



Copper-promoted cementation of antimony in hydrochloric acid system: A green protocol



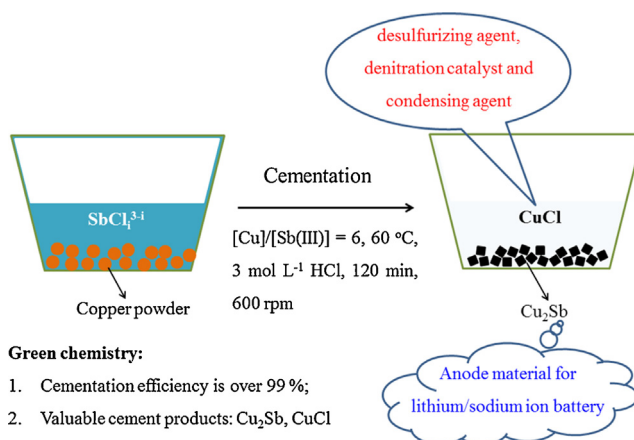
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HIGHLIGHTS

- Antimony can be efficiently removed by cementation with copper powder.
- Cemented antimony is in the form of Cu_2Sb .
- Consumed copper powder is transformed to CuCl .
- The cementation is a chemically controlled step.
- No toxic stibine generates during the cementation process.

GRAPHICAL ABSTRACT



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ABSTRACT

A new method of recovering antimony in hydrochloric acid system by cementation with copper powder was proposed and carried out at laboratory scale. Thermodynamic analysis and cyclic voltammetry test were conducted to study the cementation process. This is a novel antimony removal technology and quite meets the requirements of green chemistry. The main cement product Cu_2Sb is a promising anodic material for lithium and sodium ion battery. And nearly all consumed copper powder are transformed into CuCl which is an important industrial material. The effect of reaction temperature, stoichiometric ratio of Cu to Sb(III), stirring rate and concentration of HCl on the cementation efficiency of antimony were investigated in detail. Optimized cementation condition is obtained at 60 °C for 120 min and stirring rate of 600 rpm with Cu/Sb(III) stoichiometric ratio of 6 in 3 mol L⁻¹ HCl. At this time, nearly all antimony can be removed by copper powder and the cementation efficiency is over 99%. The structure and morphologies of the cement products were characterized by X-ray diffraction and scanning electron microscopy, respectively. Results show that the reaction temperature has little influence on the morphology of the cement products which consist of particles with various sizes. The activation energy of the cementation antimony on copper is 37.75 kJ mol⁻¹, indicating a chemically controlled step. Inductively coupled plasma mass spectrometry results show that no stibine generates during the cementation process.

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1. Introduction

As an important industrial material, antimony has been widely used in batteries, flame retardants, textiles, plastics, ammunition, ceramic opacifiers, semiconductors, infrared detectors, and glass decolorizers [1–4]. Unfortunately, antimony is also toxic and potentially carcinogenic to human [5]. The excessive exploitation and overuse of antimony have resulted in significant antimony soil and water contamination [6,7]. Antimony has been listed as a high priority pollutant by the World Health Organization (WHO). The maximum admissible antimony concentration in drinking water is 6, 10, and 5 $\mu\text{g L}^{-1}$ according to the United States Environmental Protection Agency (USEPA), European Union (EU), and WHO standards, respectively [1,4]. Till now, many approaches have been developed to remove the antimony from aqueous solution, including anion exchange [8], reverse osmosis [9], solvent extraction [10], electrodeposition [11], coagulation [12], precipitation [13], photoinduced oxidation [14], electrocoagulation [15], biosorption [16], adsorption [17–19]. Although antimony can be removed by these methods, other new problems are produced at the same time, such as the time-consuming process, the difficulty in recycle of the adsorbents or even resulting in secondary pollution.

Cementation is the simplest and oldest hydrometallurgical process and has been used in extractive metallurgy to recover valuable metals as well as to remove unwanted impurities [20–22]. Iron, zinc and copper are the most common reductants in commercial applications. Among them, copper is usually used for the recovery of noble metals, such as, gold [23], silver [24] and rhodium [20]. During the cementation process, copper is first oxidized to Cu^+ , which can further form copper complexes with chloride in HCl solution system [25], leading to the redox potential significantly reduced compared to the standard potential of pure metal ion system [26]. This makes it possible to cement other metals with relative negative potential.

In the present work, thermodynamic analysis and cyclic voltammetry test were conducted to investigate the cementation process. Then batch experiments were performed to optimize the cementation condition at laboratory scale. The structure and morphology of the cement products were characterized by X-ray diffraction (XRD) and scanning electron microscopy (SEM), and the cementation mechanism was also proposed. This novel technology quite meets the requirements of green chemistry. The main cement product Cu_2Sb and CuCl are promising anodic material for lithium/sodium ion battery and important industrial material, respectively.

2. Materials and methods

2.1. Regents and solutions

Antimony trichloride was distilled in laboratory, other reagents are analytical pure and used as received without further purification. All aqueous solutions were freshly prepared with deionized water. The Sb(III) stock solution (1.0 mol L^{-1}) was prepared by dissolving desired distilled antimony trichloride into 3.0 mol L^{-1} HCl. The working solutions containing 0.2 mol L^{-1} Sb(III) were prepared by diluting the stock solutions with 3.0 mol L^{-1} HCl immediately prior to their use.

2.2. Batch cementation experiments

The cementation of Sb(III) on copper powder was conducted in batch experiments under magnetic stirring and bubbled nitrogen through the solution all the time to avoid the oxidation of cuprous ions. When the system containing 0.2 mol L^{-1} Sb(III) reached certain temperature (30, 40, 50, 60 and 70°C), desired dosages of

Cu powder (200 mesh) was added. From then on ($t=0$), 5.00 mL solution was withdrawn after 5, 10, 15, 30, 60, 90 and 120 min, respectively, and analyzed for determining the concentration of residual antimony and generated copper ions.

2.3. Analysis and characterization

Cyclic voltammetry (CV) measurements were carried out on a CHI630b electrochemical workstation (CH Instrument, Shanghai, China) in a classical three-electrode compartment. A glass carbon (GC) electrode ($\sim 0.6 \text{ cm}$ diameter), a saturated calomel electrode (SCE) and a platinum plate with an exposed area of 2.0 cm^2 were used as the working, reference and counter electrodes, respectively. The tests were performed at 25°C with scanning rate of 0.1 V s^{-1} . CV characterization in pure copper and antimony system contains 0.6 mol L^{-1} Cu(II) and 0.2 mol L^{-1} Sb(III), respectively. While for the copper and antimony mixture system, 0.6 mol L^{-1} Cu(II) and 0.2 mol L^{-1} Sb(III) are contained.

For the detection of Sb^{3+} and Cu^+ ions with high concentrations, cerimetric titration and iodometric were conducted, respectively. While the detection of ions with low concentration was performed on inductively coupled plasma-mass spectrometry (ICP-MS).

Antimony content measured by cerimetric titration was carried out with the guidance of GB/T 15925-2010 [27] and performed as followed. 10 mL of H_3PO_4 (85%) and 25 mL of HCl (1:1) were added in sequence into 1 mL of experimental antimony solution. The solution was warmed slightly and 2 drops of methyl orange indicator was added when two bubbles were continuously emerged. Then freshly prepared $\text{Ce}(\text{SO}_4)_2$ (0.02 mol L^{-1}) was titrated until the red color of the solution disappeared and a clear yellow end-point reached. The amount of antimony was calculated from the volume of $\text{Ce}(\text{SO}_4)_2$ used.

Copper content measured by iodometric was carried out with the guidance of GB/T 15249.3-2009 [28] and performed as followed. 5 mL of HCl (37%) and 5 mL of H_2O_2 (30%) were added in sequence into 1 mL of experimental copper solution. The mixture solution was heated until $\sim 2 \text{ mL}$ solution remained and cooled down. Then dilute the solution with 30 mL deionized water. Ammonia (1:1) was added until white precipitation appeared. Concentrated phosphoric acid was added until all precipitation was dissolved. Then 5 mL phosphoric acid was extra added. Cooling down the solution to room temperature and dilute by 40 mL deionized water. 5 mL of 20% KI solution was added. Then freshly prepared $\text{Na}_2\text{S}_2\text{O}_3$ (0.02 mol L^{-1}) solution was titrated when most of the iodine has reacted (the color of the solution became light yellow). At this time 10 mL of 20% KSCN was added and keep on titrate with $\text{Na}_2\text{S}_2\text{O}_3$ solution until the yellow disappeared. Then 5 mL of 0.5% starch solution was added and the color of the solution turned to be blue. The addition of $\text{Na}_2\text{S}_2\text{O}_3$ was continued until blue color disappeared. The amount of copper was calculated from the volume of $\text{Na}_2\text{S}_2\text{O}_3$ used. All titrations were repeated three times.

The change in the solution volume before and after cementation and the component taken away by nitrogen was ignored during the calculation of the cementation efficiency (%) of antimony.

A scrubber containing 4 mol L^{-1} HNO_3 solution was used to oxidize the possible generated stibine, which was flushed out by bubbling N_2 . The contents of antimony in the tail solutions were analyzed by ICP-MS (USA, Thermo X Series II).

XRD patterns of the cement products and crystal generated from the resulting solution were recorded on a RIGAKU D/Max 2550 PC diffractometer equipped with $\text{Cu K}\alpha$ radiation ($\lambda = 1.54059 \text{ \AA}$) at 40 kV and 30 mA. The morphologies and composition of the cements were characterized by SEM (VEGA3, operated at 15 kV) equipped with energy dispersive X-ray (EDX) microanalysis (Oxford EDS Inca Energy Coater 300, operated at 15 kV).

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