The Effect of Sodium Silicate as pH Modifier and Depressant in the Froth Flotation of Molybdenite Ores

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In flotation of porphyry molybdenite ores or copper-molybdenite ores using oil collector, a molybdenite (MoS$_2$) concentrate has mainly been separated by combination of sodium silicate (Na$_2$SiO$_3$) and lime (CaO) at about pH 9–11. In this research, the role of sodium silicate and the effect of collector (kerosene) in flotation of Dong-won molybdenite ores from Korea have been observed. It was confirmed that sodium silicate could adjust the pH of pulp to 11. Furthermore, flotation efficiency using sodium silicate was better more than that using lime in the alkaline conditions (pH 9.5–11). It was demonstrated that sodium silicate could be used not only as pH modifier but also as depressant/dispersant of slime. Also Mo grade of 54.1% and recovery of 92.5% were successfully obtained at 75 g/t kerosene and 1.25 kg/t Na$_2$SiO$_3$ (pH 10).

Keywords: molybdenite, flotation, Na$_2$SiO$_3$, collector, depressant, potential of hydrogen (pH)

1. Introduction

Korea imports molybdenum of about 3.3 thousand ton per year from abroad, owing to a development of steel manufactures. Hence the development of flotation technology for Dong-won molybdenite ores (the only mine) in Korea has been demanded. Molybdenum is mainly used as an alloying agent for superalloys, stainless steels, cast irons, refractories, pigments, lubricants and others, due to its unique physical and chemical properties.

The primary source of molybdenum is the mineral molybdenite (MoS$_2$) and it is contributed from porphyry molybdenite and porphyry copper-molybdenite ores. The molybdenite is hydrophobic, due to the perfect cleavage and micaceous form of mineral, and then its natural floatability is high more than other minerals. The broken (crushed or ground) in sulphur-molybdenum bonds generates “edges” sites and van der Waals bonds “faces” sites. Thus the “edges” are highly polar but the “faces” are not and are naturally hydrophobic. The quantity of polar areas “edges” is smaller and non-polar “faces” represent the predominant part when comminuted.

Thus the floatability of molybdenite is enhanced if an insoluble, nonpolar hydrocarbon oil is added to flotation cell. Collectors in molybdenite flotation have mainly been used to a fuel oil and stove oil (kerosene) like hydrocarbon compounds than xanthates to be used as collector of sulfide minerals. Molybdenite and quartz particles are negatively charged at the pH commonly. Calcium ions are found to exhibit a strong affinity to adsorb onto surface of molybdenite and quartz, and then calcium ions are able to reverse or to reduce their zeta potential. Physicochemical investigations regarding the role of depressants in molybdenite flotation are very few. Sodium silicate has quite often been used to disperse the slime layers formed on the mineral particles, and as depressants of gangue minerals (quartz, clay minerals, etc.) to be particularly detrimental to the molybdenite recovery.

This work aims at developing a reliable flotation technique that can separate up to 52% Mo grade (MoS$_2$, 87%) with 90% recovery from Dong-won molybdenite ores, based on the control of the hydrophobic and hydrophilic of target mineral and gangue minerals. Particularly, our study is focused on estimating variables such as pH modifier and dosage of collector that affect the molybdenite flotation.

2. Experimental

2.1 Materials and agents

Molybdenite ores used in this study were obtained from a local plant (Dongwon, Co., Ltd.). Figure 1 shows XRD pattern on raw sample using Cu K$_\alpha$ target. Target mineral was molybdenite (MoS$_2$) and gangue minerals were silicate minerals such as quartz (SiO$_2$), hedenbergite (CaFe(SiO$_3$)$_2$), and grossular (Ca$_3$Al$_2$(SiO$_4$)$_3$). Chemical analysis of raw sample is reported in Table 1. The content of Mo was 0.35% and calcium oxide (CaO) was 27%, and impurities such as Pb, Zn, and Cu that can consist in sulfide minerals were relatively low as 0.0005%, 0.042% and 0.022%, respectively.

Reagents used in flotation tests were sulfuric acid (H$_2$SO$_4$), and lime (CaO) or sodium silicate (Na$_2$SiO$_3$, 9H$_2$O, Junsei chemical, Co. Ltd) for adjusting pH, and fuel oil (kerosene, Junsei) as flotation collector.

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Table 1 Chemical analysis of raw molybdenite ores used in this study.

<table>
<thead>
<tr>
<th>Metal elements (mass%)</th>
<th>Mo</th>
<th>Pb</th>
<th>Zn</th>
<th>Fe</th>
<th>Cu</th>
<th>Re</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mo</td>
<td>0.35</td>
<td>&lt;0.0005</td>
<td>0.042</td>
<td>8.64</td>
<td>0.022</td>
<td>—</td>
</tr>
</tbody>
</table>

Chemical compositions (mass%): SiO₂, CaO, Al₂O₃, MgO, MnO, K₂O

SiO₂: 46.07 CaO: 27.00 Al₂O₃: 2.91 MgO: 1.41 MnO: 1.64 K₂O: 0.59

2.2 Method

Froth flotation machine used in this study was Denver sub-A flotator of lab-scale. Figure 2 shows a flow sheet of froth flotation for the recovery of molybdenite. The sample was crushed and ground, and the minus 150 mesh fraction was used for flotation tests, and then the sample were fed into flotation cell and agitated in 20% (solids) pulp concentrate for 5 min. Reagents in sequence of pH modifiers (CaO or Na₂SiO₃, depressant (Na₂SiO₃), collector (kerosene) and frother (Aerofoth 65) were added into pulp, and final molybdenite was floated with adsorbed onto bubbles. At this time, a reaction time per reagent was 3 min and final concentrate was obtained through rougher flotation of 1 time and clean flotation of twice, and recovery time of concentrates was 10 min.

Grade and recovery were mainly used as standard for estimating the separation efficiency and mass balance of valuable mineral (or target material). Grade is the content (%) of valuable mineral in raw ores, concentrate or tailing. Recovery is the mass (%) of valuable mineral transferred from raw ores to concentrate. Molecular weight ratio of Mo and S₂ is 59.9:40.1, and hence “critical” Mo grade is 59.9% (a dotted line in graph). Mo grade is the content (mass%) of Mo material in the concentrate, and its recovery eq. (1) is in the following:

\[
Re = \frac{cC}{fF} = \left(\frac{f-t}{c-t}\right) f \times 100(\%) \tag{1}
\]

Where, Re is the recovery of Mo in the concentrate separated from feed (raw ores), and f: the content of target material in the feed; c: the content of target material in the concentrate (product fraction); t: the content of target material in the tailing (reject fraction); F: mass of the feed; C: mass of concentrate (product fraction); T: mass of the tailing (reject fraction).

Fig. 2 Flow sheet of froth flotation for recovery of molybdenite.

3. Results and Discussion

3.1 Effect of sodium silicate in alkali pH

The effect of pH on grade and recovery of molybdenite in froth flotation is shown in Fig. 3. Experiments were performed at 20% (solids) pulp concentrate, pulp temp. of 20°C, 1.25 kg/t kerosene, 75 g/t AF65, and cleaning of twice. The natural pH of pulp was relatively high as 8.7. This is attributed to limestone skarn minerals (calcic-hedenbergite, grossular) as shown in Fig. 1 and Table 1. Mo recovery curve decreased considerably as pH decreased toward acid and Mo grade decreased gently. The molybdenite concentrate was strongly agglomerated at pH 4 close to the isoelectric point (pH 3) of molybdenite. The results showed that Mo grade and recovery decreased with decreasing pH of pulp. The reason may be, first: agglomeration between minerals owing to a decrease of electrostatic repulsion between the negatively charged gangue minerals (quartz) and molybdenite, second: a slime coating the surface of molybdenite. Particularly, Hemlund affirmed that a slime coating prevents the adsorption of collector onto the surface of molybdenite and then it deteriorates the floatability of molybdenite.

In the range of alkali (pH 9.5–11), lime and sodium silicate were individually used as pH modifier. In case of lime, Mo grade in pH 10 increased over 3% than that of natural pH, whereas recovery continually decreased from pH 9.5 to 11. This may be attributed to the interaction between minerals and the introduced calcium ions in pulp. At high pH, calcium ions form the calcium hydroxy complex Ca(OH)₂ and then heterocoagulation of molybdenite and quartz particles are formed and their surface potential is decreased. It appears that heterocoagulation of molybdenite and quartz particles in pulp containing large amounts of lime impaired the floatability of molybdenite.
The role of sodium silicate and the dosage of kerosene which could affect molybdenite flotation have been observed. From test results, it was confirmed that sodium silicate to be used with depressant/dispersant could adjust the pH of pulp to 11. Furthermore, flotation efficiency using sodium silicate was better more than that using lime in the alkaline conditions (pH 9.5–11). It was demonstrated that sodium silicate could be used not only as pH modifier but also as depressant/dispersant of slime. The separation efficiency of molybdenite was effective when the dosage of kerosene was adjusted to 75 g/t. A Mo grade of 54.1% and a recovery of 92.5% were successfully obtained from gangue minerals at 75 g/t kerosene and 1.25 kg/t Na$_2$SiO$_3$ (pH 10).

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