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Hydrochloric Acid Leaching Behaviors of Copper and Antimony in Speiss Obtained from Top Submerged Lance Furnace

Sujin Chae¹, Kyoungkeun Yoo^{1,*}, Carlito Baltazar Tabelin² and Richard Diaz Alorro³

- ¹ Department of Energy & Resources Engineering, Korea Maritime and Ocean University (KMOU), 727, Taejong-ro, Yeongdo-gu, Busan 49112, Korea; sujin.chae.082@gmail.com
- ² School of Minerals and Energy Resources Engineering, University of New South Wales, Sydney 2052, NSW, Australia; c.tabelin@unsw.edu.au
- ³ Western Australian School of Mines: Minerals, Energy and Chemical Engineering, Faculty of Science and Engineering, Curtin University, Kalgoorlie 6430, WA, Australia; richard.alorro@curtin.edu.au
- * Correspondence: kyoo@kmou.ac.kr

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Abstract: Copper (Cu) has been recovered from speiss generated from top submerged lance furnace process, but it was reported that the leaching efficiency of Cu in sulfuric acid solution decreased with increasing antimony (Sb) content in the speiss. Scanning electron microscopy (SEM)–energy-dispersive X-ray spectroscopy (EDS) results indicate that Sb exists as CuSb alloy, which would retard the leaching of Cu. Therefore, hydrochloric acid leaching with aeration was performed to investigate the leaching behaviors of copper and antimony. The leaching efficiency of Cu increased with increasing agitation speed, temperature, HCl concentration, and the introduction ratio of O₂, but also with decreasing pulp density. The leaching efficiency of Cu increased to more than 99% within 60 min in 1 mol/L HCl solution at 600 rpm and 90 °C with 10 g/L pulp density and 1000 cc/min O₂. The leaching efficiency of Sb increased and then decreased in all 1 mol/L HCl leaching tests, and precipitate was observed in the leach solution, which was determined to be SbOCl or Sb₂O₃ by XRD analyses. However, in 2 mol/L–5 mol/L HCl solutions, the leaching efficiency of Sb increased to more than 95% (about 900 mg/L) and remained, so more than 2 mol/L HCl could stabilize Sb ion in the HCl solution.

Keywords: copper; antimony; hydrochloric acid leaching; speiss

1. Introduction

Top submerged lance (TSL) technology has been used to recover valuable metals from the by-product of zinc smelting or industrial waste [1–3]. The valuable metals are concentrated in speiss, and impurities such as Fe are discarded as slag [4]. Although the composition of the speiss generated in the TSL process varies depending on input materials, generally, in South Korea, the speiss contains Cu, Sb, and precious metals as the main components. The recovery process of valuable metals from the speiss is summarized as shown Figure 1. From the speiss, Cu component is leached with sulfuric acid, and so the precious metals are concentrated in leach residue. Other impurities, such as Sb and Pb, are discarded pyrometallurgically, and Ag and Au components are recovered by electrorefining processes in turn.





Figure 1. Schematic diagram of metal recovery process from speiss of top submerged lance process.

The high leaching efficiency of Cu from the speiss was required during the sulfuric acid leaching process because Cu in the residue reduces the purity of precious metal during the Au and Ag recovery process. Recently, as various secondary resources have been added to the TSL process, it was observed that the amount of antimony (Sb) increased and the leaching efficiency of Cu decreased. These facts, as a result, reduced the recovery efficiency of Au and Ag from subsequent processes. Therefore, although the leaching process of the speiss containing Cu and Sb should be improved, the leaching behaviors of materials containing Cu and Sb have been rarely reported.

The standard reduction potential of Cu is found to be 0.34 V [5,6], which indicates that Cu metal cannot be oxidized and dissolved by sulfuric acid. Additional oxidants such as Fe³⁺ [7,8], O₂ [9], Cl₂ [10] and H₂O₂ [11] or leaching media such as HNO₃ [12,13], HCl [14–17], and NH₃ [18,19] have been used to leach Cu metals. The leaching of Sb in sulfuric acid solution has rarely been investigated, and the solubility of Sb₂O₃ or Sb₂O₅, which could be generated from the oxidation of Sb, was found to be low [20]. The leaching of Sb has been investigated in sulfides using alkaline solution with Na₂S [21,22] and HCl with ozone [23], and from Pb dross [24] or fly ash [25] using hydrochloric acid. However, there have been few reports regarding Sb leaching, and the effect of Sb on the Cu leaching has not been reported.

Therefore, in the present study, the leach residue of the speiss was examined with SEM-EDS to understand the effect of Sb on the sulfuric acid leaching of the speiss, and then hydrochloric acid leaching tests with oxygen were performed to enhance the Cu leaching efficiency from the speiss. The effects of leaching factors such as temperature, agitation speed, HCl concentration, pulp density, and the flow rate of O_2 on the leaching behaviors of Cu and Sb were investigated in hydrochloric acid solution.

2. Materials and Methods

The speiss samples used in this study were obtained from a zinc smelter in Korea, and the D_{50} and D_{90} of the speiss samples were 307.4 µm and 795.5 µm, respectively. The speiss contained 77.16% Cu, 8.82% Sb, and 5.15% Pb as main components. Sulfuric acid (H₂SO₄, 95%, Junsei Co., Ltd.: Tokyo, Japan) and hydrochloric acid (HCl, 35%, Junsei Co., Ltd.: Tokyo, Japan) were used as leaching media, and purities of O₂, and N₂ were 99.99% and 99.5%, respectively.

 O_2 , air, and N_2 were introduced at 200 cc/min–1000 cc/min, and 3 cm³ of the solution was withdrawn periodically at desired time intervals (5–360 min) with a syringe. The samples were filtered with a 0.22 µm membrane filter and then the filtrate was diluted with 2% HNO₃ solution for Cu analysis and 3 mol/L HCl solution for Sb measurement, respectively.

The concentration of Cu and Sb in the solutions was measured with an inductively coupled plasma-atomic emission spectrometry (ICP-OES, Optima-8300, Perkin Elmer Inc.: Waltham, MA, USA). The precipitate generated during the leaching test was filtered and then dried at 105 °C. The precipitate was analyzed with an X-ray diffractometer (XRD, Smartlab, Rigaku Co.: Tokyo, Japan). The leaching residue obtained from the sulfuric acid leaching test was polished and then analyzed with a Scanning Electron Microscope (SEM, MIRA-3, Tescan Co.: Brno, Czech).

3. Results and Discussion

After sulfuric acid leaching of the speiss had been performed in 2 mol/L sulfuric acid solution at 400 rpm and 90 °C with 1% pulp density and 1000 cc/min introduction of O₂, the leaching residue was obtained and then examined with SEM-EDS. Figure 2 shows the SEM image of the leaching residue, and the center and outer parts of the particle shows different shapes. A net shape was observed in the entire cross section of the particle, and the net shape was found to be a CuSb intermetallic alloy, based on the result of SEM-EDS analysis. In the center of the particle, the net shape is full of dark parts, which were found to be Cu, while only the net shape was observed, without Cu, in the outer part of the particle. These results indicate that Cu was leached from the outer of particle, but Cu remained inside the CuSb alloy net shape in the center of particle because CuSb would prevent leaching of Cu. It has been reported that the leaching efficiency of Sb is lower or slower than Cu [26], and that the solubility of Sb is low in sulfuric acid [20]. Therefore, Sb should be dissolved to enhance the leaching efficiency of Cu, so hydrochloric acid leaching tests were performed because chloride ion could make complex ions with metal, thus enhancing the solubility of the metal [27].



Figure 2. SEM image of sulfuric acid leaching residue of the speiss.

Leaching tests of the speiss at agitation speeds in the range of 200–800 rpm were performed to investigate the effect of the liquid film boundary diffusion surrounding the particles on the leaching efficiency of Cu and Sb in 1 mol/L HCl at 90 °C with 1% pulp density and 1000 cc/min O₂. As shown in Figure 3a, the leaching efficiency of Cu increased rapidly, and then gradually. The efficiency increased when the agitation speed was increased from 200 rpm to 600 rpm, while the efficiencies show similar leaching behaviors at 600 rpm and 800 rpm, so working agitation speed was fixed at 600 rpm to ensure effective particle suspension in the solution in all the subsequent leaching tests. Figure 3b shows the leaching behaviors of Sb, where the leaching efficiency of Sb increased to more than 99% and then decreased with time. The efficiency at 200 rpm decreased more slowly than those between 400 rpm and 800 rpm, and, at 360 min, lower leaching efficiency of Sb was observed at higher agitation speeds. When the concentration of Sb began to decrease, precipitate was observed in the solution. Figure 4 shows the XRD pattern of the precipitate, which was determined to be antimony oxychloride (SbOCl). These results indicate that Cu was leached from the speiss by HCl leaching, while Sb dissolved and was then precipitated as SbOCl.



Figure 3. Leaching efficiencies of (a) Cu and (b) Sb with time in the function of agitation speed.



Figure 4. XRD pattern of leaching residue obtained from HCl leaching test in Figure 3.

In the TSL process, the metal product was generated as elemental metal or intermetallic alloy, as shown in Figure 1. The leaching of Cu metal can be summarized using the following equation [28]:

$$Cu^{2+} + Cu = 2Cu^+,$$
 (1)

where cupric ion (Cu^{2+}) could oxidize Cu metal in hydrochloric acid or ammonia solution [18,19,28] into cuprous ion (Cu^{+}) . This Cu⁺ ion is unstable, an so is easily oxidized into Cu²⁺ as follows [6]:

$$2Cu^{+} + 2H^{+} + 1/2O_{2} = 2Cu^{2+} + H_{2}O$$
(2)

The regenerated Cu²⁺ could be reused as an oxidant for Cu metal leaching. Therefore, it is important to introduce oxygen into the leaching solution for Cu metal leaching. The leaching tests of the speiss were performed to investigate the effect of gas introduction on the leaching efficiency of Cu and Sb in 1 mol/L HCl at 90 °C and 600 rpm with 1% pulp density. The O₂ introduction rate was adjusted from 200 cc/min to 1000 cc/min, and 1000 cc/min air and N2 were also introduced into the solution for comparison. As shown in Figure 5a, the leaching efficiency of Cu increased to more than 99% within 60 min in the cases of O_2 introduction, whereas the efficiency with air introduction increased rapidly and then gradually to 99% within 360 min. When N₂ was introduced, the efficiency increased gradually to 18% within 360 min. These results indicate that the anoxic condition prevents leaching of Cu, because the regeneration of Cu²⁺, as shown in Equation (2), is suppressed, although 18% of Cu dissolved under the N_2 introduction, which is due to partly oxidized surface of Cu [9]. Therefore, O_2 should be introduced into the leach solution for Cu metal leaching, but the leaching efficiency of Cu increased regardless of the O2 introduction rate. Figure 5b shows that the leaching efficiency of Sb increased and then decreased with time except with the introduction of N₂, where the leaching efficiency of Sb was very low. An introduction rate of 1000 cc/min of O₂ could retard the decrease in Sb concentration, so the gas introduction rate was fixed at 1000 cc/min O₂ in all subsequent leaching tests.



Figure 5. Leaching efficiencies of (a) Cu and (b) Sb with time in the function of gas introduction rate.

The effects of HCl concentration on the leaching efficiency of Cu and Sb were investigated under the following leaching conditions: 600 rpm at 90 °C with 1% pulp density and 1000 cc/min O₂. In the case of Cu leaching, as shown in Figure 6a, higher leaching efficiency of Cu was observed at higher HCl concentrations at 15 min, and then similar leaching behaviors of Cu were observed except for the test in 0.1 mol/L HCl. In Figure 6b, low leaching efficiency of Sb was observed in 0.1 mol/L HCl solution over the entire leaching time, and the efficiency increased and then decreased with time in the 1 mol/L HCl solution. When HCl concentration was increased to more than 2 mol/L, the leaching efficiency of Sb increased to more than 95% and then remained there. The concentration of Sb was measured to be about 900 mg/L. These results indicate that more than 2 mol/L HCl could stabilize Sb ions in the solution with the Sb concentration range, and this fact has rarely been reported in conventional studies.

The leaching tests of the speiss were performed to investigate the effect of temperature on the leaching efficiency of Cu and Sb in 1 mol/L HCl at 30–90 °C and 600 rpm with 1% pulp density and 1000 cc/min O_2 . Figure 7a shows that the leaching efficiency of Cu increased more rapidly at higher temperature, and that the efficiency increased to more than 99% within 120 min at 50–90 °C and within 360 min at 30 °C. In the case of Sb leaching as shown in Figure 7b, the leaching efficiency of Sb increased more rapidly at higher temperature during the early leaching time, except the test at 30 °C, and the efficiency decreased gradually. Although the leaching efficiency of Sb at 30 °C increased to 53% at 60 min, that of Cu increased as shown in Figure 7a. Since the precipitate of Sb was observed in the solution during the leaching test at 30 °C, Cu continued to dissolve while Sb dissolved and then precipitated.



Figure 6. Leaching efficiencies of (a) Cu and (b) Sb with time in the function of HCl concentration.



Figure 7. Leaching efficiencies of (a) Cu and (b) Sb with time as a function of temperature.

The effects of pulp density on the leaching efficiency of Cu and Sb were investigated in 1 mol/L HCl solution at 90 °C and 600 rpm with 1000 cc/min O₂. As shown in Figure 8a, the leaching efficiency of Cu decreased when increasing pulp density from 10 g/L to 50 g/L. In the case of Sb leaching, except the pulp density of 10 g/L, Figure 8b shows that the concentration of Sb increased and then decreased rapidly to about 10%, and that the concentration of Sb in the leaching test with 10 g/L increased and then decrease gradually to 40%. The precipitates formed in the leaching test with 20 g/L to 50 g/L were collected and analyzed with XRD. As shown in Figure 9, CuCl₂·3Cu(OH)₂ was observed in the precipitate formed in the test with 50 g/L, and, in the test with 20 g/L or 30 g/L, the precipitate is determined to be Sb₂O₃. The pHs of the leaching solution increased to 3.8 and 4.2 in the leaching tests with 20 g/L resulted from the higher pH and pulp density.



Figure 8. Leaching efficiencies of (a) Cu and (b) Sb with time in the function of pulp density.



Figure 9. XRD pattern of leaching residue obtained from HCl leaching test in Figure 8.

4. Conclusions

SEM-EDS analysis of the leaching residue obtained from H_2SO_4 leaching of speiss and HCl leaching of speiss was performed to enhance the leaching efficiency of Cu and to investigate the leaching behavior of Sb in HCl solution.

The SEM-EDS results showed that CuSb alloy remained in the leaching residue even after Cu was leached by H_2SO_4 leaching, which indicates that the leaching rate of CuSb is slower than Cu, and that CuSb could retard the leaching of Cu. Therefore, HCl was used as a leaching agent to leach the speiss. The leaching efficiency of Cu increased with increasing agitation speed, temperature, HCl concentration, gas introduction rate but with decreasing pulp density. More than 99% of Cu was dissolved for 60 min in 1 mol/L HCl solution at 600 rpm and 90 °C with 10 g/L pulp density and 1000 cc/min O₂. The leaching efficiency of Sb increased, and then was precipitated in all 1 mol/L HCl leaching tests, and the precipitate was determined to be SbOCl. However, since more than 95% of Sb (about 900 mg/L) was dissolved and remained in 2 mol/L–5 mol/L HCl solutions, this result indicates that 2 mol/L or more concentrated HCl could stabilize Sb ion in the HCl solution after 60 min.

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