; Oghai et al., 1998). Arsenic metal and arsenic in copper arsenide on the cobalt seed are also available to react with cobalt in solution to form cobalt arsenide as long as there is zinc available with a sufficient exposed anodic surface area to provide electrons, either in the seed or in zinc dust galvanically coupled with the seed, such that zinc oxidation does not become rate limiting (Fugleberg et al., 1993). The mixed potential is reduced via more noble plating of cobalt in an intermetallic compound with arsenic requiring a lower excess of zinc dust and leading to a decrease in hydrogen evolution. Formation of basic zinc sulfate and zinc hydroxide is therefore reduced via a decrease in localized increases in pH, leading to a decrease in passivation of active surface area.

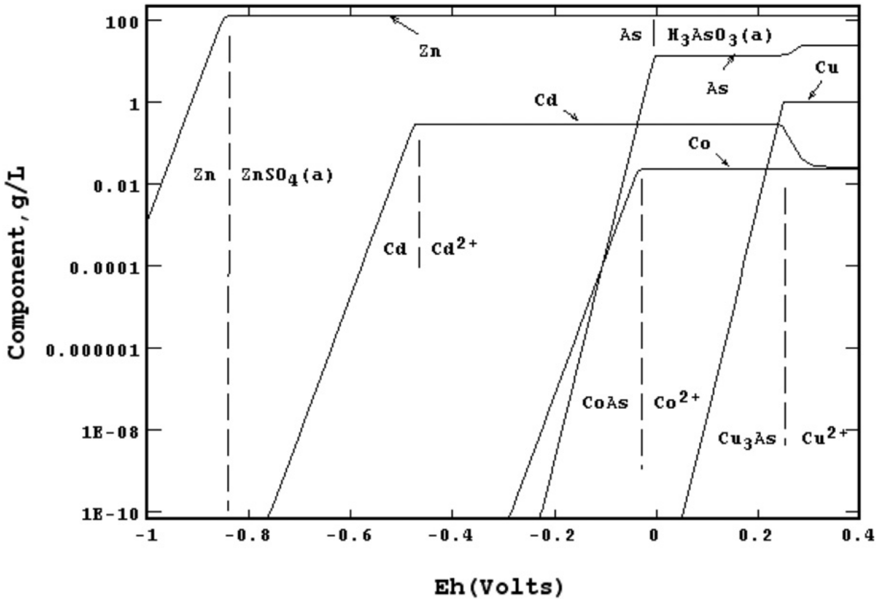

Fig. 2. Calculated equilibrium concentrations of some metal impurities and arsenic in zinc sulfate solutions as a function of the electrochemical potential (solution 3, Table 1). Temperature: 25 °C. Constructed with Stabcal using data from the NBS database and ΔG_f CoAs = −67 kJ/mol from Tozawa et al. (1992).