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Electrowinning of antimony from model sulphide alkaline solutions

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ABSTRACT

The influence of initial antimony concentration, cathode current density, concentrations of Na_2S and NaOH, gas sparging and electrolyte temperature on average cell voltage, specific energy and current efficiency of antimony deposition has been studied. The experiments were conducted in a nondiaphragm electrolytic cell. The anode and cathode were made in such a way that the anode current density was ten times higher than the cathode current density so that a vigorous production of oxygen is promoted at the anode with lesser amounts of polysulphide; and concurrently decreasing the propensity of producing hydrogen at the cathode. Increasing the initial concentration of antimony from 25 g/L to 45 g/L increased the current efficiency by 18%. The average cell voltage decreased from 2.78 V to 2.21 V when the electrolyte temperature was raised from 45 °C to 90 °C. The results showed that increasing the sulphide concentration from 0.77 M to 1.92 M decreased the current efficiency by 13% due to the formation of polysulphide and thiosulphate ions which have negative effect on the current efficiency. Sparging of the electrolyte promotes a smooth and adherent antimony deposit; and the purity of deposited antimony was raised from 99.2% to 99.6%. The specific energy consumed per kilogram of deposited antimony decreased by 74% when the cathode current density was decreased from 250 to 50 A/m^2. Based on sulphate formation, anodic current efficiencies of 85% and 90% were obtained at sodium hydroxide concentrations of 8.75 M and 10 M, respectively. The preferred crystallographic orientations of the antimony deposit obtained at 2.5 M NaOH concentration are in the order (012) (202) (110) (104), but the order becomes (012) (110) (104) (202) when NaOH concentration is increased further. The order of crystal orientations for antimony electrodeposition at 50 A/m^2 cathodic current density is (012) (110) (104) (202), which does not change with increasing cathode current density but the peaks at (110) (104) (202) crystal planes become more broadened and suppressed as current density increased.

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1. Introduction

Antimony is a silvery, white, brittle and shiny metal that exhibits poor conductivity of heat and electricity. At room temperature, antimony does not change in air; and it is not tarnished in humid air or pure water. Antimony metal is extensively used globally to harden and increase the mechanical strength of lead which is used in wet-cell batteries. Apart from its use as alloying element, antimony compounds are used as a flame retardant in fabrics and plastics; decolorizing and refining agent in glass; opacifier and emulsifier for enamel; and pigments in paints and ceramics (Awe and Sandström, 2011; Tian-cong, 1988).

Antimony had been recovered as a metal through electrolysis of alkaline sulphide solution at the Sunshine plant, Idaho, USA, while at the Equity Silver plant, antimony was produced solely as sodium hydroxyl antimonate ($NaSb(OH)_6$) (Filippou et al., 2007). Electrodeposition of antimony from pregnant alkaline sulphide solution can be conducted in either diaphragm electrolytic cells (Anderson et al., 1991; Holmes, 1943, 1944) or nondiaphragm cells (Anderson et al., 1994; Harrison, 2007; Lindström, 1959, 1977). Anderson et al. (1991) recovered antimony by electrolysis of purified pregnant solution containing about 60 g/L Sb in special diaphragm cells at 50–55 °C. The electrolytic process was performed at cell potential of 3–5 V and current density of approximately 320 A/m^2. The deposited antimony metal was brittle and non-adherent. During the electrolysis, sulphur species (especially $S_2O_3^{2-}$ and SO_4^{2-}) get accumulated in the anolyte and approximately 10% of total antimony input reported to the fouled anolyte. To avoid significant antimony losses, the fouled anolyte was treated in an autoclave at 105 °C to precipitate sodium hydroxy antimonate and convert the thioarsenate ion to arsenate. The solution containing the sodium arsenate and the residual antimony was treated with ferrous sulphate at pH 8–8.5 to precipitate ferrous arsenate ($Fe_3(AsO_4)_2$), which was sent to a tailing pond (Filippou et al., 2007). However, the complexity and high maintenance cost of using diaphragm electrolytic cells has made it less attractive.

Besides, Anderson et al. (1994) used a nondiaphragm electrowinning cell to recover antimony metal from crystallized antimony compounds produced by crystallization purification of the pregnant leach liquor. The crystallized antimony compound was redissolved in sodium hydroxide solution and used as the electrolyte. The current densities at both anode and cathode were 843 A/m^2 and 813 A/m^2, respectively. The electrowinning process was conducted

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for 6 h at 50 °C. A Faradaic current efficiency of 51.4% was achieved. The average power consumed was 6673 kWh/ton of antimony metal produced with 99.7% antimony purity. The cell voltage ranged from 3.5 V to 5 V. It was concluded that the following parameters — addition of Na_2CO_3 and Na_2SO_3, lower temperatures, higher cathodic and anodic current densities, and lower agitation, increase the cell current efficiency and also reduce power usage. The process is advantageous because the crystallized antimony compound is clean and customized, therefore, the creation of sodium sulphate build-up which is prevalent in most electrowinning situations is eliminated (Anderson et al., 1994).

Similarly, Lindström (1977) recovered antimony in a nondiaphragm electrolytic cell at high current yield (> 80%) from alkaline sulphide solutions and at the same time regenerated the leaching liquid without requiring the use of separate precipitation operations. During the electrowinning process, it is ensured that the anodic current density exceeds 1500 A/m^2 and the electrolyte is characterized by high ionic strength. At this condition of the electrolyte, the total quantity of oxygen–sulphur compounds formed constitutes SO_4^{2-} ion which reacted with Na^+ and formed a saturated solution of sodium sulphate, which was precipitated and removed as sludge from the electrolytic cell. Therefore, the problem of low current efficiency caused by the formation of polysulphide and thiosulphate ions at the anode in a nondiaphragm electrolytic cell is abruptly curtailed. For this process to be efficient and effective, Lindström (1977) concluded that the electrolyte should contain at least one equimolar quantity of hydroxide ions in relation to the sulphide ions in the solution meaning that the ion ratio $OH^-:S^{2-}$ is at least 1:1. To prevent the crystallization of the electrolyte components, the electrowinning process was conducted at a temperature between 50 °C and 90 °C.

In this study, the optimization of electrolysis parameters for antimony electrodeposition at the cathode from model alkaline sulphide solutions is reported. The anode and cathode were made in such a way that the anode current density was ten times higher than the cathode current density so that a vigorous production of oxygen is promoted at the anode with lesser amounts of polysulphide; and concurrently decreasing the propensity of producing hydrogen at the cathode. The influence of the parameters including the initial antimony concentration, cathode current density, concentration of Na_2S and NaOH, electrolyte temperature and nitrogen gas sparging on antimony electrowinning in a nondiaphragm electrolytic cell is investigated. Also, the influence of the aforementioned parameters on the crystallographic orientations of antimony deposits is examined.

2. Mechanism of the electrolytic process

During the electrolytic recovery of antimony from alkaline sulphide solutions in a nondiaphragm cell, several electrochemical reactions do occur, some of which affect the process adversely depending on the prevailing electrowinning conditions.

2.1. The cathode process

The possible chemical reaction processes that do occur at the cathode during antimony electrodeposition are given in the following sections (Tian-cong, 1988).

2.1.1. Antimony deposition

Usually, the dominating negatively charged antimony complex ions in the leaching solution are SbS_4^{3-} and SbS_3^{3-} ions. These antimony ions migrate to the cathode and get reduced (Eqs. (1)–(2)). During antimony deposition in a nondiaphragm electrolytic cell, SbS_4^{3-} ions generally dominate the electrolyte due to SbS_3^{3-}ion oxidation by the sulphur species in the solution. Therefore the current efficiency of a nondiaphram electrolytic process is usually low (in the range 45–55%) due to the oxidation (Eqs. (3)–(4)) and reduction (Eq. (1)) processes that occur during electrolysis (Tian-cong, 1988).

$$SbS_4^{3-} + 2e^- \rightarrow SbS_4^{3-} + S^{2-} \qquad E^o = -610\,mV \tag{1}$$

$$SbS_3^{3-} + 3e^- \rightarrow Sb^0 + 3S^{2-} \qquad E^o = -900\,mV \tag{2}$$

$$S_2^{2-} + SbS_3^{3-} \rightarrow S^{2-} + SbS_4^{3-} \tag{3}$$

$$S_2O_3^{2-} + SbS_3^{3-} \rightarrow SbS_4^{3-} + SO_3^{2-} \tag{4}$$

2.1.2. Reduction of electrolyte components

All the reduction reactions of the oxidized sulphur species at the cathode as given in Eqs. (5)–(7) consume energy to no purpose and hence reduce the current efficiency. The effect of these oxidized sulphur species on antimony deposition was investigated by the authors and reported in their communication submitted for publication (Awe et al., 2013).

$$S_2^{2-} + 2e^- \rightarrow 2S^{2-} \qquad E^0 = -480\ mV \tag{5}$$

$$S_2O_3^{2-} + 2e^- \rightarrow S^{2-} + SO_3{}^{2-} \qquad E^0 = -631\ mV \tag{6}$$

$$S_2O_3^{2-} + 3H_2O + 8e^- \rightarrow 2S^{2-} + 6OH^- \qquad E^0 = -612\ mV \tag{7}$$

2.1.3. Evolution of hydrogen

The hydrogen evolution potential is more negative than the deposition potential of antimony. However, this process will occur at the cathode if the concentration of antimony is too low in the solution. In practice, this reaction is reported to occur when the antimony concentration is less than 20 g/L. Due to low antimony concentration, antimony complex ions may be so depleted that the antimony deposition potential will shift to the negative, and hence decreasing hydrogen overvoltage to cause hydrogen evolution at the cathode (Anderson et al., 1991; Nordwick and Anderson, 1993; Tian-cong, 1988). This reaction will adversely affect the current efficiency. The evolved hydrogen may react with the antimony cathode to form dangerous stibine gas (Eq. (9)). Therefore, this process needs to be monitored and controlled.

$$2H_2O + 2e^- \rightarrow H_2 + 2OH^- \qquad E^0 = -828\ mV \tag{8}$$

$$3H^+ + Sb^o + 3e^- \rightarrow SbH_3 \qquad E^0 = -510\ mV \tag{9}$$

2.2. Anodic process

Reactions 10 and 11 are the major anode reactions during the electrolysis of alkaline sulphide solution. At a higher hydroxide concentration, reaction 10 will preferentially take place at the anode, but at a lower OH^- ion concentration, reaction 11 will prevail. If reaction 11 dominates, the elemental sulphur formed will react with S^{2-} ion in accordance with Eq. (12) to produce polysulphide in the solution. Formed polysulphide will further oxidize by the evolved oxygen at anode producing $S_2O_3^{2-}$ (Eq. (13)) in the electrolyte (Tian-cong, 1988).

$$4OH^- \rightarrow 2H_2O + O_2 + 4e^- \qquad E^o = +400\ mV \tag{10}$$

$$S^{2-} \rightarrow S^o + 2e^- \qquad E^o = -476\ mV \tag{11}$$

$$S^{2-} + S^o \rightarrow S_2{}^{2-} \tag{12}$$

$$S_2^{2-} + 6OH^- \rightarrow S_2O_3^{2-} + 3H_2O + 6e^- \qquad E^0 = -353\ mV \tag{13}$$

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