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STUDIES ON HYPOCHLORITE LEACHING OF MOLYBDENITE

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ABSTRACT

The response of molybdenite to hypochlorite leaching has been known for some time. However, sufficient information on the mechanism of the process has not been available for this technique to be utilized effectively in practice for exploiting low-grade molybdenum deposits. Experimental data are presented which reveal that nine moles of hypochlorite are consumed in leaching one mole of molybdenite, both with pure concentrates and with natural low-grade ores. The leaching rates and extractions of molybdenum as a function of hypochlorite concentration and ore particle size have also been established. Molybdenum extractions of 50 to 70 percent can be expected from sized (-1/2 inch) low-grade ores in 48 hours of leaching time at moderate concentrations of hypochlorite.

INTRODUCTION

Increased importance of molybdenum in high-temperature alloy applications, as evidenced by the recent rise in price and demand, has resulted in increased interest in the recovery of this metal from low-grade sources. These include porphyritic, or disseminated, copper ores of the Southwest from which molybdenum is recovered as a by-product; and the comparatively higher-grade deposits that contain molybdenite as the principal valuable mineral in quartz veins and stockworks as exemplified by the Climax and Questa deposits.

Although froth flotation recovery of molybdenite from its ores, either as the major metal or as a by-product, is relatively simple and effective, current economics impose a cut-off limit, which is generally considered to be about 0. 20 percent MoS_2, especially when molybdenum is the only metal recovered. At the present time, deposits containing less than this minimum grade are considered waste, and any procedure that would enable the economic recovery of molybdenum from such low-grade ores would be of considerable interest to the industry.

In view of the recent developments in the technology of leaching molybdenum-bearing ores, it was felt that this approach to molybdenum recovery from low-grade sources merited further study. Since hypochlorite leaching of molybdenite has been known for some time, the current investigation was initiated to determine the feasibility of such a process.

Only the first phase of the investigation, that is, leaching, is reported in detail in this paper. Further work on the recovery of molybdenum values from pregnant solutions is under way in our laboratory, and the results of this second phase will be reported at a later date.

THEORETICAL CONSIDERATIONS

Oxidation of pyrite (1), sphalerite (2), galena (3), and molybdenite (4) in alkaline solutions has been reported. Dresher et al. (5) have shown that molybdenite could be leached in an alkaline solution of potassium hydroxide using an oxygen pressure of from 100 to 200 psi at elevated temperatures ranging from 100° to 175° C. Under these conditions, molybdenite is oxidized to molybdate which is soluble in alkaline leach solutions.

The employment of sodium hypochlorite for leaching of molybdenite has also been explored briefly. Cox and Schellinger (6) investigated this possibility recently and found that the optimum conditions for leaching MoS_2 were: 3 percent solution of NaOCl, pH = 10, and a 30-minute leaching period at a temperature of 70° F. Under these conditions, 90 to 100 percent extractions were reported. The mechanism suggested by these investigators for the oxidation of MoS_2 was

$$7NaOCl + MoS_2 + 4e^- \rightarrow MoO_4^= + S_2O_3^= + 7NaCl. \qquad [1]$$

They reported a significant amount of thiosulfate ion ($S_2O_3^=$) when measured by a standard iodine titration. A similar presence of thiosulfate ion in oxidation reactions has also been reported by Forward et al. (7) in their work with cobalt, nickel, and copper sulfides in ammoniacal solutions.

It would appear, however, that the mechanism suggested by Cox and Schellinger does not represent completely the over-all reaction between NaOCl and MoS_2 when hypochlorite is present in excess. As will be shown, thiosulfate, $S_2O_3^=$, is probably just one of a series of steps in the oxidation of sulfur to sulfate, with the thiosulfate as a relatively stable intermediate state in the absence of excess NaOCl in solution.

Elemental sulfur has been found to be a product of metallic sulfide-hypochlorite reactions according to the following equation:

$$6ClO^- + MoS_2 + 4OH^- \rightarrow MoO_4^= + S^0 + SO_4^= + 6Cl^- + 2H_2O. \qquad [2]$$

Choppin and Faulkenberry (8) on leaching aqueous Na_2S with NaOCl found sulfur and sulfate as end products in quantities depending upon the concentration of the reactants, the temperature, and hydrogen ion concentration of the reaction medium. When the reactants are of approximately the same concentration, the relative amount of sulfur and sulfate produced are constant for dilute solutions. High sulfide concentration increases the formation of sulfur, while high hypochlorite concentrations increase the formation of sulfate.

In order to obtain further information on this subject, experiments were conducted to study the reaction of Na_2S and NaOCl using a potentiometric titration. A buffered solution (0. 1M Na_2CO_3-0. 1M $NaHCO_3$) containing 0. 25 gm Na_2S per 100 ml was titrated with a 0. 1 percent solution of NaOCl, and the resulting voltage readings were recorded. For titration, 3. 20 millimoles of Na_2S required 3. 22 millimoles of NaOCl, thus indicating a 1:1 molar ratio of NaOCl to Na_2S, according to Eq. 3, sulfur being the only possible end product.

$$ClO^- + S^= + H_2O \rightarrow S^o + Cl^- + 2OH^-. \qquad [3]$$

A similar titration with 0. 5 percent NaOCl gave a molar ratio of 1. 02:1 indicating that some sulfur had been oxidized to a higher state than free sulfur, which is in agreement with the results obtained by Choppin and Faulkenberry. These results are presented graphically in Figure 1.

A similar titration was made for the $Na_2S_2O_3$ — NaOCl system under identical conditions as reported in the previous test, except for the strength of titrant used. In this instance, a 1. 0 percent NaOCl solution was used. As shown in Figure 2, the results of this test indicated a mole ratio of 4:1, NaOCl to $Na_2S_2O_3$. This ratio suggests the following reaction:

$$4ClO^- + S_2O_3^= + 2OH^- \rightarrow 4Cl^- + 2SO_4^= + H_2O \qquad [4]$$

sulfate being the only possible end product.

Such titration was also attempted on the MoS_2-NaOCl system. In this instance, however, a 5. 35 percent solution of NaOCl was used for titration. One-ml portions of titrating solution were added at about 15-minute intervals to 100 ml of buffered solution containing 0. 1 gm MoS_2, and the potentials were recorded on a strip-chart recorder. A saw-tooth curve was obtained, indicating that the reaction rate was too slow to be studied by this technique.

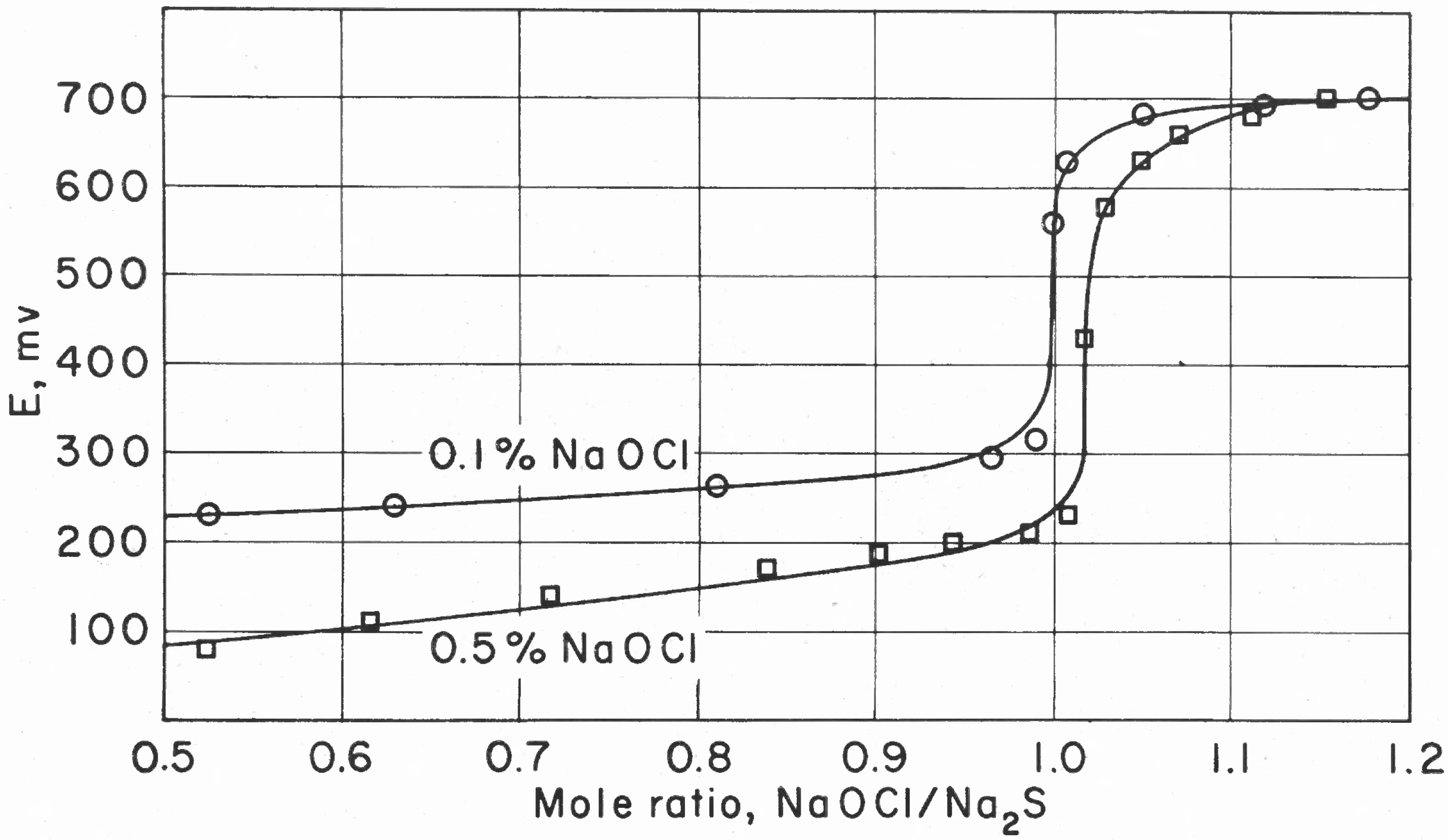

Fig. 1 Potentiometric titration curves, NaOCl vs. Na_2S

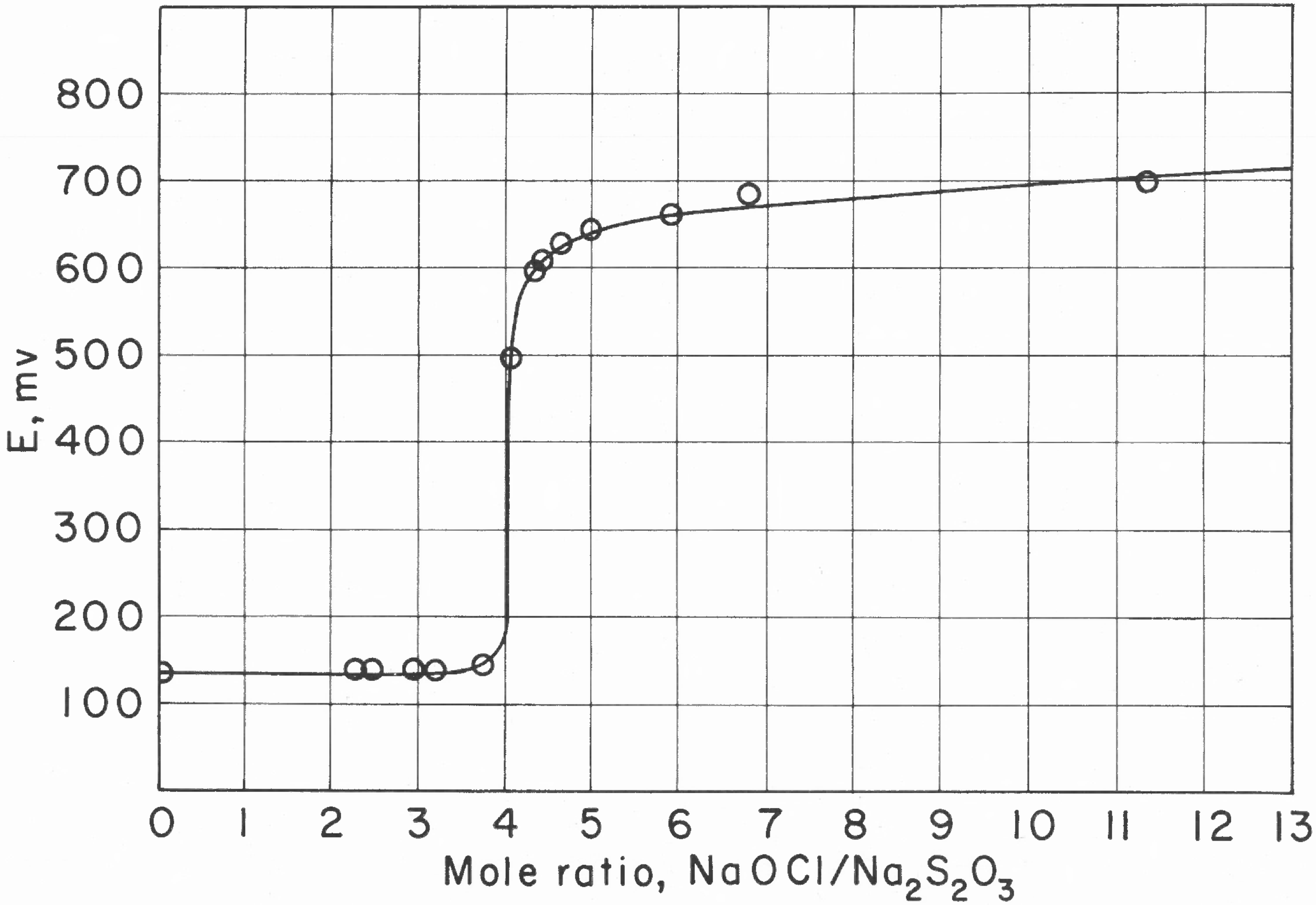

Fig. 2 Potentiometric titration curve, NaOCl vs. $Na_2S_2O_3$

Assuming that in leaching low-grade molybdenite ores, an excess of NaOCl would normally be used, it would seem that the sulfur, S^o, if any, produced in the reaction would be oxidized to sulfate, $SO_4^=$, as follows:

$$3ClO^- + S^o + H_2O \rightarrow SO_4^= + 3Cl^- + 2H^+. \qquad [5]$$

If this is the case, the over-all stoichiometric reaction between MoS_2 and NaOCl may then be represented by combining Eqs. 2 and 5 as follows:

$$9ClO^- + MoS_2 + 6OH^- \rightarrow MoO_4^= + 2SO_4^= + 9Cl^- + 3H_2O. \qquad [6]$$

This is in exact agreement with the stoichiometric relationship (Eq. 7) proposed by Dresher et al. for the oxidation of MoS_2 in the aqueous $KOH\text{-}O_2$ system:

$$MoS_2 + 9/2\ O_2 + 6OH^- \rightarrow MoO_4^= + 2SO_4^= + 3H_2O. \qquad [7]$$

From these theoretical considerations, it would be expected that the molar ratio of NaOCl to MoS_2 would be about 9:1 rather than 7:1, as proposed by Cox and Schellinger. Actually, if thiosulfate were the principal end product of their reaction, it would seem that Eq. 8 rather than Eq. 1 should describe the reaction.

$$5NaOCl + MoS_2 + 4OH^- \rightarrow MoO_4^= + S_2O_3^= + 5NaCl + 2H_2O. \qquad [8]$$

The resulting thiosulfate is then rapidly oxidized to sulfate by an excess of NaOCl as follows:

$$4NaOCl + S_2O_3^= + 2OH^- \rightarrow 2SO_4^= + 4NaCl + H_2O. \qquad [9]$$

On combining Eqs. 8 and 9, resulting in Eq. 10, the over-all reaction between NaOCl and MoS_2 is obtained:

$$9NaOCl + MoS_2 + 6OH^- \rightarrow MoO_4^= + 2SO_4^= + 9NaCl + 3H_2O. \qquad [10]$$

Eq. 10 is identical to Eq. 6 proposed by the authors. It should be stressed that as long as there is an excess of NaOCl present in the system, thiosulfate and other intermediate oxidation states of sulfur probably do not exist, or, if so, only for infinitesimal time intervals. Sulfate, $SO_4^=$, is always the final product.

During the course of the investigation, it was thought that the only possibility of decreasing the molar ratio of NaOCl to MoS_2 would be through the use of lower hypochlorite concentrations. This premise was based on the fact that low concentrations of NaOCl would favor the formation of free sulfur and retard its oxidation to higher states. The results of preliminary tests showed that it was possible to decrease the mole ratio; however, there was a corresponding retardation in the leaching rates and decrease in recoveries at lower concentrations so as to render the process uneconomical. For this reason, this approach was not pursued further. Nevertheless, the idea shows merit and will be explored more thoroughly in the future.

Experimental Procedure and Results

Samples of molybdenite used in the experimental work were obtained from the Questa, New Mexico, operation of the Molybdenum Corporation of America and from E. H. Sargent and Company. Both products were high-grade concentrates and contained 96 to 98 percent MoS_2. The low-grade ore samples were obtained from waste dumps of the Questa Operation, and contained 0. 17 to 0. 75 percent MoS_2. In addition to the valuable mineral, the ore samples contained quartz and aplite as principal gangue constituents.

Two different lots of sodium hypochlorite solutions were employed in the test work: (1) a "reagent grade" solution obtained from E. H. Sargent and Company containing 5. 25 percent NaOCl and (2) a commercial bleach labeled Clorox obtained locally and containing 5. 25 percent NaOCl. These materials were analyzed chemically and spectrographically and were found to be comparable. On this basis, Clorox was used throughout the investigation.

The experimental work was designed, first, to determine the stoichiometric reaction between NaOCl and MoS_2 and, second, to establish the reaction rates of the leaching process on molybdenite concentrates and low-grade ores under various conditions. The variables investigated were (1) effect of hypochlorite concentration, (2) type of leaching employed, stagnant, agitation, and percolation, and (3) ore-particle size.

All of the experiments were conducted at room temperature, while the pH of the solutions were held between 9 and 11 by buffering with sodium carbonate (15 grams/liter). This particular range in pH has been shown by others (6) and confirmed by the authors to be optimum for molybdenum extraction with hypochlorite.

The molybdenum content of various products was determined spectrophotometrically from a phenylhydrazine hydrochloride-molybdenum complex using a Bausch & Lomb "Spectronic 20" spectrophotometer, according to the analytical method developed by Ayres and Tuffly (9). The hypochlorite content in the solution was determined by titration with sodium thiosulfate according to ASTM D-62T (10).

Test Series I

The purpose of this series of experiments was to establish the mole ratio of NaOCl to MoS_2 at various concentrations of hypochlorite and to determine the end products of the reaction. In addition, the effect of hypochlorite concentration on leaching efficiencies was to be examined.

The experimental procedure consisted of digesting, by stirring in a beaker, 0. 5 g of -100 + 150 mesh fractions of molybdenite concentrate assaying 96. 4 percent MoS_2, in 100-ml hypochlorite solutions containing 3. 14, 1. 10, 0. 46, and 0. 099 percent NaOCl, respectively. In each leach test involving a given concentration of hypochlorite, small samples of solution were withdrawn at specified intervals up to 70 minutes and analyzed for molybdenum and hypochlorite contents.

The results of this series of experiments are listed in Tables 1-A, 1-B, 1-C, 1-D. These results are also presented graphically in Figure 3. A mole ratio of approximately 9:1 of NaOCl to MoS_2 is indicated for all of the concentrations of hypochlorite investigated, confirming the stoichiometric reaction suggested by the authors in Eq. 6.

Analytical tests made on selected samples of solution for the presence of end-product ions revealed that sulfate, $SO_4^{=}$, was the only species of sulfur-oxidation product present when hypochlorite was in excess. Furthermore, in these tests the amount of sulfur as sulfate was found to be stoichiometrically equal to the sulfur contained in the consumed molybdenite.

As shown in Figure 3, the dissolution rates of molybdenite are dependent upon hypochlorite concentrations, the higher concentrations extracting more molybdenum in a given period of time. The slopes of the curves for varying hypochlorite concentrations indicate that the leaching rate is very fast for the first 10 minutes, then slows down somewhat, and finally becomes constant for each hypochlorite concentration.

Table 1. Leaching Molybdenite Concentrates

Cum. Contact Time (min.)	Cum. Mo Ext. (gm)	Cum. NaOCl Used (gm)	pH	Mole Ratio NaOCl/MoS$_2$	Cum. Mo Ext. (%)
Table 1-A. NaOCl Concentration, 3.14%					
5	0.105	0.74	10.5	9.1	36.3
10	0.142	1.04	10.3	9.4	49.1
20	0.195	1.43	10.1	9.5	67.3
35	0.256	1.83	9.9	9.2	88.5
50	0.280	2.09	9.7	9.6	96.8
70	0.289	2.11	9.5	9.4	100.0
Table 1-B. NaOCl Concentration, 1.10%					
5	0.041	0.30	10.4	9.4	14.2
15	0.089	0.61	10.1	8.9	30.8
30	0.118	0.89	10.9	9.7	40.8
50	0.141	1.03	9.7	9.5	48.7
70	0.144	1.09	9.5	9.8	49.8
Table 1-C. NaOCl Concentration, 0.461%					
5.0	0.025	0.19	10.6	9.8	8.6
12.5	0.037	0.25	10.6	8.7	12.8
30.0	0.052	0.40	10.5	9.9	18.0
45.0	0.059	0.45	10.3	9.8	20.4
Table 1-D. NaOCl Concentration, 0.099%					
5.0	0.0053	0.036	10.5	8.8	1.8
15.0	0.0102	0.069	10.5	8.7	3.5
30.0	0.0135	0.089	10.4	8.4	4.7
50.0	0.0142	0.098	10.2	8.9	4.9

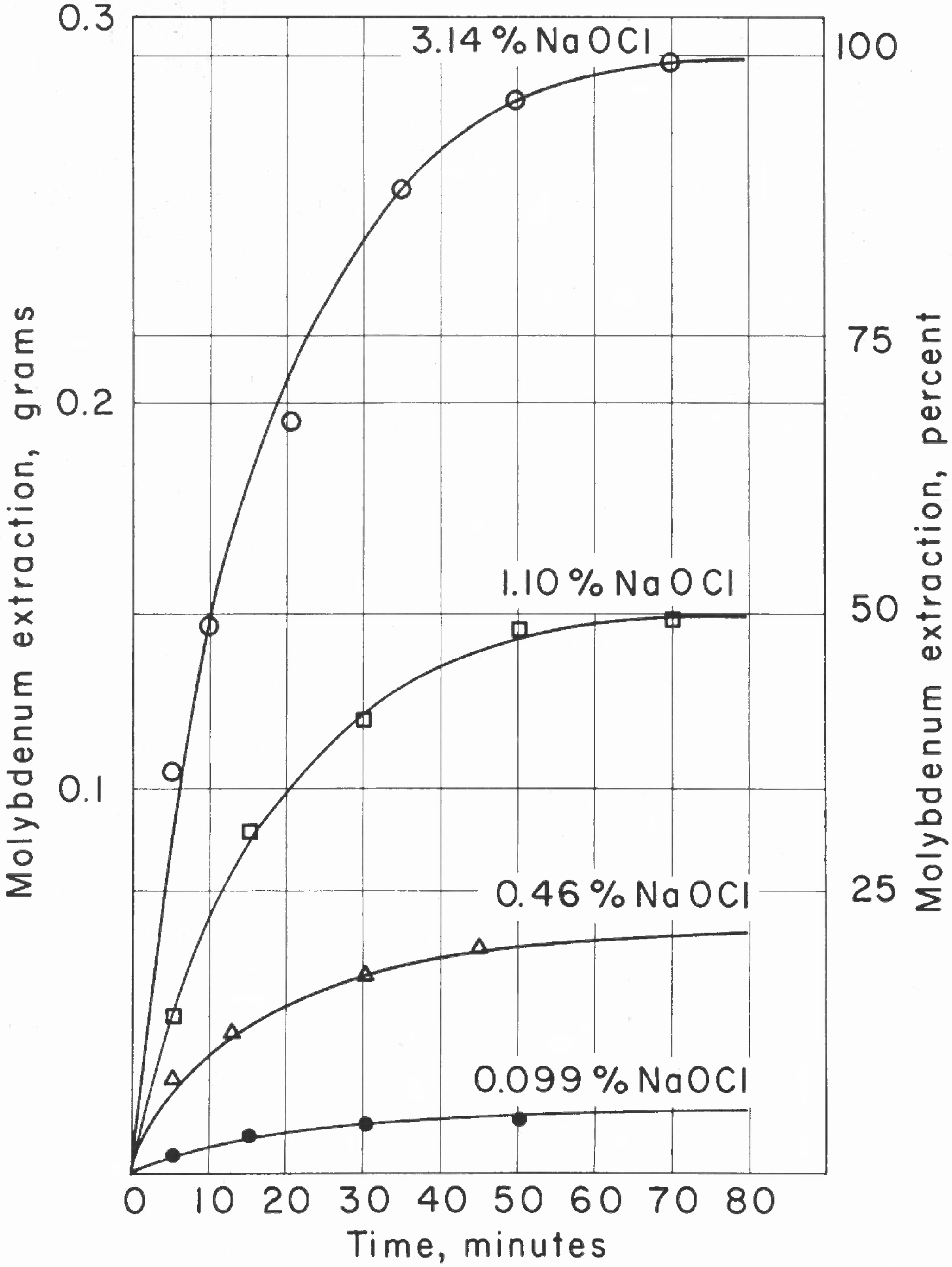

Fig. 3. Effect of Na O Cl Concentration on leaching of high grade molybdenite concentrate

In general, it appears that as long as there is hypochlorite remaining in solution, stoichiometric amounts of molybdenite will continue to be leached but at a decreasing rate.

With reference to Table 1-A, with a 3.14 percent NaOCl solution, it is found that 2.11 grams of NaOCl are consumed in extracting 100 percent of the molybdenite containing 0.289 gram of molybdenum. Thus, the leaching solution still contained about 1.03 gm NaOCl which would be capable of extracting an additional 0.144 gram of the metal. This fact is confirmed by the results shown in Table 1-B in which a 1.10 percent NaOCl solution was used for extracting 0.5 gram of MoS_2 (0.289 gm Mo). In this case, after the same leaching period of 70 minutes, essentially all the hypochlorite present in the solution was consumed in extracting 0.144 gram of molybdenum which is equivalent to about 50 percent of the molybdenite present in the feed. Such analogies can be extended to the results with weaker hypochlorite solutions, as shown in Tables 1-C and 1-D. In these tests, essentially all the hypochlorite present in the solutions was consumed in leaching stoichiometric amounts of molybdenite but with decreasing rates.

Test Series II

In these tests, the rate of leaching relatively large pieces of molybdenite with fresh hypochlorite solutions under stagnant conditions was examined. Experimentally, about 1-1/2-inch square pieces of high-grade molybdenite samples containing about 60 percent MoS_2 were immersed in 100-ml portions of buffered hypochlorite solutions containing 3.01 percent NaOCl for different time intervals. After a given time, the specimens were reimmersed in a fresh solution, while the previously leached solution was analyzed for molybdenum and hypochlorite contents.

The results indicate that the mole ratio of NaOCl to MoS_2 was again nearly constant at 9:1. The leaching rate was fast for the first 10 hours, after which the rate was retarded, as shown in Figure 4. Upon completion of the leaching test, siliceous material was noted within the piece of molybdenite. The specimen was then broken to examine the depth of leaching below the surface. Examination revealed that dissolution had progressed more or less uniformly toward the center. The remaining outer portion consisted of a porous siliceous mass, indicating fair penetration of lixiviant into the solid mass.

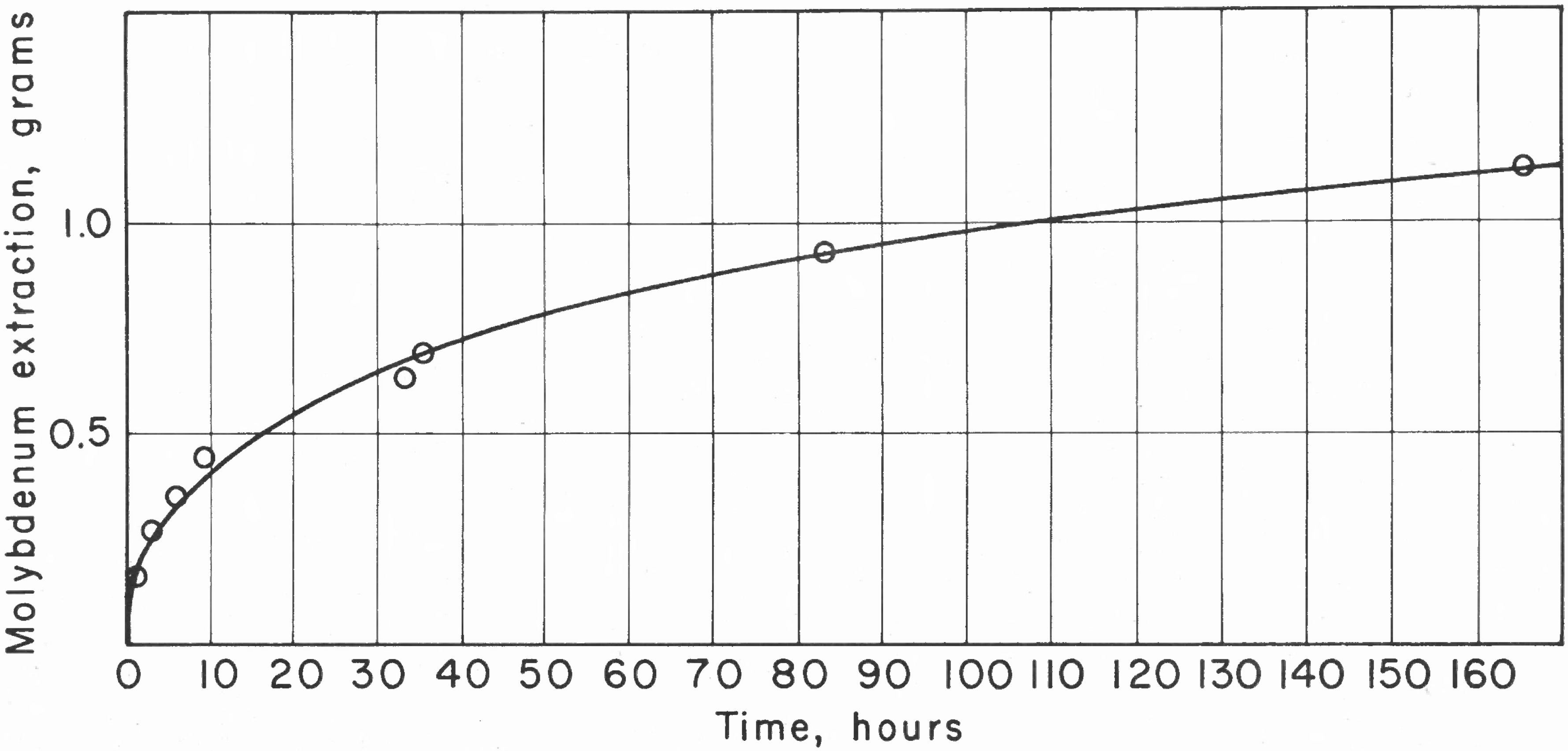

Fig. 4 Rate of leaching for a large piece of molybdenite

Test Series III

This particular series of experiments was conducted with low-grade molybdenite ore samples to determine the mole ratio of NaOCl to MoS_2 and to establish the leaching rate with varying concentrations of hypochlorite solutions. Four samples containing approximately 340 gms of sized or (-0.525" + 0.185") assaying 0.41 percent Mo was contacted with 5.04, 2.92, 1.92, and 0.98 percent of buffered hypochlorite solutions under stagnant conditions. After the leaching had progressed for a certain time, the solutions were drained and analyzed for molybdenum and hypochlorite contents. Fresh solutions were added after each draining for continued leaching of the samples.

As shown by the data listed in Tables 2-A, 2-B, 2-C, and 2-D, the mole ratio of NaOCl to MoS_2 for low-grade molybdenite ores is again constant at about 9:1. The consistency of this mole ratio for low-grade ores indicates that there is little or no consumption of hypochlorite by the gangue constituents.

The effect of hypochlorite concentrations on the extraction of molybdenum is shown in Figure 5. From the curves, it appears that the leaching rate is relatively faster for the first few hours and is proportional to the initial hypochlorite concentration. After this period, the leaching rates appear to be constant regardless of the concentration.

Test Series IV

The experiments in this series were conducted to determine the leaching rate of molybdenite in low-grade ore samples by employing a percolation leaching procedure. The effect of particle size on leaching rates was also explored in this test series.

About 2600 gms of (-0.525" + 0.185") low-grade molybdenite ore (sample A) containing 0.427 percent Mo was placed in a 4-inch diameter, 5-foot long glass column, and the desired volume of 3.08 percent NaOCl solution was percolated upward at the rate of 2 ml per minute for 57 hours. The overflow from the column was collected periodically and analyzed for molybdenum and hypochlorite contents. After this test, the column was allowed to leach under stagnant conditions for four days to determine the amount of additional molybdenite that could be leached during this period.

Table 2. Leaching Low-Grade Molybdenite Ores

Cum. Contact Time (Hrs.)	Cum. Mo Ext. (gm)	Cum. NaOCl Used (gm)	pH	Mole Ratio NaOCl/MoS$_2$	Cum. Mo Ext. (%)
Table 2-A. NaOCl Concentration, 5.04%					
2	0.268	1.90	9.4	9.1	19.1
4	0.362	2.56	10.0	9.1	25.9
6	0.430	3.02	10.2	9.0	30.7
8	0.477	3.38	10.2	9.1	34.1
19	0.617	4.54	9.8	9.5	44.1
Table 2-B. NaOCl Concentration, 2.92%					
2	0.174	1.24	9.5	9.2	12.7
4	0.255	1.80	10.0	9.1	18.6
6	0.319	2.24	10.2	9.1	23.3
8	0.376	2.62	10.2	9.0	27.5
19	0.536	3.76	9.7	9.0	39.2
Table 2-C. NaOCl Concentration, 1.92%					
2	0.152	1.08	9.4	9.2	11.0
4	0.232	1.62	9.9	9.0	16.8
6	0.281	2.02	10.1	9.3	20.4
8	0.331	2.36	10.2	9.2	24.7
19	0.467	3.32	9.6	9.2	33.8
Table 2-D. NaOCl Concentration, 0.98%					
2	.090	0.64	9.5	9.2	6.7
4	.144	1.02	9.9	9.1	10.7
6	.194	1.38	10.0	9.2	14.4
8	.237	1.70	9.9	9.3	17.6
19	.379	2.64	9.0	9.0	28.1

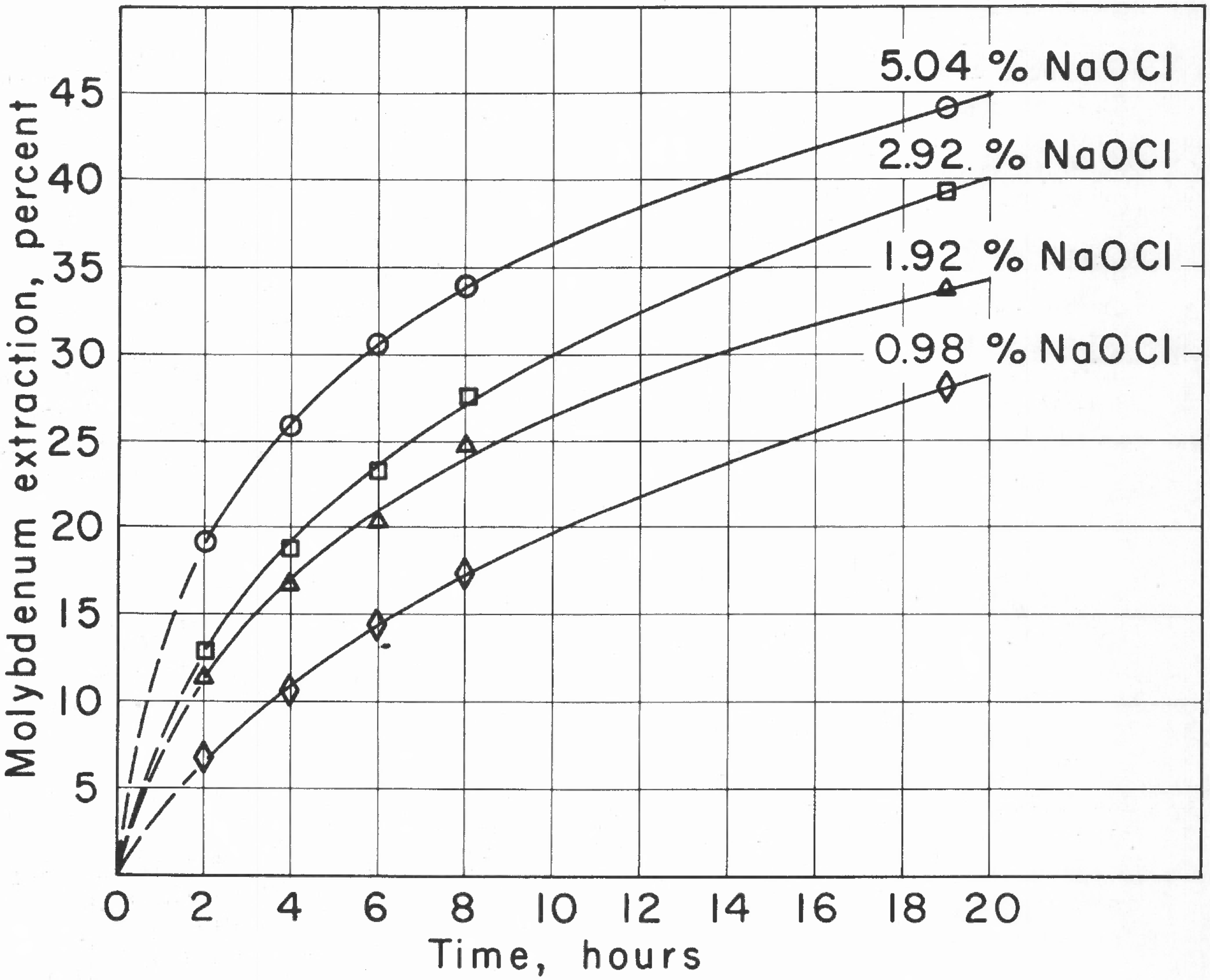

Fig. 5 Effect of NaOCl concentration on leaching of low grade molybdenite ore containing 0.41 percent molybdenum

A similar column-leaching test was performed using a molybdenite ore of lower grade (sample B) assaying 0.169 percent Mo. In this case, however, a somewhat finer-sized product, namely (-0.375" + 0.151"), was subjected to leaching for 40 hours with a 3.02 percent NaOCl solution.

The results of the tests on ore samples A and B are presented graphically in Figure 6. The results again show mole ratios for NaOCl to MoS_2 equal to about 9:1. The percent extraction of molybdenum in the two ore samples tested, however, is different. For ore sample A, an extraction of about 50 percent was obtained in 48 hours, while for ore sample B, an extraction of about 70 percent was possible during the same period. Actually, sample A contained a higher grade of molybdenum (0.427%) than sample B (0.169%); yet, the extraction for B was about 20 percent higher. This increase in extraction can only be attributed to the finer size of the particles in sample B, resulting in a relatively greater exposure of molybdenite to lixiviant. In regard to the leaching rates for the two samples tested with 3.02 percent NaOCl, much faster initial rates were noted again for the first five hours with gradual retardation until nearly constant rates were achieved after about 40 hours.

DISCUSSION OF RESULTS

In all of the experiments a mole ratio of approximately 9:1, NaOCl to MoS_2, was obtained consistently. This suggests that the reaction between NaOCl and MoS_2 is in accordance with the stoichiometric Eq. 6 as proposed by the authors.

$$9ClO^- + MoS_2 + 6OH^- \rightarrow MoO_4^= + 2SO_4^= + 9Cl^- + 3H_2O.$$

Moreover, in the presence of excess NaOCl, as was the case for almost all the experiments, the oxidation of sulfide goes to completion with sulfate, $SO_4^=$, as the only end product. Thiosulfate and other intermediate oxidation states of sulfur probably do not exist, or, if so, only for infinitesimal time periods.

The nearly constant consumption of 9 moles of NaOCl per mole of MoS_2 for both the high-grade concentrates and low-grade ores investigated indicates that the hypochlorite is consumed almost entirely by the molybdenite and very little, if any, by the gangue contained in the ore. This indication is of economic importance.

The nonlinear leaching rates observed for molybdenite concentrates in Figure 3 can probably be explained in terms of hypochlorite concentration and particle size. The higher initial rate of leaching for

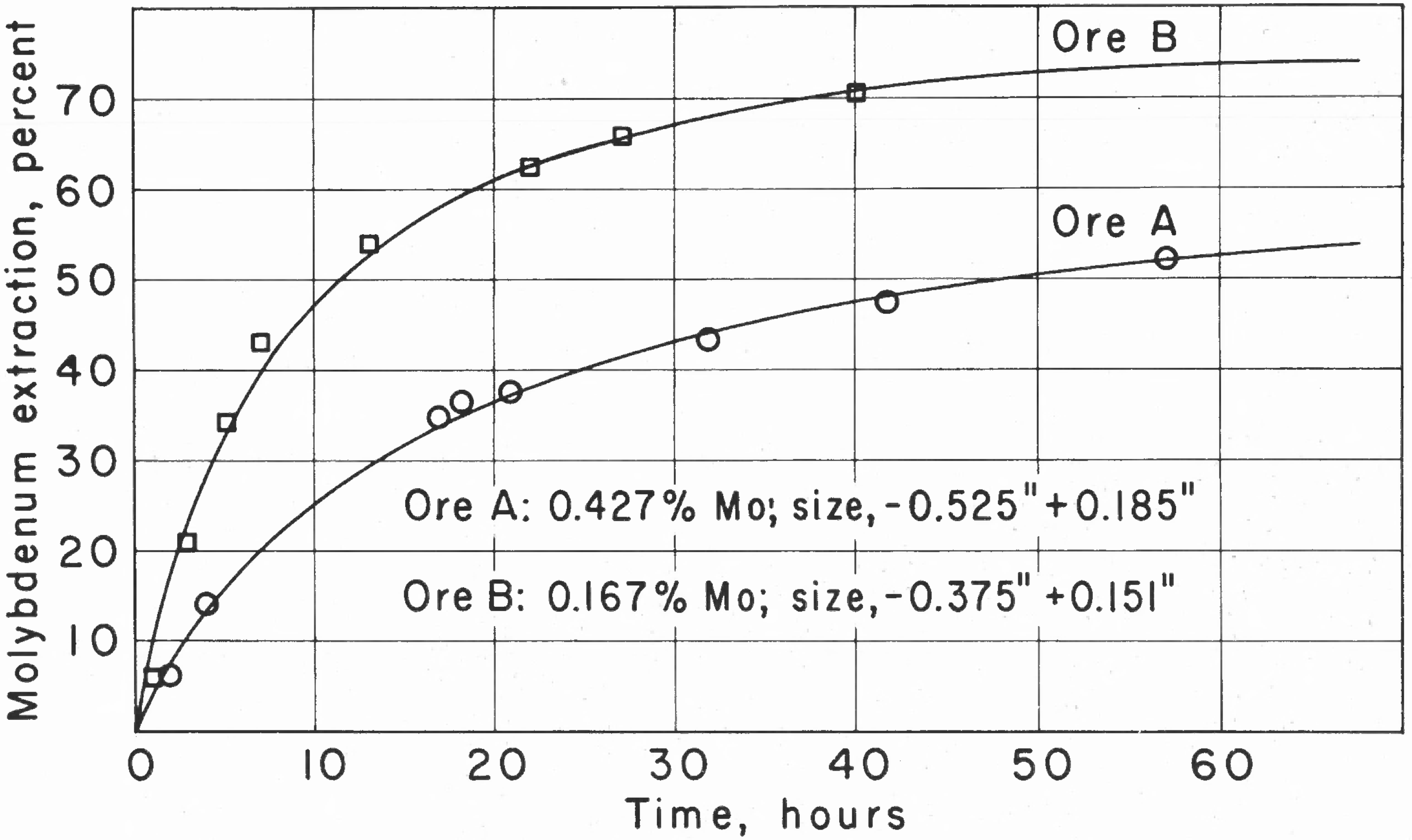

Fig. 6 Results of percolation column leaching of low grade ores of different sizes

all hypochlorite concentrations is probably due to the faster dissolution of finer particles. On the other hand, the differences in molybdenum dissolution shown by systems containing different initial concentrations of hypochlorite, that is, 0.05, 0.12, and 0.24 gm Mo/ml at 0.456, 1.10, and 3.14 percent NaOCl, respectively, after 30 minutes of leaching, can probably be attributed to differences in concentrations of hypochlorite at that time.

In the case of stagnant leaching of a relatively large piece of molybdenite with fresh hypochlorite solution (Fig. 4), the higher initial rate can probably be attributed to concentration phenomena in the immediate vicinity of the particle and perhaps to irregularities in the particle surface. Furthermore, the presence of gangue impurities within the solid piece of molybdenite may also have retarded leaching.

In the case of stagnant leaching of crushed low-grade ore samples, the results indicate that the extraction is dependent on the hypochlorite concentration during the earlier stages of leaching. During the later stages of leaching (e.g. after 8 hours in Figure 5), the higher extraction rates obtained initially, together with subsequent retardations in leaching, can probably be explained on the same basis as was suggested for relatively large pieces of molybdenite.

The results also reveal that the over-all extraction of molybdenite from low-grade ores is a function of particle size (total molybdenite exposure). See Figure 6. This is shown clearly in the case of leaching ore samples A and B under Test Series IV. Although sample A contained a higher grade of molybdenum (0.427%) than sample B (0.169%), the over-all extraction and leaching rate for sample B was higher than that of sample A because of the finer particle size of sample B. The two samples were leached under identical conditions.

These extraction studies indicate that it should be possible to leach 50 to 70 percent of the molybdenum contained in the low-grade ores in about 48 hours. The extractions were determined for ore samples crushed through 1/2-inch. Different extractions and rates are to be expected for samples of different size, and the effect of particle size will be investigated at a later date.

PRACTICAL CONSIDERATIONS

In view of these experimental results, hypochlorite leaching of molybdenite would seem to offer attractive possibilities for treating some low-grade ore bodies. Of special importance might be the leaching of submarginal ore left in place after the exploitation of higher-grade ores by conventional mining. The submarginal waste dump material accumulated during the development and mining phases of the operation might also make ideal feed for such a process. Other suitable feed for such a process might be (1) high-grade molybdenite concentrates when another compound of molybdenum is desired as the final product, (2) lower-grade middlings from flotation plants in order to avoid their recirculation in the flotation circuit, and (3) tailings from other operations in which molybdenum values have not been fully recovered.

The results of this investigation have shown clearly that both the leaching rate and efficiency depend upon the concentration of NaOCl and on the amount of molybdenite exposed to the solution. This precludes the possibility of treating those ores in which the molybdenite is very finely disseminated and which have not been comminuted to liberate or expose the molybdenite values.

The utility of this process probably would be in the treatment of quartz vein and stockwork deposits in which molybdenite occurs as large or small rosettes and as fissure fillings in the form of films, thin plates, and veinlets in the host rock. In such ores the molybdenite-enriched zones form planes of weakness. When the rock is broken, either by explosion or caving, it tends to fracture along the planes of weakness, exposing molybdenite values throughout the broken mass. This would naturally be the normal occurrence when a block-caving system of mining is used for recovering higher-grade ores from the deposit.

It would appear that upward percolation of lixiviant through caved-in blocks, followed by a suitable period of contact and subsequent draining, would be very effective in leaching economic amounts of molybdenite. Such cycles could be repeated as often as found necessary. For dump leaching, a conventional downward percolation, as practiced in copper leaching, could be employed effectively. In this case, however, it would appear that lower NaOCl concentrations, as low as one percent, would be more desirable for leaching in order to avoid air locks and subsequent channeling. For higher grades, that is, middlings or even molybdenite concentrates, agitation leaching in vats or tanks would probably be more suitable.

ECONOMICS

In regard to the economics of hypochlorite leaching of low-grade molybdenite ores, sufficient data have not yet been collected to make a fair evaluation. On the basis of this investigation, however, we are justified in making a number of generalized statements concerning the economics of the leaching phase of this process.

The results of the current investigation have shown that 9 to 10 moles of sodium hypochlorite are required to leach one mole of molybdenite. This is equivalent to 4.2 to 4.7 pounds of NaOCl per pound of MoS_2 or 7 to 8 pounds of NaOCl per pound of molybdenum recovered.

The current market price of molybdenum is \$1.40 per pound of contained Mo in a concentrated product. On the other hand, the cost of sodium hypochlorite is dependent on the method involved in its procurement or manufacture. If purchased on the open market, the cost would undoubtedly be too high for economical use. However, the cost of producing hypochlorite at the plant location by combining caustic soda and chlorine may be low enough to justify an economic operation. The production of hypochlorite locally by the electrolysis of common salt (NaCl) might also prove economical, especially if the required salt and power could be obtained readily and cheaply. In the Southwest, with the availability of relatively cheap sources of salt, such as tailings from the Carlsbad potash operations and salt lakes in Utah, and with reasonably cheap power, electrolysis would appear to be the most attractive technique for producing hypochlorite locally. In such installations, there is also the possibility of using reclaimed NaCl, a by-product of the reaction between hypochlorite and molybdenite (Eq. 6).

On the basis of recovering one pound of molybdenum per ton of ore treated and assuming 50 percent recovery of the molybdenum contained in the ore, the minimum grade that could be treated economically would be about 0.17 percent MoS_2. Since the cut-off grade for mining and flotation operations is about 0.20 percent MoS_2, ores of this grade or somewhat lower may be amenable to economic leaching using hypochlorite.

In regard to the recovery of molybdenum from copper concentrates containing 0.25 to 0.75 percent MoS_2 (3 to 9 lb. Mo per ton), the economics of employing hypochlorite leaching might be very favorable. In this instance, liberation of molybdenite would be very nearly complete, and when this material is subjected to an agitation leach, very high recoveries of molybdenum would be effected.

CONCLUSIONS

Molybdenite was found to respond readily to leaching in sodium hypochlorite solutions according to the following stoichiometric equation:

$$9ClO^- + MoS_2 + 6OH^- \longrightarrow MoO_4^= + 2SO_4^= + 9Cl^- + 3H_2O.$$

in which 9 moles of NaOCl are required to leach one mole of MoS_2. In the presence of excess hypochlorite, as was the case in almost all of the experiments, the oxidation of sulfide goes to completion with sulfate, $SO_4^=$, as the only end product. Thiosulfate and other intermediate oxidation states of sulfur probably do not exist, or, if so, only for infinitesimal time periods.

In the case of hypochlorite leaching of natural low-grade ores, the experimental results showed that hypochlorite was consumed almost entirely by the molybdenite and very little, if any, by the gangue minerals in the ores investigated.

Leaching rates and extractions of molybdenum from both concentrates and low-grade ores are dependent upon the initial hypochlorite concentrations and ore particle size (total molybdenite exposure). For low-grade ores crushed through 1/2-inch, about 50 to 70 percent extraction of the contained molybdenum was obtained in about 48 hours leaching time.

Under optimum conditions, it may be possible to employ this process in treating low-grade ores which have been sufficiently broken to expose the molybdenite. Further research, however, will have to be conducted on both the leaching and the metal recovery phases before the utility of the process can be definitely established.

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REFERENCES

1. J. F. Stenhouse and W. M. Armstrong: Canadian Mining and Metallurgical Bull. 45, 1952, p. 49.

2. V. Tronev and S. Bondin: Comptes Rendus Acad. Science, URSS, vol. 23, p. 541.

3. J. E. Anderson, J. Halpern, and C. S. Samis: AIME Trans., 1953, vol. 197, p. 554.

4. E. S. Usataya: Zapiski Vsesoyuz Mineral Obschschestva, 1952, vol. 81, pp. 298.

5. W. H. Dresher, M. E. Wadsworth and W. M. Fassell, Jr.: AIME Trans., 1956, vol. 205, p. 738.

6. H. Cox and A. K. Schellinger: Engineering and Mining Journal, vol. 159, No. 10, p. 101.

7. F. A. Forward and V. N. Mackiw: AIME Trans., 1955, vol. 203, p. 457.

8. A. R. Choppin and L. C. Faulkenberry: Journal of the American Chemical Society, 1937, vol. 59, p. 2203.

9. G. H. Ayres and B. L. Tuffly: Analytical Chemistry, 1951, vol. 23, p. 304.

10. ____________________, American Society for Testing and Materials, 1962, ASTM Designation D-62T.