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Efficient separation and recovery of metal components from metal-bearing sludge by hydrometallurgical route

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--ABSTRACT--

During the primary acid leaching of the sludge containing copper, manganese and zinc, the leachate composed of manganese and zinc ions as major components was obtained, isolating copper components. Zinc and manganese were separated from the primary leachate by oxalic acid precipitation and carbonate precipitation, respectively. The copper sulfate was recovered from the primary leaching residue by secondary acid leaching. Any harmful solid waste and wastewater (metal ion concentration<5mg/L) were not generated in the proposed process.

KEYWORDS; *Metal-bearing sludge, Hydrometallurgical route, Leaching, precipitation, Metal recovery, Environmental management*

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I. INTRODUCTION

Due to scarcity of metal resource worldwide, recycling valuable heavy metals from wastes is a very important issue for protection of resources and eliminating the negative impact of solid waste to the environment. It is necessary to develop a comprehensive recycling technology for secondary metal resources. Hydrometallurgical methods are superior and more reliable compared to the other methods for metal recovery. For example, hydrometallurgy can be considered as an effective method to treat metal-bearing waste due to its advantages such as low energy consumption, waste minimization, low cost [1, 2]. Because the nonferrous metals are expensive in the market, there is an imposing interest in developing improved hydrometallurgical processes for them [3]. Many studies [4, 5] determined the acid leaching operating parameters to maximize the leaching efficiency of metals to be recovered.

It is necessary to determine a reasonable leaching method according to the combined state and compound morphology of the metal components in solid wastes, in order to separate readily individual metals from leachate containing various metal ions. It is difficult to separate copper from other metal elements because it is reduced during sulfide precipitation. The oxidation state of copper is variable. It forms complex compounds during the sulfide precipitation process, and redox reaction occurs between Cu^{2+} and sulfide ions (S^{2-}) [6]. Also, the formation of small CuS particles that are not filtered by 0.45 mm membrane filtration results inhigh saturation and rapid nucleation rate, because the copper ions form products of CuS (or Cu_2S) with too low solubility. In addition, the simultaneous precipitation of zinc and copper oxalates will occur when oxalate precipitation methods are applied. On the other hand, manganese in solid wastes is generally present as a mixture of divalent, trivalent and tetravalent manganese compounds. The divalent manganese oxides are considerably soluble in acid solutions, and the tetravalent manganese oxides are stable under acidic and alkaline conditions, so it is important to choose a proper leaching method for the recovery of manganese. It is difficult to separate heavy metal ions forming compounds with similar solubility. This study describes a hydrometallurgical method to recover copper, manganese and zinc from metal-bearing sludge at high separation efficiency.

II. MATERIALS AND METHODS

A. Extraction and recovery of metal

Metal-bearing sludge including several metals such as Cu, Zn and Mn was used in the experiments. In the first stage leaching, sulfuric acid was used as the leaching agent, and the leaching was carried out for 2 h with the addition of iron sulfate as the reducing agent. At that time, copper remained in the leaching residue by adding excess reduced iron powder, and manganese and zinc were dissolved into the leaching solution. The residual reduced iron powder was separated using a permanent magnet after leaching. The primary leachate (L-

1) was stirred for 15 min at 40 °C under the addition of 2 mol/L oxalic acid. After solid-liquid centrifugation, iron ions in the leachate were separated at 180 °C for 10 h in the reaction vessel after adding 15 mol/L nitric acid. Sodium carbonate was added to the remaining residual solution to adjust a pH of 8.5 for the carbonate precipitation. Meanwhile, the primary leaching residue (R-1) was dissolved in 3 mol/L H_2SO_4 solution by adding 30% hydrogen peroxide. After leaching, centrifugation was carried out to obtain the secondary leachate (L-2) and the secondary leaching residue (R-2). L-2 was concentrated to recover Cu as $CuSO_4 \cdot 5H_2O$ crystals.

B. Characterization

The samples and the obtained solid products (R-1 and R-2) were analyzed by X-ray diffraction (XRD, Rigaku, Rint2200, Japan) and the Mn valence of the samples was analyzed by X-ray photoelectron spectroscopy (XPS, ADES-400, VG, UK). The metal ion concentrations in liquid samples (L-1 and L-2) were measured by inductively coupled plasma optical emission spectrometer (ICP-OES, AVIO-200, Perkin Elmer, USA).

III. EXPERIMENTAL RESULTS AND ANALYSIS

A. Composition of sludge.

According to XRD analysis of the samples, rhodochrosite ($MnCO_3$), vernadite [MnO_2 $(H_2O)_2$], zincite (ZnO), and atacamite [$Cu_2Cl(OH)_3$] were observed. XPS analysis was carried out to confirm the chemical state of manganese in the samples.

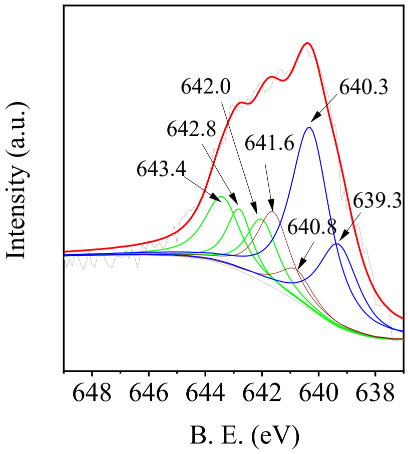

Fig.1.High-resolution XPS spectrum of Mn2p3/2 of sample

The spectra were best fitted by the Gaussian-Lorentzian peak determination method after Shirley background subtraction. The appropriate high-resolution Mn2p3/2 XPS spectra of the samples were analyzed by separating seven peaks (Fig. 1). The characteristic peaks of Mn (IV) were recorded at 643.4 eV, 642.8 eV, and 642.0 eV. Furthermore, the peaks observed at 640.3 eV and 639.3 eV are related to Mn (II). On the other hand, 29.8% Mn (IV), 17.7% Mn (III), and 52.5% Mn (II) were analyzed. These results indicate the existence of manganese compounds with different oxidation states in the sample.

B. Leaching experiments

Experiments were carried out to determine the optimum leaching conditions. As a result, the leaching efficiency of manganese reached more than 99% and copper was less than 0.5% at the following conditions. The addition ratio of $FeSO_4 \cdot 7H_2O$ to the sample was 1.0, and addition ratio of the reduced iron was 0.035 in the primary leaching. The concentrations of Zn, Mn and Fe in L-1 were 10.2 g/L, 42.8 g/L, and 55.9 g/L respectively, and the purity of Zn and Mn precipitates was above 99%. Copper and gypsum were observed in the primary leaching residue (R-1), while only gypsum was detected in the secondary leaching residue (R-2) (Fig.2).

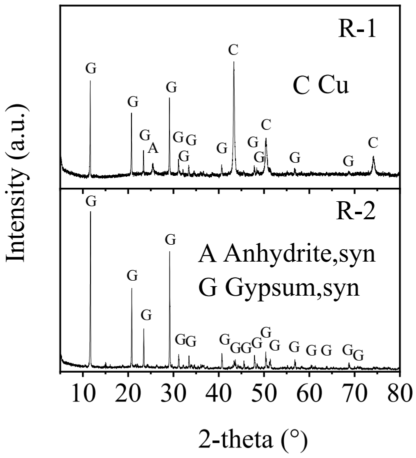

Fig.2. XRD patterns of R-1 and R-2

C. Metal recovery mechanism

The reduction process of tetravalent manganese under acidic system can be expressed as Eq. 1.

$$MnO_2 + 4H^+ + 2e = Mn^{2+} + 2H_2O \quad \varphi_1^0 = 1.224V \tag{1}$$

Ferrous sulfate with a standard electrode potential of 0.771 V can be used as a reducing agent to reduce MnO_2 (Eq. 2).

$$Fe^{3+} + e = Fe^{2+} \quad \varphi_2^0 = 0.771V \tag{2}$$

$$E = E^0 + \frac{0.0592}{2}\ln(\frac{[Fe^{2+}]^2 \cdot [H^+]^4}{[Mn^{2+}] \cdot [Fe^{3+}]^2}) \tag{3}$$

$$Cu^{2+} + Fe = Fe^{2+} + Cu \downarrow \tag{4}$$

The Fe^{2+} produced during copper substitution by reduced iron increases the reduction leaching efficiency of manganese (Eqs. 3 and 4). On the other hand, the reduction leaching of Mn (IV) by metallic iron is thermodynamically possible according to the Gibbs free energy calculation (Eqs. 5 and 6).

$$MnO_2 + 1.333Fe + 6H^+ = Mn^{2+} + 1.333Fe^{3+} + 2H_2O + H_2 \uparrow \quad \Delta G^0 = -262.067kJ/mol \tag{5}$$

$$1.5MnO_2 + Fe + 6H^+ = 1.5Mn^{2+} + Fe^{3+} + 3H_2O \quad \Delta G^0 = -375.897kJ/mol \tag{6}$$

The manganese carbonate and zinc oxide in the sample dissolve in sulfuric acid, while Ca^{2+} remains with metallic copper in R-1, forming calcium sulfate (Eqs. 7~9) (Fig. 2).

$$MnCO_3 + H_2SO_4 = Mn^{2+} + SO_4^{2-} + CO_2 \uparrow + H_2O \tag{7}$$

$$ZnO + H_2SO_4 = Zn^{2+} + SO_4^{2-} + H_2O \tag{8}$$

$$Ca^{2+} + SO_4^{2-} = CaSO_4 \downarrow \tag{9}$$

The remaining copper in R-1 is oxidized by hydrogen peroxide and sulfuric acid (Eqs. 10 and 11).

$$HO_2^- + H_2O + 2e = 3OH^- \quad \varphi^0_{HO_2^-/OH^-} = 0.878V \tag{10}$$

$$H_2O_2 + 2H^+ + 2e = 2H_2O \quad \varphi^0_{H_2O_2/H_2O} = 1.776V \tag{11}$$

The existence of metal components in a given system was concerned to the electrochemical potential (Eh) and pH.H_2O_2 is used as an oxidant. Hence, Cu is converted to Cu^{2+}. As a result, copper is readily converted to copper sulfate in acidic solution, as shown in Fig. 3.

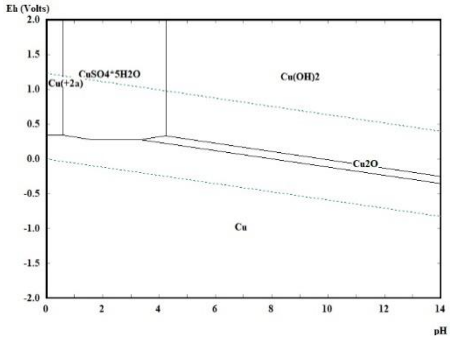

Fig. 3. Eh-pH relationship in the Cu-S-H_2O system at 25°C.

The Gibbs free energy calculation results show that the oxidation of metallic copper by hydrogen peroxide is a thermodynamically possible reaction under acidic system (Eq. 12).

$$Cu + H_2O_2 + H_2SO_4 = CuSO_4 + 2H_2O \ \Delta G^0 = -326.146 kJ / mol \qquad (12)$$

IV. CONCLUSION

Based on the mineral composition of the solid waste, the reductive acid leaching of the tetravalent manganese was carried out, and the reduced iron was added to separate the copper from the leachate. Zinc and manganese in L-1 were recovered by oxalic acid precipitation and carbonate precipitation. The copper in R-1 was recovered as copper sulfate during the second leaching process, and the product remaining in the final leaching residue was gypsum. The hydrometallurgical method proposed in this study is an eco-friendly method that minimizes the harmful impact of solid waste to the environment by recycling all the metallic components in solid waste.

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