STUDY ON SEPARATION OF CHALCOPYRITE AND MOLYBDENITE USING FLOTATION IN SEAWATER AND HYDROGEN PEROXIDE SOLUTION

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https://doi.org/10.15017/1866284

出版情報：Kyushu University, 2017, 博士（工学）, 課程博士
バージョン：
権利関係：

（様式２）

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論文名　：STUDY ON SEPARATION OF CHALCOPYRITE AND MOLYBDENITE USING FLOTATION IN SEAWATER AND HYDROGEN PEROXIDE SOLUTION
（海水及び過酸化水素水中における黄銅鉱と輝水鉛鉱の分離に関する研究）

区　　分　：甲

論 文 内 容 の 要 旨

The increased demand of molybdenum in the last 5 years has resulted in a necessity for a better recovery of molybdenum. Approximately, 50% of molybdenum production comes from copper-molybdenum (Cu-Mo) ores. Molybdenum, as a by-product from Cu-Mo flotation plants, plays a very important role in making the flotation plants economically viable. This is triggered by the up-floating molybdenum price which was up to three times higher than the price of copper in 2016. However, the existing Cu-Mo flotation plants demonstrate imperfect molybdenum recovery, ranging from 25% to 85%. Due to the deposit location, several mining operations are located in desert areas (i.e., Atacama Desert, Chile), the usage of seawater for Cu-Mo flotation plants could not be avoided and has been reported to be able to depress the floatability of molybdenum at pH>9.5. The cause of this phenomenon might be due to the effects of $Mg(OH)_2$ precipitate formed in seawater at pH>9.5. However, several studies show contradictive results, therefore further study is needed to clarify this phenomenon.

Other existing Cu-Mo flotation processes use sodium hydrosulfide (NaHS), a toxic depressant, to depress the floatability of copper ores, causing environmental and health issues. For this reason, other safer methods are required to replace the NaHS reagent. The methods should be able to deliver comparable results (i.e. mineral recoveries and grades) to the existing Cu-Mo flotation plants.

In order to provide a reliable method as well as using non-dangerous reagents, in this thesis, the depression effect of seawater on flotation performance of chalcopyrite and molybdenite at alkaline conditions was examined. Moreover, the possibility for selective flotation of chalcopyrite and molybdenite was investigated by employing various flotation reagents. To clarify the flotation mechanisms, mineral surface characterizations and observation on bubble-particle interactions were carried out.

This dissertation consists of 7 chapters. **Chapter 1** presents the background and objectives of this study. Moreover, an overview of froth flotation, zeta potential, and bubble-particle interactions are presented in order to provide the basic understanding of this study. Surface characterization using atomic force microscopy is briefly discussed in this chapter.

Chapter 2 focuses on the development of an image analysis software. In froth flotation, bubble-particle interactions play a crucial factor that affect the mineral recoveries. The bubble-particle interactions are usually studied using a high-speed camera followed by image analysis. However, the available image processing software (i.e., Interface Measurement and Analysis System (FAMAS), and ImageJ) analyze the image frame-by-frame and are not able to analyze the dynamic bubble parameters automatically. Moreover, FAMAS is only able to measure the contact angle. Therefore, an image analysis software was developed in this thesis. The software was built in Matlab platform and was programmed to be able to analyze thousands images of bubble movement and its dynamic interactions with the solid surface automatically and rapidly. The software is called Bubble-Solid Surface Interactions Analyzer (Bsolina). Bsolina is a stand-alone software which does not necessarily require network connection to function or another existing process to run. A comparison study was conducted between Bsolina and FAMAS to test the accuracy of Bsolina. The contact angle results showed that Bsolina has similar accuracy level as FAMAS and has the advantage of being able to analyze the dynamics bubble parameters.

Chapter 3 intensively discusses the effects of artificial seawater, a seawater model solution, on the floatability of molybdenite and chalcopyrite, the main minerals in Cu-Mo flotation process. Floatability tests using a column flotation in the absence of flotation reagents (i.e., frothers and collectors) demonstrated that artificial seawater has a detrimental effect on the floatability of molybdenite at pH>9. Surprisingly, however, the similar detrimental effect was observed on the floatability of chalcopyrite under the same alkaline conditions, which contradict several studies. The floatability results are in agreement with low contact angle readings and the reversal of zeta potential signs of both minerals at pH>9, indicating the adsorption of hydrophilic species on the particle

surfaces. Furthermore, the floatability tests of single mineral showed that there is a possibility for selective flotation of both minerals at pH 10 by the addition of kerosene emulsion in artificial seawater, which might be caused by the increasing of surface hydrophobicity of molybdenite owing to the adsorption of kerosene as indicated from higher contact angle values. Finally, a $MgCl_2$ aqueous solution was employed to clarify the effect of $Mg(OH)_2$ on the floatability of chalcopyrite and molybdenite in both with and without kerosene addition. The low floatability results of both minerals in a $MgCl_2$ aqueous solution at pH>9 confirms the depression effect of $Mg(OH)_2$ on the floatability of chalcopyrite and molybdenite.

In **Chapter 4**, surface characterizations of molybdenite and chalcopyrite in artificial seawater and in a 0.01 M $MgCl_2$ solution both with and without kerosene addition were examined. The surface characterizations were carried out using atomic force microscopy (AFM). In addition, the bubble interactions with both mineral surfaces are also discussed in this chapter. The bubble-particle interactions results and AFM images show that both mineral surfaces were covered dominantly by $Mg(OH)_2$ precipitate and a small concentration of $CaCO_3$ precipitate from seawater at pH 11 with and without kerosene addition, altering the surfaces hydrophobicity and preventing the formation of three-phase contact (TPC) on the surfaces, thus depressing the floatability of both minerals as presented in Chapter 3. These results are supported by the reversal of zeta potential of both minerals at pH>9 owing to the adsorption of positively charged $Mg(OH)_2$ particles on the surface as discussed in Chapter 3. In addition, the AFM images show that the selective flotation of chalcopyrite and molybdenite at pH 10 with the addition of kerosene emulsion in artificial seawater might be due to the lower adsorption of $Mg(OH)_2$ on molybdenite surface compared to that on chalcopyrite surface. From the study of bubble-particle interactions, kerosene was found to change the bubble shape from oblate to spherical and was found to reduce the bubble rise velocity by ~50%. Moreover, kerosene could accelerate the formation of TPC at natural pH of both treatment solutions by one order of magnitude (from ~200 to ~40 ms). The reason for these phenomena is likely caused by the adsorption of kerosene at air/liquid interface and on the mineral surface, which improved the mineral surface hydrophobicity and destabilized the thin liquid film on the surface. The implications of all of these effects for flotation process are a longer contact time between bubble and particle, a higher probability of bubble-particle attachment and therefore, a higher flotation recovery in the presence of kerosene as can be observed from flotation results of chalcopyrite and molybdenite at pH<9 from Chapter 3.

Chapter 5 focuses on investigating an oxidation treatment to replace the NaHS treatment using a mixture of hydrogen peroxide (H_2O_2) aqueous solution and ferrous sulfate ($FeSO_4$). $FeSO_4$ was employed to improve the oxidation performance of H_2O_2 aqueous solution via Fenton-like reaction in flotation process at pH 9. It was observed that the addition of $FeSO_4$ into H_2O_2 aqueous solution could increase the concentration of dissolved oxygen in the solution, indicating a stronger oxidizing power compared to that of without the addition of $FeSO_4$. Moreover, the oxidizing power increased with an increase in concentration of $FeSO_4$. This phenomenon might be caused by the reaction between FeOOH precipitate with the H_2O_2 produces oxygen (O_2) and hydroxyl radicals (•OH) at pH 9. The contact angle readings showed that chalcopyrite surface was more sensitive to surface oxidation compared to that of molybdenite in H_2O_2 aqueous solution both with and without the addition of $FeSO_4$. In addition, selective oxidation was observed in a mixture of 0.1 mM $FeSO_4$ and 10 mM H_2O_2 aqueous solution. Under this condition, the contact angle of chalcopyrite and molybdenite was 0° and ~60°, respectively. Indeed, the flotation test confirm the contact angle readings, showing that H_2O_2 exhibited a detrimental effect on floatability of chalcopyrite in a mixture of 0.1 mM $FeSO_4$ and 10 mM H_2O_2 aqueous solution. On the other hand, molybdenite remained floatable under the same condition, suggesting a possibility for selective flotation of both minerals.

Chapter 6 explains the effects of H_2O_2 aqueous solution both with and without the addition of $FeSO_4$ on the surface characteristics of chalcopyrite and molybdenite were studied. The topography of the mineral surfaces was scanned using AFM. Meanwhile, the chemical species on the surface was characterized using X-ray photoelectron spectroscopy (XPS). The AFM images of chalcopyrite surface show that the surface was covered with mountainous features after the oxidation treatment with a mixture of H_2O_2 aqueous solution and $FeSO_4$ at pH 9. Furthermore, the XPS results suggest that these mountainous features were the hydrophilic oxidation products (i.e., CuO, $Cu(OH)_2$, $Fe_2(SO_4)_3$, and FeOOH), reducing the surface hydrophobicity and floatability of chalcopyrite as shown in Chapter 5. In addition, the XPS results indicate that the molybdenite surface was slightly oxidized into MoO_3 and MoO_2. However, the surface topography images of molybdenite show clean surfaces after the oxidation treatment. This phenomenon might be caused by the oxidation of MoO_3 and MoO_2 forming a dissolvable MoO_4^- ion at pH 9 as indicated by Eh-pH diagram of molybdenite. Indeed, elemental analysis of the filtrate after the oxidation treatment indicates the dissolved molybdenum species in the solution. This mechanism supports the contact angle readings and flotation results, showing the molybdenite remained hydrophobic and floatable after the oxidation treatment as discussed in Chapter 5.

In **Chapter 7**, conclusions and recommendations for future work are presented.