CIRCULAR 106

Selective Flotation of Molybdenite from Chalcopyrite Concentrates by Potassium Permanganate

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STATE BUREAU OF MINES AND MINERAL RESOURCES NEW
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INTRODUCTION

It is well known that potassium permanganate has excellent oxidizing characteristics in flotation systems. The exact mechanism by which the permanganate performs its useful functions in the process has been the subject of recent studies at the New Mexico State Bureau of Mines and Mineral Resources.

Treatment of collector-coated flotation concentrates with $KMnO_4$ oxidizes the organic constituents of the adsorbed layer on the mineral surface and renders the floated particles nonfloatable (Escalera, Bhappu,. and Reidies, 1970). In addition to its tendency to oxidize selectively, permanganate, when chemically reduced, also forms a hydrous manganese oxide ($MnO_x \cdot XH_2O$) that may precipitate on the surfaces of certain components of the concentrate, thereby serving further to depress the floatability of these components.

The theoretical aspects of sulfide depression by permanganate oxidation have been discussed by Escalera, Bhappu, and Reidies, and this study investigated the oxidizing characteristics of permanganate on actual flotation-plant concentrates by comparing it with two other oxidizers used in the selective flotation of molybdenite.

EXPERIMENTAL WORK

In the flotation of copper sulfide ores, xanthates are usually added for collecting copper minerals. Molybdenite, being naturally hydrophobic, is easily floated with the copper minerals and must then be separated from them. In a large number of laboratory experiments and in several plant applications, $KMnO_4$ has been used to destroy the xanthate coating on the copper sulfide minerals by oxidation.

To determine the extent of copper sulfide depression by permanganate, the following variables were taken into account:

(1) concentration of reagent
(2) pH
(3) temperature
(4) time of oxidation

To ascertain depression effectiveness, two other well-known oxidants, hydrogen peroxide (H_20_2) and sodium hypochlorite (NaClO), were used for comparison.

Reagents and Mineral Sample

The $KMnO_4$ used was the technical or commercial grade, assaying 97 percent (minimum), supplied by Carus Chemical Company. The H_20_2 used was a reagent-grade (30 percent) peroxide obtained from Baker Chemical Company. The NaClO used was a commercial-grade (5.25 percent active) Clorox bleach. For all the experiments, we used tap water containing about 150 ppm hardness, from the Socorro, New Mexico, municipal water supply. The water temperature was about 30°C. Reagent-grade sulfuric acid and calcium hydroxide were used to adjust the pH.

The mineral sample used was from the Pima mine, near Tucson, Arizona; it consisted principally of chalcopyrite and pyrite with about 0.5 percent molybdenite. Potassium amyl xanthate (Z-6), lime, methylisobutylcarbinol (MIBC), and a fuel oil constituted the reagents used in the copper - flotation circuit at Pima. For all practical purposes, we considered the copper sulfide minerals to be collector-coated with xanthate.

Procedure

All tests followed this procedure:

A 100-gram sample was repulped with 1,000 ml tap water in a Denver Laboratory flotation machine. The required amount of oxidant was added **and** the pulp allowed to condition for 5 minutes. The flotation reagents (0.2 lb/ton fuel oil and 0. 1 lb/ton MIBC frother) were added and an additional 5 minutes of conditioning allowed. Flotation of molybdenite then proceeded for 3 minutes. Both the concentrates and tailings were saved, dried, and weighed to determine the copper-depression percentages.

RESULTS AND DISCUSSION

The results were plotted showing copper-flotation percentage (%F) as a function of reagent amount, the lower the percent flotation the more effective the depression.

To compensate for the strength of the different oxidants investigated, the amounts of reagent reported correspond to the total amount of oxidants added on a 100-percent active basis.

Figure 1 shows an initial effective depression at 100 mg potassium permanganate (equivalent to 0.5 lb/ton concentrate, 100 percent reagent basis), a 55 percent flotation, corresponding to 45 percent copper sulfide depression, being obtained. This initial depression becomes less effective at higher concentrations and up to 500 mg (6. 0 lb/ton) of oxidant. Above this point, depression gradually and steadily increased with increasing amounts of reagent before attaining a constant 92 percent at and above 1, 000 mg (20 lb/ton).

The reason for this decrease in depression above the first critical amount of permanganate followed by increase in depression above 500 mg and optimum depression above 1,000 mg is not clear. Oxidation of xanthate to dixanthogen obviously causes the initial depression at the lower reagent concentration. The subsequent decrease in depression may result from partial oxidation of copper sulfide mineral surfaces, which may adsorb neutral dixanthogen as a collector, thereby increasing floatability. Dixanthogens have proved to be good collectors for partly oxidized copper sulfides and cement copper under certain conditions.

The increasing oxidation of the sulfide minerals, which reduces their tendency to float, may explain the gradual and steady increase in depression above 500 mg. With excess permanganate above 1,000 mg (20 lb/ton), complete oxidation of mineral surface, plus an increasing oxidative destruction of the dixanthogen, may result in maximum depression.

Possibly, MnO2, a reaction product of permanganate and xanthate (Escalera, Bhappu, and Reidies, 1970) selectively adsorbed on the surface of the sulfide minerals, may prevent their flotation at higher permanganate amounts. Manganese dioxide has an isoelectric point at about pH 3 or 4; above this pH value it becomes negatively charged and would therefore selectively adsorb on sulfide mineral surfaces under suitable conditions. Also, more MnO_2 would be available at higher concentrations of reagent, thus increasing the depression of sulfide minerals.

Figure 2 shows the comparative depression effectiveness of the three oxidants; percentage flotation is plotted against the concentration of reagents (100 percent reagent basis). Compared to $KMnO_4$ (fig. 1), the optimum depression with $H2O_2$ occurred at 25 mg (0.5 lb/ton) of reagent with a 60

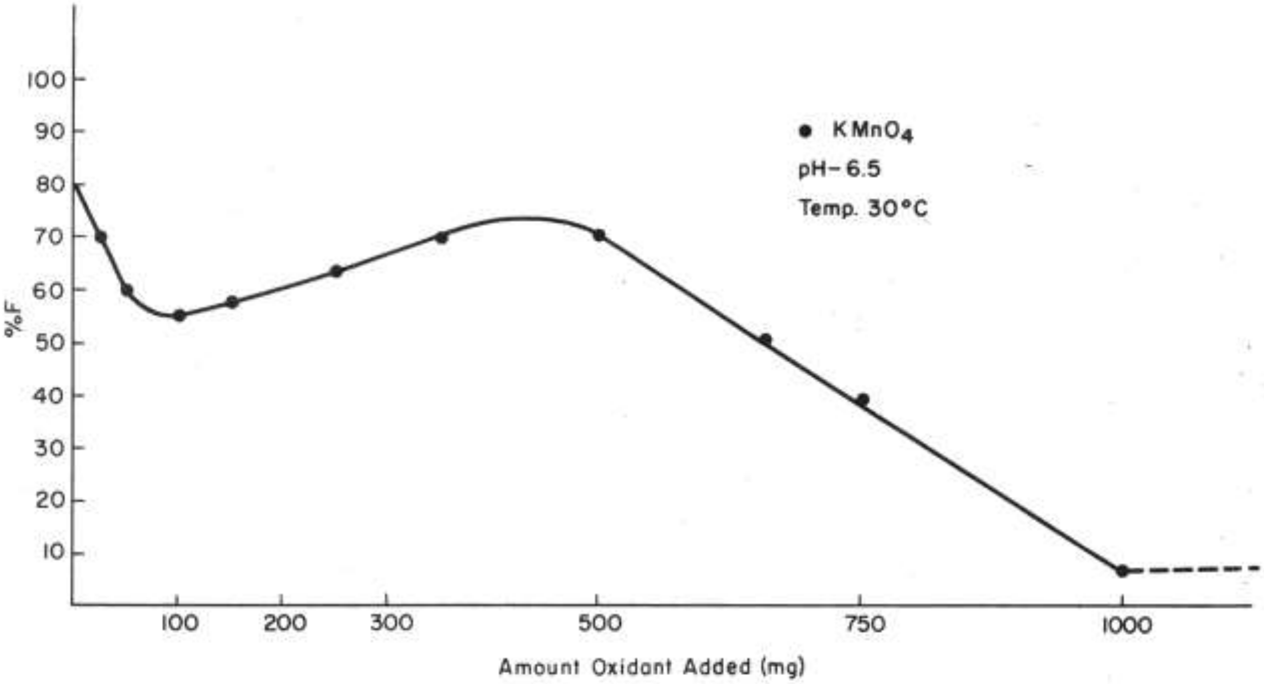

Figure 1. Depression as a function of amount of $KMnO_4$.

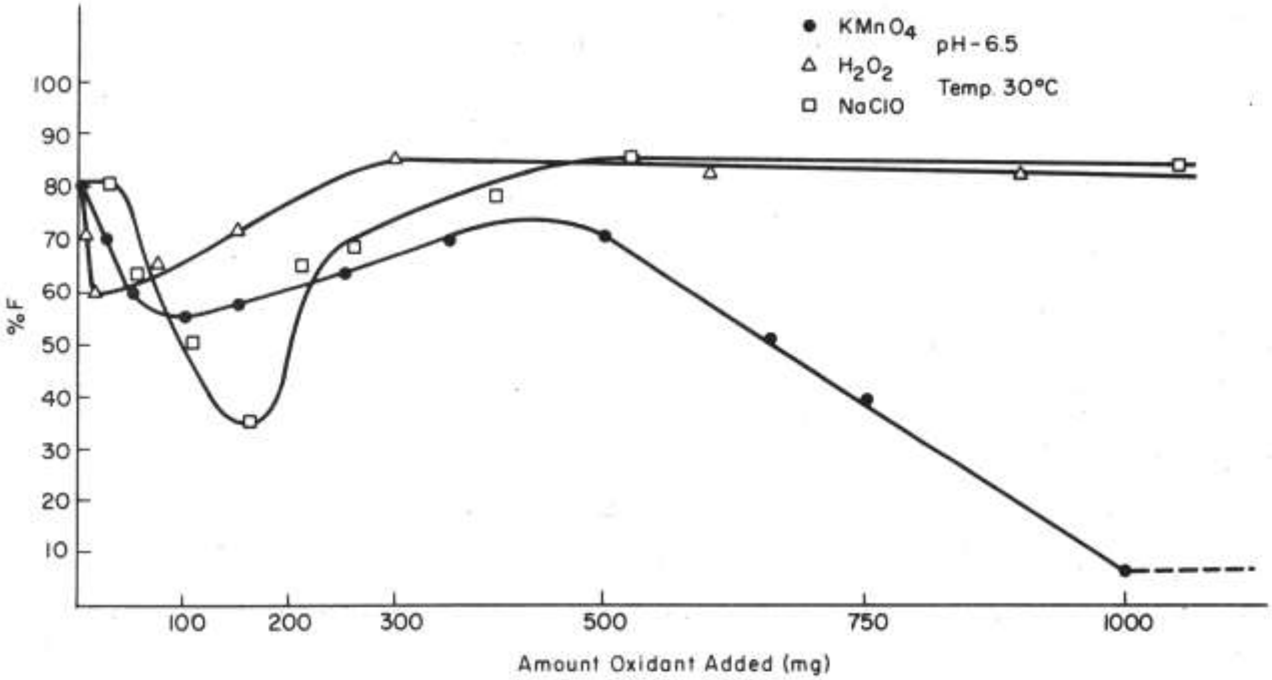

Figure 2. Depression as a function of amount of various oxidants.

percent flotation—about 15 percent better than the depression obtained with $KMnO_4$ at 25 mg. Increasing the peroxide concentration, however, did not result in improved depression, regardless of the amount used. Hypochlorite showed the best performance at lower concentrations, giving a 65 percent depression at 160 mg (3. 2 lb/ton). Neither H_2O_2 nor NaClO exhibited the increased depression at higher concentrations that was observed with KMnO4.

Figure 3 shows the same data on the basis of the oxygen content in the three oxidants. The initial maximum depression in all tests occurred at about 35 mg oxygen content, NaC1O showing the best depression (65 percent) and permanganate and peroxide showing about equal depression at this low content. $KMnO_4$ is the best depressant at higher oxygen content (400 mg); beyond this point it maintains a constant 92 percent depression regardless of the amount of oxidant used.

The above data indicate that, from a practical viewpoint, none of the reagents acts as an effective depressant at lower amounts; NaC1O, the best, achieved only a moderate 65 percent depression. At high concentrations, however, $KMnO_4$, the optimum depressant, gave an excellent 92 percent depression at 1,000 mg (20 lb/ton). Of course, this high reagent requirement would be economically unattractive in rougher flotation circuits but quite acceptable in cleaner circuits, especially in the final cleaners.

In regard to a possible explanation for depression at higher $KMnO_4$ concentrations, we ruled out the mechanism of complete oxidation of sulfide mineral surfaces with excess oxidants because the data in Figures 2 and 3 revealed that $H2O_2$ and NaClO do not exhibit depression at higher concentrations. Therefore, some other factor indigenous to or specific for permanganate must account for optimum depression. The depression effect involving slime-coating of sulfide minerals by MnO_2 seems a plausible explanation.. The presence of excess MnO_4 ions in the system may also influence the depression phenomenon.

Effect of pH

To determine the effect of pH on depression with different oxidants, standard flotation test conditions were selected on the basis of previous results; they included the amount of reagent at which best depression was observed, 100 mg (2.0 lb/ton) and 1,000 mg (20 lb/ton). The temperature of the pulp was kept constant at 30°C.

Figure 4 shows that the optimum depression for all three reagents occurs at about pH 6.5. The depression decreases on both sides of this critical point; all three curves following a somewhat similar pattern.

Of the reagents used, NaC1O gave the best depression of about 62 percent at the critical pH; it more effectively depressed at the lower amount (100 mg) of reagent as well.

Permanganate yielded only a moderate 45 percent depression at 100 mg concentration, but, with concentration of 1,000 mg or more, the depres-

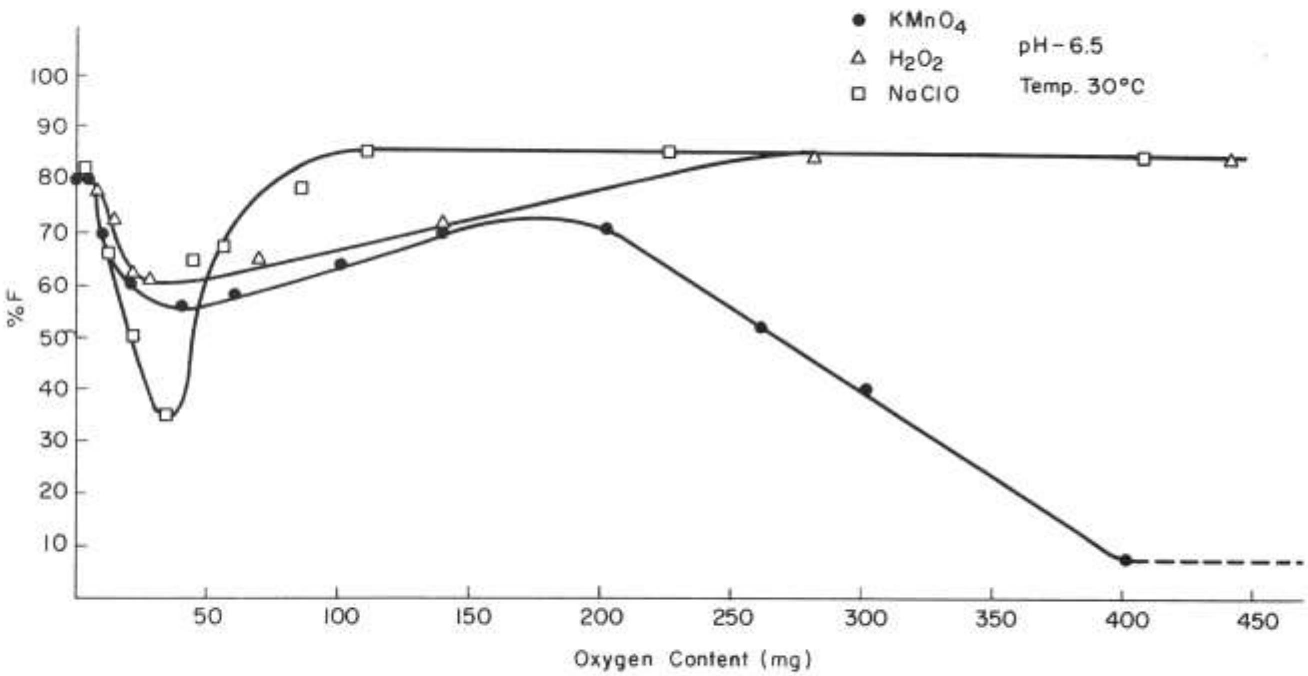

Figure 3. Depression as a function of oxygen content in the oxidants investigated.

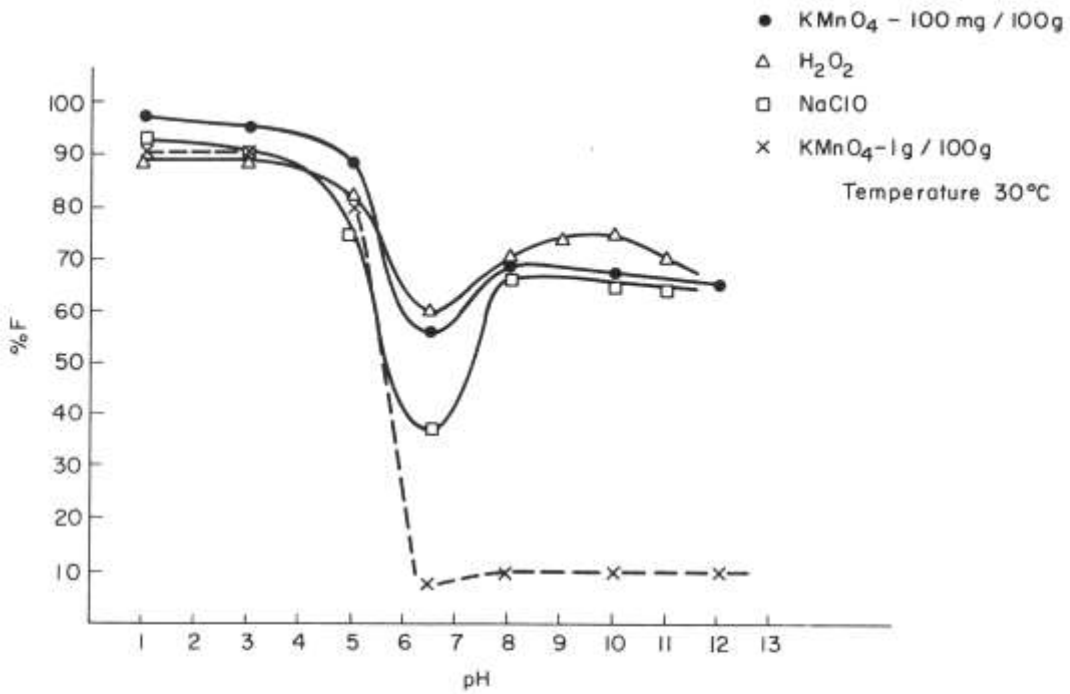

Figure 4. Depression as a function of pH of the pulp.

sion was 98 percent at pH 6.5. Hydrogen peroxide and NaClO did not show a similar effective depression at higher reagent concentrations.

The existence of this critical pH for maximum depression for all the oxidants seems to indicate that they are all stable at this pH value and that the reagents decompose in high acid and alkaline solutions. We know that permanganate is less stable in acid solutions, the decomposition being roughly proportional to the acidity; the presence of MnO_2 also promotes this degradation. In alkaline solutions, the permanganate decomposes very slowly to give oxygen and manganate. Quite probably, the other two oxidants decompose similarly. Of course, at very high concentrations of $KMnO_4$, the alkaline circuit contains enough reagent to obtain maximum depression. An additional explanation for the lack of depression on both sides of the critical pH value involves the collection mechanism of xanthate and dixanthogen.

Solutions of xanthate become saturated with respect to dixanthogen at different pH values, depending on the concentration of the xanthate ion. Every concentration of xanthate ion has a saturation pH value. Under conditions below this saturation pH value, the excess dixanthogen does not tend to convert to xanthate, provided that the equilibrium values exceed the solubility value of 1.3 x 10^{-5} moles per liter, as suggested by Pomianowski and Leja (1963). However, with an excess of dixanthogen initially present at a higher pH value, where the equilibrium values are smaller than the solubility value, the reaction of converting dixanthogen to xanthate takes place until the concentration of dixanthogen equals the equilibrium value.

The equations

$$RXH \rightleftharpoons RX^- + H^+ \qquad K_1 = \frac{[RX^-]\,[H^+]}{[RXH]} = 2 \times 10^{-2} \tag{1}$$

and

$$(RX)_2 + 2\,OH^- \rightleftharpoons 2RX^- + H_2O + \tfrac{1}{2}O_2 \quad K_2 = \frac{[RX^-]^2\, P_{O_2}^{1/2}}{[OH^-]^2\,[(RX)_2]} = 3.3 \times 10^{10} \tag{2}$$

together with

$$H_2O \rightleftharpoons H^+ + OH^- \qquad K_w = [H^+]\,[OH^-] = 10^{-14} \tag{3}$$

have a definite implication in the dixanthogen-xanthate ratio. Using the K values for the equations, the ratio of dixanthogen to xanthic acid present in xanthate solutions at different pH values and different concentrations of xanthate ions (in solutions saturated with air at 1 atm. pressure) can be expressed by

$$\frac{[(RX)_2]}{[RXH]} = \frac{1}{K_2}\;\frac{[RX^-]^2}{[OH^-]^2}\;\frac{K_1}{[RX^-]\,[H^+]} = 6 \times 10^{15}\,[RX^-][H^+] \tag{4}$$

It appears, therefore, that for the amount of xanthate present (10^{-5} to 10^{-4} M xanthate solution), on the acidic side, the concentration of dixanthogen always exceeds the xanthic acid. Even in slightly alkaline solutions, it is greater by several orders of magnitude (10^3 times). On the highly acidic side, the predominant species is dixanthogen with no xanthic acid present.

This would suggest that the dissolved dixanthogen is the active species responsible for the rise in flotation response of the mineral as the pH of the system lowers, according to

$$MS + (RX)_2 + \tfrac{1}{2}O_2 + H_2O \longrightarrow M(RX)_2 + S^0 + 2\,OH^- \qquad (5)$$

$$MSO_4 + (RX)_2 \longrightarrow M(RX)_2 + SO_4^{-2} \qquad (6)$$

or the alternate suggested by Leja (1957):

$$MS + (RX)_2 \longrightarrow M(RX)_2 + S^0 \qquad (7)$$

Adsorption of dixanthogen by the mineral surface would satisfy the theoretical deduction of Cook and Nixon (1950) that the active species in adsorption from oxidized xanthate solutions is the molecular dixanthogen rather than the xanthic acid.

Effect of Temperature

We determined the effect of temperature on permanganate and the other two oxidants examined by running a series of tests at pH 6.5 and using two reagent concentration levels, 100 mg (2 lb/ton) and 1,000 mg (20 lb/ton). The results (fig. 5) indicate little correlation, suggesting that the influence of temperature on depression depends on the characteristics of the individual reagent. Maximum depressions at the 100 mg concentration level for the different reagents were

$KMnO_4$	45 percent depression at 30°C
H_2O_2	60 percent depression at 40°C
NaClO	80 percent depression at 50°C

Clearly, hypochlorite depressed best at lower reagent concentration. At higher concentrations (20 lb/ton), however, permanganate is an exceptionally effective depressant. The depression is most effective at lower temperatures (15 to 30°C), with a maximum at 30°C; above this critical temperature, depression is very poor.

The general U shape of the curves in Figure 5 corresponds to that obtained for reagent concentration and pH, differing mainly in the occurrence of maximum depression at different temperatures. Moreover, the depression shown by H_2O_2 and NaClO increases at higher temperatures up to critical values.

The differences in the critical temperatures of maximum depression shown by the oxidants cannot be explained on the basis of thermal decompo-

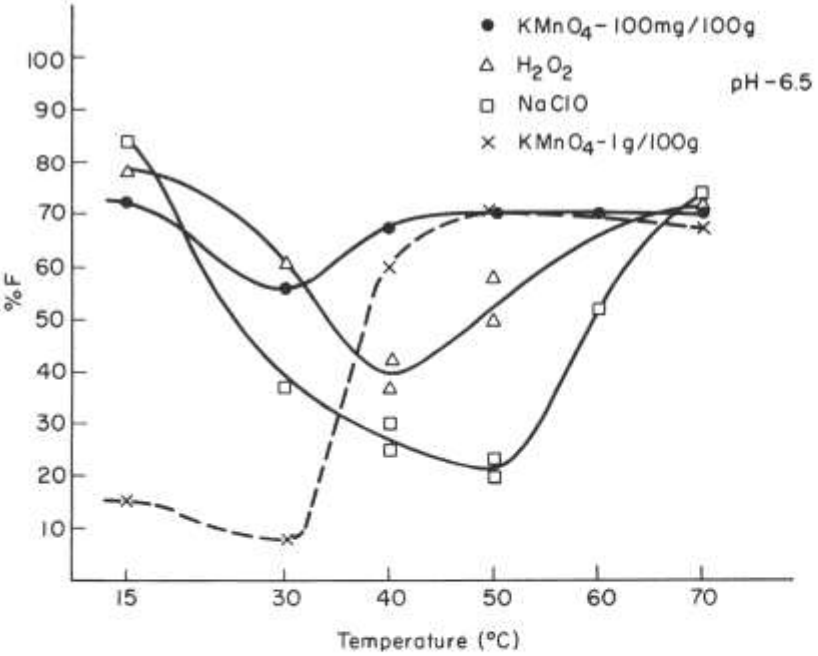

Figure 5. Depression as a function of temperature.

sition of the reagents alone, since oxidants such as permanganate are quite stable at neutral pH even at 100°C in the absence of impurities. However, their decomposition at higher temperature becomes critical in the presence of reducing materials and fine particles (Wiberg, 1965, p. 20), and it seems logical to assume that this is the case in our flotation system.

In the case of aqueous permanganate, for example, the decomposition being autocatalytic, due to the precipitation of MnO_2, which acts as a catalyst, there is a better chance for the decomposition to occur at lower temperature (about 30°C) than for the other oxidants. Hydrogen peroxide decomposes somewhat slowly at 40°C. As for hypochlorite, it does not appear to decompose at all up to 50°C and may act as a superior depressant not only because of its oxidation power but also because of the contained chlorine available upon decomposition.

Effect of Time

In some flotation systems, time of conditioning and time of flotation play important parts in either floating or depressing the minerals and generally influencing the over - all results. With sulfide minerals especially, the depressed sulfides begin to float after 7 to 10 minutes of flotation time. Because of the importance of this variable in molybdenite flotation systems, we tried to determine the effect of time under standard flotation conditions:

pH 6.5, 30°C, and reagent concentration levels of 100 mg and 1,000 mg. The pulp was conditioned for selected periods of time up to 1 hour and floated for 3 minutes.

Figure 6 shows the effectiveness of depression as a function of conditioning time for the three oxidants. Permanganate at the 100-mg concentration level showed a constant depression of about 45 percent for 10 minutes, after which the effectiveness decreased about 15 percent over the next 50 minutes. At the 1,000-mg level, permanganate produced about 90 percent depression for the first 8 minutes, after which the depression decreased rapidly to about 30 percent in the next 15 minutes, then decreased gradually during the rest of the hour.

In comparison, NaClO at the lower concentration level showed improvement in depression over an hour's conditioning period. Depression of a mere 30 percent occurred in the first 3 minutes, followed by a significant depression increase up to 80 percent after one hour. Hydrogen peroxide showed similar behavior, except for a less effective over-all depression.

Permanganate decomposes and loses its oxidizing capacity within 10 minutes, even at a very high concentration. This decomposition is probably due to further oxidation of the dixanthogen with possible formation of CO_2, H_20, and $SO_4^=$. For this reason, practical applications employing perman-

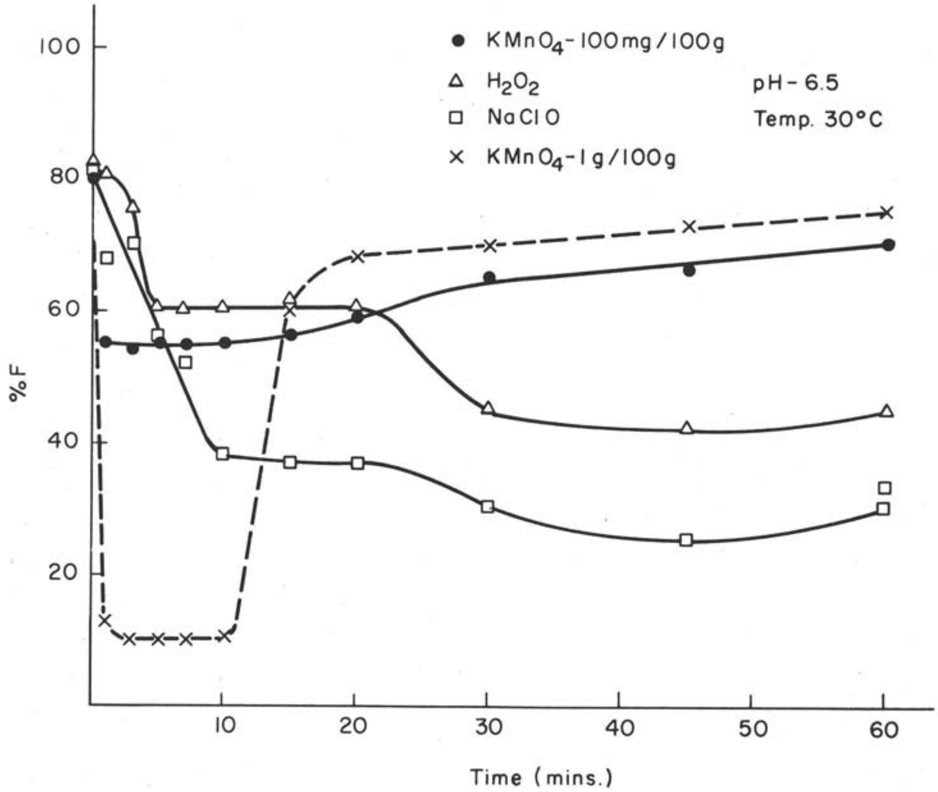

Figure 6. Depression as a function of conditioning time.

ganate must make provisions to limit the conditioning and the flotation time to 10 minutes. Operators would find it beneficial to add the required reagent separately to each cleaner circuit to obtain maximum depression effectiveness.

Hydrogen peroxide and hypochlorite do not appear to decompose with time; on the contrary, they act as slow but stronger oxidants.

SUMMARY AND CONCLUSIONS

The study evaluated depression effectiveness of $KMnO_4$ compared to H_2O_2 and NaClO in the selective flotation of molybdenite from bulk concentrates, investigating the effects of reagent concentration, pH, temperature, and conditioning time.

Depression of xanthate collector-coated copper sulfide minerals involves oxidation of xanthate to dixanthogen by the oxidants investigated. However, under certain favorable conditions, dixanthogen acts as a collector, thereby overcoming depression. The depression curves showed that all three reagents require higher concentrations (2 lb/ton and above) to obtain even moderate depression initially. With further increase in concentration, once again only permanganate showed increase in depression, optimized at 20 lb/ton and above.

The higher concentrations (20 lb/ton and above) required for optimum depression mean that KMnO4 would be economically attractive in the cleaner flotation circuits rather than in the rougher circuits.

All three reagents produced maximum depression at pH 6. 5; it appears that the reagents decomposed above and below this critical value. At lower concentrations, NaClO showed the best depression. At higher concentrations (20 lb/ton and above), $KMnO_4$ was the most effective reagent and was unaffected by increases in pH values.

Examination of the effect of temperature indicated that the extent of depression depended on the characteristics of the individual oxidant. At lower concentrations, maximum depression for all three reagents occurred at different temperatures: KMnO4 at 30°C, H_2O_2 at 40°C, and NaClO at 50°C. At higher concentrations, $KMnO_4$ gave optimum depression at 30°C but was relatively ineffective above this critical temperature.

The depression effectiveness for permanganate definitely depended on time, with depression decreasing after 10 minutes for both low and high concentration levels. For this reason, the application of $KMnO_4$ in plant practice would involve careful manipulation and stage additions of reagent to otain optimum depression. In comparison, H_2O_2 and NaClO showed increasing depression with time, hypochlorite showing better depression than hydrogen peroxide.

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