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Effects of pH and pulp potential on selective separation of Molybdenite from the Sungun Mine Cu-Mo concentrate

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ABSTRACT

In this research, selective flotation of Mo from the Sungun mine Cu-Mo concentrate was evaluated in different operating conditions. It was found that the addition of 16 kg/t Na_2S into the flotation pulp and aeration rapidly decreased the initial oxidiation-reduction potential (ORP) of the pulp from +228mV to -597 mV (with reference to standard Ag/AgCl electrode), and increasing the amount of Na_2S by 50kg/t did not change the pulp potential. The highest metallurgical and selective separation of Molybdenite from Mo-Cu concentrate were achieved at pH= 10.5 and ORP<-300 mV. Nitrogen aeration in the frothing stage caused that pulp potential became more reducing, resulting in decreasing Na_2S consumption from 16kg/t to 6kg/t at a constant metallurgical efficiency in rougher flotation. In such a condition, the recovery of 92.88% and the separation efficiency of 90.03% were achieved in flotation of molybdenite, comprising only 3% of copper minerals.

Keywords : *Cu-Mo concentrate, Nitrogen, Pulp potential, Separation efficiency, Sodium sulphide*

1. Introduction

Molybdenite (MoS_2) is naturally a hydrophobic mineral and is the most important molybdenum source to be usually associated with copper sulfide ore as a trace mineral [1-4]. Because of large differences between the surface properties of molybdenite and other sulfides, molybdenite can be recovered from Cu–Mo ores as a by-product with copper at levels as low as 0.01% Mo. Approximately half of the world's molybdenum production comes from porphyry Cu–Mo ores [5-7]. Since molybdenite is a valuable mineral, high recovery and efficient separation from copper sulfide is very important. Molybdenite floatability is influenced by a number of factors such as particle size and shape, face/edge ratio, degree of crystallization, pH, pulp potential, reagents, etc. [7]. Conventional separation of copper sulfide and molybdenite has been achieved with sulfide bulk flotation followed by selective molybdenite flotation by Na_2S/NaSH addition, because Na_2S/NaSH acts as a depressant for copper sulfide in the appropriate pulp potential [7].

It was found that changes in pulp potential as an effective factor resulted in dual effects of Na_2S and NaSH on flotation and depression behavior of sulphide minerals. In other words, both flotation and depression of sulphide minerals could be achieved through controlling the pulp potentials [1, 8]. Several studies, investigated the effect of potential in chalcopyrite-molybdenite separation. The potentials were reported with reference to the standard Ag/AgCl electrode. The results demonstrated that the flotation of chalcopyrite was large only when the potential exceeded 100 mV [9-11]. Based on thermodynamics, it is expected that dixanthogen will form at potentials greater than 100 mV at a pH of 10.5 –11 [11]. In other word, chalcopyrite depression occurs due to inability of the collector to be oxidized under pulp reducing conditions, and therefore, monitoring pulp potential is a key parameter in the reagent adsorption and the species formed on the surface [9-13].

In addition, it has been reported that the hydrosulfide ion (HS^-), which is the result of hydrolysis and dissociation of Na_2S, removes the collectors from chalcopyrite surface in an appropriate reducing condition as follow [1, 8]:

$$2CuX + HS^- + OH^- \rightarrow Cu_2S + H_2O + 2X^- \qquad (X = \text{Xanthate})$$

However, in presence of air for achieving reducing potential and depression of chalcopyrite, a considerable amount of Na_2S/NaSH is required. The use of nitrogen in the flotation of different ores has been tested in the past two decades and it was established that in presence of nitrogen, improved (a) in some cases, floatability of certain minerals (gold sulfides) and (b) depression of certain minerals (pyrrhotite and copper in copper–moly separation) [1]. Using nitrogen instead of air in the flotation systems changed the pulp potential and suggested that Na_2S/NaSH consumption could be reduced. After using nitrogen in the Sarcheshmeh copper complex over 21 months, the consumption of sodium sulphide was reduced from 17.7 to 14.2 kg/t at constant metallurgy account [14].

The final produced Cu- Mo concentrate in the Sungun plant contains 0.5% of Mo and 25% of Cu. In the molybdenite plant, Cu minerals are depressed by Na_2S and molybdenite is floated with addition of diesel oil. However, a large amount of Na_2S is required for reducing the pulp potential and selective flotation.

Based on previous studies as mentioned above, it can be concluded that controlling pH and ORP (with addition of Na_2S or nitrogen gas) play a key role in the selective separation of copper minerals and molybdenite as well as in the amount of reagent consumption. In other words, by adjusting pH and pulp potential at an appropriate level, the consumption of Na_2S could be reduced significantly. Accordingly, Mo plants operation costs could be reduced significantly with decreasing the Na_2S consumption. The objective of this research is to find the appropriate flotation conditions wherein the maximum selectivity in the separation of copper mineral and molybdenite is achieved. To achieve this objective, considering the reduction of Na_2S consumption in the

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flotation, the effects of pH, pulp potential, aeration by nitrogen and air during the Mo- Cu flotation were investigated.

2. Materials and Methods

Through a systematic sampling program, a representative Cu-Mo concentrate sample was collected from the Sungun Cu-Mo concentrate thickener underflow which is the Mo plant feed. In the sampling process, increments were collected in equal time intervals of 1 h. The gross samples were obtained by mixing 168 increments collected in equal time intervals within one week. The weight of collected samples from the plant's feed was more than 185 kg.

The chemical analysis of collected gross samples indicated that the concentrate contained 25.2% Cu and 0.49% Mo. Mineralogical studies were performed on polish sections prepared for each size fraction under an optical microscope (U-LH100, Japan). Mineralogical studies revealed that chalcopyrite and molybdenite were the major Cu and Mo minerals, respectively. Covellite, bornite and chalcocite were identified as the minor sulphide copper phases in the concentrate. Particle size analysis by a Cyclosizer (*Warman International Cyclosizer, USA)* indicated that 90% of particles size was minus 44 µm and 28.14% minus 11 µm. Fig. 1 presents the particle size distribution of the initial sample. D_{80} of the gross sample was 37.3 µm using trend line in EXCEL.

Flotation experiments were performed in a 2.5l Denver laboratory flotation cell. The pH was adjusted by lime and Merck sulfuric acid. Na_2S was applied as copper minerals depressant and also flotation pulp potential adjustment. 50 g/t diesel oil was used as molybdenite collector. Flotation pulp potential measured with an ORP electrode (Ag/AgCl) in presence of nitrogen gas and air. Air/nitrogen flow rate was adjusted at 2.25 l/min. The pulp potential including pH and oxidized- reduction potential were measured by pH and ORP electrodes (Metrohm 827, Switzerland), respectively. Mo and Cu content of samples were analyzed by ICP-OES instrument (Varian 735, Australia).

The recovery of Mo, Cu and the separation efficiency of molybdenite (S.E) were calculated and reported in graphs. Separation efficiency is the metallurgical efficiency of the separation. In other word, it deals with quality of separation between gangue and valuable mineral. It can can be calculated by [15]:

$$S.E = 100\,\frac{C}{F}\left(\frac{c}{f} - \frac{m-c}{m-f}\right)$$

Where c, f and m denote the content of Mo in the concentrate, feed and molybdenite structure, respectively. C and F respectively refer to the weight of concentrate and feed.

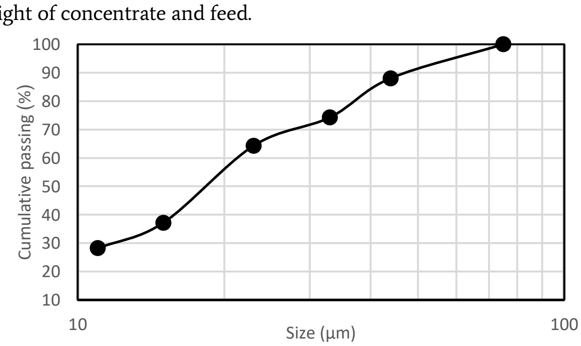

Fig. 1: Particle size distribution of Cu- Mo concentrate.

3. Results and discussion

Changes in ORP and pH were recorded and monitored as a function of Na_2S dosage as shown in Fig. 2A. The results illustrate that adding 16 kg/t Na_2S to pulp with aeration decreases the initial potential from +228mV to -597 mV. Increasing Na_2S from 16kg/t to 50kg/t did not change significantly the pulp potential. In other words, the pulp initial potential remained in a steady state when more than about 16 kg/t Na_2S was consumed.

Effects of Na_2S addition on pH factor is also given in Fig. 2B. It is obvious that adding up to 10 kg/t Na_2S increased the pH up to 12. Afterwards pH remained almost unchanged. It has been thought that, sodium sulfide, in solution hydrolyzes and releases OH^-, S^{2-}, and HS^- ions. As a result, the pulp becomes alkaline and more reducing condition [15].

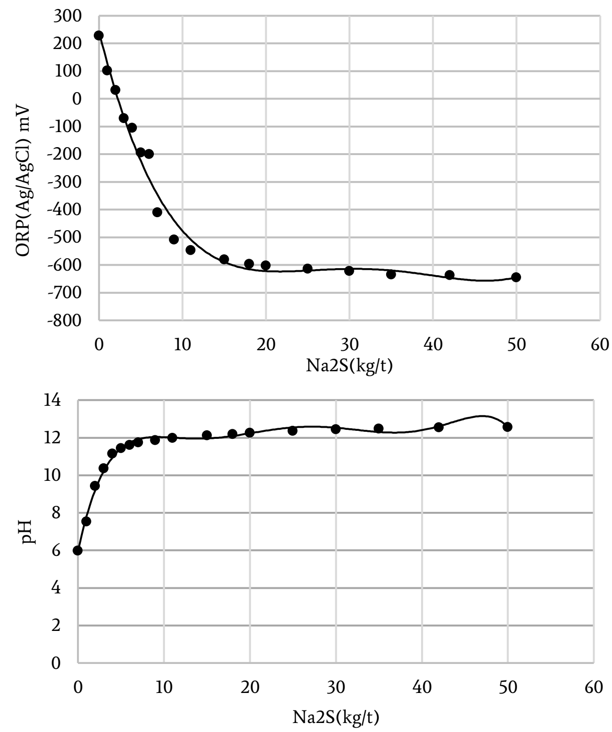

Fig. 2: A: Initial pulp potential, B: pH variations vs. Na_2S addition in aeration.

Changes in pulp potential after Na_2S addition, as a function of time was monitored and presented in Fig. 3. It can be seen that adding 16 kg/t Na_2S, dropped the initial potential from+220 mV to -585mV after 30s. By opening, then, the aeration valve, the pulp potential gradually increased directly as a function of time. After lasting 240s (4mins) from the beginning, pulp potential raised to -400mV. Previous investigators proposed that an appropriate pulp potential in selective flotation of Mo from Cu-MO concentrate should be lower than -400mV [8, 11, 16]. Therefore, Na_2S addition was made in a stepwise procedure during the flotation experiments, including the addition in the flotation conditioning stage and 4 minutes lasting frothing.

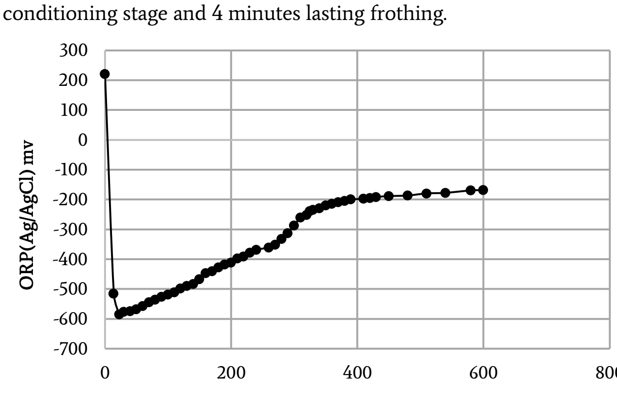

Fig. 3: The variation of the pulp potential as a function of time after addition of 16kg/t Na_2S and aeration.

3.1. Effects of solid percent and pH at low level of Na_2S

The recovery of Cu and Mo minerals in presence of air/nitrogen gas as a function of pH is shown in Fig. 4. The obtained results show that at low levels of Na_2S (6kg/t), 67.08% and 80.84% Mo was floated at pH of

10.5 and 12.5, respectively. However, in turn, 2% and 7% of copper minerals were floated besides the Mo concentrate. It means that the floatability of copper minerals at pH=10.5 is 3-4 times lower than that of pH=12.5 in presence of air. Nitrogen aeration in the frothing stage improved the recovery of Mo by 10-25%. Consequently, 92.88% Mo was floated at pH=10.5 and Na_2S= 6 kg/t. The comparison of results at pH=12.5 by air and Nitrogen aeration indicated that the floatability of Cu minerals decreased significantly from 7% to about 2.2%, and higher selectivity in separation of Mo from Cu minerals achieved in presence of nitrogen while applying less amounts of Na_2S in the flotation tests.

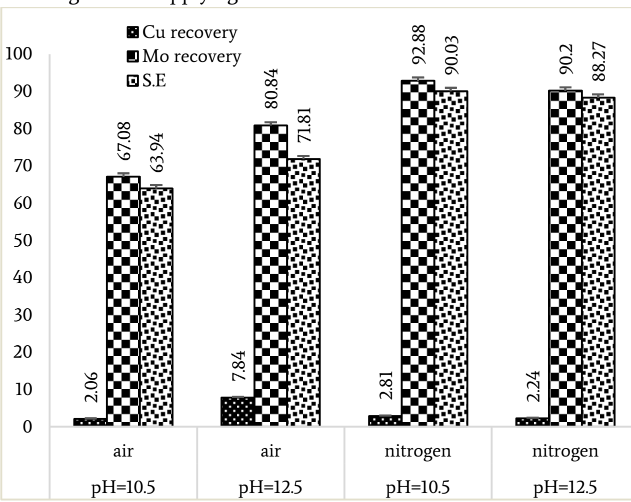

Fig. 4: Effects of pH on Mo and Cu recovery and separation efficiency (solid percent (s.p)=18% , Na_2S=6kg/t).

Fig. 5 illustrates Cu and Mo recoveries as a function of the pulp solid percent at low level of Na_2S (6kg/t). It is clear that increasing the pulp solid from 18% to 28% enhances the recovery of Mo and also the separation efficiency. This can be attributed to the fact that at high level of solid, the more Na_2S in a fixed volume, the more reducing pulp potential. In addition, using nitrogen gas in the frothing stage caused that the reducing conditions always to be maintained in the range of -200 and -300 mV (Fig. 5B), wherein 92% of Mo was recovered while only 3% Cu minerals were floated along with Mo concentrate for minimum dosage of Na_2S (6kg/t). As mentioned previously, Na_2S was added into the pulp in two stages: (1) conditioning and (2) 240s lasting frothing. It can be seen form Fig. 5B that the pulp potential significantly dropped after 240s frothing. It is because of adding Na_2S after 240s.

3.2. Effects of Na_2S quantity on the selectivity

Fig. 6 presents the variation in the separation efficiency and pulp potential at two levels of Na_2S dosage. Increasing Na_2S from 6 to 16kg/t in a pulp of 18% solid and pH=10.5 decreased the pulp potential from -100 mV to -400 mV, i.e., more reducing condition persists in the pulp. Consequently, Mo recovery increased from 67.08% to 91.74% while the floatability of copper minerals decreased from 2.04% to 0.44%. It can be concluded that pulp potential remains in a more reducing state (-400mV) when higher dosage of Na_2S is employed. Consequently, the separation efficiency for Mo improved from 63.94% to 90.98%. However, higher operation costs will persist as a result of much more Na_2S usage.

As seen from Fig. 6, the use of nitrogen in the frothing stage leads to more reducing state in pulp, resulting in reduction of Na_2S consumption. Subsequently, the separation efficiency was improved in Mo flotation from Cu-Mo concentrate. By using only 6kg/t Na_2S, the recovery of Mo peaks up to 92.88%. Similar results were obtained using 16 kg/t Na_2S in the same condition as mentioned above. In fact, nitrogen application in the frothing stage at pH= 10.5, decreased Na_2S dosage from 16 kg/t to 6kg/t without changes in metallurgical accounts.

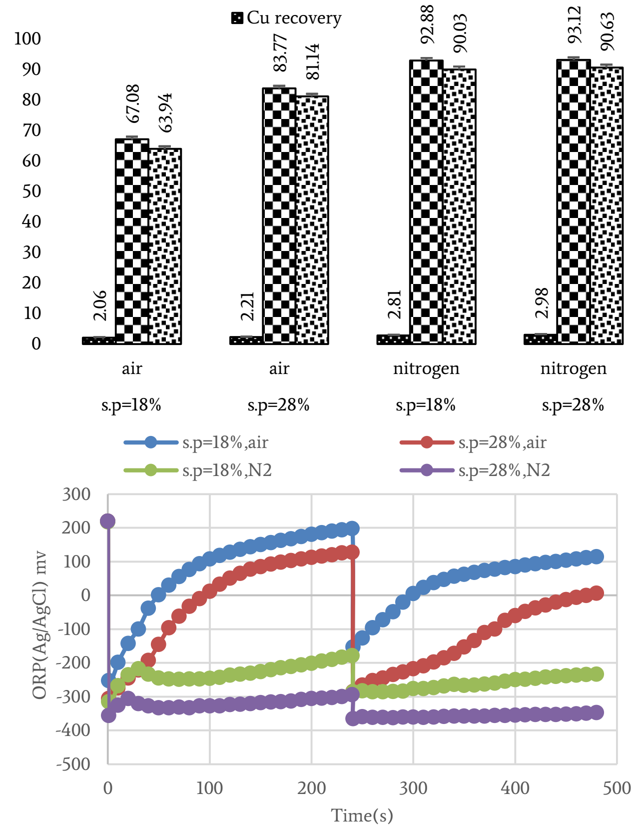

Fig. 5: A) Cu and Mo recovery, B) Changes in pulp potential vs. solid percent (s.p) changes (Na_2S =6kg/t ‹pH=10.5).

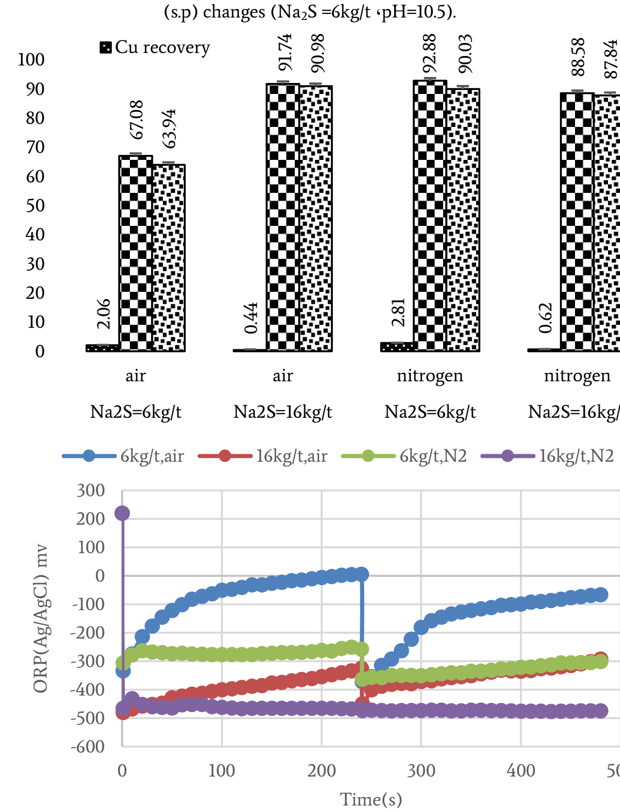

Fig. 6: A: Mo – Cu recovery and separation efficiency changes in the and low dosages of Na_2S,; B: pulp potential (pH= 10.5, solid percent=18%).

4. Conclusion

Selective separation of molybdenite from Cu-Mo concentrate was successfully performed by manipulating pH, pulp potential, solid percent, Na_2S and aeration gas. The following major conclusions can be made based on this study:

1. Na_2S addition increased pH in the pulp and led to more reducing condition in pulp. The use of more than 16kg/t Na_2S did not change the initial pulp potential significantly.
2. The highest selectivity in the separation of Mo from Mo- Cu was achieved at pH= 10.5 and ORP< -300mV.
3. Applying nitrogen gas instead of air in the frothing stage significantly decreased the consumption of Na_2S from 16kg/t to 6kg/t at pH=10.5 by preserving the same metallurgical results.

Based on the obtained result, it is strongly recommended that the Sungun Mo plant decreases pH from 12 to 10.5 in the rougher flotation stage. At such condition, Na_2S consumption can be decreased in the rougher stage. Furthermore, the possibility of applying nitrogen gas in the plant flotation cells will be evaluated.

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