1. Introduction

Galvanic interactions among different minerals are well-known phenomena. Rath and Paramguru investigated galvanic interaction between sphalerite and manganese (IV) oxide (MnO2) in sulfuric acid solution and found a substantial increase in leaching of both the minerals1. Galvanic leaching of manganese nodule and cobalt-rich crust, which contain MnO2, has been investigated using sulfide minerals2–4. Nakazawa et al. showed that the dissolution rate of manganese in cobalt-rich crust was accelerated in the presence of pyrite4. Since MnO2 is nobler than pyrite, MnO2 acts as a cathode to be reduced resulting in release of manganese from the crust in the contact with pyrite. On the other hand, pyrite acts as an anode to be oxidized.

Gantayat et al.5 investigated galvanic interaction between chalcopyrite and MnO2 in sulfuric acid medium using compact disc electrodes of both materials. They reported that chalcopyrite and MnO2 form a galvanic corrosion couple where the former acts as anode and the latter as cathode leading to strong interaction between the minerals. Devi et al.6 studied the dissolution in the presence of MnO2 in hydrochloric acid medium. They found that chalcopyrite didn’t dissolved independently but underwent oxidative dissolution with MnO2 by (i) galvanic interaction (ii) cyclic action of F3+/Fe2+ redox couple and (iii) chlorine gas by MnO2 dissolution. The last one was observed to be most effective. But so far, no study is reported on galvanic leaching of chalcopyrite particles using MnO2 in sulfuric acid solution.

Dixon et al. developed the ferric sulfate leaching process of chalcopyrite using pyrite (Galvanox process)7. In this process, the rapid rate of chalcopyrite has been attributed to the galvanic interaction between pyrite and chalcopyrite. Since pyrite is nobler than chalcopyrite, pyrite acts as a cathode, accept electrons from chalcopyrite and reduce ferric ions in ferric sulfate medium.

Spent zinc-carbon batteries are mostly collected as incombustible waste by municipal authorities and are buried in landfill sites without recycling them in Japan. Zinc-carbon battery contains a carbon rod cathode with a moist paste (hereafter, black paste) of MnO2 and NH4Cl mixed with...
carbon powder to improve conductivity and retain moisture in the acid electrolyte. During discharging of zinc-carbon batteries, the zinc is oxidized and MnO₂ is reduced. A simplified overall cell reaction is:

$$Zn + 2MnO_2 \rightarrow Mn_2O_3 + ZnO$$  \hspace{1cm} (1)

In sulfuric acid solution, Mn₂O₃ dissolves to form MnO₂ as follows:

$$Mn_2O_3 + H_2SO_4 \rightarrow MnO_2 + MnSO_4 + H_2O$$  \hspace{1cm} (2)

In this study, we have examined the feasibility of the galvanic leaching of chalcopyrite using black paste obtained from spent zinc-carbon batteries and chemical reagent MnO₂ in sulfuric acid solutions.

2. Experimental

Chalcopyrite concentrate (−100 μm) used in this study was provided by Atakama mining in Chile. The XRD pattern of the sample was collected with a diffractometer (Regaku Corp., Rint2100) and small peaks of pyrite were observed as well as peaks of chalcopyrite (Figure 1). The chemical compositions are as follows; Cu: 28.9%, Fe: 28.9%.

MnO₂ powder (extra pure grade reagent) was provided by Kanto chemical Co. Ltd. Black paste was collected from the dismantled spent zinc-carbon batteries. In order to remove the zinc from the black paste, the original black paste was washed with 1 N sulfuric acid solution at 1/10 solid/liquid ratio by mixing at 200 rpm for 1 h with a magnetic stirrer. The black paste was recovered with filtration and dried at 80°C for 24 h followed by grinding with a porcelain mortar and a pestle. XRD patterns of MnO₂ and black paste are shown in Figure 1. XRD analysis of the black paste indicates the presence of graphite that is used as a conductive material in zinc-carbon batteries. Due to the chemically inert and electrically conductive nature of carbons, carbons are used as the conductive additive. The chemical compositions of the black paste and MnO₂ were measured according to the following procedure: 0.5 g samples were digested with aqua regia (20 mL of HNO₃ : HCl = 1 : 3) by gentle boiling on a hot plate for 4 h. The solutions were filtered and the residue of the black paste on the filter paper was rinsed with distilled water. Mn, Zn and Fe in the filtrates were analyzed with an atomic absorption spectrophotometer (Hitachi Z-5000). Table 1 shows the chemical compositions of MnO₂ and black paste. The residue of the black paste was dried at the 40°C for 24 h and weighed. The residue was observed with scanning electron microscope equipped with an energy dispersive X-ray spectrometer (Oxford Instruments, Inca x-act). A SEM micrograph and EDX spectrum of the residue are shown in Figure 2. The residue could be graphite and amounts to 16.4 weight percent of the black paste. The SEM micrograph indicates that graphite particles are smaller than 200 nm.

Leaching experiments were carried out in 300 mL erlenmeyer flasks with 200 mL sulfuric acid solution. Samples were added into the flask and stirred on magnetic stirrer at 200 rpm at the room temperature unless otherwise described. At desired interval the pH and the redox potential of the leaching solution were measured. The redox potential was measured using Pt electrode with Ag-AgCl (3.3 N KCl) reference electrode and it was converted and reported with respect to NHE. Then an aliquot was withdrawn and centrifuged.

Table 1: Chemical compositions of black paste and MnO₂

|             | Mn   | Fe   | Zn   |
|-------------|------|------|------|
| Black paste | 40.7%| 2.3% | 0.4% |
| MnO₂        | 54.6%| N.D. | N.D. |
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3. Results

3.1 Rest potential of MnO₂ and chalcopyrite

The steady-state rest potentials of MnO₂ and chalcopyrite after one hour in pH 0.8 sulfuric acid solution were 1171 mV and 527 mV (NHE), respectively. These materials are expected to form galvanic couple in contact with each other. MnO₂ can act as a cathode while chalcopyrite serves as an anode, suggesting that chalcopyrite could be oxidized to dissolve.

3.2 Effect of MnO₂ on chalcopyrite leaching

Figure 3 shows the effect of the MnO₂ on the chalcopyrite leaching. The leaching rate of chalcopyrite increased in the presence of MnO₂. The extraction yield of copper was 52% in 24 days, while 17% in the absence of MnO₂. MnO₂ dissolution was also accelerated in the presence of chalcopyrite and the extraction yield was 23%. Chalcopyrite and MnO₂ could be leached through galvanic interaction between them according to equation (3) and (4).

\[ \text{CuFeS}_2 \rightarrow \text{Cu}^{2+} + \text{Fe}^{2+} + 2\text{S}^0 + 4\text{e}^- \]  

\[ \text{MnO}_2 + 4\text{H}^+ + 2\text{e}^- \rightarrow \text{Mn}^{2+} + 2\text{H}_2\text{O} \]  

Iron ions occurred as ferrous ions in the absence of MnO₂, whereas ferric ions existed in the presence of MnO₂. Ferrous ions dissolved from chalcopyrite were oxidized to ferric ions by MnO₂ according to the reaction (5):

\[ 2\text{Fe}^{2+} + \text{MnO}_2 + 4\text{H}^+ \rightarrow 2\text{Fe}^{3+} + \text{Mn}^{2+} + 2\text{H}_2\text{O} \]  

Overall reaction between chalcopyrite and MnO₂ is described as follows:

\[ 2\text{CuFeS}_2 + 5\text{MnO}_2 + 20\text{H}^+ \rightarrow 2\text{Cu}^{2+} + 2\text{Fe}^{3+} + 5\text{Mn}^{2+} + 4\text{S}^0 + 10\text{H}_2\text{O} \]  

The molar ratio of dissolved Mn ions to Cu ions was 3.9 at the experiment, which is higher compared to the stoichiometric ratio. Since the chalcopyrite concentrate contains pyrite, this may be due to some excess manganese dissolution by the galvanic interaction between MnO₂ and pyrite. Pyrite has lower rest potential than MnO₂ and forms a galvanic couple with MnO₂ where it becomes the anode of the couple and dissolves according to reaction (7):

\[ \text{FeS}_2 + 8\text{H}_2\text{O} \rightarrow \text{Fe}^{3+} + 2\text{SO}_4^{2-} + 16\text{H}^+ + 14\text{e}^- \]
The redox potential in the presence of MnO$_2$ remained over 900 mV during the experiments whereas it was about 600 mV without MnO$_2$.

MnO$_2$ accelerates the kinetics of chalcopyrite leaching, but leaching rate of chalcopyrite was not so adequate that it would require a long period of time to complete the leaching.

3.3 Effect of black paste on the leaching of chalcopyrite

The leaching experiments were carried out with the additions of 1 g and 2 g black paste to observe the effect of black paste on the chalcopyrite leaching. The results in Figure 4 show that the kinetics of chalcopyrite leaching was enhanced dramatically in the presence of black paste. The dissolution rate of copper increased with increase in the black paste dosage. The extraction yield of copper in the presence of 2 g black paste was 83% in 40 h, while that was 5% in the absence of black paste. After then copper dissolution rate slowed down and 90% of copper in the concentrate dissolved in 116 h. Extraction yield of Mn increased remarkably and was 63% at the end of the experiment. For the addition of 1 g black paste, copper dissolution from chalcopyrite halted at the extraction yield of 67% because complete manganese dissolution from the black paste was almost achieved.

Iron ions occurred as ferrous ions in the absence of black paste whereas ferric ions existed in the presence of black paste. Ferrous ions dissolved from chalcopyrite were oxidized by MnO$_2$ in the black paste according to the reaction (5). The pH rose with time in the presence of black paste because H$^+$ ions were consumed according to the reactions (6). The redox potential increased up to over 900 mV in the presence of the black paste while it decreased without the addition of black paste because of increase in ferrous concentration. Figure 4 shows the XRD patterns of the residue with the addition of 2 g black paste. The peaks of element sulfur were observed, but the peaks of chalcopyrite were not. Following experiments were carried out using the black paste.

3.4 Effect of initial pH on the chalcopyrite leaching in the presence of black paste

In order to investigate the effect of initial pH, leaching experiments were carried out at initial pH 0.8 and 1.2. The results are shown in Figure 5.
There are no so much differences in the rate and extent of copper extraction between them. For initial pH 1.2, pH increased to 2.4 in 116 h and iron concentration was lower than that for initial pH 0.8 after the leaching of 65 h. The reason for lower iron concentration is that ferric ions could precipitate as jarosite.

3.5 Effect of temperature on the chalcopyrite leaching in the presence of black paste

Leaching experiments were conducted at 50°C and room temperature to study the effect of temperature on the leaching of chalcopyrite. The results are shown in Figure 6. Elevating temperature increased extraction rate at the middle stage of the experiment, but the extraction yield of copper was the same as that at the room temperature in 50 h. Total iron concentration decreased after 20 h at higher temperature. Ferric ions could precipitate as jarosite because jarosite tend to form with increase in temperature.14

3.6 Effect of amount of chalcopyrite on the chalcopyrite leaching in the presence of black paste

The experiments were carried out by varying chalcopyrite dosage 0.5 g and 1 g at a black paste-to-chalcopyrite ratio of 4. The results are shown in Figure 7. It is found that the extraction rate of

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**Fig. 4** Effect of black paste dosage on the chalcopyrite leaching. (a) Cu extraction, (b) Mn extraction, (c) Fe concentration, (d) pH, (e) Redox potential
copper increased with increase in chalcopyrite dosage. For the chalcopyrite dosage of 0.5 g and 1 g, extraction yields of copper were 65% and 81% in 23 h respectively.

3.7 Effect of graphite collected from the black paste on the chalcopyrite leaching in the presence of MnO₂

The black paste contains graphite to increase the electric conductivity of zinc-carbon batteries. Effect of graphite was examined on the chalcopyrite leaching. Leaching experiment was conducted using graphite collected from black paste in the way described above. 0.16 g graphite, which is equivalent to the amount of the graphite included
in 1 g black paste, was added into the leaching solution with the 0.5 g chalcopyrite in the absence of MnO₂ and a leaching experiment was conducted. After sample solution was withdrawn at 22 h, 0.84 g MnO₂ was added into the leaching solution. The results are presented in Figure 8. The graphite didn’t accelerate the kinetics of chalcopyrite leaching in the absence of MnO₂. The redox potential was about 600 mv before the addition of MnO₂.

Adding MnO₂ triggered the dissolution reaction of chalcopyrite. In 4 h after the addition of MnO₂, extraction yield of copper increased from 5% to 11% and the redox potential rose from 590 mv to 837 mv. The kinetics of chalcopyrite leaching was enhanced extremely in the presence of MnO₂ and graphite, and the extraction yield was 85% at the end of the leaching experiment.

3.8 Effect of the graphite in the black paste on the chalcopyrite leaching in ferric sulfate medium

In the chalcopyrite leaching with addition of the black paste, iron ions occurred as ferric ions in leaching solutions because ferrous ions dissolved from chalcopyrite were oxidized to ferric ions. In order to examine the effect of graphite on ferric sulfate leaching of chalcopyrite, leaching experiments were carried out in ferric sulfate medium (Fe(III) 511 mg/L) in the absence or presence of the graphite collected from the black paste. The
results presented in Figure 9 indicate that graphite powder doesn’t improve the kinetics of the chalcopyrite leaching in the presence of ferric ions. The graphite doesn’t have catalytic effect to dissolve the copper from chalcopyrite.

4. Discussion

Since MnO₂ is noble than chalcopyrite, chalcopyrite and MnO₂ form a galvanic corrosion couple in sulfuric acid solution where the former acts as anode and the latter as cathode leading to simultaneous dissolution of both materials. In the presence of MnO₂, the kinetics of chalcopyrite leaching was enhanced, but the leaching rate was not so adequate that it would require a lot of time to complete the leaching. The dissolution rate of copper from chalcopyrite could depend on electron transfer from chalcopyrite to MnO₂.

The black paste collected from spent zinc-carbon dry batteries contains manganese dioxide and graphite. Adding the black paste increased the rate and extent of chalcopyrite leaching significantly. Graphite is used as conductive material in black paste. Generally about 55 volume% carbon is mixed with MnO₂ to improve electric conductivity. In order to determine the effect of graphite on chalcopyrite leaching, experiments were conducted using the graphite obtained from the black paste. The graphite accelerated the kinetics of chalcopyrite leaching in the presence of MnO₂, but it didn’t improve ferric sulfate leaching of chalcopyrite with 510 mg/L of ferric ions in the absence of MnO₂, indicating that the graphite could play an important role in the galvanic interaction between chalcopyrite and MnO₂.

Chalcopyrite is refractory in ferric sulfate media. Low dissolution rate of copper from chalcopyrite could be attributed to the formation of passive layers such as elemental sulfur layer, a copper-rich polysulfide layer and layers consisting of iron salt on the chalcopyrite surface. Elemental sulfur layer formed on the surface of chalcopyrite by the oxidation of ferric ions is extremely low electrical conductivity. This layer could prevent transfers of electron and ions to the chalcopyrite core and hinder dissolution of copper from chalcopyrite. Nazari et al. found that silver-enhanced pyrite accelerated the kinetics of chalcopyrite leaching dramatically in the Galvanox process, and investigated the mechanism of silver-enhanced pyrite leaching of chalcopyrite. It has been shown that miniscule amount of silver dissolved from the pyrite react with the sulfur layer on the chalcopyrite and increase the conductivity of this layer significantly. It allows the transfer of electrons from chalcopyrite to pyrite resulting into enhancing the leaching rate of chalcopyrite dramatically.

Graphite particles in the black paste is very fine and electrical conductive. One of reasons for the acceleration of extraction rate of copper from chalcopyrite is that electron transfer from chalcopyrite to MnO₂ could be facilitated through graphite. Increase in electron transfer could enhance the galvanic interaction between the both materials, resulting in increasing the kinetics of chalcopyrite leaching. At presence, effect of carbon on the chalcopyrite leaching has been investigated using several carbon materials in the presence of MnO₂.

5. Conclusions

The feasibility of galvanic leaching of chalcopyrite was examined using black paste collected from spent zinc-carbon batteries and chemical reagent MnO₂ in sulfuric acid media. Black paste mainly contains MnO₂ and graphite. Obtained results are summarized as follows:

1. MnO₂ increased the leaching rate of chalcopyrite by galvanic interaction between chalcopyrite and MnO₂, and extraction yield of copper was 52% in 24 days whereas 17% without MnO₂.
2. Black paste accelerated the kinetics of chalcopyrite leaching dramatically and the extraction yield of copper was 83% in 40 h.
3. The graphite obtained from the black paste enhanced chalcopyrite leaching in the presence of MnO₂, but did not in the absence of MnO₂.
4. The graphite is so fine and conductive that it could facilitate electron transfer from chalcopyrite to MnO₂, resulting in accelerating the galvanic leaching of chalcopyrite.

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