Selective Precipitation of Copper and Zinc over Iron from Acid Mine Drainage by Neutralization and Sulfidization for Recovery

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In order to selectively precipitate copper (Cu) and zinc (Zn) over iron (Fe) for recovery from an acid mine drainage (AMD) generated from an abandoned copper mine located in east Japan, the feasibility of a treatment process combining lime neutralization with sodium hydrosulfide (NaHS) sulfidization was investigated. First of all, lime neutralization was applied to the AMD to find the precipitation behaviors of Cu, Zn, and Fe. Next, NaHS sulfidization as well as the integration with lime neutralization were conducted to selectively precipitate Cu, Zn, and Fe from the AMD. The results show that by adding more than 20 mg/L NaHS into the AMD at pH 2.8 without pH adjustment, all of the Cu precipitated whereas Fe and Zn did not. Fe could be selectively precipitated over Zn afterwards by lime neutralization at pH 5; however, the addition of an oxidizing agent such as 0.02 vol.% H2O2 was needed. On the other hand, after Fe was fully precipitated previously by lime neutralization at pH 5, all of the Cu precipitated when 10-15 mg/L NaHS was added whereas Zn did not. After Cu and Fe were precipitated, Zn could be precipitated by lime neutralization at above pH 9.

Key Words : Acid Mine Drainage (AMD), Copper, Zinc, Neutralization, Sulfidization, Recovery

1 INTRODUCTION

Mine development brings out the metal resources needed for human society. However, it has caused several serious environment problems such as the production of large amounts of mine waste, the dispersion of beneficiation tailings, and the acid mine drainage (AMD) [1]. Among them, AMD is the most serious hazard since it contains high acidity and a broad range of heavy metals which have adverse effects on aquatic life and human beings [2-3]. Besides, the hazards of AMD continue even after the mine was abandoned. Generally, AMD is treated by neutralization method such as lime neutralization or limestone neutralization to neutralize the acidity and remove the heavy metals [4-5]. However, it is also accompanied by the treatment of metal hydroxide precipitates. Recently, many researchers have studied several advanced methods such as the biogenic sulfide since most base metals in acidic solution precipitate in contact with sulfide [6-10]. Even though, the most popular method for AMD treatment today is still lime neutralization.

One abandoned copper mine located in east Japan discharges about 12 m³/min of AMD which is gathered and treated in the downstream purification plant. The main heavy metals contained in the AMD are copper (Cu), zinc (Zn), and iron (Fe). The present treatment process is lime neutralization, where lime slurry is introduced to adjust the pH of AMD to about pH 10 to precipitate all of the heavy metals. After solid-liquid separation by gravitation sedimentation, sulfuric acid (H2SO4) is introduced to adjust the pH of the AMD to about pH 7. All of the heavy metal concentrations in the effluent can meet the Japanese effluent standards. The precipitate generated in the treatment process is pumped to a landfill disposal site. Because of the decrease in the capacity of landfill disposal site as well as the increase in the price of base metals such as Cu in recent years, it is expected that not only to treat but also to recover these base metals from the AMD. For the subsequent Cu and Zn smelting process, the major issue is how to separate Cu and Zn from Fe in the AMD selectively as well as possible.

In this study, we attempted to selectively precipitate Cu and Zn from the AMD by combining the present lime neutralization treatment method with NaHS sulfidization. First of all, lime neutralization was applied to the AMD to find the precipitation behavior of Cu, Zn, and Fe in the AMD. Then, NaHS sulfidization as well as the integration with lime neutralization was conducted to separately precipitate Cu, Zn, and Fe from the AMD. Furthermore, the chemical species of Cu, Zn, and Fe in the precipitates generated by neutralization and sulfidization was also characterized.

2 MATERIALS AND METHODS

2.1 Materials

AMD sample taken from the inlet of the AMD purification plant located in east Japan was utilized in this investigation.
Before experiment, filtration was carried out to remove the brown precipitates presented in the sample. Table 1 shows the pH and the concentrations of Cu, Zn, and Fe in the AMD. Lime (calcium hydroxide (Ca(OH)_2), Nacalai Co., Ltd., Japan) was used in the neutralization experiment and for pH adjustment. NaHS (70% sodium hydrosulfide, Nacalai Co., Ltd., Japan) was used in the sulfidization experiment. When necessary, 30 wt.% hydrogen peroxide (H_2O_2) solution (Wako Co., Ltd., Japan) was used as the oxidizing agent to adjust the redox condition of the AMD. All reagents were analytical grade.

<table>
<thead>
<tr>
<th>pH</th>
<th>Cu</th>
<th>Zn</th>
<th>Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>As received AMD sample</td>
<td>2.8</td>
<td>4.05</td>
<td>9.86</td>
</tr>
</tbody>
</table>

(Unit of metal concentration: mg/L)

2.2 Methods
All experiments were carried out at room temperature (i.e. at about 293 K). In each experiment, 200 mL of AMD was poured into a 300 mL beaker equipped with a stainless magnetic stirrer. After the addition of reagent, the liquid was mixed with the stirrer at 400 rad/min. The neutralization experiment was conducted by introducing lime powder into the beaker to adjust the pH of the AMD. In the sulfidization experiment, 10 g/L of NaHS solution was freshly prepared beforehand. The needed volume of the NaHS solution was introduced into the AMD whose pH had been previously adjusted by lime. When the desired pH in the neutralization experiment was reached or the sulfidization experiment was completed, 5 mL of liquid was sampled and filtrated through a 0.2 μm membrane filter for metal analysis. The concentrations of Cu, Zn, and Fe in the AMD precipitated were collected by using vacuum filtration, dried, and analyzed with an X-ray diffractometer (XRD, Rigaku, SmartLab). In addition, in order to characterize the chemical species of Cu, Zn, and Fe in the precipitates generated by neutralization and sulfidization, the precipitates were collected by using vacuum filtration, dried, and analyzed with an X-ray diffractometer (XRD, Rigaku, SmartLab).

3 RESULTS AND DISCUSSIONS
3.1 Precipitation of Cu, Zn, and Fe by lime neutralization
First of all, the lime neutralization was applied to the AMD to find the precipitation behavior of Cu, Zn, and Fe in the present treatment process. Figure 1 shows the concentrations of Cu, Zn, and Fe in the AMD as a function of pH adjusted by lime. The concentration of Fe in the AMD started to decrease when the pH of the AMD increased from initial pH 2.8 to pH 4, and all of the Fe precipitated above pH 5. The concentration of Cu started to decrease between pH 5-6, and all of the Cu precipitated above pH 8. On the other hand, the concentration of Zn barely changed below pH 6 but started to decrease at pH 7, and all of the Zn precipitated above pH 9. According to these results, both Cu and Zn in the AMD precipitated between pH 6-8, which suggested that these two metals can not be separated from each other in the present lime neutralization treatment process.

3.2 Precipitation of Cu, Zn, and Fe by NaHS sulfidization
In this work, we attempted to integrate the present lime neutralization process with the sulfidization treatment for selectively precipitating Cu and Zn, over Fe from the AMD. According to the results in section 3.1, the sulfidization treatment for the AMD should be conducted below pH 5, since Cu and Zn started to precipitate when the pH of the AMD was adjusted to above pH 5 and pH 7, respectively. Figure 2 and Figure 3 show the concentrations of Cu, Zn, and Fe in the AMD as a function of NaHS dosage at pH 2.8 (where pH has not been adjusted) as well as at pH 5 (where pH has been adjusted by lime and Fe has been fully precipitated), respectively.

At pH 2.8, the concentration of Cu in the AMD started to decrease when more than 5 mg/L NaHS was added, and all of the Cu precipitated when more than 20 mg/L NaHS was added. On the other hand, the concentration of Fe and Zn remained unchanged. The results suggest that the addition of more than 20 mg/L NaHS into the AMD sample directly at pH 2.8 can selectively precipitate Cu over Fe and Zn from the AMD.
min, whereas Zn and Fe did not. Although the NaHS sulfidization for precipitating Cu from the AMD reacted quickly, it was observed that the black Cu precipitates flocculated over time. Therefore, a longer reaction time, e.g. more than 30 min, would be helpful for the subsequent solid-liquid separation process.

It is needed to notice that the addition of NaHS solution into the AMD cause the generation of H\textsubscript{2}S especially at pH 2.8, since part of the HS\textsuperscript{-} reacts with H\textsuperscript{+} in low pH acid solution.

The XRD pattern of the precipitate generated by sulfidization with a dosage of 20 mg/L NaHS at pH 2.8 is shown in Figure 6. The peaks of CuS and Cu\textsubscript{2}SO\textsubscript{4} \cdot 5H\textsubscript{2}O are characterized, which implies the main chemical species of Cu in the precipitate are CuS and Cu\textsubscript{2}SO\textsubscript{4} \cdot 5H\textsubscript{2}O.

3.3 Precipitation of Zn and Fe by lime neutralization after Cu was precipitated by NaHS sulfidization

After Cu was precipitated from the AMD by NaHS sulfidization at pH 2.8, lime neutralization was conducted to selectively precipitate Zn and Fe. Figure 7 shows the concentrations of Zn and Fe in the AMD as a function of pH adjusted by lime. Zn started to precipitate at pH 7, and fully precipitated above pH 9. On the other hand, Fe somewhat precipitated at pH 5-7, and fully precipitated above pH 9. Comparing the results with those given in section 3.1, it was found that the precipitation behavior of Zn was almost the same, i.e. started to precipitate at pH 7. However, Fe began to precipitate at pH 7 instead of pH 4, and could not fully precipitate until pH 9. As a result, Fe co-precipitated with Zn at pH 7-9, which suggests that Zn and Fe can not be precipitated individually by lime neutralization after Cu was precipitated by NaHS sulfidization at pH 2.8.

The co-precipitation of Fe and Zn is considered as follows. According to the Eh-pH diagram of the Fe-H\textsubscript{2}O system as shown in Figure 8, the chemical specie of Fe in aqueous solution at pH 4-7 is Fe (II) ion (when in a comparatively reductive condition) or FeO\textsubscript{2}H\textsuperscript{-} (when in a comparatively oxidative one). Since the sulfidizing agent NaHS has the characteristic of reductive ability, the redox condition of the AMD became comparatively reductive after 20 mg/L of NaHS was added to precipitate Cu at pH 2.8. As a result, Fe was difficult to be precipitated and co-precipitated with Zn at pH 7-9.
In order to promote the precipitation of Fe, an attempt was made by introducing H$_2$O$_2$ (30 wt.% hydrogen peroxide solution) to transform the comparatively reductive condition of the AMD to comparatively oxidative condition. Figure 9 shows the effect of H$_2$O$_2$ dosage on the precipitation of Zn and Fe at pH 5 where Cu was previously precipitated by NaHS sulfidization at pH 2.8 followed by pH adjustment using lime. By adding more than 0.02 vol.% H$_2$O$_2$, all of the Fe precipitated at pH 5 whereas none of the Zn did. The efficacy of H$_2$O$_2$ addition in promoting the precipitation of Fe over Zn after Cu was previously precipitated by NaHS sulfidization was confirmed. After Cu and Fe were precipitated, Zn could be precipitated by lime neutralization at above pH 9. The concentrations of Fe, Cu and Zn in the solution after the treatment were below the detection limit (0.005 mg/L), which could meet the effluent standards in Japan (Cu: 3.0 mg/L; Zn: 2.0 mg/L).

On the other hand, in the case after all of the Cu precipitated by 10-15 mg/L NaHS dosage at pH 5 where Fe had been fully precipitated during pH adjustment from 2.8 to 5, Zn could also be fully precipitated by lime neutralization at above pH 9. The concentrations of Fe, Cu and Zn in the solution after the treatment were below the detection limit (0.005 mg/L), which could also meet the effluent standards in Japan.

The XRD patterns of the Fe precipitate at pH 5 and Zn precipitate at pH 10 generated by lime neutralization with 0.1 vol.% H$_2$O$_2$ dosage, where Cu was previously precipitated by NaHS sulfidization at pH 2.8, are shown in Figure 10. The chemical species of Fe and Zn in each precipitate are both amorphous thus can not be characterized. Nevertheless, according to the Eh-pH diagrams of the Fe-H$_2$O$_2$ system as shown in Figure 8 and the Zn-H$_2$O system as shown in Figure 11, the possible chemical species of Fe and Zn might be FeOOH and ZnO, respectively.

Figure 8: Eh-pH diagram of Fe-H$_2$O$_2$ system (Molarity: Fe 0.12 mmol/L, temperature 293 K, pressure 1 Pa)

Figure 9: Concentrations of Zn and Fe in the AMD as a function of 30 wt% H$_2$O$_2$ solution dosage at pH 5, where Cu was previously precipitated by NaHS sulfidization at pH 2.8 followed by lime neutralization to pH 5

Figure 10: XRD patterns of the Fe precipitate at pH 5 and Zn precipitate at pH 10 generated by lime neutralization with 0.1 vol.% H$_2$O$_2$ dosage, where Cu was previously precipitated by NaHS sulfidization at pH 2.8

Figure 11: Eh-pH diagram of Zn-H$_2$O$_2$ system (Molarity: Zn 0.15 mmol/L, temperature 293 K, pressure 1 Pa)

4 CONCLUSION

For the purpose of selectively recovering Cu and Zn over Fe from the AMD generated from an abandoned copper mine located in east Japan, the feasibility of integrating the present lime neutralization process with NaHS sulfidization treatment was investigated. The following results were obtained:

1. By lime neutralization treatment, Fe started to precipitate when the pH of the AMD was adjusted from initial pH 2.8 to pH 4, and fully precipitated above pH 5. Cu started to precipitate between pH 5-6, and fully precipitated above pH 8. Zn started...
to precipitate at pH 7, and fully precipitated above pH 9. As a result, Cu and Zn coprecipitated at pH 6-8 and could not be precipitated individually.

(2) By adding more than 20 mg/L NaHS into the AMD at pH 2.8 without pH adjustment, all of the Cu precipitated whereas Fe and Zn did not. Fe could be selectively precipitated over Zn afterwards by lime neutralization at pH 5; however, the addition of an oxidizing agent such as 0.02 vol.% H₂O₂ was needed. After Cu and Fe were precipitated, Zn could be precipitated by lime neutralization at above pH 9.

(3) After Fe was fully precipitated by lime at pH 5, all of the Cu precipitated when 10-15 mg/L NaHS was added whereas Zn did not. However, Zn started to precipitate when more than 15 mg/L NaHS was added. After Cu and Fe were precipitated, Zn could be precipitated by lime neutralization at above pH 9.

(4) The two processes proposed in conclusion (2) and (3) are both based on modifying the existing neutralization treatment process, which are easy to be applied in practical. The former is considered to be more preferable in practical application although the addition of an oxidizing agent is needed after Cu is precipitated by NaHS sulfidization. The latter is effective only when Fe can be fully precipitated below pH 5. If not, Cu and Fe will co-precipitate since Cu begins to precipitate at pH 5.

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References


