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# Catalytic production of antimonate through alkaline leaching of stibnite concentrate

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ABSTRACT

A hydrometallurgical treatment based on leaching and oxidation of trivalent antimony in hydroquinone-catalyzed alkaline electrolyte and precipitation of sodium hydroxyantimonate was elucidated. The influences of temperature and hydroquinone concentration on both the leaching and oxidation processes were discussed. Similar trends for recovery curves of antimony were obtained at different temperatures and hydroquinone concentrations in oxygen-rich alkaline electrolyte. The antimony recovery was calculated to be 90% within 1 h at 80 °C in 0.4 $g \cdot L^{-1}$ HQ. The complete trivalent to pentavalent antimony oxidation was achieved within 4 h under optimum conditions in a single-stage process. The oxidation rate equation is as follows:

$$r_{Sb(III)} = -\frac{dC_{Sb(III)}}{dt} = 5.09.C_{Sb(III)}^{1.02}.C_{HQ}^{1.05}$$

The precipitation product was found to be sodium hydroxyantimonate (mopungite) with pseudo-cubic crystal morphology. It is concluded that $O_2$ was unlikely to be the most powerful oxidant, but rather the HQ is responsible for the rapid oxidation of Sb (III) by the formation of $H_2O_2$. The leaching and oxidation reaction mechanism for the formation of pentavalent antimony was proposed, resulting in intermediate species such as $SbS_3^{3-}$, $SbO_2^-$ and $Sb_2O_3$.

## 1. Introduction

Antimony oxides ($Sb_2O_3$, $NaSb(OH)_6$, $Sb_2O_5$) have received interest as an antistatic additive and as flame-resistant compounds in coatings, nanowires, plastics, fiber and textiles; a base for a new type of glass and ceramics; and a co-catalyst for PET production (Anderson, 2012; Binions et al., 2006). High-grade antimony oxides are commercially produced from sulfide ores by the processes of roasting in a blast furnace and volatilizing/reducing in a reverberatory furnace (Lager and Forssberg, 1989; Xikuangshan Administration of Mines, 1964). Recently, stringent roaster emission-control legislation has resulted in developing hydrometallurgical methods as an alternative to pyrometallurgical `processes for antimony oxide production.

Several leaching reagents are implemented to extract Sb(III) from a sulfide ore (tetrahedrite, stibnite, andorite, jamesonite and zinkenite) and/or a flotation concentrate in acidic solution ($H_2SO_4$, $HNO_3$, HCl and $C_4H_6O_6$) (Correia et al., 2000; Havlik et al., 1994; Madkour and Salem, 1996) and alkaline solution ($Na_2S$ and NaOH) (Ackerman et al., 1993; Anderson, 2003; Baláž and Achimovičová, 2006; Baláž et al., 1992; Celep et al., 2011; Raschman and Sminčáková, 2012; Ubaldini et al., 2000).

The hydrochloric acid electrolyte with ferric ion is commonly used to recover the antimony (III) chloride from sulfide ores. The ferric ion provides an oxidizing environment, while the hydrochloric acid complexes and extracts the antimony. In the meantime, the sulfide in stibnite ($Sb_2S_3$) is oxidized to elemental sulfur by controlling the leaching potential. The hydrolysis of antimony chloride results in the precipitation of antimony oxychloride (SbOCl). The final product, antimony oxide ($Sb_2O_3$), is produced by treatment of the solid precipitate with ammonia (Thibault et al., 1997). In the process proposed by Yang and Wu (2014), $SbCl_5$ was used as an oxidant to obtain the oxychloride species at 85 °C. Orthorhombic cubic antimony oxide crystals were obtained after the neutralization and crystallization with ammonia and ethylenediaminetetraacetic acid tetrasodium salt. Although the chloride system is being performed successfully, alkaline sulfide technology is more often utilized due to minimal corrosion, high selectivity and easy full-scale application (Anderson, 2012).

The dissolution of stibnite in a conventional alkaline sodium sulfide electrolyte may form various aqueous species including antimonites, thioantimonites ($SbS_2^-$, $SbS_3^{-3}$, $Sb_2S_4^{2-}$ and $Sb_2S_5^{-4}$) oxothioantimonites ($SbOS^-$), polysulfides, thiosulfates, etc. (Arntson et al., 1966), depending on the reaction conditions ($E_h$, pH and T). When the lixiviant is a

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mixture of $Na_2S$ and NaOH, the reaction producing thioantimonite is as follows (Anderson, 2001; Ubaldini et al, 2000):

$$Sb_2S_{3(s)} + 2NaOH_{(aq)} \rightarrow NaSbOS_{(aq)} + NaSbS_{2(aq)} + H_2O \quad (1)$$

$$NaSbS_{2(aq)} + Na_2S_{(aq)} \rightarrow Na_3SbS_{3(aq)} \quad (2)$$

The primary purpose of the addition of sodium hydroxide with sodium sulfide is the prevention of the hydrolysis reaction path that produces toxic hydrogen sulfide gas and creates the sodium polysulfide species in the leaching medium (Anderson and Twidwell, 2008; Ubaldini et al., 2000).

Recently, Raschman and Sminčáková (2012) achieved 90% leaching of a natural stibnite ore (49.3% Sb) in less than 30 min at 19 °C using an electrolyte containing 2 wt.% $Na_2S$ and 2 wt.% NaOH. The antimony leaching was reported to be controlled by the surface chemical reaction with an apparent activation energy of 44 $kJ.mol^{-1}$. Vegliò and Ubaldini (2001) studied the optimization of the leaching conditions of pure stibnite in a solution of sodium sulfide and sodium hydroxide at 40 °C. Findings from the surface response method revealed that the ideal concentrations maximizing antimony recovery (98%–100% Sb) were 1 g $Na_2S$ and 1 g NaOH per gram of pure stibnite.

A complete hydrometallurgical process for antimony recovery from refractory gold-bearing stibnite ore was proposed by Ubaldini et al. (2000). Similar antimony recovery (85%) was obtained in 5 min with alkaline sulfide electrolyte (20 $g \cdot L^{-1}$ $Na_2S$ and NaOH) at 80 °C. The electrowinning process provided antimony and gold recoveries as 70% and 75%, respectively.

Although metallic antimony is a common final product of the alkaline leaching-electrowinning process (Awe, 2013; Nordwick and Anderson, 1993), there are also some applications producing marketable antimony oxides from leach liquors such as in the Sunshine Mine and Equity Silver Mines (Dayton, 1982; Nordwick and Anderson, 1993). The leachate was produced on site by the dissolution of elemental sulfur in sodium hydroxide. The resulting electrolyte contained polysulfides. The antimonate was precipitated from the electrolyte by following reaction:

$$Na_3SbS_{4(aq)} + 4O_{2(g)} + 2NaOH_{(aq)} + 2H_2O \rightarrow NaSb(OH)_{6(s)} + 2Na_2S_2O_{3(aq)} \quad (3)$$

An alternative antimonite production route from ores and concentrates was proposed in the patent of Vogt (1977). The study claimed that the antimony could be oxidized in the presence of a catalyst such as a mixture of copper and hydroquinone by a two-step procedure. Initially, the antimony was extracted from sulfides and then isolated as pentavalent antimony. After the filtration, the antimonate product was obtained by the addition of various metal halide salts (NaCl and $CaCl_2$). It was reported that this process prevented the formation of the undesirable gases $SO_2$ and $H_2S$.

The primary catalyst used in the procedure was hydroquinone, $C_6H_6O_2$ (HQ), which is widely used as a reducing agent forming a reversible redox system with quinone, $C_6H_4O_2$ (Q). HQ forms Q by a two-electron, two-proton reversible oxidation process, as shown below (Cameron, 1938; Sirajuddin et al., 2010):

$$C_6H_6O_2 = C_6H_4O_2 + 2H^+ + 2e^- \qquad E_{h,\ 20^\circ C} = 0.03\ V\ \ (pH\ 13.01) \quad (4)$$

$$C_6H_6O_2 + O_2 \rightarrow C_6H_4O_2 + H_2O_2 \qquad \Delta H_{rxn} = -13.85\ kJ \cdot mol^{-1} \quad (5)$$

The complex auto-oxidation mechanism of this benzene derivative has several steps that depend on the pH. In alkaline solution ($pH > 7.8$), HQ is readily oxidized to Q exothermically in the presence of oxygen to produce hydrogen peroxide, as shown in Eq. (5) (Mandal et al., 2005). The hydrogen peroxide species may provide the necessary oxidizing environment for other species in the electrolyte.

The present work focused on investigating the single-stage method for sodium hydroxyantimonate production involving catalytic extraction of antimony metal from stibnite concentrate and subsequent oxidation of Sb(III) to Sb(V). This study contributes to the literature by describing the kinetics of single-stage leaching and oxidation that is monitored under various operating conditions, the oxidation reaction rate equation, the characterization of the sodium hydroxyantimonate product by chemical and physical analyses, and a proposed reaction mechanism for the antimonate production from stibnite ore in the presence of oxygen and HQ.

## 2. Material and methods

The investigation was conducted with the sample of stibnite concentrate obtained from the Ödemiş–Halıköy (Turkey) concentrator plant. The chemical and mineralogical composition of the sample is shown in Table 1. The interfering elements (Fe, Cu, etc.) affecting the oxidation reaction are observed to be negligible. The mineralogical composition was obtained with the combination of elemental analysis using an atomic absorption spectrometer (AAS) and X-ray diffraction (XRD) analysis.

The XRD and scanning electron microscopy (SEM) analyses were performed using a Rigaku Miniflex II diffractometer with Cu $K_\alpha$ radiation and a JEOL JXA-733 Superprobe, respectively. A mineralogical characterization by SEM coupled with energy-dispersive spectroscopy (EDS) and qualitative XRD analysis of the head sample (Fig. 1) revealed the presence of stibnite, $Sb_2S_3$, quartz and small amounts of elemental sulfur, valentinite, chalcopyrite, pyrite and galena in the sample. The particle size of the received samples as determined by a HORIBA/Partica LA-950 V2 Particle Size Analyzer was below 96 μm ($d_{80}$).

The experiments were conducted in a 0.50-L four-necked glass reactor equipped with a condenser. The temperature was controlled within ±2 °C using a glass-coated temperature sensor in conjunction with a hot plate. Typically, the vessel was charged with an electrolyte containing KOH, HQ and sample with 4% wt/v pulp density ($L/S = 25$). The alkaline electrolyte was oxidized with air (0.27 $m^3 \cdot h^{-1}$) on a continuous basis to maintain the oxidation of trivalent antimony and HQ. The addition of HQ immediately produces a brown-colored solution indicating the dissociation of HQ to the meta-stable quinone species. The experiments were initiated by introducing HQ salt into the electrolyte in the concentration range of 0.2 to 0.8 $g \cdot L^{-1}$. The temperature of the solution was varied over the range of 30 °C to 90 °C, and the reaction was sustained for 4 h. Because the sodium compounds of antimony oxides have low solubility above pH 11, potassium hydroxide was selected to create the alkaline medium during the process. The initial free hydroxide concentration was 0.30 M, and the reaction was mixed well at an agitation rate of 10 $s^{-1}$ by a magnetically driven twin impeller. The oxidized antimony was precipitated from the leach liquor as sodium hydroxyantimonate $NaSb(OH)_6$ at 30 °C for 60 min using 0.50 M NaCl solution. The final solid sample was dried at 70 °C for 5 h.

**Table 1**
Chemical composition of the stibnite flotation concentrate (%).

| Chemical analysis | | Mineralogical analysis | |
|---|---|---|---|
| Element | % | Mineral | % |
| Sb | 69.21 | $Sb_2S_3$ | 92.37 |
| Fe | 0.54 | $Sb_2O_3$ | 3.50 |
| Pb | 0.28 | $FeS_2$ | 1.12 |
| As | 0.20 | $SiO_2$ | 2.06 |
| Zn | 0.03 | PbS | 0.32 |
| Cu | 0.02 | CaO | 0.07 |
| S | 27.02 | $CuFeS_2$ | 0.05 |