Molybdenite flotation from copper/molybdenum concentrates by ozone conditioning

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Abstract—Typically, rougher molybdenite flotation and recovery from bulk copper/molybdenum concentrates involves the use of alkalifluorides, Nokes reagents, cyanides, oxidants, and/or thermal treatment to depress copper sulfide minerals. The bulk copper/molybdenum feed generally varies from 0.2%-0.4% Mo to 1.0%-Mo, and with traditional reagents the single-stage rougher flotation recovery of molybdenite varies between 40% and 90% at a concentrate grade of 5% to 10% Mo.

With ozone conditioning for copper depression, however, improved separations appear to be possible, as demonstrated by tests with Cu/Mo concentrates from both the Phelps Dodge Morenci Operations and the Kennecott Copperton Operations. Single-stage rougher flotation after ozone conditioning can provide a molybdenum concentrate at a recovery of more than 90% and a rougher concentrate grade higher than 20% Mo in some cases.

Subsequent cleaner flotation with additional ozone conditioning results in relatively copper-free molybdenum concentrates containing as much as 52% Mo.

Preliminary analysis indicates that, with a multistage ozone conditioning flotation strategy, the process is technically and economically viable and should be suitable for industrial application.

Introduction

One of the primary sources for molybdenum is the byproduct recovery of molybdenite by flotation from bulk copper/molybdenum concentrates. For this flotation system a number of different reagents are used, including alkali sulfides, Nokes reagents, cyanides, chemical oxidants, and/or thermal treatment for depression of the copper sulfide minerals (Sutulov, 1970; Castro, 1979; Crozier, 1979; Shirley, 1979; Nagara et al., 1983).

In a few cases, the molybdenite is depressed by dextrin or starch, and the copper sulfide minerals are floated away from the molybdenite (Salter, 1964; Sutulov, 1970; Castro, 1979; Shirley, 1979).

Existing flotation practice for the separation of molybdenite from copper/molybdenum concentrates generally results in low Mo recovery and requires many stages of flotation. This practice is often associated with high reagent addition, which leads to concern with respect to health, safety, and environmental issues (Jang, 1989). Thus even marginal improvements in molybdenite flotation practice would be of significant importance. In view of this situation, other techniques for the depression of copper sulfide minerals would be worthy of further investigation.

The objective of this research was to investigate and evaluate the effectiveness of ozone conditioning for the depression of copper sulfide minerals and the selective flotation of molybdenite from copper/molybdenum concentrates. The results of this research program were quite successful, and the University of Utah is now seeking patent protection for this flotation technology (Miller, Ye, and Jang, 1990).

The utilization of ozone in the flotation of sulfide minerals was first studied by Ishii et al. (1970). Since then, there has been limited study on the utilization of ozone conditioning in the flotation of sulfide minerals.

Ozone can oxidize organic compounds rapidly, thereby destroying flotation collectors adsorbed at sulfide mineral surfaces. It was reported that ozone was found to be quite effective in removing residual xanthates in alkaline solutions (Natarajan and Iwasaki, 1985), and this finding led to the differential flotation of copper/nickel sulfide concentrates by destroying residual xanthate in the pulp (Iwasaki and Malicsi, 1985). The effectiveness of ozone in removing xanthate from sulfide mineral surfaces was also reported by Matsubara et al. (1978).

In the case of coal flotation, Miller and Ye (1988, 1989) recently reported the utilization of ozone as a depressant for the selective flotation of resinite macerals from other coal macerals. In addition, ozone is commonly used in waste water treatment to remove organic matter as described in the literature (Murphy and Orr, 1975).

Experimental

Two different bulk copper/molybdenum concentrates were selected for this study, one from the Phelps Dodge Morenci Plant and the other from the Kennecott Copperton Concentrator. The Morenci sample contained chalcocite as the predominant copper sulfide mineral, while the Copperton sample contained chalcopyrite as the predominant copper sulfide mineral. Thus, these two different copper/molybdenum concentrates were quite appropriate for the evaluation of the ozone conditioning process. Both samples were final flotation products from the respective copper flotation circuits and were taken before entering the molybdenum circuit. The Morenci copper/molybdenum concentrate analyzed 0.2%-0.4% Mo and 28%-33% Cu, while the grade of the Copperton copper/molybdenum concentrate was 2.5%-4.1% Mo and 32%-34% Cu. The concentrates were received at 20%-35% solids. The particle size data show that the Copperton concentrate is of a substantially finer size (62% passing 400 mesh) than the Morenci concentrate (46% passing 400 mesh).

Slurry preparation

In general, a slurry sample for testing was first diluted with an equivalent amount of fresh water and agitated for several minutes. After agitation, the slurry was filtered. The filter cake was then repulped with fresh water to create a suspension containing 20% solids.

The purpose of this slurry preparation procedure was to remove residual flotation reagents contained in the as-received slurry samples and thus reduce their effect in the ozone conditioning and molybdenum flotation process, such that a fair comparison of the effectiveness of ozone conditioning could be obtained.

Ozone conditioning and flotation

The repulped slurry was transferred into a 4-L Galigher flotation machine. The air inlet on the flotation machine was first connected to the outlet of an ozone generator (Model 03B2-0, Ozone Research and Equipment Co.). The ozone with oxygen as the parent gas was introduced into the copper/molybdenum slurry through the air inlet and sparged naturally into the stirred suspension. The ozone was added at a rate of 0.18 g/min for various lengths of time (the conditioning time). Before and during conditioning, the pulp pH was adjusted by H2SO4 or Ca(OH)2 to the desired value. The frother then was added and flotation conducted at 1000 rpm and an air flowrate of 6 L/min.

The frother type and level of addition were examined as a process variable. In general, for single-stage flotation isopropyl alcohol was added first and flotation carried out for 4 min. After that, MIBC was added and the flotation carried out for an additional 4 min. The overall flotation time for one experiment was, therefore, 8 min. After flotation, both the concentrate and tailings products were filtered, dried and analyzed. The purpose of this two-step frother addition will be discussed later.

Product analyses

The chemical analyses of the flotation products (% Cu or Mo) was accomplished with an X-Met 820, which, after appropriate calibration, measures the elemental composition based on energy dispersive X-ray fluorescence. Using 22 standard samples provided by the Morenci plant with known chemical analyses, calibration curves were established for Cu (primarily chalcocite) and Mo. These curves were subsequently used to determine the chemical composition of the flotation products.

For the copper/molybdenum concentrate from the Copperton concentrator, calibration curves for Cu (primarily chalcocite) and Mo were constructed with 22 standard samples obtained from the Copperton concentrator for the same purpose. The Cu/Mo analysis using the X-Met 820 involves a maximum error at about 5% of the chemically analyzed value, i.e.,

\[
\left( \frac{\text{X-Met 820 analysis} - \text{chemical analysis}}{\text{chemical analysis}} \right) = \pm 0.05
\]

In many instances, the error was considerably less. In the case of rougher concentrates, the error from analysis was usually less than 2%. Finally, for reclaimer flotation experiments to produce a final high-grade molybdenum concentrate, chemical analysis was provided by Phelps Dodge.

Experimental results

There were two major objectives in this present study of selective molybdenite flotation by the ozone conditioning process. One objective was to investigate the effectiveness of the process and to determine the best conditions for separation during single-stage batch flotation. Economics were not taken into consideration during this phase of the research program.

The second objective was to search for a rational process strategy for industrial utilization. In this case, multistage flotation is required, since each stage of ozone conditioning and flotation is not necessarily controlled at optimal separation efficiency. Economic considerations are the key issue throughout this phase of the research involving process design. As a result of these two objectives, over one hundred tests were conducted (Jang, 1989). Only relevant results of greatest significance are presented in this paper.

Single-stage batch flotation

In these tests, ozone conditioning time, pulp pH, and reagent schedule were the major parameters investigated. Experimental results are given separately for the Morenci and Copperton samples.

Morenci copper/molybdenum concentrate: Typical experimental results from single-stage batch flotation of the Morenci copper/molybdenum concentrate are presented in Fig. 1, which describes the effect of ozone conditioning time on flotation recovery and concentrate grade.

Chalcocite is quickly depressed upon contact with ozone, as is evident by the significant drop in copper recovery during the first six minutes. Molybdenum recovery, however, is initially improved during short ozone conditioning times and then gradually decreases when the conditioning time is extended. The initial increase in Mo recovery appears to be related to a bubble-loading effect. Basically, molybdenite is more resistant to ozone oxidation than chalcocite (compare Mo flotation recovery at 3 min ozone conditioning time with that at 60 min conditioning time).

Surface oxidation and depression of molybdenite by ozone conditioning is slow. On the other hand, chalcocite particles are depressed almost instantaneously, and consequently more bubble surface is available for the attachment of molybdenite particles, bringing an increase in Mo recovery. With the extension of the ozone conditioning time, the bubble-loading effect is not further
improved, since the majority of the chalcocite particles have already been depressed. Eventually, some surface oxidation of molybdenum begins to occur, causing a drop in Mo flotation recovery.

Fig. 2 gives the flotation recovery and concentrate grade for molybdenum as a function of pulp pH at a fixed ozone conditioning time of 30 min. Mo grade in the concentrate is found to be highest at a pH of 7 to 10. However, further experiments revealed that there is a relation between optimal ozone conditioning time and pulp pH for selective Mo flotation. Such a relationship, based on experimental data, is given in Figs. 3, 4 and 5 as response surface and contour plots for the Mo grade, flotation recovery, and coefficient of separation, respectively.

![Fig. 2—Effect of pulp pH on single-stage flotation for the Morenci Cu/Mo sample at a constant ozone conditioning time of 30 min.](image1)

![Fig. 3—Response surface and contour plots for Mo grade as a function of pH and ozone conditioning time.](image2)

![Fig. 4—Response surface and contour plots for Mo recovery as a function of pH and ozone conditioning time.](image3)

![Fig. 5—Response surface and contour plots for the coefficient of separation as a function of pH and ozone conditioning time.](image4)
These results are discussed later, but it is evident that further research will be required to fully explain the observed behavior.

The results presented in Fig. 6 provide an example of a general rule of thumb for the effect of frother on Mo flotation recovery and concentrate grade. Unlike other single-stage flotation experiments, in this case, only one stage of frother addition was made at a dosage of 0.3 kg/ton in each test. As the hydrocarbon chain length of the frother increases, the flotation recovery of Mo is improved, while the concentrate grade drops. The frothers used in this study were ethyl alcohol (C2), isopropyl alcohol (C3), isobutyl alcohol (C4), and MIBC (C6).

Copperton copper/molybdenum concentrate: Both molybdenite and chalcopyrite in the Copperton copper/molybdenum concentrate have a relatively poor floatability in comparison with the molybdenite and chalcocite from the Morenci copper/molybdenum concentrate. Since neither molybdenite nor chalcopyrite floated well in the laboratory, kerosene was added and the pulp conditioned in the flotation cell before ozone conditioning.

The purpose of the kerosene addition was first to make both molybdenite and chalcopyrite easy to float prior to subsequent chalcopyrite depression by ozone conditioning. Thus, the selective flotation of molybdenite from chalcopyrite was achieved.

Experimental data from this phase of the work are presented in Fig. 7. As can be seen from the figure, with 0.4 kg/ton kerosene addition prior to the ozone conditioning, both molybdenite and chalcocite became more hydrophobic, and flotation recoveries of about 95% and 87% were achieved for Mo and Cu, respectively. After ozone addition, chalcopyrite was depressed quickly, resulting in a selective flotation of molybdenite. For example, with 15 min of ozone conditioning, Mo recovery still remained at 86.2%, while the Cu recovery dropped to only 29.3%.

Obviously, there should exist a certain correlation between optimum kerosene dosage and ozone conditioning time for the best separation of molybdenite from chalcopyrite. However, single-stage flotation experiments on this matter were not carried out; because the search for such a correlation would be exhaustive, and only a general demonstration of the effectiveness of ozone conditioning for selective molybdenite flotation from the copper/molybdenum concentrate was desired. In any event, the optimum conditions for single-stage flotation are probably not the optimum conditions for a multistage process strategy ultimately required for industrial utilization.

Multistage flotation

As can be noted from the single-stage batch flotation testing for both the Morenci and Copperton Concentrate, the ozone conditioning time needed to achieve satisfactory flotation separation of molybdenite from copper sulfide minerals is relatively long, and the process under these circumstances is not economical. Since the Mo content in the Morenci copper/molybdenum feed is only 0.2%-0.4% and the majority of the copper sulfide mineral particles can be effectively depressed at short ozone conditioning times, it is quite natural to suggest a multistage flotation process in which the majority of the copper sulfide mineral particles is rejected first in a rougher flotation at a short ozone conditioning time. The copper sulfide mineral particles which are not depressed and are collected in the rougher concentrate with molybdenite can be reconditioned and depressed during cleaner and re-cleaner flotation. With this process strategy, ozone consumption will be reduced significantly over that required for single-stage flotation.

This phase of the research was conducted with two different Morenci samples, the low-grade copper/molybdenum concentrate being fed to the molybdenum plant containing 0.25% Mo, and an intermediate product, the rougher flotation concentrate, from the molybdenum plant, containing about 34% Mo.
Flotation of low-grade copper/molybdenum feed: For this low-grade feed material, the experimental flowsheet is given in Fig. 8. The feed material, containing about 0.25% Mo, was first conditioned and floated with 2 min ozone conditioning time and 0.01 kg/ton MIBC addition at 20% solids in a 4-L Galigher flotation machine. This rougher flotation was repeated for many batch experiments until enough rougher concentrate was collected.

An average Mo recovery of 89.5% was obtained during rougher flotation, with 10.5% of the Mo rejected to the rougher tailings. The rougher concentrates were repulped, mixed together, and placed in a 2-L Galigher flotation cell at 20% solids by weight. The composite slurry was conditioned for an additional 3 min with ozone, and then 0.1 kg/ton isopropyl alcohol was added (dosage is with respect to rougher feed), and cleaner flotation was carried out.

Cleaner flotation yielded a cleaner concentrate containing 26.0% Mo at 92.2% recovery from the rougher concentrate, which corresponds to an overall Mo recovery of 82.5% from the feed to the molybdenum plant. The cleaner flotation tailings contained about 0.23% Mo and in practice could be recycled back to rougher flotation.

The tailings rejected from rougher flotation were also reconditioned with ozone for 1 min, and a scavenger flotation step was conducted without addition of any flotation reagent. During scavenger flotation, 89.9% Mo in the rougher tailings was recovered in the scavenger concentrate at a grade of 1.64%. In plant practice, this scavenger froth product might be sent to cleaner flotation.

With the above flotation strategy, an overall molybdenum recovery of 98.9% might be expected at a cleaner concentrate grade of 26.0% Mo with 0.01 kg/ton MIBC and 0.1 kg/ton MIBC addition.
The ozone consumption for this phase of work was 0.72 kg O$_3$/ton of molybdenum plant feed, or 0.29 kg O$_3$/kg of Mo recovered.

Flotation of intermediate product from the molybdenum plant: Since the Mo content of the molybdenum plant feed material is so low, the froth product collected during laboratory batch flotation was not enough to investigate further upgrading with regard to the concentrate by the ozone conditioning process. Consequently, another intermediate product from the molybdenum plant having a higher Mo content (34% Mo, 9% Cu) was used. Although this feed material is different from that collected during previous flotation experiments with ozone conditioning, this testing was conducted mainly to demonstrate the effectiveness of the ozone conditioning process to produce a high-purity final molybdenum concentrate.

Two stages of flotation were used for this feed material. Initial recleaner flotation was done at 10% solids in a 4-L Galigher cell, with 3 min ozone conditioning, 0.1 kg/ton isopropyl alcohol addition. The ozone consumption for this procedure was 2.1 kg O$_3$/ton of this intermediate product feed.

As shown in Fig. 9, the final recleaner flotation step can produce a low-copper molybdenum concentrate. Even at a cumulative recovery of 84.8% Mo (68.3% with respect to the feed), the Cu content in the concentrate is still below 2.3%. In the meantime, the cumulative Mo grade is at 46.3%. Product analysis during this phase of the work was provided by Phelps Dodge, Morenci Branch. The analysis shows that the final molybdenum concentrate is contaminated with insol (talc) at 14.6%, which is not separated from Mo under these conditions, although such a separation is possible (Miller, Ye and Jang, 1990).

Conditioning with ozone-saturated water

In view of the fact that most of the O$_3$ introduced into the system may actually have been dissipated to the atmosphere before reacting with the mineral particles, an experiment with ozone-saturated water was also carried out. In this experiment, 150 g of this dry intermediate product material was placed in 2 L of ozone-saturated water for 8 hr and then floated. Only one stage of flotation was done.

Experimental results with the intermediate product containing 34% Mo are given in Fig. 10 and plotted as cumulative Cu grade and cumulative Mo grade vs. Mo recovery. As a comparison, the results from blank tests without ozone are also given in the figure. As can be seen, a significant improvement in Cu rejection is achieved after conditioning with ozone-saturated water. The ozone consumption in this case according to experimental conditions and O$_3$ solubility data from the literature (Emmert and Pigford, 1963) is 0.09 kg/ton feed. However, conditioning with ozone-saturated water for the plant feed material containing 0.25% Mo only resulted in a limited improvement in copper rejection when compared to a blank test. This is probably due to the large amount of chalcocite present in the low-grade plant feed that exhausts the ozone before a significant depression of chalcocite can be realized.

Based on these two experiments, it is speculated that a minimum ozone consumption of 0.24 kg O$_3$/ton of chalcocite is required for significant Cu depression (low-grade feed contains average 30% Cu, chalcocite = 30% x 159/127 = 37.5%, minimal ozone consumption = 0.09/0.375 = 0.24 kg/ton chalcocite).

Discussion

Chemistry

Obviously, chalcocite, chalcopyrite, and molybdenite can all be oxidized by ozone. In general, the oxidation produces a variety of reaction products, many of which are hydrophilic. The exact nature of these oxidation products is a function of system pH and the extent of oxidation.

Many investigators have reported on the oxidation of sulfide minerals with various oxidants. Only limited research has been reported on the oxidation of sulfide minerals with ozone, and the exact nature of the ozone reaction products at the surfaces of chalcocite, chalcopyrite, and molybdenite are unknown.

Oxidation by ozone appears to be promoted at high pH, as suggested by the data presented in Fig. 2, which show an increase in the grade of the Mo concentrate as the pulp pH is increased all the way up to pH 10 due to a significant depression of chalcocite. In the meantime, the flotation recovery of Mo is also gradually decreased as the pulp pH is raised, showing that a slight depression of Mo occurs concurrently.

Data on response surface and contour plots for Mo grade and recovery given in Figs. 3 and 4 show that the effectiveness of
ozone depression for chalcocite and molybdenite varies with both pulp pH and ozone conditioning time. These results are understood to be indicative of specific surface reactions with ozone leading to different surface states at the minerals’ surfaces; surface reactions that occur at different rates.

It appears that the selective separation of molybdenite from copper sulfide minerals by ozone oxidation observed from this current work is possibly due to the difference in the nature of the surface oxidation reactions (particularly rate) between the molybdenite and the copper sulfide minerals. Molybdenite is more resistant to ozone oxidation and has a slower oxidation rate. This conclusion is supported by a comparison of the dependence of Cu recovery and Mo recovery on ozone conditioning time as revealed in Figs. 1 and 7. In both cases, the flotation recovery of chalcocite (Fig. 1) and chalcopyrite (Fig. 7) is quite sensitive to ozone exposure when compared to the flotation response of molybdenite. In future work, detailed study with respect to reaction mechanisms of ozone at these sulfide minerals surfaces and the nature of the reaction product will be useful in order to further develop this processing strategy.

Economics

From an economic point of view, single-stage flotation of molybdenite from copper sulfide minerals by this ozone conditioning process is not appropriate due to the high ozone consumption and waste during conditioning. However, multistage flotation makes the ozone process very attractive. In multistage flotation, the strategy used is to first reject the majority of the easily depressed copper sulfide mineral particles by rougher flotation with a short ozone conditioning time. The rest of the copper sulfide mineral particles that report to the rougher Mo concentrate can be reconditioned and depressed by ozone during subsequent ozone conditioning and flotation.

In this way, ozone consumption in terms of kilograms per ton of feed or per kilogram of Mo recovered is very low. As shown by the data given previously, for the low-grade copper/molybdenum concentrate (0.25% Mo), the feed to rougher molybdenum flotation, Mo might be upgraded to 26% at a recovery of 98.9% recovery in three stages at an ozone consumption of only 0.72 kg O3/ton of feed or 0.29 kg O3/kg of Mo recovered. Once a high-grade Mo product is obtained, further up-grading of Mo from a feed of 34% Mo and 9% Cu to a product with low copper content (2.3% Cu) consumes very little ozone (the analysis indicates only an incremental consumption of about 0.05 kg O3 per ton of low-grade feed to the molybdenum plant).

If we assume that the flotation response and product quality from the test with this 34% Mo feed material can be considered similar to that with a 26% Mo feed material obtained from the cleaner flotation shown in Fig. 8, then the total ozone consumption to produce a high-purity product of the quality shown in Fig. 9 from a feed containing 0.25% Mo with five stages of flotation is only about 0.75 kg/ton of feed to the molybdenum plant, or less than 0.5 kg O3 per kg of Mo recovered as a relatively copper-free MoS2 product.

With today’s technology, it is common to produce ozone at an energy demand of 20 kWh/kg O3 with air being used as the parent gas. In this way, the cost of ozone conditioning to produce a relatively copper-free product from a copper/molybdenum concentrate containing 0.25% Mo is less than $0.50/kg of Mo recovered, compared to the current reagent cost of about $2/kg of Mo recovered by conventional flotation practice. Other associated operating cost is not included in this calculation.

As stated before, much of the ozone introduced into the system actually may have been dissipated to the atmosphere before reaction with the mineral particles in suspension. Oxidation by ozone-saturated water is another effective way to reduce the cost associated with this conditioning process. The high solubility and stability of ozone in water (Henry’s law constant at 4570 for 25°C) makes this ozone conditioning process economically attractive. Based on experimental results presented previously, a minimum of 0.24 kg O3/ton is required for chalcocite depression. This conditioning technique using ozone-saturated water thus requires a relatively low solids concentration during conditioning. Nevertheless, there is little doubt that by appropriate control of design and operating variables the ozone conditioning process for selective molybdenite flotation from Cu/Mo concentrates is both technically and economically viable.

Conclusion

It has been demonstrated from the present work that ozone treatment is an effective and economically attractive method for the selective separation of molybdenite from copper/molybdenum concentrates. Under the experimental conditions selected, the cost of ozone conditioning is estimated at about $0.50 per kilogram of Mo recovered as relatively copper-free molybdenite flotation concentrate.

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