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Hydrometallurgical Recovery of Molybdenum from the Questa Mine

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Abstract

The dissolution of molybdenite (MoS_2) was studied leaching with acid solution or decomposing with using various oxidizing agents including hypochlorite, carbonate solution. If acid leaching is used, provisions ozone, oxygen-alkali, acid-permanganate, persulfate, should be made to prevent complexing of molybdenum acid-ferric chloride, nitric acid, chlorine dioxide, acid- with iron, calcium, and aluminum ions.

The extraction of molybdenum from leach solution was studied employing anion exchange resins, a fast and selective method for dissolving molybdenite. organic solvents, and activated carbon. The adsorption characteristics shown by all three for Mo (VI) are alike, stable reagent, difficult to handle, and troublesome to regenerate. Acid-chlorate leaching is not so rapid nor processes. The observed similarities indicate that the so selective as hypochlorite but presents less of a ionic species adsorbed may be the same for the handling problem, provides for easy extraction of molybdenum. Efforts are made to explain the irregular variation of D with pH and to establish optimum conditions for loading and elution.

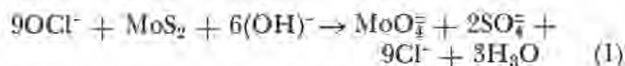
The manganese dioxide-sulfuric acid oxidation of molybdenite was studied in detail and was also found effective. Its only application, however, appears to be in dissolving molybdenum from high-grade ores or concentrates. Preliminary tests on bacterial oxidation of molybdenite indicate a favorable response of the specific species *Thiobacillus thiooxidans* and *Thiobacillus ferrooxidans*, which have been tentatively identified in the Questa mine water.

Studies of the recovery of molybdenum as a marketable product were directed toward its precipitation as the ferric-molybdenum complexes. Stable dehydrated compounds containing 70 to 80 per cent MoO_3 and 20 per cent Fe_2O_3 were produced under optimum conditions. Efforts have been made to elucidate the scheme of precipitation and composition of the precipitated iron-molybdenum compound and to compare it with the naturally occurring mineral, ferrimolybdite, in the oxidized zones of the molybdenum-bearing limonite may be extracted either by molybdenum deposits.

Dissolution of Molybdenite

HYPOCHLORITE LEACHING

In a previous publication by Bhappu, Reynolds, and Stahmann (1963), it was shown that molybdenite concentrates respond readily to leaching in basic hypochlorite solution according to the stoichiometric equation



in which 9 moles of hypochlorite are required to leach 1 mole of molybdenite.

In hypochlorite leaching of natural low-grade ores, it was found that hypochlorite was consumed almost entirely by the molybdenite and very little, if any, by the gangue minerals contained in the ores investigated. It was also shown that leaching rates and extractions of molybdenite from both concentrates and low-grade ores are dependent upon the initial hypochlorite concentrations and ore particle size.

On the basis of these results it might appear that hypochlorite is the ideal practical lixiviant for molybdenite, but the reagent cost would be very high unless it were regenerated and a cyclic process established. Regeneration of hypochlorite may be accomplished electrolytically. The reagent, almost from the start, is also decomposed by the current, and this decomposition increases as the concentration of the hypochlorite increases, until the amount decomposed is just equal to the amount produced. In commercial practice, a 66 per cent current efficiency is obtained with a yield of about 3.2 kw. hr./lb. of chlorine equivalent produced. It is apparent that the economics of hypochlorite leaching would be favorable only if the reagent is regenerated electrolytically from the brine produced as a by-product of the reaction between hypochlorite and molybdenite (eq. 1). The prime requirement in this regeneration is a reasonably cheap power supply. Regeneration of hypochlorite is under investigation.

OTHER OXIDIZERS AS LEACHING AGENTS

Efforts were made to find other oxidizing agents that might replace hypochlorite. Since the process sought is to be used in leaching tailing piles, dumps, and low-grade ore left in place, a successful leaching agent should give fair leaching rates at ambient temperatures and pressures.

To limit the field of study, all oxidizing agents were tried on a semiquantitative basis first. This was accomplished by mixing molybdenite concentrate with a solution of the oxidizing agent for several hours and analyzing the leach solution for molybdenum. Table 1 shows the results for the oxidizing agents investigated.

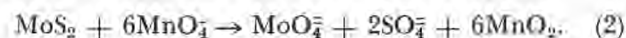
TABLE I. OXIDIZING AGENTS STUDIED

OXIDIZING AGENT	REMARKS
O ₃	No reaction in 4 hours
O ₂ + NaOH	Reaction very slow at atmospheric pressures; trace of Mo in solution after 24 hours
KMnO ₄ + H ₂ SO ₄	Rapid leaching; MnO ₂ precipitates as end product below 2 normal H ₂ SO ₄
Na ₂ S ₂ O ₈ + H ₂ SO ₄	Ag ⁺ needed as catalyst
FeCl ₃ + H ₂ SO ₄	No reaction in 24 hours
HNO ₃ (5-10%)	Fair reaction rate; H ₂ MoO ₄ precipitates as end product
ClO ₂	High leaching rates but is a very explosive gas
NaClO ₃ + H ₂ SO ₄	Fair rate
MnO ₂ + H ₂ SO ₄	Slow rate

Ozone, although generally considered a good oxidizing agent, does not produce any noticeable reaction with molybdenite at room temperature and atmospheric pressure.

A caustic solution saturated with oxygen did oxidize molybdenite, but the reaction was very slow. Work has been done on this system at higher pressures and temperatures by Dresler, Wadsworth, and Fassell (1956).

With basic or slightly acid permanganate and molybdenite, the end product is manganese dioxide, probably by the reaction



The manganese dioxide is insoluble and would be retained in leaching dumps, tailings piles, or low-grade ores in place. Such a precipitate would probably seal the channels in the ore body and make the ore body impermeable to the leaching solution. A large quantity of acid would be required to prevent precipitation of MnO₂, thereby increasing the cost of the process.

Tests with sodium persulfate indicated the necessity of a catalyst. Silver ion in solution is usually used with persulfate oxidations for analytical work. The amount of silver needed depends on the rate of reaction desired; about one gram per liter will suffice. Any loss in leach solution or presence of chloride ions would result in a loss of silver, a large economic factor. A cheaper catalyst, if available, could make this process more attractive.

Ferric chloride in acid solution did not oxidize molybdenite under the conditions investigated.

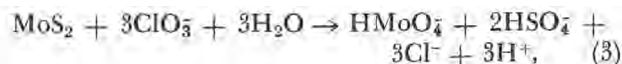
In dilute nitric acid, molybdenite is oxidized; but the oxidized form of molybdenum in nitric acid is molybdic acid (H₂MoO₄), which is not soluble to any appreciable extent unless sulfuric acid is also added to the leach solution.

A solution of chlorine dioxide in water showed high leaching rates. The gas is very explosive and must be used in dilute solution for safe operation. Chlorine

dioxide probably undergoes disproportionation in solution to chlorate and hypochlorite. The hypochlorite in basic solution would then be the oxidizing agent. As the hypochlorite reacts with the molybdenite, the solution becomes acidic and chlorate begins to oxidize the mineral.

CHLORATE LEACHING

Sodium chlorate in acid solution seems promising as leaching agent for molybdenite and other metallic sulfides. The over-all reaction probably is represented by the equation



provided neither molybdenite nor chlorate is present in excess. A ratio of 1 MoS₂ to 3ClO₃⁻ is indicated. In tests so far, the ratio observed was about 1:4. If

is in excess, some of the intermediate products of reduction, as Cl₂ and ClO₂, may escape as gases before they may be further reduced. Also, any carbonaceous matter, free sulfur, or other sulfides increase chlorate consumption. Either of these would result in observation of a higher than theoretical ratio. On the other hand, if excess molybdenite were present, some molybdenum might enter the solution in an oxidation state less than Mo(VI) or be reduced to such state near the end of reaction, with the result that a lower ratio might be found. This possibility is being investigated.

The suggested equation for the reaction indicates that the leaching rate depends upon pH and the chlorate concentration. Results of tests to measure these effects are shown in Figures 1 and 2. These indicate the rate to be directly proportional to the acid concentration and to the 1.24 power of the chlorate concentration. More work is required to optimize these effects.

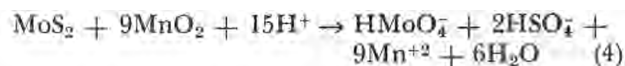
Preliminary work indicates that leaching molybdenite with aqueous acid-chlorate solutions may offer real advantages over other reagents studied. The reagents sodium chlorate and sulfuric acid are relatively low in cost. Leaching proceeds at a reasonably high rate and is done in acid solution, which, as will appear later, facilitates recovery of molybdenum from dilute solution by ion exchange, solvent extraction, or activated charcoal adsorption. Regeneration is quite efficient. A current efficiency approaching 90 per cent is reported as not unusual for making the chlorate.

Among possible disadvantages of the acid-chlorate leach are its lack of selectivity toward molybdenite and the possibly prohibitive acid consumption of a calcareous ore.

MANGANESE DIOXIDE-SULFURIC ACID LEACHING

Manganese dioxide-sulfuric acid is an effective oxidizing agent for molybdenite (Roman, 1964); however, its application appears to be limited to high-grade ores

or concentrates. When manganese dioxide and molybdenite are mixed in strong sulfuric acid solution, they react as follows:



As indicated in Figure 3, the rate-controlling step may be the dissolution of the manganese dioxide or the surface oxidation of the molybdenite, depending on the ratio of manganese dioxide surface area to

surface area. Temperature has a relatively slight effect on the rate, a 23° C increase merely doubling the rate. An increase in acid concentration will also increase the rate, as illustrated in Figure 4. The magnitude of increase in rate may be proportional to the 0.66, 1.0, or 1.5 power of the acid activity, depending on the controlling reaction.

CONCLUSIONS

From this discussion of the oxidation of molybdenite with different reagents, it appears that some of the oxidizers can be utilized effectively for the dissolution of the ore. Each lixiviant has advantages and disadvantages, and its effectiveness is dependent on the characteristics of the ore to be treated. Although significant progress has been made in determining suitable reagents, considerable additional testing is needed to establish the best oxidizer and optimum conditions for the dissolution of molybdenum from the Questa deposit.

With each of the reagents tested for leaching molybdenite, the sulfur is oxidized to sulfate, a total electron transfer of 16 for the two S atoms. The molybdenum is oxidized from Mo(IV) to Mo(VI), requiring an electron change of two and making a total electron transfer of 18 for each molybdenite unit. Sixteen of the 18 electrons transferred, or about 90 per cent of the oxidizing capacity of the reagent utilized, are used to oxidize sulfur. If a means may be found to retard or to prevent oxidation of sulfur, very important savings in reagent cost could be realized.

BACTERIAL OXIDATION OF MOLYBDENITE

The Bureau has been active in bacterial oxidation research for the last two years, using five strains of bacteria obtained from the American Type Culture Collection, Washington, D.C. The bacterial strains under investigation are *Thiobacillus thiooxidans* (ATCC 8085), *Thiobacillus ferrooxidans* (ATCC 13728), *Ferrobacillus ferrooxidans* (ATCC 13661), *Thiobacillus concretivorus* (ATCC 13730), and *Thiobacillus thio-parvus* (ATCC 8153).

In leaching experiments, test tubes and percolation columns are charged with high-grade molybdenite,

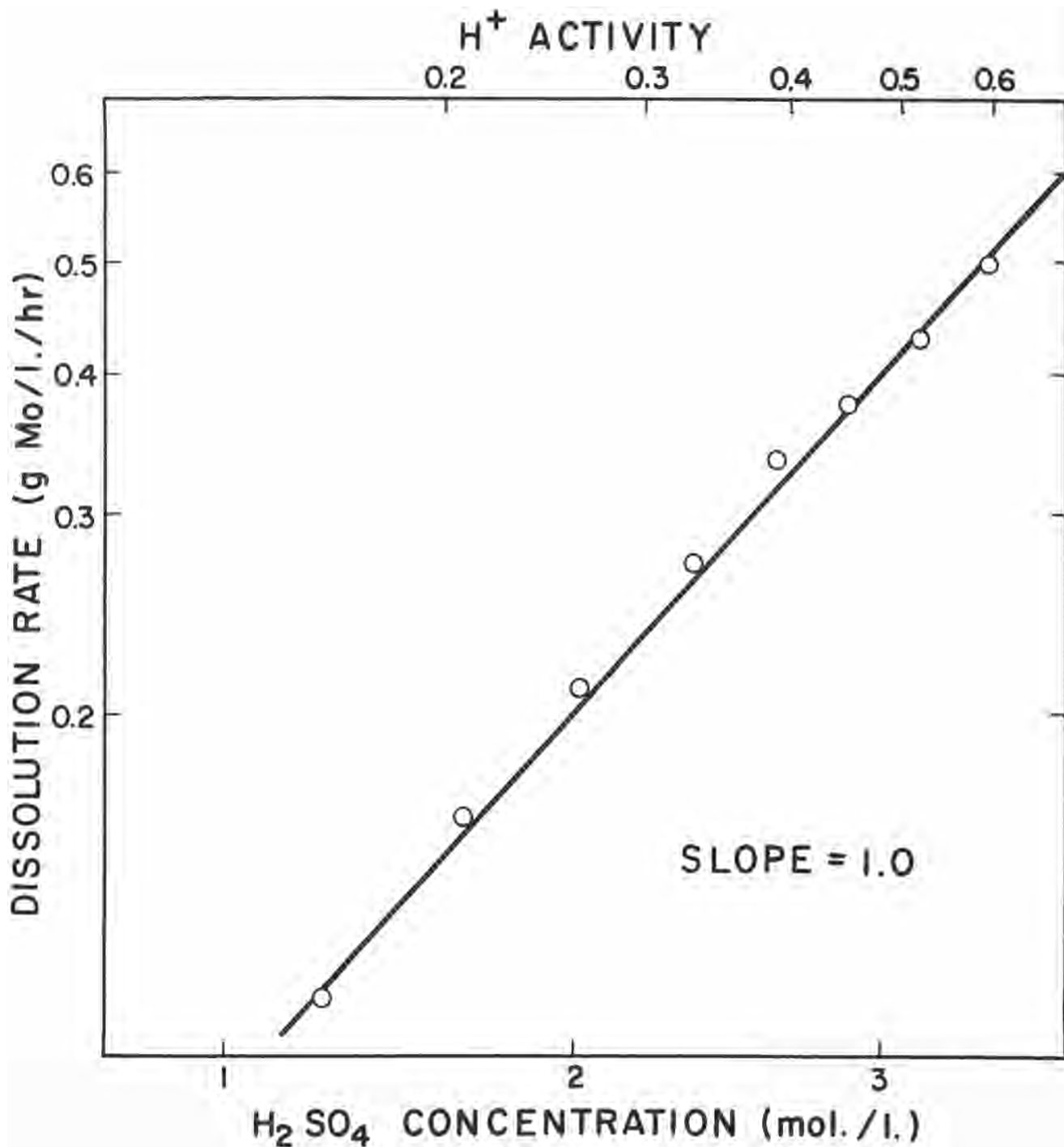


Figure 1
EFFECT OF VARYING H₂SO₄ CONCENTRATION ON THE DISSOLUTION RATE OF MoS₂ AT CONSTANT CONCENTRATION OF NaClO₃ (5%)

silicon dioxide, and nutrient solutions. After loading, the tubes and columns are inoculated with different types of bacteria, provided with a source of air bubbled through water and filtered through sterile cotton, and

kept in a dark room maintained at a constant temperature of 80° F. Small portions (3 milliliters) of the nutrient solutions are removed from the tubes or columns every seven days for pH determination and molyb-

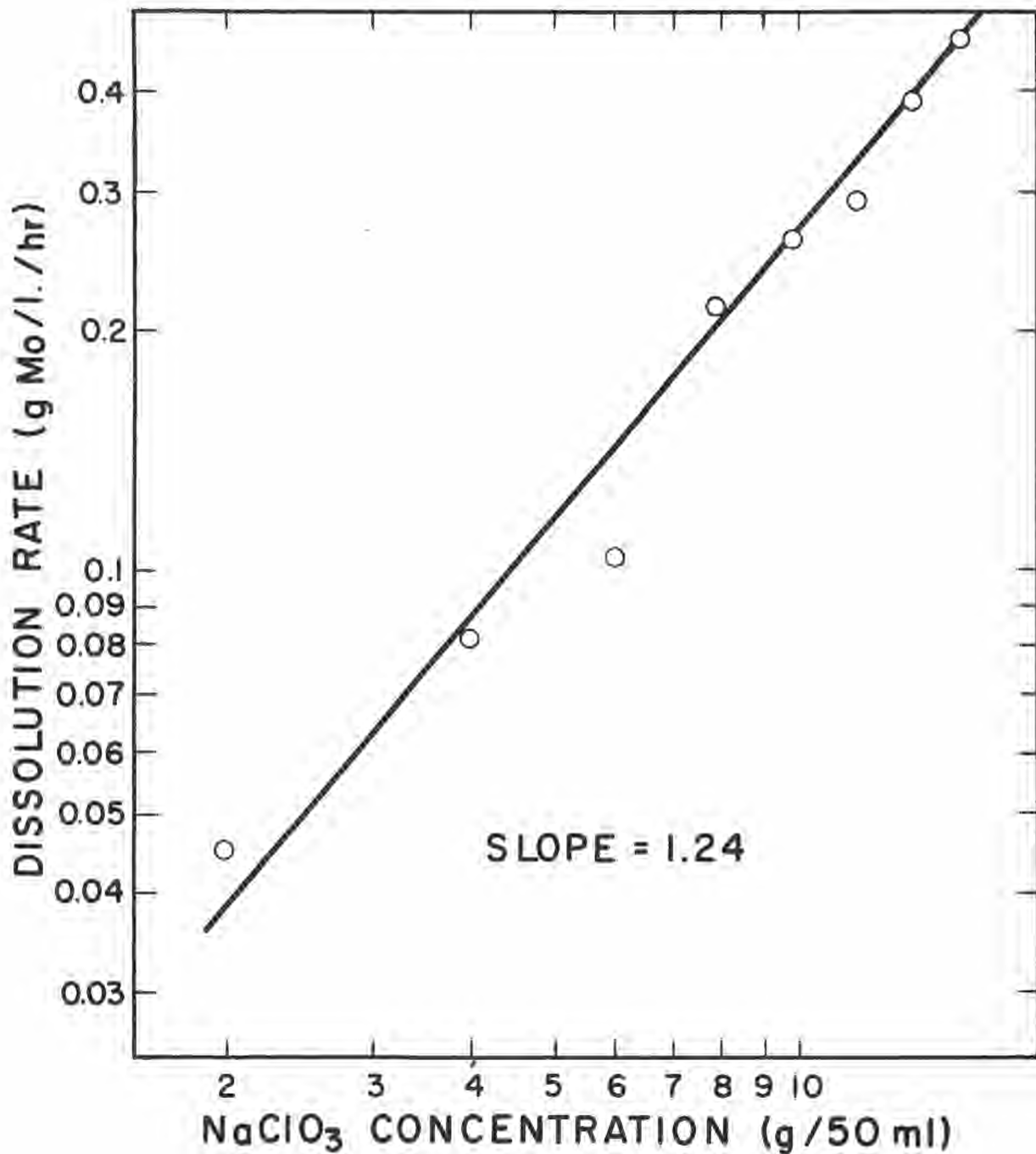


Figure 2

EFFECT OF VARYING NaClO_3 CONCENTRATION ON THE DISSOLUTION RATE OF MoS_2 AT CONSTANT CONCENTRATION OF H_2SO_4 (2% by volume)

denum analysis, replaced with fresh stock solutions, and the systems allowed to percolate continuously for a predetermined leaching period. This procedure is different from the standard method in which the solutions are drained from the systems every week and replaced with fresh nutrient media. The former

method is preferred because it gives practical data on leaching of ores by showing the effect of diverse mineralogy and interfering ions on the dissolution of the metal from ores. Slides for observing bacterial growth within the tubes and columns are made each week by using the Gram staining techniques. Also, stock cul-

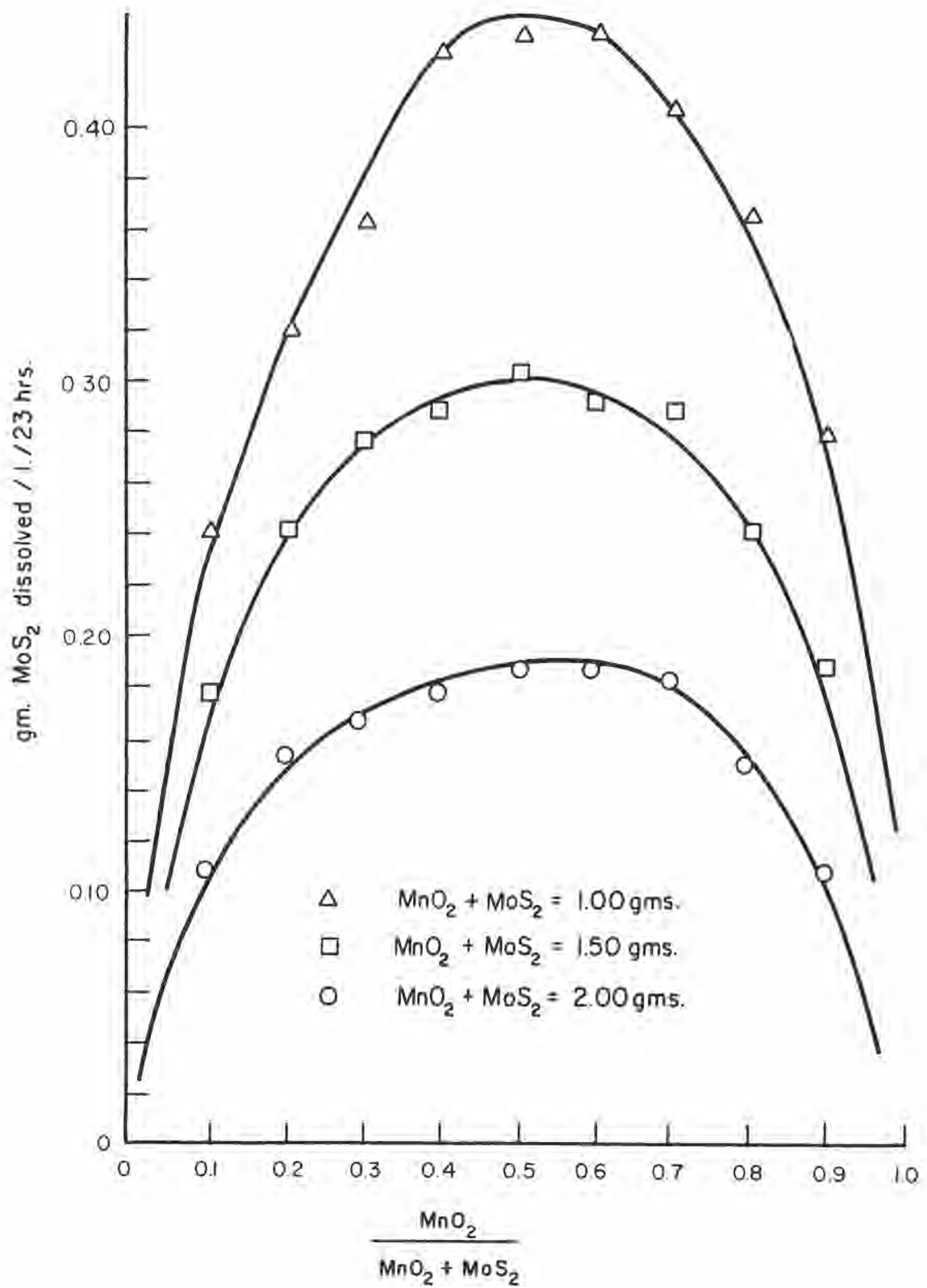


Figure 3

CURVES SHOWING DEPENDENCE OF DISSOLUTION RATE OF MoS₂ ON RATIO OF MnO₂ TO TOTAL WEIGHT OF SOLIDS (MnO₂ + MoS₂)

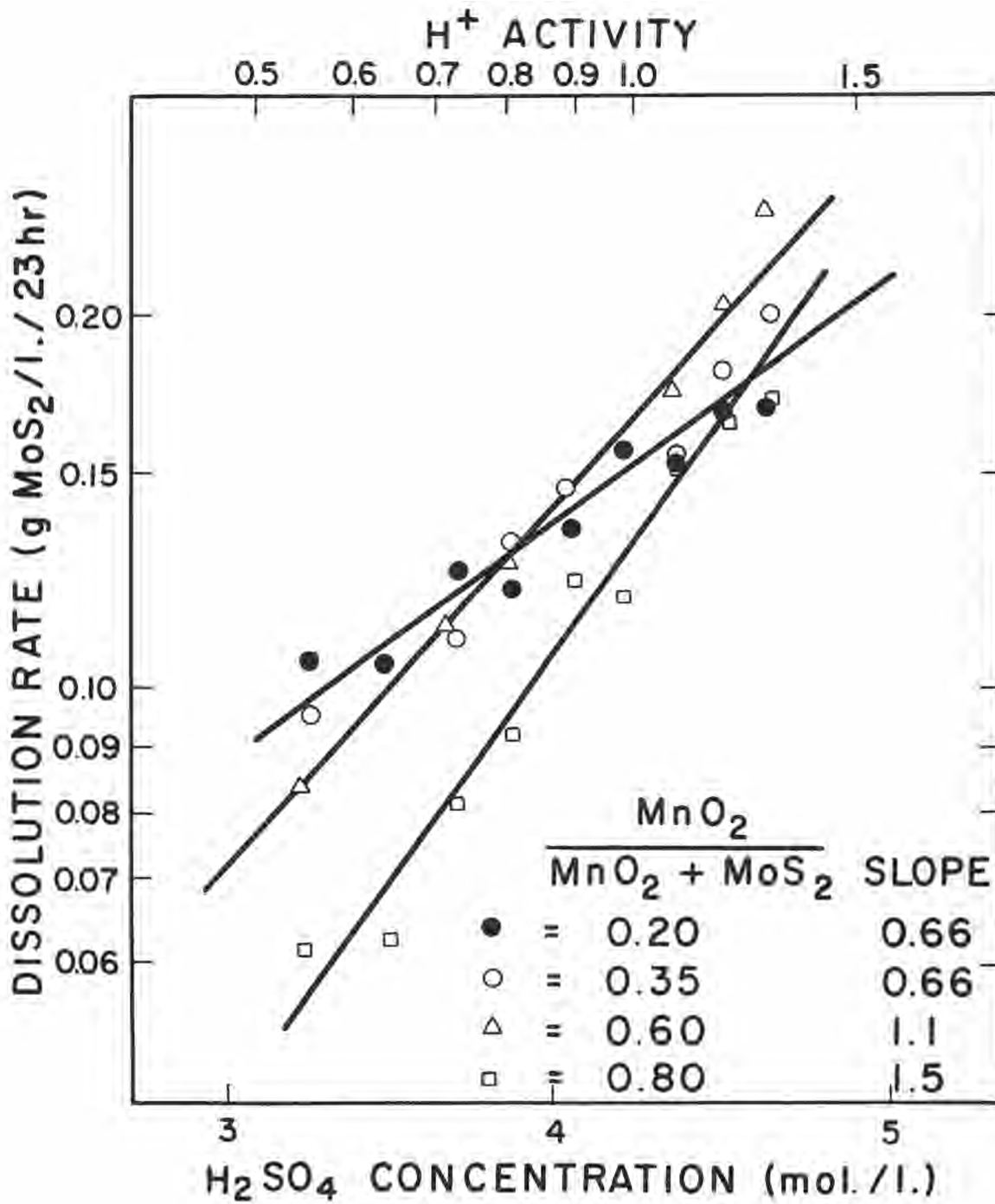


Figure 4

EFFECT OF VARYING H_2SO_4 CONCENTRATION ON THE DISSOLUTION RATE OF MoS_2 AT DIFFERENT WEIGHT FRACTIONS OF MnO_2 IN SOLIDS (g)

tures of the five bacterial strains used in the experiments are maintained and transferred to fresh stock solutions once every two weeks.

The results of bacterial leaching tests on high-grade molybdenite over a period of two months, as reported in Table 2, indicate that the action of *Thiobacillus*

TABLE 2. DISSOLUTION OF MoS₂ WITH DIFFERENT TYPES OF BACTERIA

TIME (days)	DISSOLVED MO (mg/liter)								
	*A	B	C	D	E	(A+B)	K	Q	S
14	2.05	1.26	0.87	1.37	0.80	1.83	0.70	2.15	1.16
28	3.31	3.30	2.03	1.78	1.13	3.98	1.50	2.57	1.38
42	4.36	5.62	3.10	2.66	1.46	5.63	4.55	3.04	1.43
56	5.94	6.60	3.24	3.58	1.50	7.50	7.00	5.96	1.53
70	8.32	7.22	3.70	3.96	1.72	9.26	9.16	9.17	1.64

*Type of bacteria utilized;

A—*Thiobacillus ferrooxidans*

B—*Thiobacillus thiooxidans*

C—*Ferrobacillus ferrooxidans*

D—*Thiobacillus concretivorus*

E—*Thiobacillus thioparus*

K—Kennecott culture

Q—Questa culture

S—Sterile control

ferrooxidans resulted in the oxidation of 5.1 times more molybdenite than in the sterile control. Action of *Thiobacillus thiooxidans* resulted in the oxidation of 4.4 times more, and the combination of *Thiobacillus ferrooxidans* and *Thiobacillus thiooxidans* resulted in the oxidation of 5.7 times more molybdenite than in the sterile sample. On the other hand, *Ferrobacillus ferrooxidans* and *Thiobacillus concretivorus* were found to be poor oxidizers, and *Thiobacillus thioparus* was the least active.

Identical tests were also run on a culture of the Bingham (Utah) mine water, supplied through the courtesy of Kennecott Corporation, and one obtained from the Questa mine water. The results of these tests indicate that the Kennecott culture was not successful in oxidizing molybdenite during the initial period. However, within a few weeks, the culture became adapted and acted quite favorably. The main reason for the slow action of the Kennecott culture at the beginning appears to be its lack of tolerance to the unaccustomed environment, since it was obtained from a molybdenum-free location. On the other hand, the Questa culture, already conditioned to molybdenum, was quite active from the start and resulted in the oxidation of 5.6 times more molybdenite than in the sterile sample. Although not conclusively determined, the Questa culture, like the cultures from Kennecott and other mine waters from Southwestern copper

mines, appears to contain *Thiobacillus thiooxidans*, *Thiobacillus ferrooxidans*, and *Thiobacillus concretivorus*, a strain similar to *Thiobacillus thiooxidans*.

One of the major problems faced in any bacterial leaching program is the tolerance of the specific bacterial strains to metallic ions in solution. The test results showed that the fresh strain of *Thiobacillus thiooxidans* can tolerate up to 9 ppm Mo, *Thiobacillus ferrooxidans* 8 ppm, *Ferrobacillus ferrooxidans* 6 ppm, the Kennecott culture 9 ppm, and the Questa culture 10 ppm. Such tolerances are obviously too low to be of commercial value, and efforts are under way to obtain higher tolerances by acclimatizing the bacteria to increasing molybdenum concentrations.

On the basis of the preliminary work, leach columns have been set up for investigating the dissolution of molybdenite from natural ores by all the bacterial strains, including the Kennecott and the Questa cultures. Initial results of several months of testing indicated very little molybdenum in leach solutions. At the start, it was difficult to retain the desirable pH of 2.0 in the columns because of acid-consuming gangue in the ore samples. The lack of pH control might have adversely affected the bacterial activity. This problem was overcome by preconditioning the ore with sulfuric acid to obtain a stable pH of 2.5 prior to the introduction of bacteria into the columns. Maximum activity (15 to 25 ppm Mo) was reached at the end of the second or the third week for all the strains investigated. Thereafter, the molybdenum in solution dropped abruptly to about 4 ppm Mo and then gradually to about 1 ppm Mo, over the next several weeks. Exploratory tests indicate that this might result from the formation of insoluble molybdenum complexes with iron, calcium, aluminum, and other cations present in the leach solution at pH 2.5. The maximum molybdenum concentration probably represents supersaturation. Such supersaturations are known to occur for many molybdenum complexes. To overcome this difficulty, efforts have been made to keep the iron in the reduced state by using a mixture of sulfurous and sulfuric acids for pH adjustments, lowering the pH of the solutions to about 1.0 to prevent the formation of the molybdenum complexes, and by using suitable chelating agents to tie up the detrimental ions. The latest analyses of solutions indicate a gradual increase in the molybdenum content. The complexing of molybdenum with various cations will be a serious problem in acid leaching or bacterial leaching of low-grade ores and deserves further detailed investigation to find means of overcoming this difficulty.

Dissolution of Nonsulfide Molybdenum Minerals

The molybdenum values contained in nonsulfide fractions in the oxidized zones of molybdenum deposits have in recent years been a subject of study by several investigators (Jones, 1957; Vinogradov, 1957; Mikhailov, 1962; Schaller, 1907; Kerr, Thomas, and Langer, 1963; Furbish and Sarafian, 1964). The mode of occurrence of nonsulfide molybdenum minerals is important not only from purely scientific viewpoints of geochemistry and ore genesis but also from its economic importance as an additional source of molybdenum metal. This is clearly demonstrated by the recent addition of an oxide-molybdenum plant to the Climax operation.

In the Questa deposit, a significant amount of molybdenum is present in the oxidation zone of the proposed open pit. Since a large proportion of the oxide content will be associated with the sulfide fraction during the first few years of mining, it is imperative that efforts be made to recover the oxide values along with the sulfides. Also, the oxide content left in place or in the waste dumps may constitute a substantial reserve of the metal, so some thought should be given to the extraction of metal from such oxide material.

Petrographic examinations and chemical analyses by the Bureau's laboratory and independent investigators (Carpenter, Lang, personal communications, 1964) have shown that molybdenum occurs primarily within the zone of oxidation in the following ways:

1. as *molybdenite*, increasing in grade with depth and partly unstable because of relatively high acidity;
2. as *Ferrimolybdite*, $\text{Fe}_2(\text{MoO}_4)_3 \cdot n\text{H}_2\text{O}$, the canary-yellow-colored hydrous ferric molybdate, occurring in a variety of ways, such as tiny acicular crystals disseminated in various minerals, as late crosscutting veinlets, as tufts, and as powdery coatings on molybdenite;
3. as *molybdenum-bearing hydrous iron oxides*, which have been thought to be a mechanical mixture of colloidal molybdenum oxidation products such as $\text{MoO}(\text{OH})_3$ with ferric oxide complexes, adsorption of these products on ferric oxide mineral surfaces, or a chemical combination of ferric iron and molybdate ion to form ferrimolybdite; and
4. in *association with clay assemblages*, as a crystalline precipitate of aluminum molybdate hydrate $[\text{2Al}(\text{H}_2\text{O})_4(\text{OH})_2] \text{MoO}_4$ and as molybdenum adsorbed by kaolin and amorphous allophane.

The examination also revealed that about 20 per cent of the molybdenum value in oxide minerals was contained

in ferrimolybdite and about 80 per cent in the limonite fraction, with only a minor amount contained in the clay fractions. Therefore, dissolution of ferrimolybdite and iron-oxide minerals was studied in detail.

Leaching tests were conducted on a high-grade specimen of ferrimolybdite from the Questa mine. The composition of the mineral is $\text{Fe}_2\text{O}_3 \cdot 3\text{1MoO}_3 \cdot 10\text{H}_2\text{O}$, containing 56.0 per cent MoO_3 and 73.5 per cent MoO_3 (dehydrated basis). Experiments on the solubility of the mineral were made in solutions with various pH values, the acid solutions being prepared by adding sulfuric acid to distilled water and the alkaline by adding caustic soda. Since equilibrium was attained within one day, a 24-hour contact time was allowed. Similar solubility experiments were also conducted on natural limonite containing up to seven per cent MoO_3 . The results as shown in Figure 5 indicate that it would be possible to leach oxide molybdenum values from their ores by either strong acid or alkali leaching. Naturally, the nature of the associated gangue minerals, either acidic or basic, would govern the type of leaching applied in practice.

Results of acid leaching tests on high-grade (3 to 5 per cent Mo) oxide molybdenum samples indicated good recovery with economically acceptable acid consumption of about 83 pounds H_2SO_4 per ton of ore leached. However, the results from the mine-run oxide ore (73 pounds H_2SO_4 per ton of ore assaying 0.05 per cent Mo) and initial oxide-flotation concentrate (800 pounds H_2SO_4 per ton of concentrates assaying 0.25 per cent Mo) indicated acid leaching to be impractical because of excessive acid consumption by the highly calcareous gangue in the ore.

Investigation into alkali leaching of the mine-run oxide ore and flotation concentrate indicated carbonate leaching to be most promising. As shown in Figure 6, about 94 per cent dissolution was obtained in one hour at 99° C, with 2.5 per cent Na_2CO_3 , from an oxide-flotation concentrate assaying 0.255 per cent oxide molybdenum. Three moles of carbonate are required to dissolve one mole of oxide molybdenum, giving a very favorable reagent cost for leaching. Because of the heat involved in the process, it would be necessary to treat high-grade oxide ores or concentrates obtained from lower grade material. Indications are that some of the sulfide molybdenum contained in the oxide ores is dissolved by the carbonate solution.

If leaching is attempted on a mixed sulfide-oxide ore (including in-place leaching), either a basic hypochlorite-carbonate leach or an acid-chlorate leach would dissolve molybdenum from both types of minerals. The type of leaching, alkali or acid, is governed by the associated gangue minerals contained in the de-

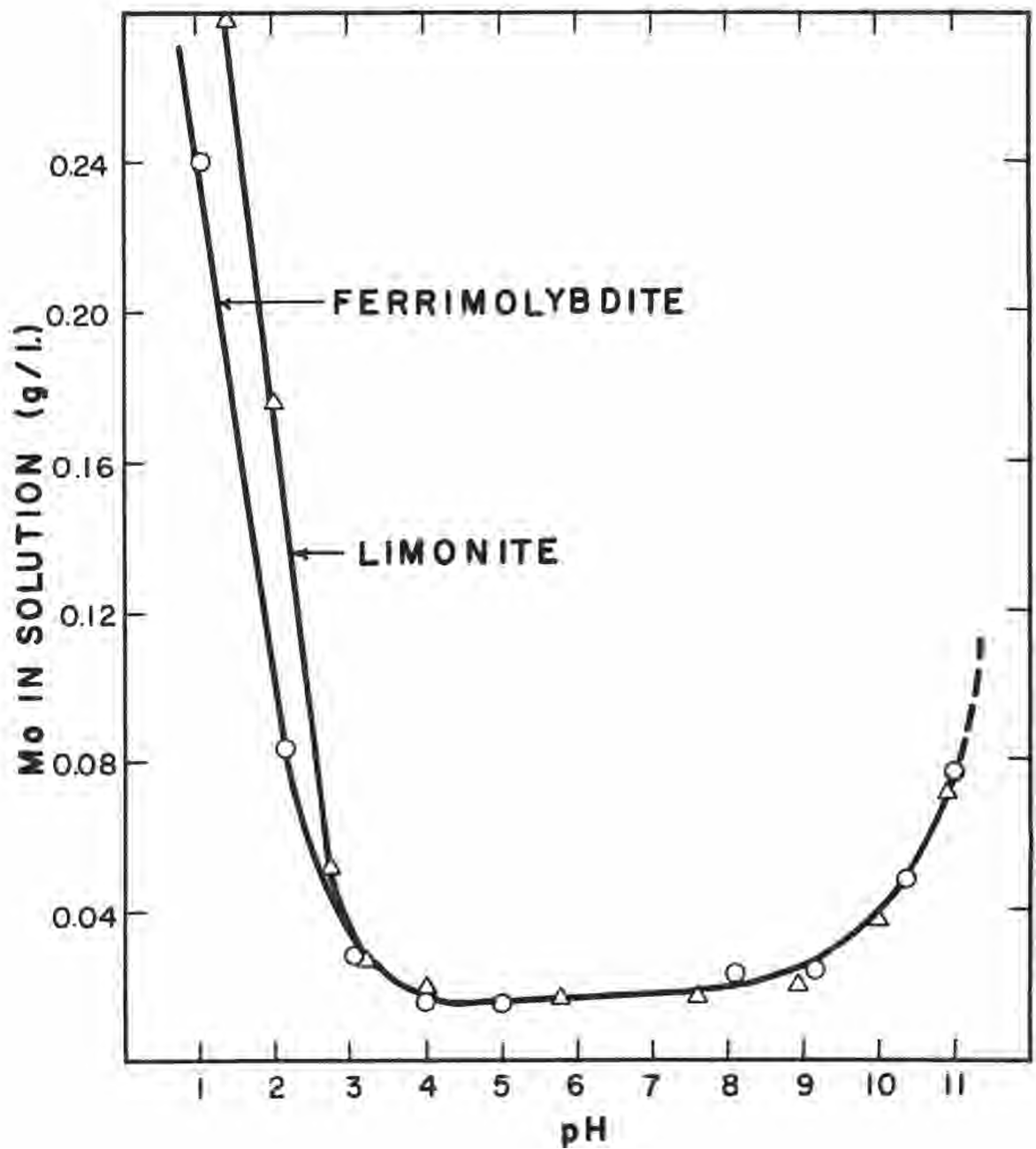


Figure 5
DISSOLUTION OF MOLYBDENUM FROM FERRIMOLYBDITE AND LIMONITE AS A FUNCTION OF THE PH VALUE OF THE INITIAL SOLUTION

posit. If acid leaching is used, it is imperative to keep the iron in the reduced state to avoid its precipitation with molybdenum ions. Because of the difficulties encountered in acid leaching, such as the precipitation of

insoluble ferric molybdate, calcium molybdate, and aluminum molybdate and the presence of acid-consuming gangue in the Questa ore, it appears that an alkali leach may be preferable.

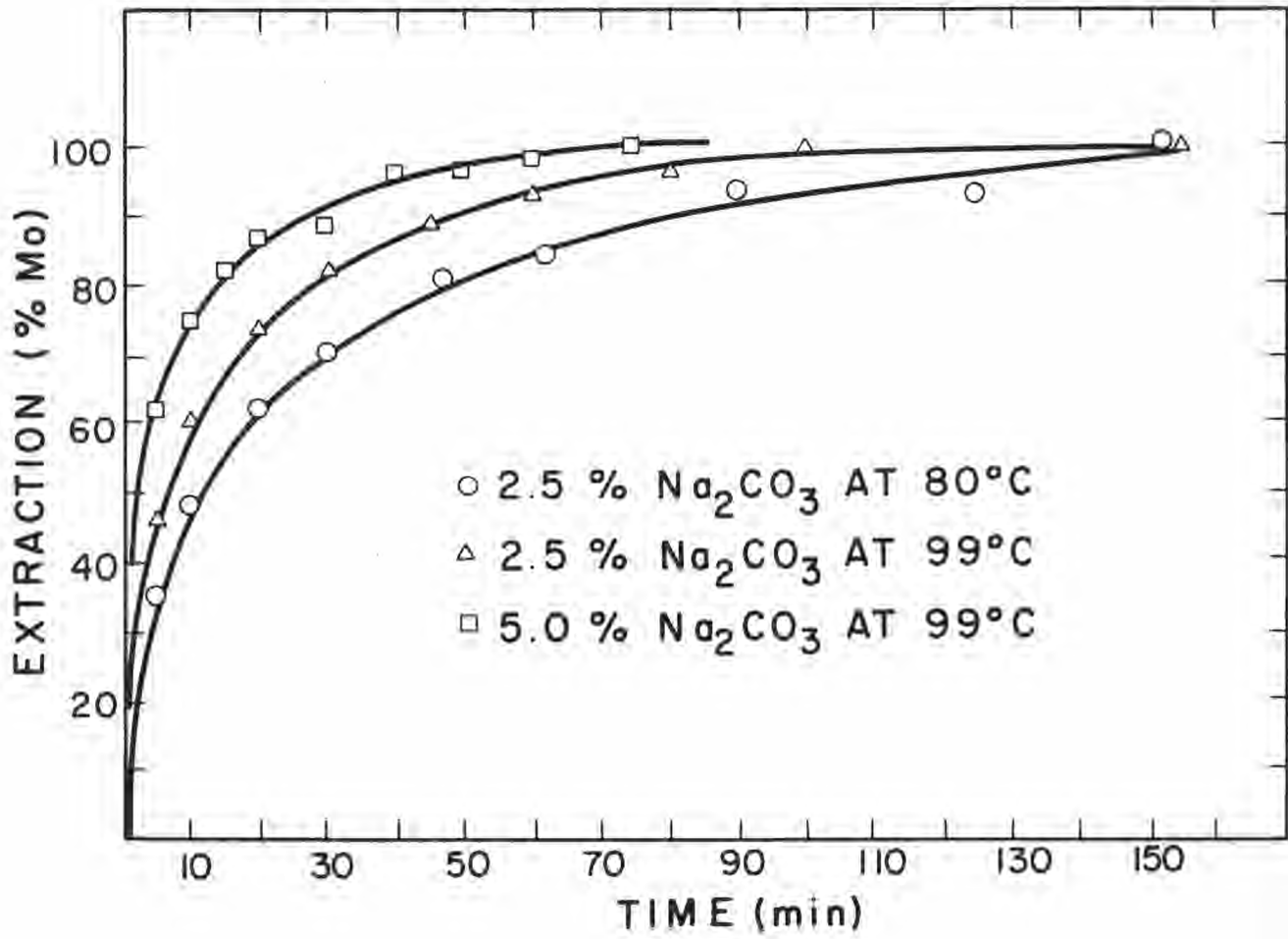


Figure 6

TYPICAL CURVES SHOWING EXTRACTION OF MOLYBDENUM FROM OXIDE FLOTATION CONCENTRATE VERSUS TIME AT VARYING Na₂CO₃ CONCENTRATIONS AND TEMPERATURES

Recovery of Molybdenum from Leach Solutions

ION EXCHANGE

Cox and Schellinger (1958) reported recovery of molybdenum from dilute sodium hypochlorite leach solutions by anion exchange. They indicated that the leach solutions were passed directly through a column of the resin, and the adsorbed molybdate eluted with 2 M sodium hydroxide.

Anion exchange was used by Fisher and Meloche (1952) to effect the analytical separation of molybdenum and rhenium. The ions were absorbed from 1 N sodium hydroxide, and the molybdenum was removed with a large volume of 2.5 N sodium hydroxide. After acidifying the column, rhenium was eluted with 7 N hydrochloric acid. The method was improved by Meloche and Preuss (1954) by eluting molybdenum with 1 M oxalate solution and recovering the rhenium with 1 M perchloric acid.

The above reports were used as guides in the work reported here. Absorption of molybdenum from hypochlorite leach solutions was attempted using conditions described by Cox and Schellinger. Little molybdenum was absorbed, and resin exchange capacity was largely destroyed by the hypochlorite. When excess molybdenite was used to remove the oxidizing agent, much of the molybdenum was reduced to a lower oxidation state, cationic in form, and was not retained, by the resin. If, however, the leach solutions were acidified and the free chlorine removed, molybdenum was absorbed quantitatively by a strongly basic anion exchange resin.

Equilibrium distribution coefficients were measured for Mo(VI) in dilute solution over a wide range of acid and base concentrations. Four commercially available resins were studied: Dowex 1-X8, Dowex 2-X8, and Dowex 21 K (Dow Chemical Co.), and Amberlite IRA-400 (Rohm and Haas). The resins, in the 50 to 100 sieve-size range and in the chloride form, were air-dried before use.

Five grams of a dry resin and 50 milliliters of a 0.01 M sodium molybdate solution adjusted to the desired pH between zero and 14 were equilibrated by continuous mixing for 24 hours. After equilibration the solution was analyzed for residual molybdenum by the phenylhydrazine spectrophotometric method of Ayres and Tuffly (1951). All tests were run in duplicate and the results averaged for graphical presentation (fig. 7). The equilibrium distribution coefficient, D , was calculated from the relation

$$D = \frac{\text{mg Mo absorbed per g resin}}{\text{mg Mo per ml of solution}} \quad \text{at equilibrium.}$$

Solutions of the same Mo(VI) content were prepared covering the range from 9 N hydrochloric acid to 9 N sodium hydroxide. These were equilibrated with por-

tions of the IRA-400 resin as described. The results, shown graphically in Figure 8, are not greatly different from those reported by Meloche and Preuss for greater than one normal concentrations of acid or base. The data for IRA-400 from Figure 7 are included in Figure 8 to show completely the anion exchange behavior of hexavalent molybdenum.

The final pH of the solution differed from the initial values for most of the tests. Figure 9 shows the variations observed for the four resins studied. A buffering action is indicated, varying from weak for Dowex 1 to strong for Dowex 2, with Dowex 21 K and IRA falling in between.

As shown in Figure 7, the absorption behavior of Mo(VI) does not differ greatly for the four resins. The differences probably represent variations in resin characteristics, since the data for each resin were quite reproducible. The irregular variation of D with pH must then be referred to changes in the molybdenum-containing ionic species predominant at the different pH values. It seems reasonable, in view of the sluggishness often observed for transformations involving molybdenum, that the initial pH may have a greater influence than does the final pH.

As shown in Figure 8, at least five regions with widely varying absorption behaviors may be differentiated. The most prominent feature is Region II, in the range 0 to 5 pH. The D values are extremely high in this range and peak about at its center. Generally such high values, 10^5 and greater, are observed only for heavy, polyvalent ions. The ionic species present here are probably polyvalent polymeric forms of the type $[(\text{MoO}_3)_x \cdot (\text{H}_{10} \text{O}_4)_y]^{y-}$, where x and y may have values from 2 to 24, the so-called "isopoly" acids. These are formed as a basic solution of molybdate is gradually acidified. The molybdate ion, $^-\text{O}-\text{MoO}_2-\text{O}^-$, is converted to the acid molybdate ion, $\text{HO}-\text{MoO}_2-\text{O}^-$, and to molybdic acid, $\text{MoO}_2(\text{OH})_2$. The OH-containing forms may condense (by elimination of water) to form the multicharged polymer ions. The smaller of these may form at about pH 5 and may grow larger with decreasing pH until at about pH 2.5 an optimum size peaks the absorption. At still lower pH, the polymer units may become too large to enter the pores of the resin, thus causing a very large drop in D . This probably would go nearly to zero, except that near zero pH, precipitation of MoO_3 (the limit of polymerization) becomes a factor. Molybdenum removed from solution by precipitation would be difficult to distinguish from that absorbed by the resin. It has also been postulated by Killeffer and Linz (1952) that in the low pH range, the Mo(VI) may become cationic (MoO_2^{+2}) and thus fail to co-operate in anion exchange. If such an ion should exist, it would most likely be "neutralized" by

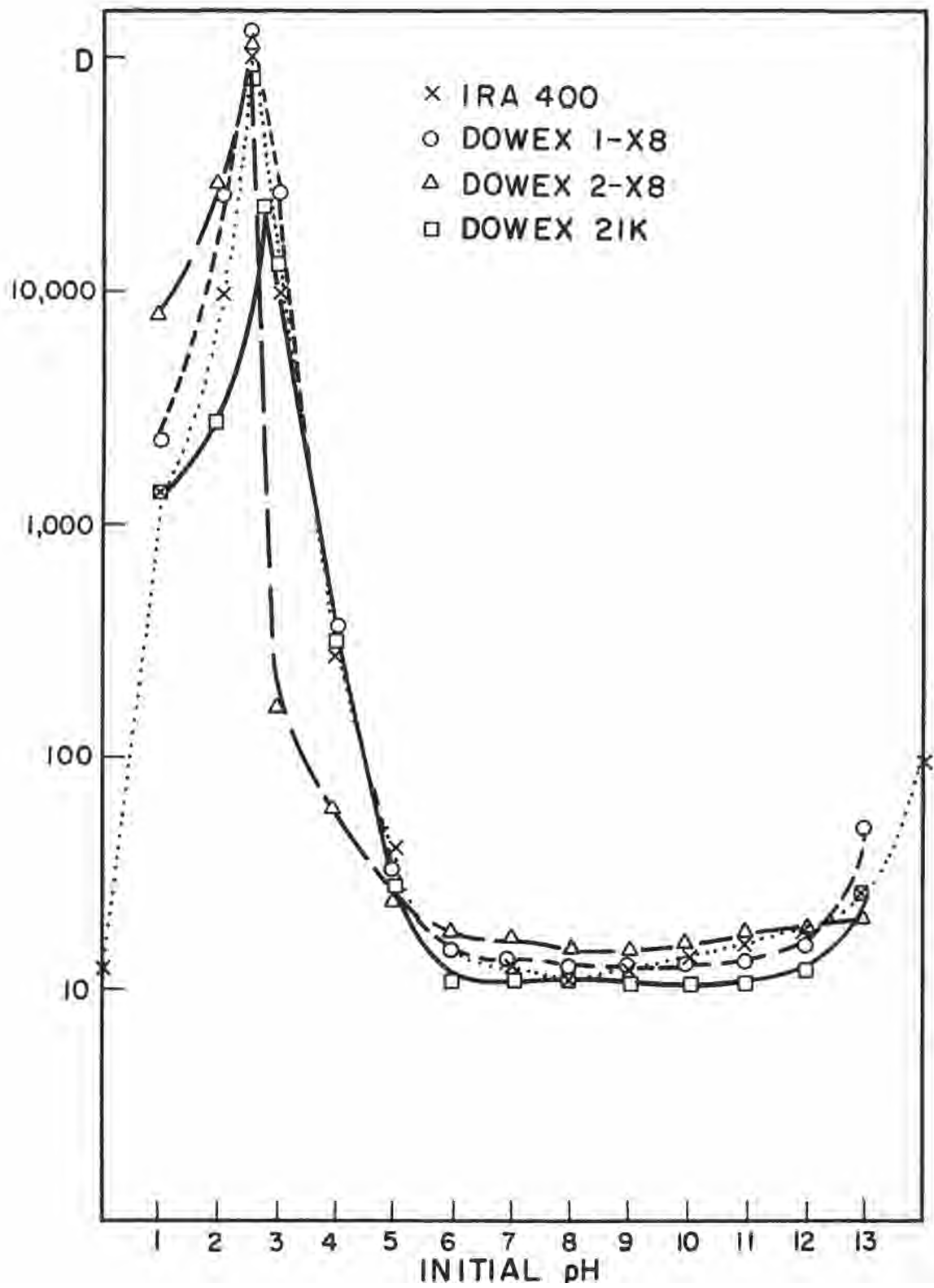


Figure 7

DISTRIBUTION COEFFICIENTS FOR $Mo(VI)$ ON SOME STRONGLY BASIC ANION EXCHANGE RESINS AS FUNCTIONS OF INITIAL PH OF THE SOLUTIONS

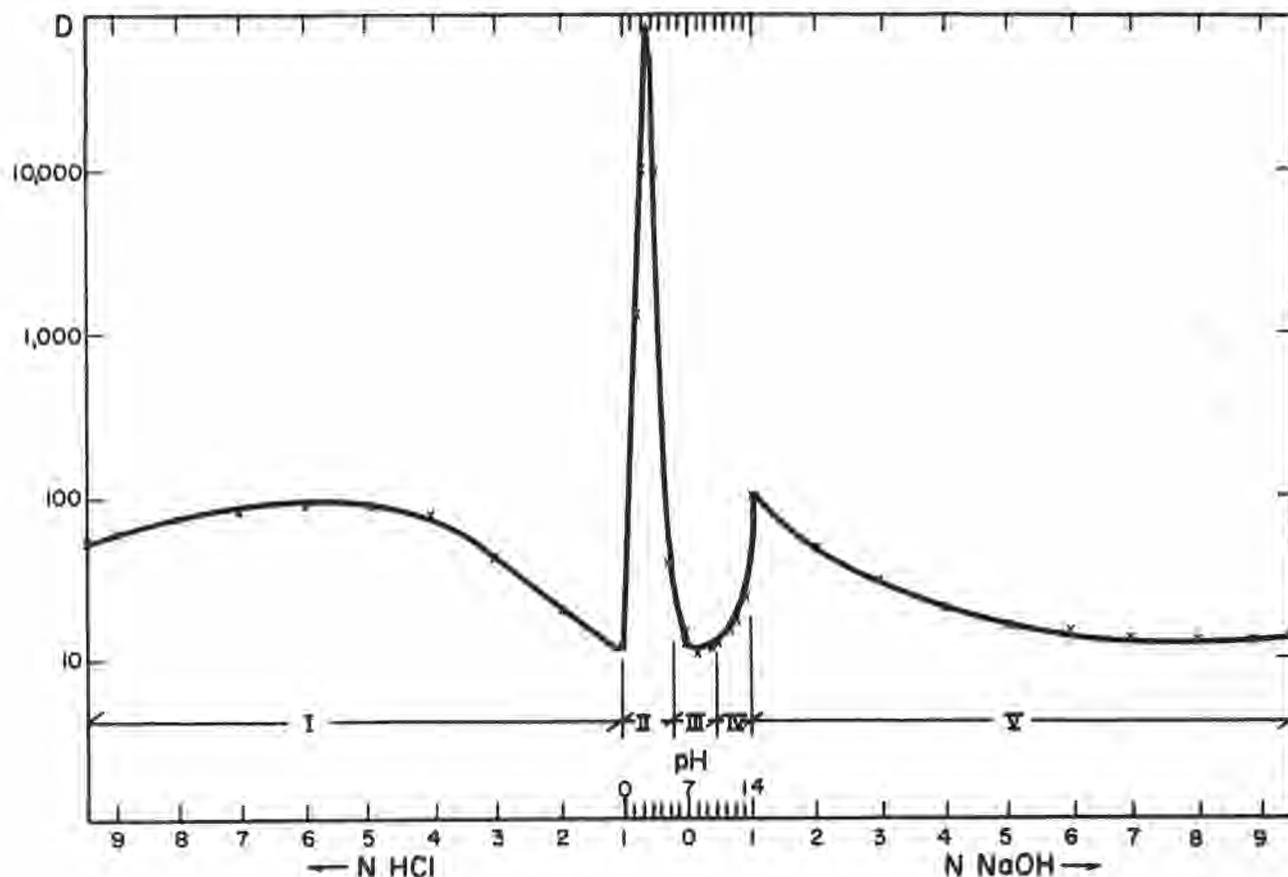


Figure 8

DISTRIBUTION COEFFICIENTS FOR Mo(VI) ON IRA-400 ANION EXCHANGE RESIN FOR A WIDE RANGE OF ACID AND BASE CONCENTRATIONS

combining with one or two of the anions present to make a polymer and would only suggest a rather improbable mechanism for the polymerization.

As the acid concentration increases above 1 N (entering Region I), precipitation may be increased by the higher acidity and at the same time offset by formation of multicharged chloro-complexes of the type $[\text{MoO}_3 \cdot \text{Cl}_3]^{-3}$. Suppression of complete ionization of such complexes could perhaps account for the decrease in D at hydrochloric acid concentrations above 6 N.

The low point of absorption of Mo(VI) is in Region III, between pH 5 and pH 10. The acid-molybdate ion, HMoO_4 , probably is predominant, its monovalency perhaps accounting for the low D values observed. Region III probably is the range in which molybdenum could be removed most easily from the resin. For IRA-400, pH 8 appears to be most favorable for stripping Mo(VI) from the resin.

Above pH 10, the divalent molybdate ion, MoO_4 , probably predominates to form Region IV and to give a marked rise in absorption at high pH values. D values are still quite high for 2 N and 2.5 N sodium

hydroxide in Region V, thus accounting for the relatively poor showing these concentrations of base make as eluants for molybdenum.

For all four resins, degradation was observed at pH 12, and it increased in degree for higher concentrations of base. Hydrolysis and removal of the amine groupings which constitute the exchange sites appear to be the main type of degradation, although definite charging of the resin was observed at pH 12 and higher base concentrations. Resin degradation may be a cause for the relatively slow decline of D in Region V, although formation of hydroxy-complexes of the type $[(\text{OH})_m \cdot \text{MoO}_4]^{-(m+2)}$ may enter the picture.

From this anion exchange behavior of molybdenum, it is evident that for optimum utilization in recovery from leach solutions, the resin should be loaded at pH 1 to 3 and stripped at pH 7 to 9. The resin could be loaded quite effectively at pH 14, but it would probably deteriorate rapidly upon reuse. Much evidence has been found that although a strongly basic anion exchange resin may be loaded relatively easily, unloading may become a considerable problem. Preliminary studies with weakly basic (amine rather than quater-

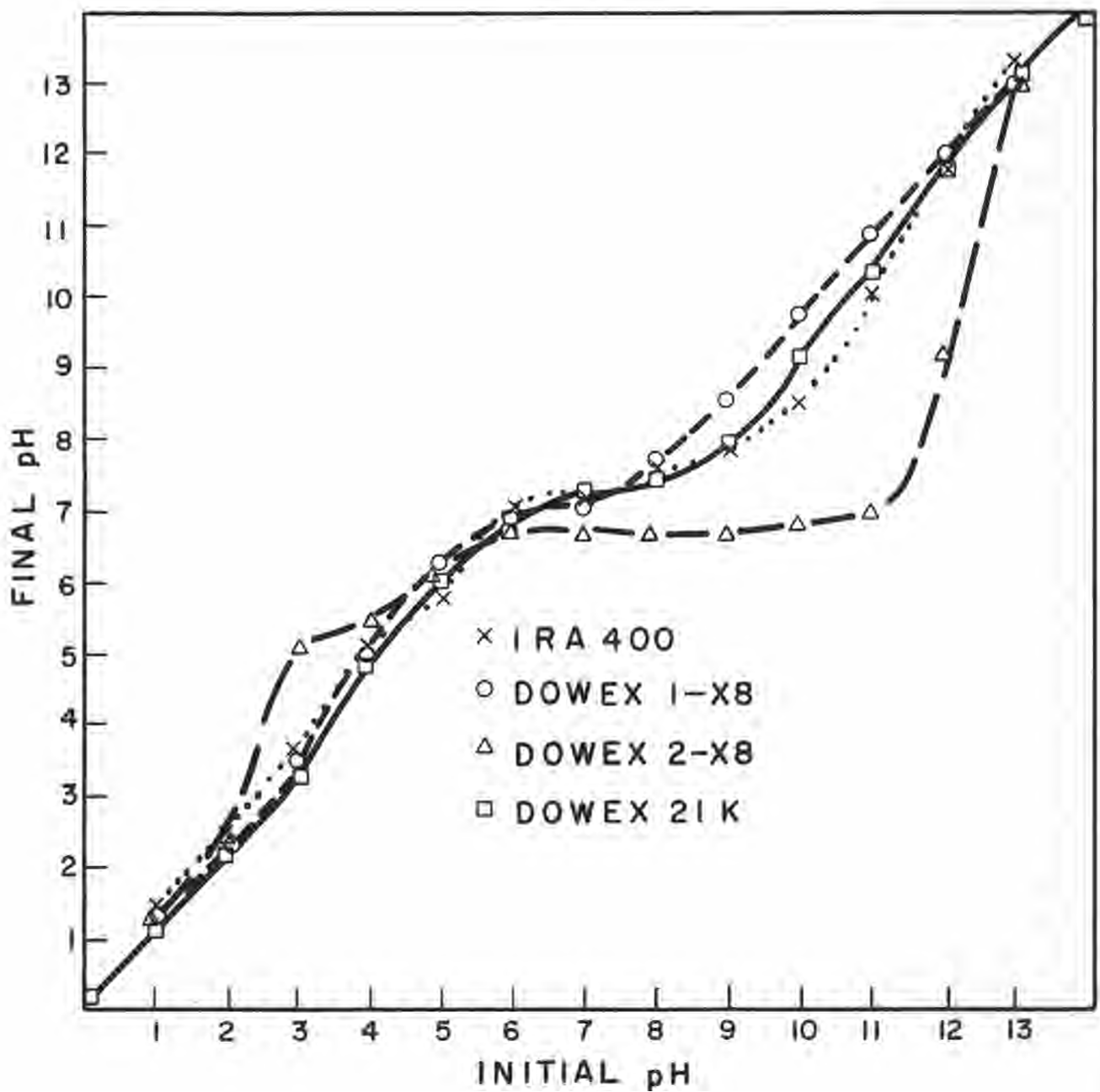


Figure 9

VARIATION OF FINAL PH WITH INITIAL PH FOR AQUEOUS Mo(VI) SOLUTIONS UPON ABSORPTION OF SOME STRONGLY BASIC ANION EXCHANGE RESINS

nary ammonium types) anion exchanges indicate that these may be more satisfactory for recovery of molybdenum. Both of these projects are being actively pursued and will be reported when completed.

SOLVENT EXTRACTION

Recovery of molybdenum from uranium mill circuits using a quarternary ammonium chloride (Aliquat

336, General Mills) in an inert hydrocarbon solvent has been reported by Lewis and House (1960). Procedures were developed for extraction from sodium carbonate scrub solutions and from uranium-barren alkaline leach solutions.

In the current investigation, solvent extraction of Mo(VI) from aqueous solutions as a function of pH was studied for three commercially available amines. The amine was dissolved to form a 0.1 solution in a

solvent consisting of 0.1 M 1-octanol in a high-boiling petroleum ether. The alcohol serves to increase the solubilities of the amine and the amine-molybdenum complex in the organic phase.

The three amines used were as follows:

1. *Aliquat 336* (General Mills), a quaternary ammonium chloride, R_3CH_3NC1 , where R is a C_8 to C_{12} straight carbon chain, with C_8 predominating. Average molecular weight is 405.
2. *Alamine 336* (General Mills), a tertiary amine, R_3N , predominantly a trioctyl amine. Average molecular weight is 355.
3. *Primene JMT* (Rohm and Haas), a primary amine, RNH_2 , containing 18 to 22 carbons in side chains of 4 to 8 carbons each. The average molecular weight is 315.

A suitable secondary amine was not available at the time these tests were made.

The aqueous phase was a 0.5 M sodium-molybdate solution adjusted to the desired initial pH. Equal volumes of the organic and aqueous phases were equilibrated by continuous mixing for at least 24 hours. The phases were then separated and analyzed for molybdenum by the phenylhydrazine spectrophotometric procedure of Ayres and Tuffly.

Equilibrium distribution coefficients were calculated using the relation

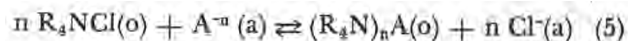
$$D = \frac{\text{concentration of Mo in the organic phase}}{\text{concentration of Mo in the aqueous phase}}$$

Data for Aliquat 336 are shown in Figure 10, in which D is plotted as a function of the initial pH of the aqueous phase. Also shown is the relationship between initial and final pH values. For comparison, the curve for Mo(VI) absorbed on a strongly basic anion exchange resin (Dowex 1-X8) is included.

The two D curves in Figure 10 are seen to be quite similar, as could be anticipated by the near identity of the absorption process for the resin and the quaternary amine. The ionic species are the same for each for a given initial pH, and the sorption in each case involves the exchange of the molybdenum-bearing ion from the aqueous phase for one or more chloride ions from a water immiscible phase. As a consequence, the curve for Aliquat 336 indicates nearly the same pH ranges for the same predominant ionic species as do the curves for absorption by the resin (*cf.* fig. 8). The strong "buffering" action of Aliquat 336 was not anticipated, but it parallels the action of the resins, as shown in Figure 9. In both cases, the pH changes probably must be related to hydrogen ions which in some manner may be associated with the ionic complex

and which may be removed from the aqueous solution by sorption of the complex.

The reaction of extraction by a solution of a quaternary ammonium salt in an immiscible solvent may be represented by



where (o) and (a) represent the organic and aqueous phases, respectively, and A^{-n} is the anionic complex being absorbed. The mass action expression is

$$k = \frac{[(R_4N)_nA]_o}{[A^{-n}]_a} \cdot \frac{[Cl^{-}]_a^n}{[R_4NCl]_o^n} = D \cdot \frac{[Cl^{-}]_a^n}{[R_4NCl]_o^n}$$

from which the distribution coefficient

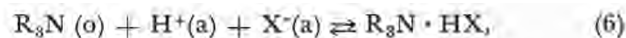
$$D = \frac{k [R_4NCl]_o^n}{[Cl^{-}]_a^n}$$

indicating that D is not a function of pH but is directly to a power of the amine concentration in the organic phase and inversely proportional to a power of the chloride concentration in the aqueous phase.

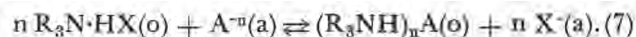
This same expression may be derived for an anion exchange resin, but it can scarcely be applied without making more or less arbitrary assumptions about ionic molecular activities in the resin phase. A fairly rigorous discussion of solvent extraction is summarized by Sandell (1959, Chap. II).

The rapid fall-off of D as the pH falls below 2 may be related to ionic dimensions, as it was for the resins, in this case the polymer complex being too large to be pulled into the organic phase (solubilized) by the amine cations.

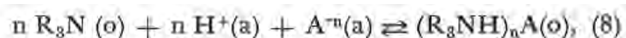
The absorption data for Alamine 336 and Primene JMT are presented as Figure 11. The D-curves are seen to be quite different from the ones obtained for the quaternary exchangers, as could be anticipated from a consideration of the differing mechanisms involved. With the amines, ion exchange can not occur until acid is transferred from the aqueous phase to form the form of the amine



which may be followed by the ion exchange of the metal-containing ionic complexes



Adding equations (6) and (7) gives



from which at equilibrium the extraction constant

$$k = \frac{[(R_3NH)_nA]_o}{[A^{-n}]_a} \cdot \frac{1}{[R_3N]_o^n [H^+]_a^n} = \frac{D}{[R_3N]_o^n [H^+]_a^n} \quad (9)$$

This distribution coefficient expression shows D to be

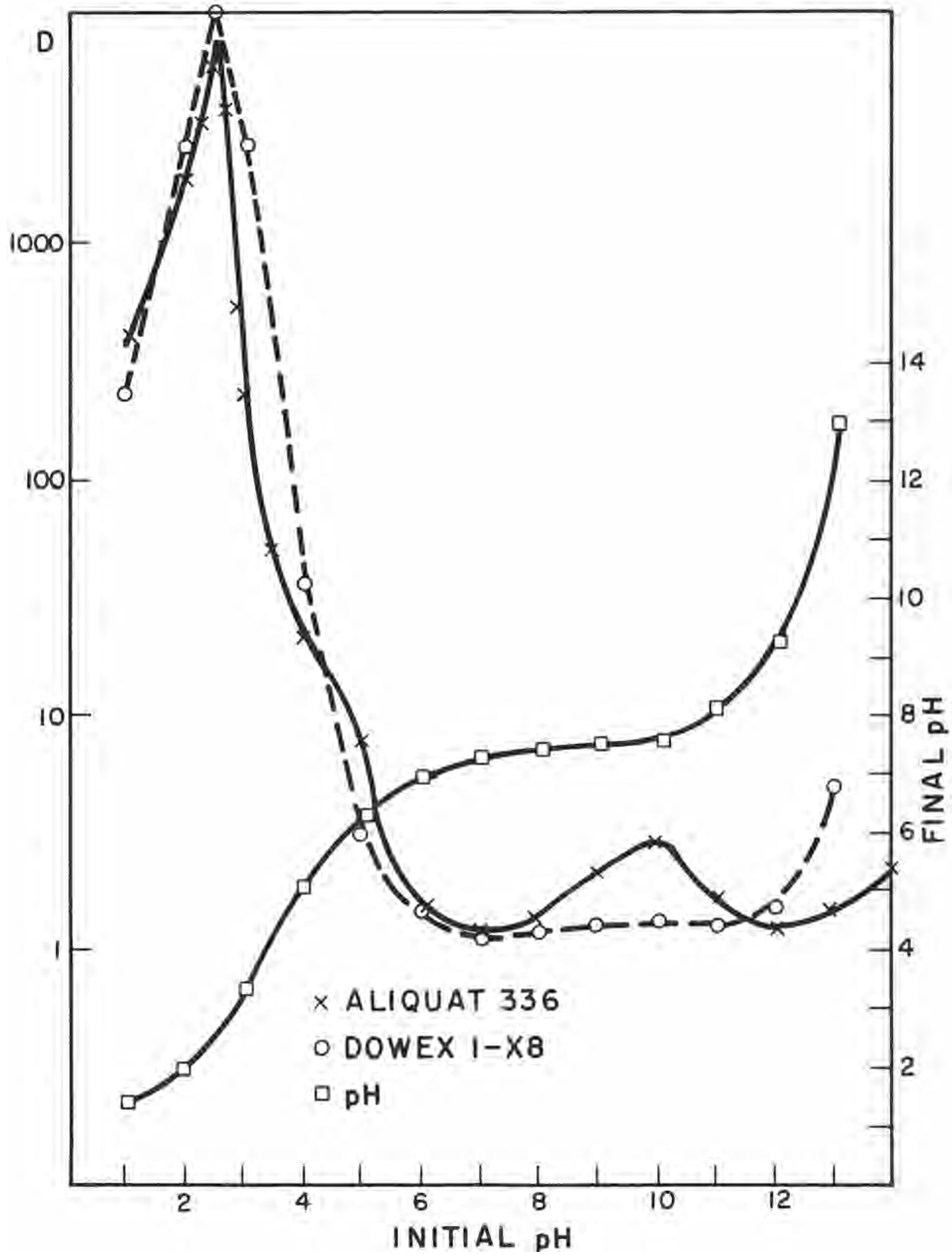


Figure 10

SOLVENT EXTRACTION OF Mo(VI) FROM AQUEOUS SOLUTION BY ALIQUAT 336 AND DOWEX 1-X8

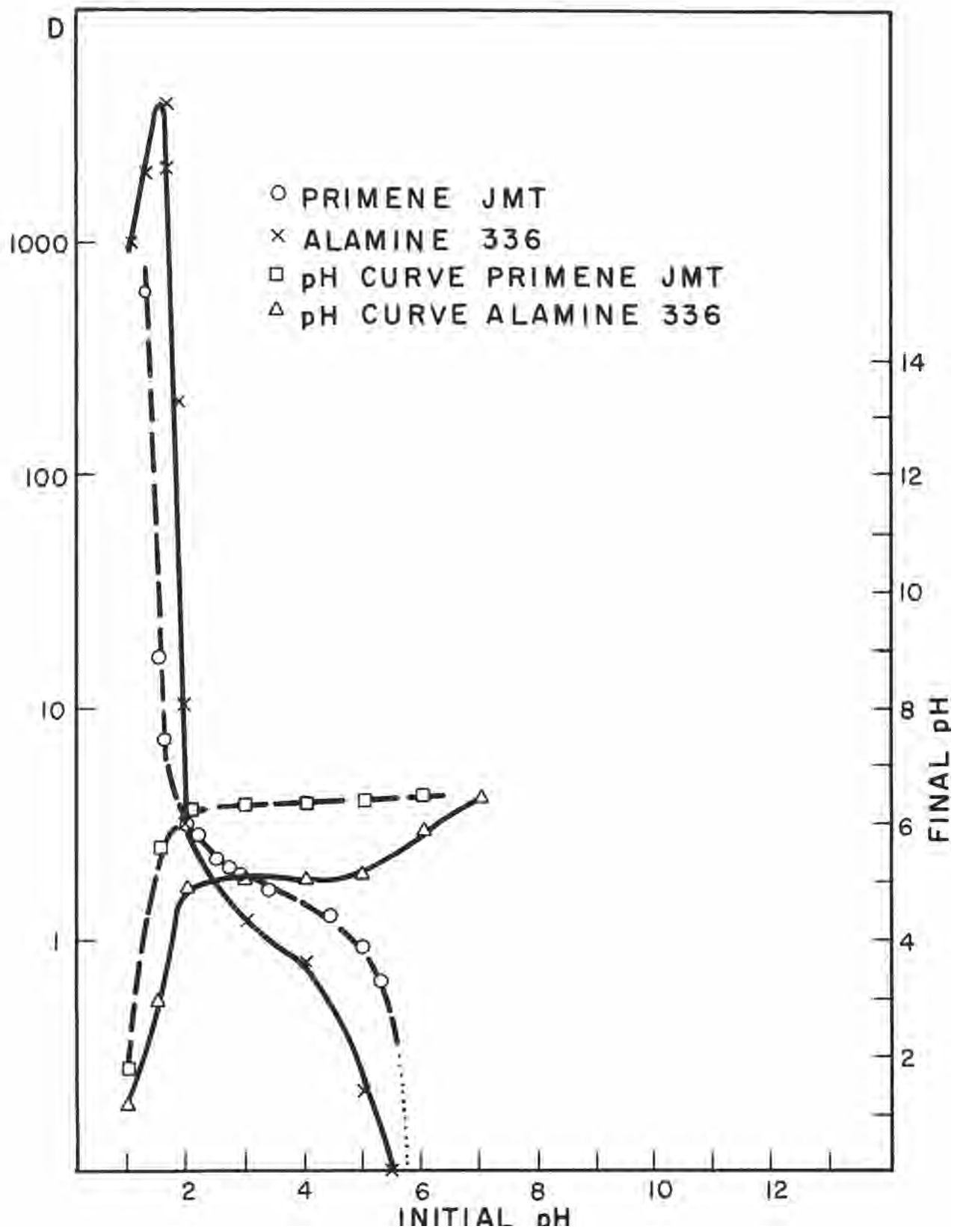


Figure 11

SOLVENT EXTRACTION OF Mo(VI) FROM AQUEOUS SOLUTION BY AMINES

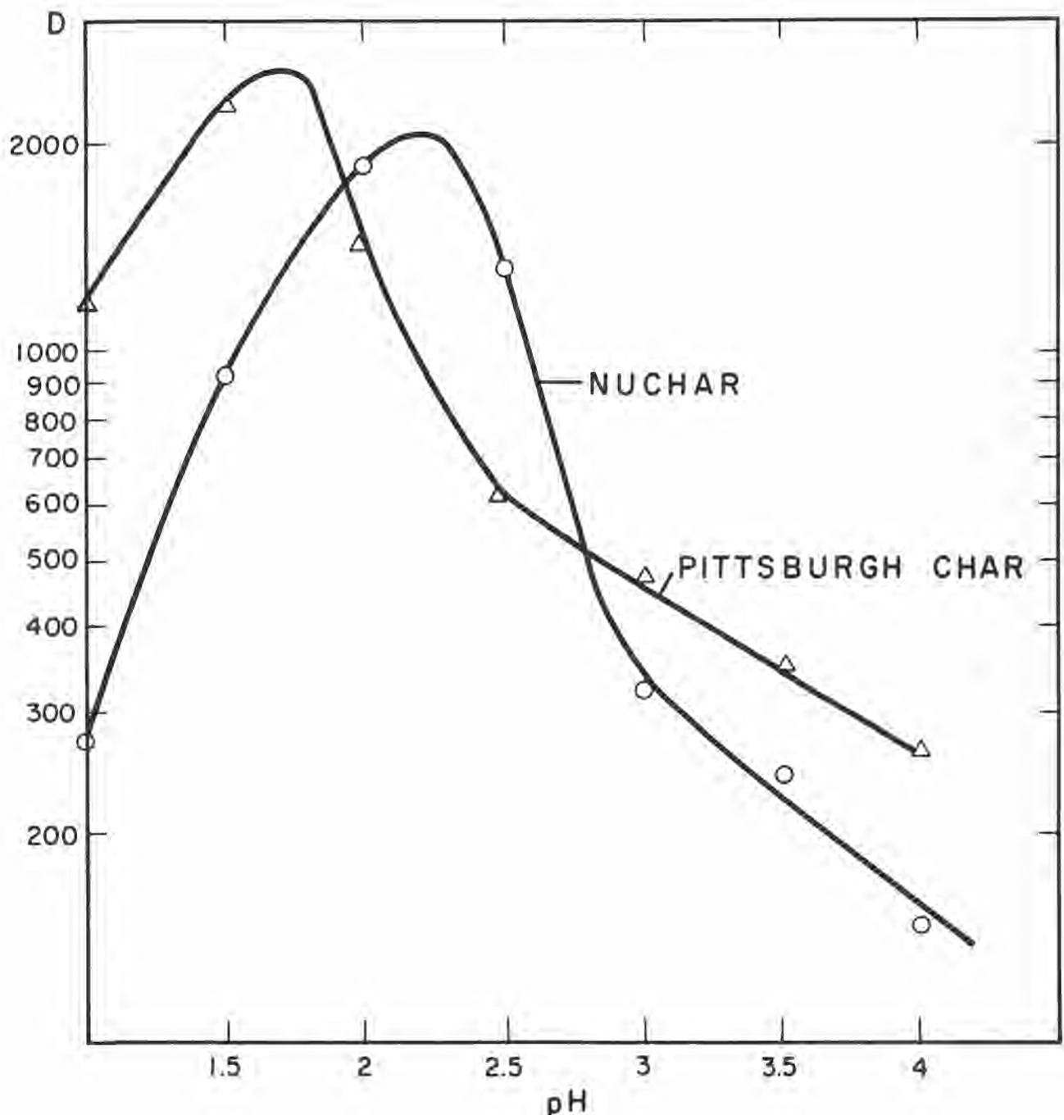


Figure 12
 ABSORPTION OF Mo(VI) FROM AQUEOUS SOLUTION BY ACTIVATED CARBONS

proportional to a power of the amine concentration in the organic phase and to a power of the hydrogen ion concentration in the aqueous phase (that is, inversely proportional to a power of the pH of the aqueous solution). In line with this, it is to be noted that the extent of extraction decreases very rapidly to negligible values at about pH 6 for the concentrations of reagents used. The variation of D with amine concentration (to determine n , perhaps) and with the Mo(VI) concentration must be known before optimum conditions may be defined for effective and efficient recovery of Mo(VI) from aqueous solutions.

From the work reported here, however, it may be seen that Aliquat 336 is subject to some of the same disadvantages that afflict the strongly basic anion exchange resins in the recovery of Mo from aqueous solutions. With the resins, a D value above 10 is generally considered impractical because of the relatively large volume of solution required for effective stripping. For solvent extraction, D above 1 is considered impractical because of the number of stages involved in effective stripping. These values may be realized fairly readily with Alamine 336 and Primene JMT. As shown in Figure 11, a relatively small change in pH causes quite a large change in D , as is suggested by the expression for D . For example, for Alamine 336, D drops from about 4000 at pH 1.5 to 3 at pH 2, to 0.8 at pH 4, and to 0.1 between pH 5 and 6, for the concentrations used in the experimental work. It may be that further work will show solvent extraction with high molecular weight amines to be the most efficient means for recovering small concentrations of Mo(VI) from dilute solutions.

ACTIVATED CARBON

Adsorption of molybdenum by activated carbon was reported by Sigworth (1962). He indicated a loading capacity of 16 pounds of molybdenum per 100 pounds of Nuchar C-190-N at an optimum loading pH of 2.0 from sulfate solutions. The Bureau, in preliminary studies, has obtained somewhat higher loading from a 1-gram-per-liter Mo(VI) solution. The optimum loading pH for Nuchar C-190-N was near 2.2, and for coarse Pittsburgh Char (Cal 12 x 40), the optimum D value was found at about pH 1.75, as shown in Figure 12. At these pH values, a loading of 22 and 23 pounds per hundred pounds of char, respectively, was obtained. The distribution coefficients were measured by the same techniques used for studying ion exchange and solvent extraction behavior of Mo(VI).

The D values fall to very low values at pH above 4, so that the adsorbed molybdenum could be removed by relatively small volumes of dilute caustic. Ammonia also proved quite effective for stripping Mo(VI) from the char.

In view of the many available activated carbons, much more work will be required to optimize the recovery of Mo(VI) from leach solutions by this means.

The adsorption of Mo(VI) by activated carbon is very like that by ion exchange and solvent extraction using long-chain amines. The highest D values are obtained at pH 1.5 to 2.5 for all three processes, and maximum loading of the resin and the char are comparable in extent (roughly 15 to 25 pounds of molybdenum per 100 pounds solid). The observed similarities suggest that the ionic species absorbed may be the same for the three processes.

Precipitation as Ferric—Molybdenum Compound

The recovery of molybdenum in the form of a marketable product was studied employing ferric iron as a complexing agent. The basis for this idea was the occurrence of ferrimolybdate and molybdenum-bearing limonite in natural ore bodies. It was hoped that by careful control of pH and concentrations of the active ions, it would be possible to produce a product containing a high molybdenum content along with iron as the other primary constituent. Such a product would be an ideal starting material or additive for producing ferromolybdenum.

Initial test results revealed that with an 8-grams-per-liter molybdenum solution and a 3.12-grams-per-liter ferric iron solution (1 Fe:3 Mo) and with careful pH control, it was possible to precipitate a yellow compound resembling natural ferrimolybdate. Such a compound assayed between 70 and 77 per cent MoO₃ in a dehydrated state, depending on the iron-to-molybdenum ratio in solution as well as on the pH. The results of this precipitation study are shown in Table 3.

The results indicate that the precipitated iron-molybdenum compound is not a true ferrimolybdate (Fe₂(MoO₄)₃ • 7.5 H₂O or Fe₂O₃ • 3MoO₃ • 7.5 H₂O) but one containing a mixture of ferrimolybdate compounds, depending upon the pH of precipitation. D.T.A., X-ray diffraction, and chemical analysis show that the probable ferrimolybdate species is the hydrated acid ferrimolybdate. The degree of hydration of this precipitated product depends on the extent of hydrolysis of ferric ions, which in turn is dependent on the pH. A possible mechanism of this precipitation phenomenon is as follows:

pH	Predominant species	Proposed products	Ratio of Fe ₂ O ₃ :MoO ₃	Designation
1.0	Fe ⁺⁺⁺ + 3HMoO ₄ ⁻	→ Fe(HMoO ₄) ₃	1:6	A
1.0 to 2.4	Fe(OH) ⁺⁺ + 2HMoO ₄ ⁻	→ Fe(OH)(HMoO ₄) ₂	1:4	B
2.4 to 3.2	(a) Fe(OH) ₂ ⁺ + HMoO ₄ ⁻	→ Fe(OH) ₂ (HMoO ₄)	1:2	C
	(b) Fe(OH) ₂ ⁺ + OH ⁻	→ Fe(OH) ₃	1:0	D
2.4 to 6.2	Fe(OH) _n + (3-n)(HMoO ₄) ⁻	+ (3-n)H ⁺ ⇌ [*] Fe(OH) _n (HMoO ₄) _{3-n} + (3-n)(H ₂ O)		E
>6.2	Fe(OH) _n (HMoO ₄) _{3-n} + (3-n)(H ₂ O)	→ Fe(OH) _n + (3-n)(MoO ₄) ⁼ + 2(3-n)H ⁺		F

*Equation reverses at pH 3.2

It is postulated that at pH below 1.0, the active ions may combine to form product A, Fe(HMoO₄)₃, containing a mole ratio of 1Fe₂O₃ : 6MoO₃. However, attempts to prove the existence of product A were not successful at the concentrations at which the tests were

TABLE 3. COMPOSITION OF FERRIC-MOLYBDENUM PRECIPITATES

PRECIPITATION (pH)	MOLE RATIO (Fe ₂ O ₃ :MoO ₃ :H ₂ O)	MoO ₃ (%) [*]	RECOVERY (% Mo)
1.11	1.0:4.15:13.10	79.0	27.7
1.53	1.0:4.14: 9.60	77.4	89.0
1.57	1.0:4.03: 9.50	77.0	89.4
2.18	1.0:3.54: 8.02	75.1	94.4
2.32	1.0:3.30: 6.49	73.6	+99.
2.35	1.0:3.28: 5.94	73.3	+99.
2.41	1.0:3.10: 5.47	72.3	+99.
2.82	1.0:2.95: 5.22	70.0	+99.

*Per cent of MoO₃ in dehydrated precipitate

performed because of the inability to obtain a precipitate at the low pH. It is seen from Table 3 that at a pH up to 1.6, the precipitated product contains a mole ratio of about 1Fe₂O₃ : 4MoO₃ and might have a composition represented by product B, Fe(OH)(HMoO₄)₂. For the precipitate obtained in the pH range 1.6 to 2.4, indications are that both B and C, Fe(OH)₂(HMoO₄), are present with B predominating. Conversely, above pH 2.4 the prevailing product in the mixed precipitate appears to be C.

In the event the ferric iron is present in excess and the pH is above 2.4, it will precipitate as Fe(OH)₃ along with ferric-molybdenum compounds B and C, thereby decreasing the Fe₂O₃ : MoO₃ ratio. This reasoning was substantiated by a test in which 2.525 grams NaMoO₄ • 2H₂O and 1.00 gram FeCl₃ • 6H₂O (10 per cent more iron than required by C) were added to 100 milliliters of water and the pH adjusted to 3.5. The precipitated compound gave a mole ratio of 1Fe₂O₃ : 1.8 MoO₃. This ratio can be explained on the basis of

complete precipitation of molybdenum with the required iron as compound C, in which the ratio would be 1Fe₂O₃ : 2MoO₃ with the excess 10-per-cent iron precipitating as Fe(OH)₃, thus lowering the above ratio

to 1Fe₂O₃ : 1.8MoO₃

The experimental boundary between $\text{Fe}_2(\text{MoO}_4)_3$ and $\text{Fe}(\text{OH})_3$ at total molybdenum concentration of 10^{-4} mole per liter as reported by Titley (1963) suggests that $\text{Fe}(\text{OH})_3$ and HMoO_4^- will react to a limited extent at pH 6.2 (and lower) to form ferrimolybdate according to designation E. However, attempts to produce the required reaction, by adding a solution containing molybdate ions to one containing precipitated $\text{Fe}(\text{OH})_3$ under prescribed conditions, were not successful, indicating that a reversal of equation E may take place before pH 6.2. Further testing showed that the minimum solubility of the ferric-molybdenum compound was at pH 3.2, which is in agreement with the recent study by Furbish and Sarafian. Finally, in more alkaline ranges (>6.2 pH), the ferric-molybdenum compound decomposes to give solid $\text{Fe}(\text{OH})_3$ and HMoO_4^- in solution according to designation F. The solubility product for ferric-molybdenum precipitates is difficult to establish because the precipitate occurs as a mixture of compounds dictated by the pH, as shown in Table 3.

The recovery of molybdenum in the precipitated product amounts to 27.7 per cent at pH 1.11 and plus 99 per cent above pH 2.32. The maximum recovery would be obtained at pH 3.2, the pH of minimum solubility. The optimum conditions for a practical process would depend on the type of leaching employed, the amount of ferric iron and molybdenum ions present in the pregnant solution, and the arrangement that might be made for recirculation of spent solution.

These conclusions indicate that such a technique may be effectively utilized for the extraction of molybdenum from solutions by the deliberate addition of ferric iron (if sufficient iron is not already present in the solution) and by adjusting the pH to form a ferric-molybdenum compound.

RELATION OF PRECIPITATION TO GEOCHEMISTRY

The results of the precipitation studies presented in this paper may explain the geochemistry of the occurrence of ferrimolybdate in the oxidized zone of molybdenum deposits. The naturally occurring mineral ferrimolybdate could be represented by a ferric-molybdenum compound having the formula $(\text{FeOH})_n(\text{HMoO}_4)_{3-n}$, where n can be 1, 2, or 3 and stands for the stage of hydrolysis of ferric iron. Moreover, the complexing of molybdenum ions with ferric iron leads one to believe that the molybdenum is tied up in the limonite occurring in the deposit as the ferric-molybdenum compound. The mode of occurrence of the oxide-molybdenum minerals in the oxidized zone may be explained on the basis of the concentration of molybdate ions (HMoO_4^-), ferric ions, and the pH existing at the time of formation, as shown in Table 4.

It is apparent that understanding of both the geochemistry of the formation of minerals and deposits and the chemistry involved in metallurgical processes may lead the mineral engineers to maximum exploitation of mineral resources.

TABLE 4. NATURAL OCCURRENCE OF MOLYBDENUM IN OXIDIZED ZONES

TYPICAL SULFIDE	BARREN ZONE	YELLOW FERRIMOLYBDITE	REDDISH YELLOW LIMONITE	REDDISH BROWN LIMONITE
MoS_2	$+\text{HMoO}_4^-$	$\text{Fe}(\text{OH})_n(\text{HMoO}_4)_{3-n}$	$\text{Fe}(\text{OH})_3(\text{HMoO}_4)_{3-n}$	MoO_4^{2-}
+	+	+	+	
FeS_2	Fe^{+++}	Fe^{+++}	$\text{Fe}(\text{OH})_3$	$\text{Fe}(\text{OH})_3$
60% Mo	—	53-47% Mo	47-0% Mo	0% Mo
	<1.0 pH	1.0-2.4 pH	2.4-3.2 pH	>3.2 pH

Summary

The research conducted on the extraction of molybdenum from sulfide and oxide ores indicates that it is possible to leach molybdenite (MoS_2) with oxidizing agents such as hypochlorite, acid chlorate, and manganese dioxide-sulfuric acid. Each oxidizer has its advantages and disadvantages, and to date the best oxidizer has not been established. Bacterial oxidation of molybdenite is also effective using *Thiobacillus thiooxidans* and *Thiobacillus ferrooxidans*, both of which have been tentatively determined to be present in the Questa mine water.

The primary oxide-molybdenum minerals in the oxidized ores investigated are ferrimolybdite, $\text{Fe}_e(\text{MoO}_4)_3 \cdot n\text{H}_2\text{O}$, and molybdenum-bearing limonite, both of which are soluble in strong acid and decompose in strong alkali solutions. However, a carbonate leach may be preferable in practice because of the difficulties encountered in acid leaching, such as the precipitation of insoluble molybdate compounds and the presence of acid-consuming gangue in the ores.

Anion exchange resins, high molecular weight amines in a hydrocarbon solvent, and activated carbon were investigated for recovery of molybdenum from leach solutions. Distribution coefficients in each instance depend on the predominant molybdenum-containing ionic species, which are controlled by the initial pH of the aqueous solution. All three means were very effective in removing Mo(VI) from solution at about pH 2, where the "isopoly" molybdic acid complexes predominate. Stripping from strongly basic anion exchange resins and from a quaternary ammonium salt proved difficult. A primary and a tertiary amine could be heavily loaded at pH 1.5 to 2.5 and stripped efficiently by aqueous solutions buffered at

pH 3.0 and higher. A loading of about 22 weight-per cent from a pH 2 solution was achieved on activated carbon. It could be stripped with 4 per cent caustic, or ammonia, to give a thirtyfold enrichment over the original aqueous solution.

The recovery of molybdenum from solutions as a marketable iron-molybdenum product was investigated and appears to be feasible. Using this technique, stable dehydrated compounds containing 70 to 80 per cent MoO_3 and 20 to 30 per cent Fe_2O_3 were produced under optimum concentration and pH conditions. It is postulated that the precipitated ferric-molybdenum compound, resembling the naturally occurring ferrimolybdite, is a mixture of hydrated ferric-molybdate complexes $\text{Fe}(\text{OH})(\text{HMoO}_4)_2$ and $\text{Fe}(\text{OH})_2 \text{HMoO}_4$, their proportions depending upon the pH during precipitation.

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