

REDUCTIVE PRECIPITATION OF MOLYBDENUM
OXIDES FOR RECOVERY OF MOLYBDENUM
FROM HYPOCHLORITE LEACH SOLUTIONS

by

DUNCAN CRAIG REID

B.A.Sc., The University of British Columbia, 1972

M.L.S., The University of British Columbia, 1974

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Department of Metallurgy

The University of British Columbia
2075 Wesbrook Place
Vancouver, Canada
V6T 1W5

Date October 5, 1979

ABSTRACT

The feasibility of reductive precipitation of molybdenum oxides as the molybdenum recovery stage of a hypochlorite leach of Cu-Mo rougher concentrates has been investigated. Hydrogen gas at elevated temperature and pressure and hydrazine at moderate temperature and atmospheric pressure were used as reductants. Reduction was performed on solutions containing 5 to 17 g/l Mo as sodium molybdate. Hydrogen reduction was successful only in the presence of a Pt catalyst, temperature = 200°C, pressure = 30 atm of H₂, and initial acidification to pH = 2. Ten hours was required to obtain 90% recovery of molybdenum as MoO₂. Reduction with hydrazine yielded an MoO(OH)₃ precipitate with 90% recovery obtained in 40 minutes at 50°C, pH = 4.5, and initial mole ratio of hydrazine to molybdenum of 4:1. Precipitation under the same conditions in the presence of 3 M NaCl gave only 70% recovery in 4 hours and the precipitate contained 3.3% sodium. The effect of NaCl is explained in terms of stabilization of mixed valent ionic molybdenum species in the presence of NaCl.

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1. INTRODUCTION

Conventional technology for the production of MoS_2 concentrates as a byproduct from processing of porphyry copper ores is based on a bulk or rougher flotation for the recovery of a copper sulfide-molybdenum sulfide concentrate. This is followed by differential flotation to produce separate copper and molybdenum sulfide concentrates. The molybdenum concentrate is then cleaned by further flotation steps to obtain a marketable MoS_2 product. According to data published by Sutulov¹ for fifty flotation plants treating such ores the mean recovery of molybdenum in the copper rougher concentrate is 64% while the mean overall recovery is only 50%. Warren et al.² have shown that selective leaching of molybdenum from rougher concentrates could be an economically favourable alternative to further flotation steps if the molybdenum recovery from the rougher concentrates approached 100% and if the residue was suitable for production of a copper concentrate by flotation. They proposed a sodium hypochlorite leach for treatment of rougher concentrates that involved on-site electrolytic generation of sodium hypochlorite using commercially available hypochlorite cells. A similar approach has been proposed by workers at the U.S. Bureau of Mines (USBM).³⁻⁸ In the USBM process hypochlorite leaching would be applied to the off-grade molybdenum sulfide concentrate produced by differential flotation of the initial rougher concentrate. This process, then, would replace only the cleaning stages of production of an MoS_2

concentrate while the process proposed by Warren et al. would also replace the differential flotation step. A further difference between the two proposals is that the USBM process involves generation of sodium hypochlorite "in-situ" by electrolysis of a brine slurry of the concentrate as it is pumped through a specially designed electrolytic cell.

The USBM process has been piloted on concentrates containing 16 to 35% Mo and 6 to 15% Cu. Warren et al. have designed their process to treat concentrates containing approximately 0.3% Mo and 12% Cu. The basic flow sheets for both processes are compared in figure 1. Both processes use Na_2CO_3 for pH adjustment. Warren et al. propose to carry out leaching at pH 9 while the USBM process operates at pH 5.5 to 7. The leach temperature for both processes is 45 - 50° C.

The stoichiometry of the leach can be represented by the equation:



which shows that 1 kg of NaOCl should be consumed to bring 0.143 kg of Mo into solution. According to Warren et al. modern hypochlorite generators require 3.52 kwh per kg NaOCl. It follows that in their process energy consumption should be 24.5 kwh per kg Mo. In a recent pilot plant study⁸ the USBM process required 19.8 to 28.6 kwh per kg Mo to treat concentrates containing 16 to 35% Mo and 6 to 15% Cu. The molybdenum recovery decreased from 93 to 97% to only 75% when the copper content increased to 15% and the power consumption correspondingly increased to the 28.6 kwh value. The decrease in molybdenum recovery was attributed to the formation of insoluble copper molybdates. Current research in this laboratory has shown, however, that the effect of copper minerals on the molybdenum recovery is

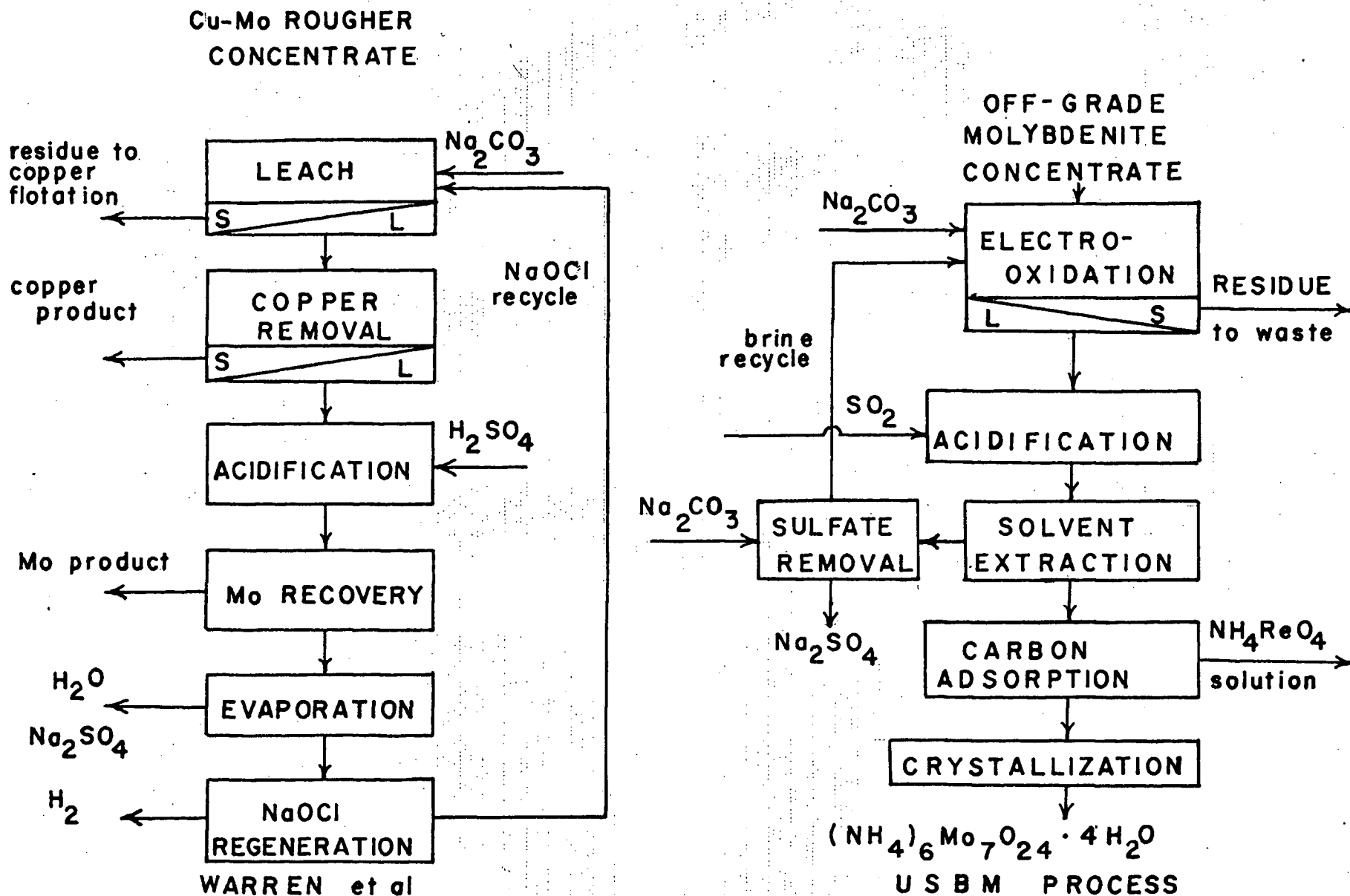


Figure 1: Proposed flowsheets for hypochlorite leaching of molybdenite containing concentrates.

more complex than this. At the pH of the USBM leach, for example, it is likely that significant decomposition of NaOCl to NaClO_3 occurs. Since NaClO_3 does not oxidize MoS_2 at this pH such decomposition reduces the energy efficiency of the leach. The use of carbonate for pH control has also been shown to be an important factor in increasing molybdenum recovery.⁹ Research in this area is continuing. On the basis of the available information, then, it seems that the process proposed by Warren et al. offers a higher recovery of molybdenum with a better leaching energy efficiency than the USBM process.

Warren et al. calculated the approximate composition of the leach solution that would result on application of their process to a rougher concentrate containing 0.3% Mo. Table I compares this with the composition resulting from application of the USBM process to a molybdenite concentrate. It can be seen that the two solutions are similar. It would thus be possible to apply the USBM solvent extraction-carbon adsorption sequence for recovery of molybdenum and rhenium to Warren et al.'s process. A disadvantage of the USBM procedure however, is the necessity to acidify the solution to $\text{pH} < 2$ for molybdenum extraction by a tertiary amine.⁴ A process capable of recovering molybdenum from alkaline solutions would be preferable for a hypochlorite leach operating at $\text{pH} = 9$.

Alternative means of molybdenum recovery have been suggested. These include reduction of molybdate solutions with hydrogen at elevated temperature and pressure to produce insoluble MoO_2 ¹⁰⁻¹⁵ and reduction with iron followed by neutralization to precipitate $\text{Mo}(\text{OH})_3$.¹⁶ As described in the literature, however, both of the processes operate in acid solution.

The feasibility of alternative routes to molybdenum recovery from

	Warren et al.	USBM
H ₂ O	1100 kg	900 kg
NaCl	170 kg	100 kg
Na ₂ SO ₄	68 kg	37 kg
Na ₂ MoO ₄	10 kg	4 - 43 kg
Cu	variable	---
NaOCl ₃	nil	5 - 13 kg
NaClO ₄	5 - 8 kg	.14 - .72 kg
Re	---	.001 - .050 kg
pH	9	5 - 7

Table I Comparison of leach liquor solutions
for molybdenum recovery

leach solutions depends on the economics of the unit operations involved and on the marketability of the resulting product. In addition the ability of a given process to recover rhenium could be a deciding factor in cases where the concentrate to be treated contained a significant amount of rhenium.

Conventionally almost all molybdenum sulfide concentrates are roasted to produce a technical grade MoO_3 . The principal use of this product is the production of calcium molybdate, molybdic oxide briquets, or ferromolybdenum for alloy steel production. Technical grade MoO_3 can also be further purified by sublimation to yield pure MoO_3 or by hydrometallurgical means to produce ammonium molybdate or sodium molybdate (Figure 2). A hydrometallurgical treatment of MoS_2 containing concentrates should at least be capable of producing a product of equal quality to technical grade MoO_3 . By way of example Table II shows technical grade MoO_3 specifications for Endako Mines Ltd. Hydrometallurgical production of a molybdenum oxide, sodium molybdate, or ammonium molybdate product of high purity directly from an off-grade or rougher concentrate could, however, eliminate not only roasting but also sublimation or other subsequent purification steps. The ability to produce such a product could influence the economic favourability of a hydrometallurgical route.

The potential-pH diagram for the molybdenum water system published by Pourbaix¹⁸ (Figure 3) is relatively simple and indicates that reductive precipitation of MoO_2 could be possible over a wide range of pH. Several reducing agents might be considered. These include H_2 , SO_2 , H_2S , CO , iron and hydrazine. The gaseous reagents and hydrazine are attractive because they offer the possibility of producing a high purity product.

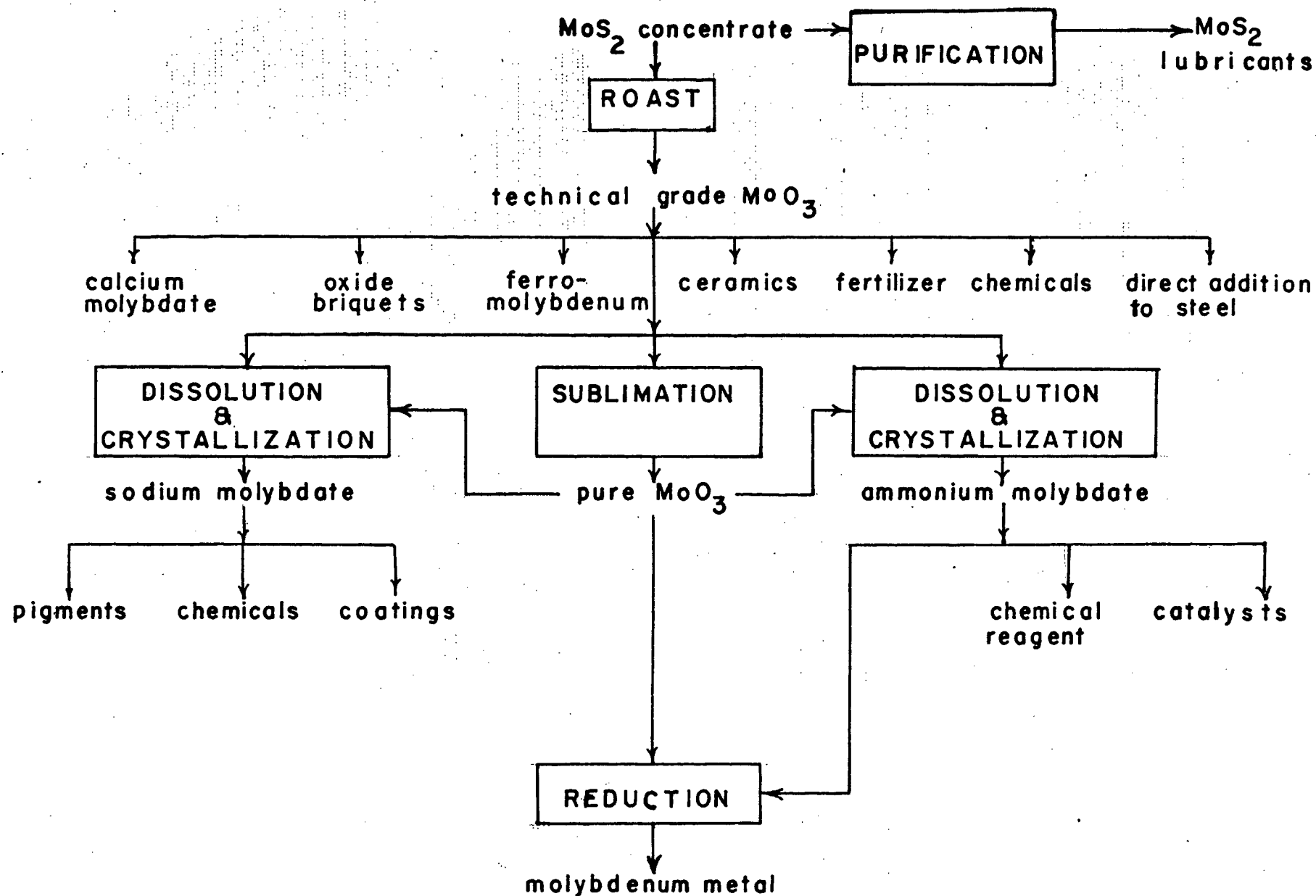


Figure 2: Principal operations and products in processing of molybdenite concentrates.

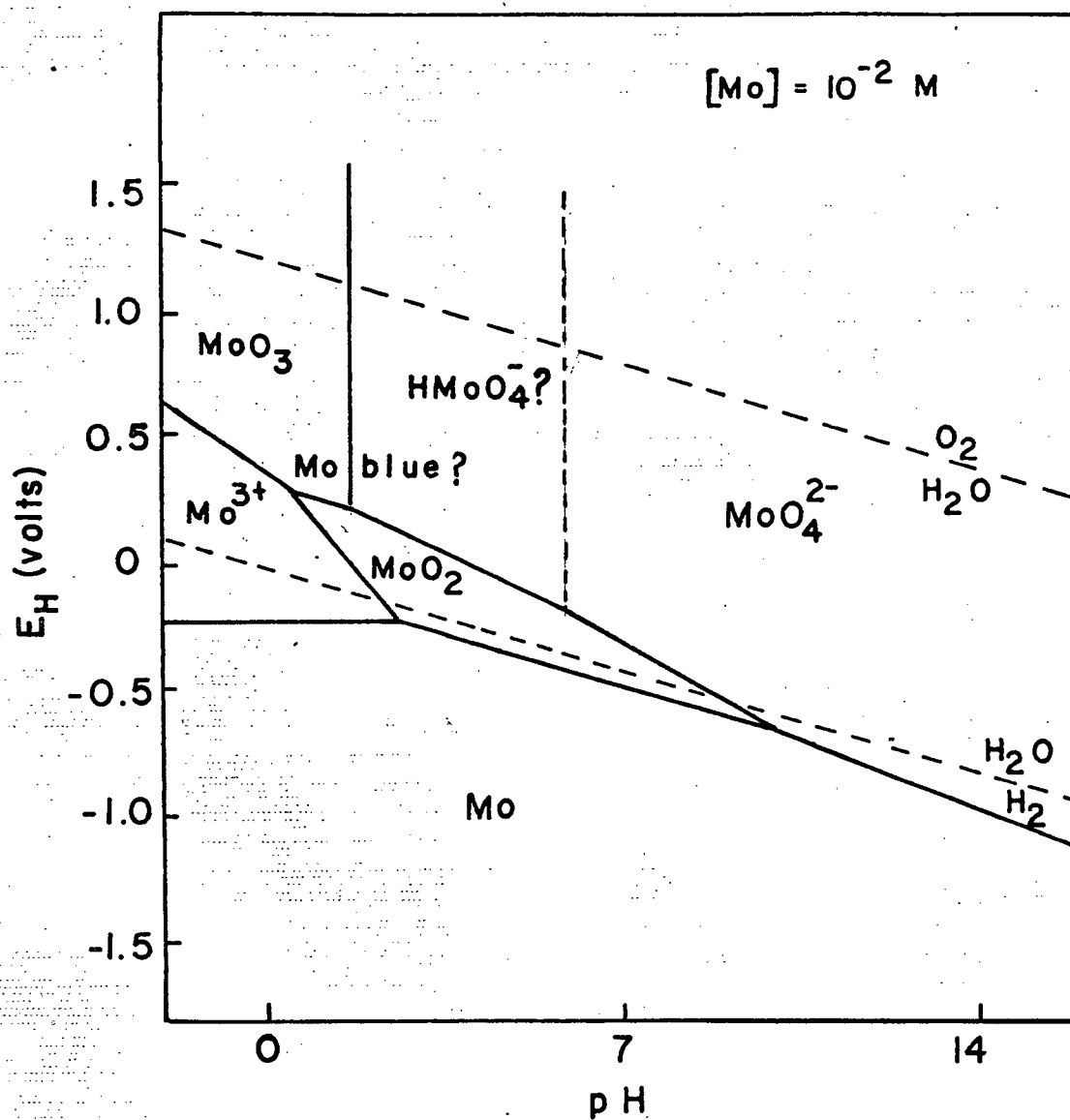


Figure 3: Potential-pH equilibrium diagram for the system Mo-H₂O at 25°C.

OXIDE			
	Range %	Typical %	Guaranteed %
Mo	57.0 - 62.0	59.0	57.0 min.
Cu	0.05 - 0.10	0.075	0.10 max.
S	0.03 - 0.10	0.06	0.10 max.
P	--	0.01	0.05 max.
Pb	0.015 - 0.050	0.025	0.05 max.
Bi	0.02 - 0.04	0.030	0.05 max.
WO ₃	--	0.030	0.16 max.
SiO ₂	5.0 - 15.0	8.0	15.0 max.
Fe	0.020 - 0.45	0.35	--
CaO	0.050 - 0.120	0.07	--

OXIDE BRIQUETTES (PITCH)			
	Range %	Typical %	Guaranteed %
Mo	50.6 - 54.0	53.0	51.6 min.
C	10.0 - 15.0	11.00	12.0 approx.
Cu	0.05 - 0.15	0.075	0.15 max.
S	0.09 - 0.15	0.11	0.15 max.
P	--	0.01	0.05 max.
Bi	0.02 - 0.04	0.03	--
Fe	0.20 - 0.40	0.29	--
Pb	0.015 - 0.050	0.025	--

Table II Technical grade MoO₃ specifications for Endako Mines

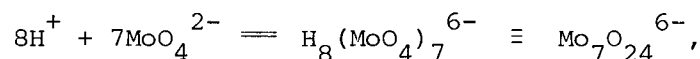
Despite the apparent simplicity of the Pourbaix diagram, however, the aqueous chemistry of molybdenum is complex. There is, in fact, a rich chemistry of polymeric molybdates and reduced molybdenum species that has resulted in an extensive and often contradictory literature. A review of this literature is necessary as a basis for considering reductive precipitation as a means of molybdenum recovery from alkaline solutions.

2. LITERATURE REVIEW

2.1 Aqueous Chemistry of Molybdenum

2.1.1 Mo^{VI}

A hypochlorite leach of MoS₂ produces Mo^{VI} in solution which for pH's greater than about six exists as the monomeric molybdate ion MoO₄²⁻. On acidification, however, molybdate ions polymerize consuming H⁺ to produce isopolymolybdates such as the paramolybdate ion Mo₇O₂₄⁶⁻. Several isopolymolybdates have been reported and the literature has been reviewed by Sasaki and Sillen.¹⁹ They characterized isopolymolybdates in terms of their acidity, *z*, defined as moles H⁺ bound per mole Mo. Thus paramolybdate formed according to the equation,



can be represented by $z = 8/7 = 1.14$.

It is generally accepted that paramolybdate is the first species to form on acidification of molybdate solutions and that it is the only isopolyanion, or at least by far predominant, up to $z = 1.14$ ²⁰⁻²² (pH ≈ 5). The nature of the polymolybdates formed on further acidification must be regarded as uncertain since there is some disagreement in the literature.^{19,23-25} Figure 4 shows a predominance area diagram constructed by Baes²² who accepted Sasaki and Sillen's¹⁹ sequence of isopolymolybdates.

For acidification up to $z = 1.5$ it has been shown that isopolymolybdate equilibria are almost instantaneous for moderate molybdenum concentrations. For $z \geq 1.5$, however, where polymerization proceeds beyond the heptamer or octamer stage, Aveston et al.²⁴ noted that the equilibria are only slowly established.

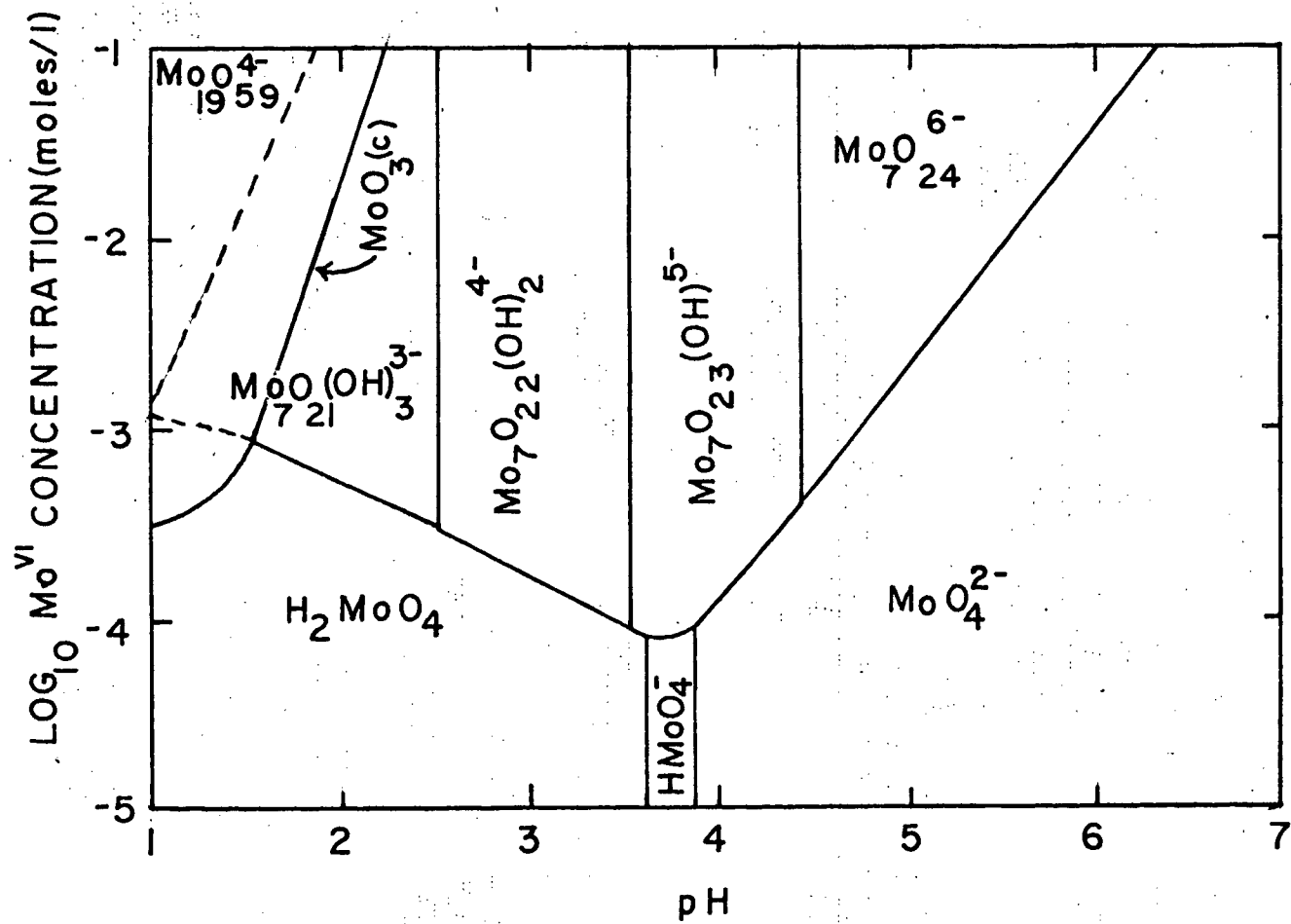


Figure 4: Predominance area diagram for Mo^{VI} in 3 N NaCl.

The formation of isopolymolybdates is significant for recovery of molybdenum from process solutions because both solvent extraction and reduction reactions appear to involve only polymerized molybdenum species. Charlot³⁰ has stated, for example, that monomeric molybdate ion is reduced infinitely slowly in alkaline solution. Polarographic studies have tended to confirm this with Mo^{VI} giving no reduction waves for $\text{pH} > 5$ ³¹⁻³³. Similarly the necessity for acidification to $\text{pH} < 2$ for solvent extraction in the USBM process indicates that the extracted species involves isopolymolybdates or even cationic molybdenum species. A review of molybdenum solvent extraction by Zelikman confirms that extraction is most efficient in acid solution and that the extracted species are isopolymolybdates or cations.³⁴

2.1.2 Reduced Species and Precipitates

For lack of thermodynamic data Pourbaix was able to consider only Mo , Mo^{3+} , and MoO_2 in his diagram. The predominance area of the mixed-valent molybdenum blue compounds could only be shown approximately based on qualitative observations. It is now well recognized, however, that Mo^{V} , Mo^{IV} , and Mo^{III} species can be prepared and are stable in aqueous solution.³⁵ Hydrated oxides of each of these valence states can be precipitated in appropriate pH intervals. Some progress has also been made in the characterization of the molybdenum blues.

Like Mo^{VI} the reduced molybdenum aquo-ions show a tendency towards polymerization. Both Mo^{III} and Mo^{IV} can form dimers³⁵ and Mo^{V} has been reported to form dimers, tetramers, and higher polymers.³⁶ The molybdenum blues are undoubtedly polymeric since their formation at a given pH is

dependent on molybdenum concentration. The reduced molybdenum species are of interest in the present study and the chemistry of each is briefly reviewed in the following sections.

2.1.2.1 Molybdenum Blue

Mild reduction of molybdate solutions in the pH range 4 to 0 yields more or less intensely coloured blue solutions. If reduction proceeds beyond the optimum for formation of the blue the colour density decreases and the colour may change from blue to green or brown.³⁷ There have been many attempts to characterize the blue colloidal precipitates that can be prepared from such solutions.³⁸⁻⁴² Glemser and Lutz³⁸ and Sacconi and Cini³⁹ concluded that molybdenum blue was neither a unique compound nor did it represent a definite oxidation state of molybdenum. This conclusion seems to have been generally accepted and is stated in several works on inorganic chemistry.^{20,21,43} On the other hand Weiser⁴⁴ has pointed out that the evidence for the existence of different compounds was based largely on analytical differences of the same order of magnitude as the experimental errors inherent in analyzing a colloidal mass.

Arnold and Walker⁴¹ avoided analyzing a colloidal precipitate by extracting the blue into butanol and determining the mean oxidation state of molybdenum by potentiometric titration. They obtained the formula Mo_6O_{17} which agreed with the earlier results of Treadwell and Schaeppi.⁴⁰

Ostrowetsky⁴² studied the formation of molybdenum blue by mixing solutions of Mo^{V} and Mo^{VI} in varying ratios and at varying pH's. Total molybdenum in solution was also varied. The formation of the blue was analyzed by spectrophotometry, by isolation of its rubidium salt, and by

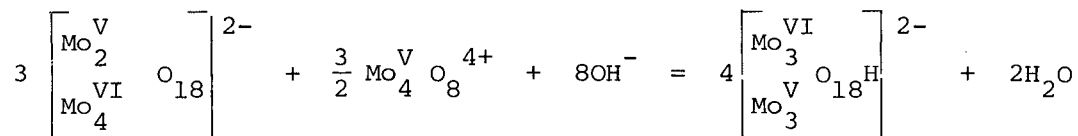
potentiometry. Electrolytic preparation of the blue gave the same results.

Optimum conditions for formation of the blue were $\text{pH} = 1.22$, $\text{Mo}^{\text{V}}/\text{Mo}^{\text{VI}} = 0.5$,

and $[\text{Mo}]_{\text{total}} = 0.015 \text{ M}$. The blue species was formulated as $\left[\begin{array}{c} \text{Mo}_2^{\text{V}} \\ \text{Mo}_4^{\text{VI}} \\ \text{O}_{18} \end{array} \right]^{2-}$.

The corresponding acid, $\text{H}_2\text{Mo}_6\text{O}_{18}$, agreed with the results of Arnold and Walker and Treadwell and Schaeppi. Decrease of total molybdenum concentration inhibited formation of the blue.

If a solution of the blue, under the optimum conditions for its formation mentioned above, was titrated with NaOH the solution became green, then brown. The brown solution was found to correspond to $\text{HMo}_6\text{O}_{18}^{2-}$ and its formation from the blue written as



The brown solution could also be prepared directly by mixing Mo^{V} and Mo^{VI} .

Maximum yield was obtained at $\text{pH} = 2.7$.

A third mixed compound, also brown, was found to be formed at

$\text{pH} = 3$ to 4 and $\text{Mo}^{\text{V}}/\text{Mo}^{\text{VI}} = 2.0$. It was formulated as $\left[\begin{array}{c} \text{Mo}_4^{\text{V}} \\ \text{Mo}_2^{\text{VI}} \\ \text{O}_{17}\text{H} \end{array} \right]^-$.

For $\text{pH} > 4$, however, its concentration decreased and at $\text{pH} = 4.5$ a precipitate of $\text{MoO}(\text{OH})_3$ was observed.

The work of Ostrowetsky permits a logical interpretation of the colour changes observed on reduction of molybdate solutions in the pH range 0 to 4.5. For $\text{pH} < 0$ the blue compound cannot form and no colour change is

observed until the Mo^{V} stage or lower is attained. For pH between 0 and 4 the first colour to appear is blue for low values of $\text{Mo}^{\text{V}}/\text{Mo}^{\text{VI}}$. As reduction proceeds the solution becomes green or brown as the two brown $\text{Mo}^{\text{V}}/\text{Mo}^{\text{VI}}$ species form. The solution precipitates $\text{MoO}(\text{OH})_3$ as the Mo^{V} stage is approached more closely. If a solution containing any of the mixed valent species is neutralized $\text{MoO}(\text{OH})_3$ is precipitated and molybdates are formed in solution.

In addition the mixed valent species can coexist in various proportions in solution with varying amounts of excess Mo^{VI} or Mo^{V} depending on the particular conditions. This probably explains the range of mean oxidation states for molybdenum obtained by different workers using different means of preparation of the colloidal blue.

Partial confirmation of Ostrowetsky's work was provided by Filippov and Nuger⁴⁵ who observed that the character and intensity of the molybdenum blue spectrum observed during reduction of molybdic acid by hydrazinium chloride varied according to the pH at which the reduction was performed. The maximum absorbance observed by Filippov and Nuger occurred at $\text{pH} = 1.31$ which corresponds to the optimum pH for formation of the blue compound proposed by Ostrowetsky. As the pH of reduction was increased the absorbance due to formation of the blue decreased. Unfortunately Filippov and Nuger did not record the spectra in the region of absorbance of the two brown species so it is not possible to tell if the absorbances due to these two species increased as would be expected if the overall degree of reduction obtained was independent of pH. In the case of Filippov and Nuger's work it is likely that the degree of reduction did depend on pH since for $\text{pH} > 4$ no reduction was observed. The latter observation is likely the

result of a kinetic effect since, as will be shown later, hydrazine in sufficient excess can reduce molybdate almost quantitatively to Mo^{V} for pH between 4.5 and 5.0.

Ostrowetsky proposed that since the mixed valent species were hexamers it was likely that they were formed by reduction of hexameric molybdate species. Filippov and Nuger also assumed that molybdenum blues were isostructural with the molybdate species from which they were formed.

2.1.2.2 Mo^V

Mo^V and its chloride salts, R₂MoOCl₅ (where R = NH₄⁺, Rb⁺), can be prepared in acid solution by standard procedures.⁴⁶ On neutralization or dilution the green chloride solutions hydrolyze rapidly to give a brown colour for [Mo] > 0.1 M which becomes amber or yellow on increasing dilution. Complete neutralization yields a brown Mo^V precipitate.

According to Mellor⁴⁷ Klason obtained MoO(OH)₃ by adding 3 moles of ammonia to a solution containing one mole of (NH₄)₂MoOCl₅ while Debray found that if excess ammonia was used the precipitate was partially decomposed and the filtered solution contained Mo^{VI}. The anhydrous oxide was obtained by several workers by heating the precipitate in vacuo or in inert gas streams.

Simon and Souchay⁴⁸ performed a detailed spectrophotometric study of the hydrolysis and concluded that below 2 M HCl and 3 M H₂SO₄ Mo^V was not complexed by the anion of the acid used. Titration of (NH₄)₂MoOCl₅ with NaOH suggested the hydrolysis product immediately before precipitation could be formulated as (MoO₂⁺)_x where x indicated an unknown degree of polymerization.

Ardon and Pernick⁴⁹ confirmed this work concluding that the predominant Mo^V species in dilute HCl, HClO₄, and other acids is a binuclear cation with charge 2+ and is not coordinated to chloride. Their work involved analysis of its elution behaviour from a cation exchange column and cryoscopy of a 0.02 M solution in eutectic HClO₄.

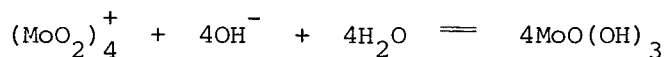
Subsequently Viossat and Lamache³⁶ proposed that for [Mo^V] > 10⁻² M the predominant species is a tetramer which transforms into (MoO₂⁺)₂ on dilution. They also reported that if a solution of Mo^V was neutralized to pH = 1.2 and heated at 80°C a significant fraction of the molybdenum

precipitated while $(\text{MoO}_2^+)_2$ and $(\text{MoO}_2^+)_4$ coexisted in solution with a previously unknown chestnut coloured species. The chestnut species could be removed from solution on an anion exchange resin. It was found that it was highly polymerized. One manifestation of this polymerization was that small concentrations of it suppressed the polarographic maximum observed for Mo^{VI} in 2 N HCl. Viossat and Lamache proposed that the chestnut Mo^{V} species was actually cationic but had an overall negative charge resulting from strongly adsorbed chloride ions.

Only two studies of the precipitation of Mo^{V} appear to have been published. They are in fair agreement with each other. Katsobashvili et al. produced Mo^{V} in HCl solution using zinc as a reductant. The resulting solutions contained 0.021 M Mo and were 0.03 N in AlCl_3 . Titration with 0.02 N NaOH showed precipitation was complete between pH 6 and 6.5. Molybdenum remaining in solution was beyond the limit of sensitivity of colorimetric analysis. It was observed, however, that between pH 8 and 10 hydroxyl ions were adsorbed by the precipitate and the molybdenum concentration in solution increased. They found that Mo^{VI} was dissolving from the precipitate so the phenomenon was not simply a question of increasing solubility of Mo^{V} at a higher pH. Mo^{VI} also appeared in solution if NH_3 was used for neutralization. The amount appearing increased with time and temperature of standing for a given pH and with increasing pH for constant time and temperature. It was noted that plots of Mo^{VI} appearing vs time for constant pH's between 6.5 and 9 had positive intercepts indicating that at least part of the dissolution occurred almost instantaneously on neutralization.

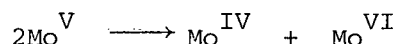
Souchay et al.⁵¹ neutralized aliquots of 0.03 M Mo^{V} solutions in HCl

with varying amounts of NaOH, agitated them for 10 minutes, and separated the precipitate by filtration. The pH of the filtrate was measured and Mo^{V} remaining in solution was determined polarographically in 6 N HCl after oxidation to Mo^{VI} with Ce^{4+} . Sodium and chloride ions in the precipitate were determined after dissolving it in 3 N HNO_3 . The results indicated the precipitation of Mo^{V} was complete for $\text{pH} > 6$ but that the consumption of NaOH exceeded the one equivalent expected from the equation

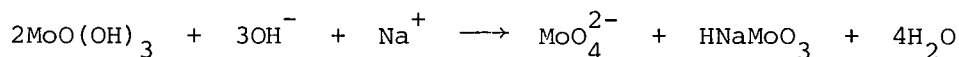


It was concluded that the precipitate acted as an ion exchanger absorbing Na^+ and releasing H^+ . The pickup of sodium increased when NaCl was added to the solutions.

Souchay et al. also observed dissolution of the precipitate but only after a solution of $\text{pH} = 12.65$ was agitated for several hours. It was found by polarographic analysis that after such dissolution the precipitate contained a mole of Mo^{IV} for each mole of Mo^{VI} appearing in solution. The appearance of Mo^{VI} thus resulted from the dismutation of Mo^{V} according to:



In 5 N NaOH complete dismutation was almost instantaneous yielding a precipitate in which the mole ratio of molybdenum to sodium was one to one. The reaction proposed was:



which involved formation of an insoluble molybdate identified in a similar study of the precipitation of Mo^{IV} .⁵¹

2.1.2.3 Mo^{IV}

The behaviour of Mo^{IV} in aqueous solution has been a matter of controversy. According to Mellor several workers reported obtaining various hydrates of MoO₂ by neutralization of reduced molybdate solutions. Conversely, Klason maintained these precipitates were probably impure Mo^V products and hydrated oxides of Mo^{IV} did not exist. This opinion was reinforced by Haight and coworkers who concluded, on the basis of polarographic work⁵² and analysis of the kinetics of the reduction of Mo^{VI} by Sn^{II},⁵³ that Mo^{IV} was unstable in aqueous solution and disproportionated into Mo^{III} and Mo^V.

Guibe and Souchay,⁵⁴ however, had previously demonstrated the existence of Mo^{IV} using polarography. Souchay, Cadiot, and Duhamiaux⁵⁵ subsequently neutralized a Mo^{IV} solution to precipitate MoO(OH)₂ and formulated the predominant Mo^{IV} ion before precipitation as MoO(OH)⁺.

Ardon and coworkers suggested Mo^{IV} was actually dimeric based on ion exchange experiments⁵⁶ and cryoscopy.⁵⁷ Recently Chalilpoyil and Anson⁵⁸ reported that a dimeric assignment is consistent with the behaviour of Mo^{IV} during electrochemical oxidation and reduction.

Souchay, Cadiot, and Viossat⁵⁷ studied the precipitation of Mo^{IV}. Varying amounts of NaOH were used to neutralize aliquots of 0.03 M Mo^{IV} in the same procedure as already described for their work on Mo^V. Precipitation began at pH = 1.5 and was complete at pH = 2.8. Sodium and chloride ions could be eliminated from the precipitate by washing with water. The product was analyzed as MoO₂ · 2H₂O. It could be easily dissolved in 2 N HCl to give the spectrum and polarogram characteristic of Mo^{IV}. After drying at 130°C, however, it took on a grainy appearance and could no longer

be dissolved in acid. Insolubility in acid is a characteristic of anhydrous MoO_2 .⁴⁷

If neutralization was carried out with an excess of NaOH giving a final pH of 11.5 the product was an insoluble monoalkaline molybdate. The reaction proposed was



where $\text{M} = \text{Na}^+, \text{Li}^+, \text{K}^+$. In 5 N NaOH the molybdate partially redissolved to give Mo^{IV} in solution. The ion MoO_3^{2-} was proposed by analogy with molybdate.

Lagrange and Schwing^{59,60} obtained an $\text{MoO}_2 \cdot 2\text{H}_2\text{O}$ precipitate by electrolysis of 0.125 M Na_2MoO_4 solutions on a mercury cathode at -0.6 V (vs SHE) and pH 5 - 6. The precipitate only formed for pH > 2. At lower pH molybdenum blue was formed and no deposition occurred. The precipitate gave the ASTM diffraction pattern for MoO_2 after drying at 500°C in nitrogen.

Lamache⁶¹ found that electrolysis at -.29 to -.38 V (vs SHE) in an acetic buffer of pH 4.6 gave Mo^{III} in solution and a precipitate containing equal amounts of Mo^{V} and Mo^{IV} .

2.1.2.4 Mo^{III}

Mo^{III} can be produced in acid solution by reduction with Cd, Zn, Hg or by electrolysis.^{31,46} Mo^{III} deposits have been formed by electrolytic reduction in alkaline or neutral solution but the rate of deposition is slow.⁶²⁻⁶⁶

No detailed studies of the precipitation of Mo^{III} to yield $\text{Mo}(\text{OH})_3$

have been made. Mo(OH)_3 and the anhydrous oxide are poorly characterized. Smith⁶² verified that electrolysis in alkaline and neutral solutions led to Mo(OH)_3 by preparing enough of the deposit for analysis. Mellor⁴⁷ reported that Mo(OH)_3 dissolves only with difficulty in acids.

Watt and Davies⁶⁴ obtained anhydrous Mo_2O_3 by reduction of Mo^{VI} oxide with solutions of potassium in liquid ammonia. They reported that Mo_2O_3 dissolves readily in 6 N HCl. Mo_2O_3 was converted to insoluble black Mo(OH)_3 by agitation in water for 15 minutes at 25°C. Mo(OH)_3 prepared from Mo_2O_3 was found to have the same properties as Mo(OH)_3 prepared by electrolysis of Mo^{VI} solutions at pH 3.1 to 4.4. Neither Mo(OH)_3 nor Mo_2O_3 gave X-ray diffraction patterns. On heating to 325°C in an inert atmosphere, however, Mo(OH)_3 gave diffraction patterns for Mo and MoO_2 while Mo_2O_3 still gave no pattern.

Messner and Zimmerly¹⁶ reduced Mo^{VI} solutions with iron at pH 1 to 3.5 and precipitated Mo(OH)_3 by neutralization to pH 3.6 to 4.5. The MoO_3 produced by roasting the precipitate contained 2.12% Fe and 0.14% Cu.

2.1.3 Summary

The preceding review of aqueous molybdenum chemistry suggests that reductive precipitation could lead to various products including mixed valent precipitates. It also illustrates the complex nature of molybdenum species in aqueous solution. Which aqueous species or precipitate predominates in a given situation is likely to be dependent on total molybdenum concentration, pH, and potential. Furthermore as these conditions change during a reaction the predominant species and hence reaction path might be

expected to change. A review of the literature on hydrogen reduction and reduction with hydrazine serves to illustrate these points.

2.2 Reduction with Hydrogen and Carbon Monoxide

Paal and Brunjes⁶⁷ and Paal and Buttner⁶⁸ studied reduction of ammonium paramolybdate solutions by hydrogen in the presence of a colloidal palladium catalyst. Figure 5 shows percent reduction to Mo^{IV} (calculated on the basis of H_2 consumed) vs time for the initial period of reduction carried out at 30°C and atmospheric pressure. The Mo^{IV} stage was attained after two days at which point the reaction stopped. Reduction was continued by heating to 50° to 60°C and applying a slight overpressure of hydrogen. The reaction proceeded slowly and stopped again after three days when the H_2 consumption corresponded to Mo^{III} . The end solution was yellow and the fine black precipitate formed was very difficult to dissolve in cold or hot concentrated HCl or H_2SO_4 . The small quantity that did dissolve gave a light red solution.

The brown black slurry formed at the Mo^{IV} stage gave a weight between $\text{Mo}(\text{OH})_4$ and $\text{MoO}(\text{OH})_2$ when dried in vacuo without heating. When dried with mild heating the weight approximated MoO_2 . The precipitate was analyzed for molybdenum after dissolution in aqua regia. These results seem to be in accord with those of Souchay et al.⁵¹ who found that neutralization of Mo^{IV} yielded $\text{MoO}_2 \cdot n\text{H}_2\text{O}$ with n very nearly 2.

Paal and Buttner did not analyze the precipitate corresponding to the Mo^{III} stage. The difficult solubility in, and the red colour imparted to, concentrated acid is in accord with the reported properties of $\text{Mo}(\text{OH})_3$. The yellow colour of the end solution could have been that of the $\text{Mo}^{3+}(\text{H}_2\text{O})_6$ monomer.⁵⁸

The abrupt decrease in the rate of reaction can be attributed to

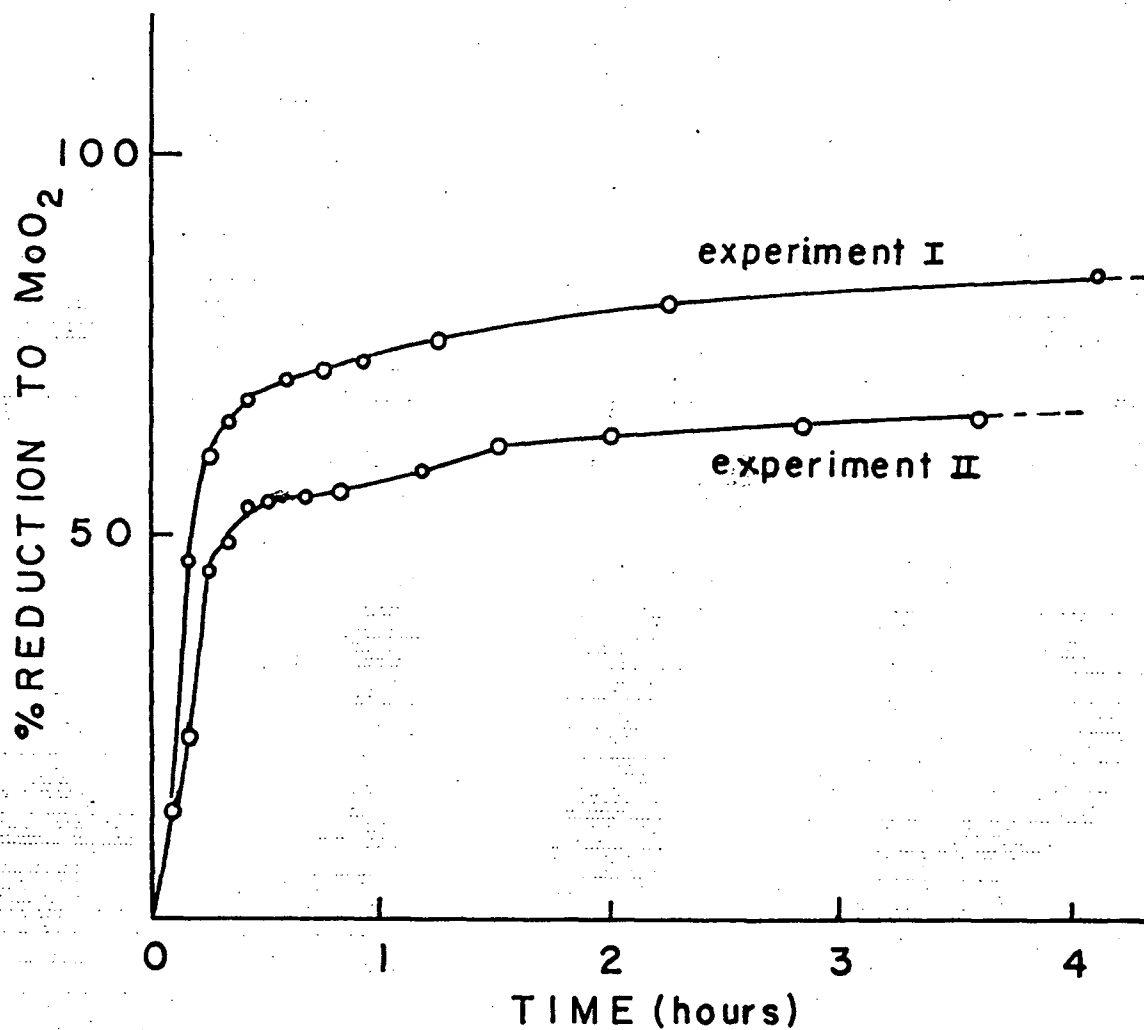
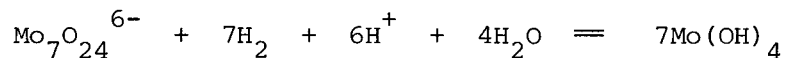
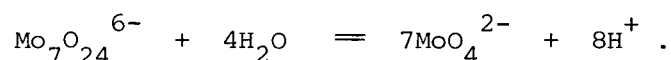


Figure 5: Reduction of ammonium paramolybdate solutions by hydrogen in the presence of a colloidal palladium catalyst.

depolymerization of molybdate occurring when reduction has consumed sufficient acid. For example the reduction can be written:



from which it follows that reduction consumes acid. The paramolybdate itself buffers the reaction in the pH range 5 to 6 by its own dissociation according to:



It can be shown that after 57% of the total molybdenum has been reduced to $\text{Mo}(\text{OH})_4$ the remaining Mo^{VI} exists only as MoO_4^{2-} . In this particular system the pH is then held between 9 and 10 by the $\text{NH}_4^+/\text{NH}_3$ buffer. Since it seems apparent that MoO_4^{2-} is reduced only very slowly the reaction proceeds to completion at a very slow rate.

It was found that the precipitates formed absorbed the palladium catalyst almost completely.

Iyapina and Zelikmann¹⁰ studied hydrogen reduction of 0.05 M sodium molybdate solutions at 100° to 200°C and 10 to 60 atm hydrogen pressure. Figure 6 shows their results for solutions of initial pH 2 and 7 at 40 atm and 200°C. The recommended optimum pH was 2 which corresponds to complete acidification of MoO_4^{2-} . This initial pH assures the reaction is buffered between pH 5 and 6 up to completion. It should be noted, however, that in this work it was found that the solutions contained iron. Thus for lower pH's some of the reduction was performed by the walls of the autoclave. In subsequent runs a quartz liner was used but in these runs various catalysts were also added. The product of reduction was identified

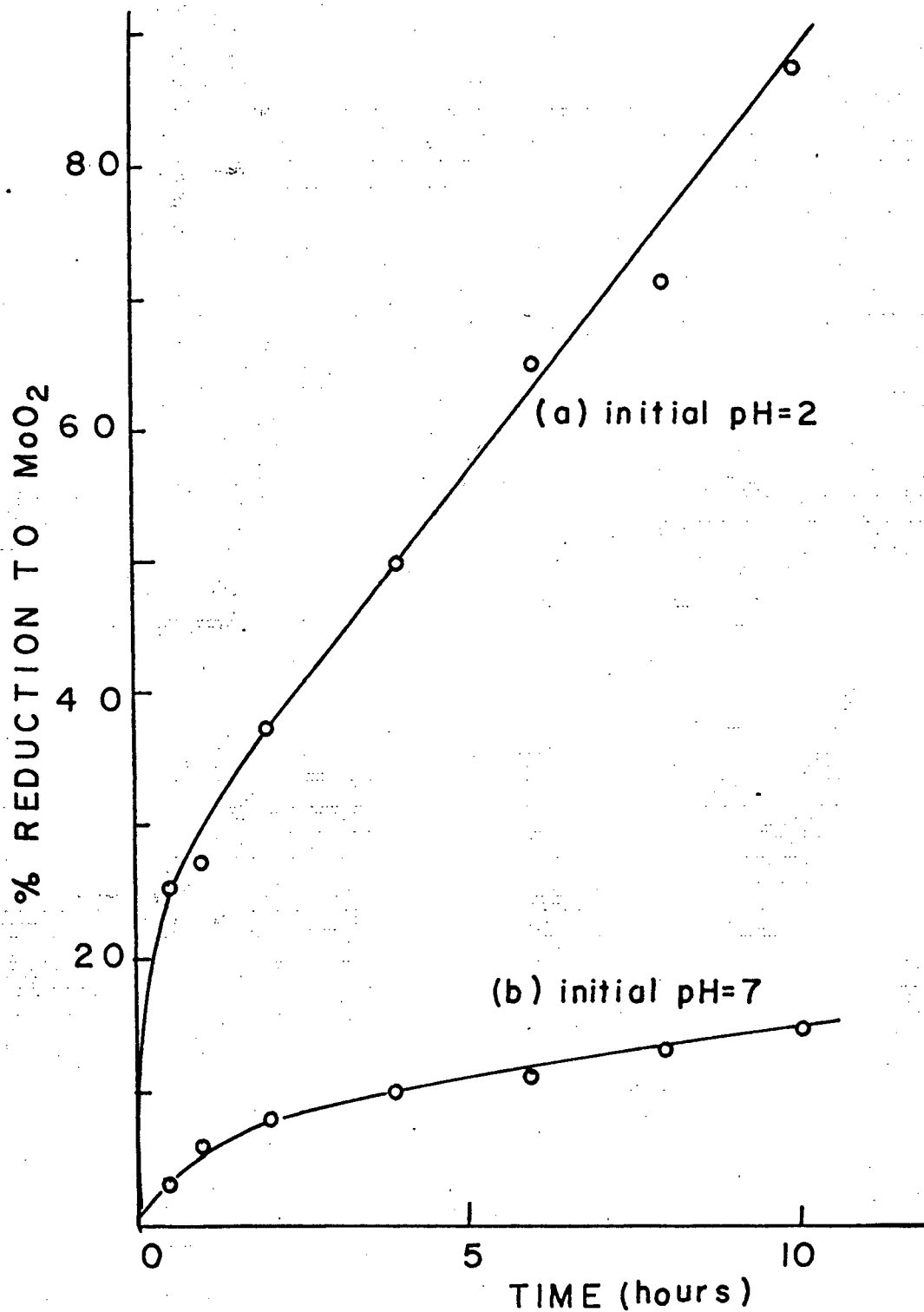
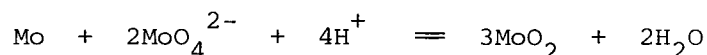


Figure 6: Reduction of sodium molybdate solutions by hydrogen at 200°C and 40 atm H₂.

as MoO_2 by X-ray diffraction and analysis for molybdenum.

The effect of MoO_2 slurry from a previous reduction and metallic molybdenum as catalysts is shown in Figure 7 curve a and Figure 7 curve b, respectively, for initial $\text{pH} = 3$, 40 atm H_2 , and 200°C . MoO_2 was added in a concentration of 67 g/l and metallic molybdenum as 7% of the amount theoretically necessary for the reaction



It was proposed that the reaction of metallic molybdenum with the solution formed "active" MoO_2 particles which served as centres of crystallization. It is apparent from Figure 7 that MoO_2 from previous reductions was not an efficient catalyst. Figure 7 curve c shows the results for no added catalyst (also, however, with no liner).

Complete reduction was obtained in four hours using metallic molybdenum as a catalyst and operating with initial $\text{pH} = 2$, 60 atm H_2 , and 200°C (Figure 7 curve d). Under these conditions decreasing the initial molybdenum concentration from 44 g/l to 5 g/l decreased the time required for complete reduction from 4 hours to less than $\frac{1}{2}$ hour. In no case was complete reduction obtained with an initial $\text{pH} > 2$. This is in accord with the assumption that polymolybdates are necessary for an appreciable rate of reduction.

In a later review Zelikmann³⁴ noted for 200°C , 7% of stoichiometrically necessary metallic Mo, and 40 g/l molybdenum that the rate of reduction was linearly dependent on $\sqrt{\text{PH}_2}$. He concluded that hydrogen participated in the rate controlling step in atomic form.

Sobol¹² studied reduction by both H_2 and CO at elevated temperature

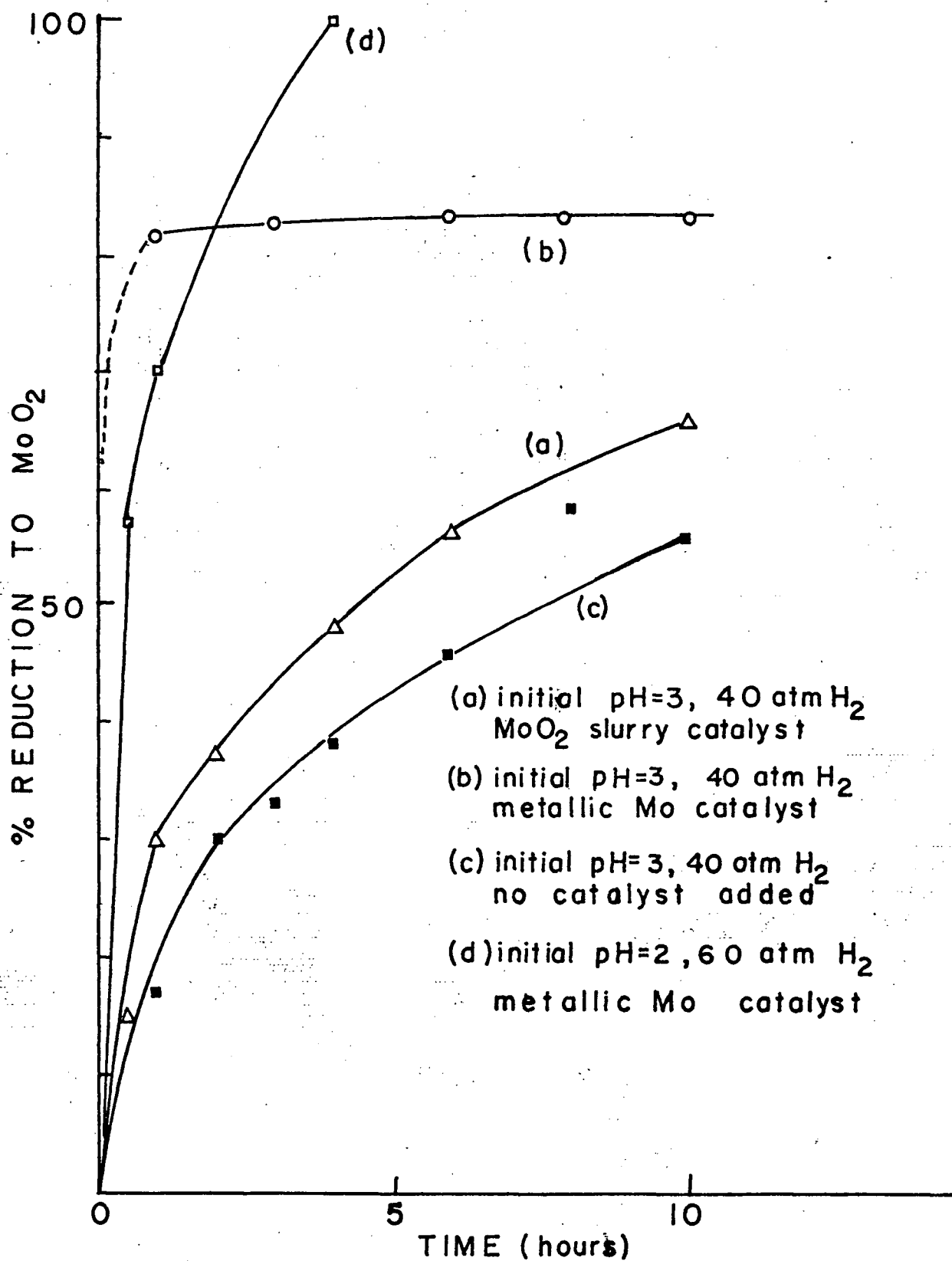


Figure 7: Effect of various catalysts, initial pH, and hydrogen pressure on hydrogen reduction of sodium molybdate solutions at 200°C.

and pressure. Using CO at 80 - 85 atm pressure and 200 - 220°C temperature almost complete reduction of molybdate could be obtained in times approaching one day. This was attributed to the buffering action of formic acid produced according to the reaction $\text{CO} + \text{H}_2\text{O} = \text{HCOOH}$. Hydrogen reduction was found to require preliminary acidification to $\text{pH} = 2$ in agreement with Zelikman and Lyapina. It was concluded, however, that the kinetics of gaseous reduction were slow and catalysis was required. An MoO_2 pulp produced by hydrogen reduction of molybdate solutions was found to have no significant catalytic effect. Sobol, therefore, proposed the use of metallic molybdenum as reductant and his further work did not consider gaseous reduction.

Kunda and Rudyk¹⁵ proposed hydrogen reduction at 180°C and 23 atm H_2 in the presence of 0.025 g/l PdCl_2 catalyst for molybdenum recovery from solutions containing about 1 M molybdenum, 1.54 M $(\text{NH}_4)_2\text{SO}_4$, and mole ratio free $\text{NH}_3/\text{Mo} = 2$. Under these conditions essentially complete reduction was obtained in less than one-half hour. The resulting oxide powder absorbed the palladium chloride catalyst but retained enough catalytic activity for use in two "densifications" with fresh molybdate solutions. From the solution composition given it is apparent that the hydrogen ion activity in this system was controlled by the $\text{NH}_4^+/\text{NH}_3$ buffer. The fact that reduction went rapidly to completion in these conditions can perhaps be explained by the effect of temperature on the molybdate polymerization and $\text{NH}_4^+/\text{NH}_3$ equilibria. No data is available for the polymolybdates but using free energy data from Barner and Scheuerman's⁶⁹ compilation it can be shown that the pH of the $\text{NH}_4^+/\text{NH}_3$ buffer falls from 9.27 at 25°C to 5.75 at 200°C. Presumably this fall was sufficient to ensure that the system was buffered in a pH range where polymolybdates could exist.

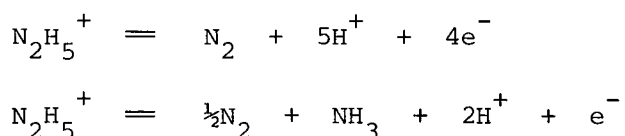
The oxide product analyzed 60 - 65% Mo, 4 - 5% NH_3 , and 0.5% S compared to 59% Mo for $\text{MoO}(\text{OH})_3$, 75% for MoO_2 , and 65% for $\text{Mo}(\text{OH})_3$. Solid state hydrogen reduction of this product gave 99.9% molybdenum metal.

The precise nature of the oxide product was not determined. X-ray diffraction was not mentioned. They did report that when reduction was carried out under milder conditions than those listed above intermediate steps were observed; the solution became marine blue, then molybdenum precipitated as a brown amorphous residue which later agglomerated into black, oval-shaped particles of lower molybdenum oxide. It may be supposed that the brown residue was $\text{MoO}(\text{OH})_3$ and it is possible that in this case complete reduction to the Mo^{IV} state did not proceed. It was observed in the present study that under some conditions $\text{MoO}(\text{OH})_3$ precipitated from molybdenum blue solutions had a blue-black colour rather than its customary brown.

Wagenmann¹⁴ patented a process involving hydrogen reduction to recover molybdenum from 1.5 - 3.0 g/l molybdenum and 60 - 120 g/l sulfate solutions acidified to pH = 2. Reduction was carried out at 180°C and 20 - 25 atm H_2 in a flow through reactor with a residence time of 4½ hours. The solution exiting the reduction vessel was cooled to 80°C and expanded to 0.1 atm before filtration to recover the molybdenum product. The filtrate contained 0.05 g/l Mo thus molybdenum recovery was 97%. The analysis of the product was not given. No catalysis was mentioned. These results are considerably better than those obtained by Zelikmann and Lyapina (Figure 7) at a higher temperature and hydrogen pressure. Since Wagenmann did not describe the construction of his reactor it is not possible to determine whether the walls of the reactor played a role in the reduction.

2.3 Reduction with Hydrazine

The behaviour of hydrazine, N_2H_4 , as a reducing agent has been the subject of much work, the general aim of which was to determine the reasons for the wide variation of stoichiometry with different oxidants and experimental conditions. Hydrazine was shown to react according to two limiting reactions:*



which could often occur in parallel giving stoichiometries between the two limits. Some oxidizing agents added slowly to boiling highly acid hydrazine solutions also gave a significant yield of hydrazoic acid, HN_3 .

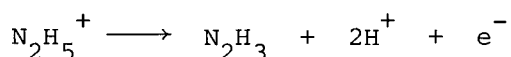
Browne and Shetterly,⁷⁰ in summarizing the results of a series of investigations, recognized three classes of oxidizing agents for hydrazine in hot acid solution:

class a	class b	class c
produce fairly large amounts of NH_3 and HN_3	little or no HN_3 but much NH_3	little or no HN_3 or NH_3
H_2O_2	KMnO_4	KIO_3
KClO_4	MnO_2	HgO
$\text{K}_2\text{S}_2\text{O}_8$	Fe_2O_3	HgCl_2

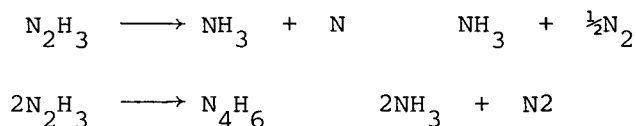
*Most of the work to be discussed was performed in solutions of $\text{pH} < 7$ where the protonated form of hydrazine, N_2H_5^+ , predominates.

They stated that so many different factors influenced the course of the reactions that it was impossible to establish a simple relationship between the potential of the various oxidizing agents and their ability to produce HN_3 , NH_3 , or N_2 .

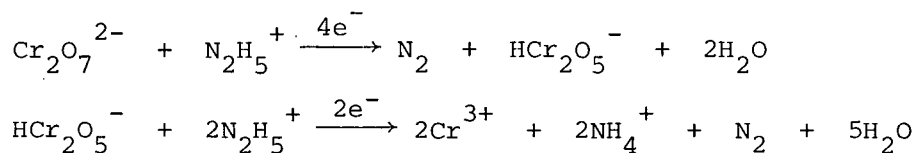
Cuy et al.⁷¹ summarized a further series of investigations by suggesting there were two classes of oxidizing agents. Those undergoing a change of one equivalent per mole reacted according to:



followed by one of the two reactions:



If either of these two subsequent reactions occurred faster than further oxidation of N_2H_3 a limiting stoichiometry of one equivalent per mole of hydrazine ought to obtain. For oxidizing agents undergoing a change of more than one equivalent per mole a mixed stoichiometry (i.e. between 1 and 4 equivalents per mole of hydrazine) was explained in terms of the generation of another oxidizing agent as an intermediate undergoing only one equivalent reduction, for example:



giving the overall stoichiometry of 1.5 moles N_2H_5^+ per mole of $\text{Cr}_2\text{O}_7^{2-}$.

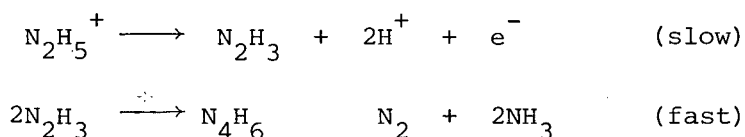
An observed tendency of the stoichiometry, R, (defined as moles of

electrons/mole of hydrazine) to increase in alkaline solution was thought due to a higher rate of further oxidation of intermediate N_2H_3 in alkaline solutions as opposed to a higher rate of its decomposition in acid solutions.

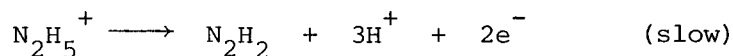
Kirk and Browne⁷² likewise proposed division of oxidizing agents into two classes:

1. Those that accept only one electron per "active" unit (atom, ion, molecule) were termed monodelectronators;
2. Those that accept more than one electron per "active" unit were termed polydelectronators, i.e. didelectronators, tridelectronators, etc.

With monodelectronators complete oxidation to nitrogen could be obtained but in cases where R was less than four the sole byproduct was ammonia formed according to:

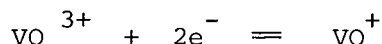
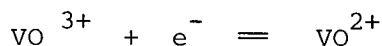


With didelectronators complete oxidation to nitrogen was predominant but for incomplete oxidation ammonia and a small quantity of hydrazoic acid were formed. The reaction sequence in this case involved initial formation of N_2H_2 according to:



followed by a series of fast subsequent reactions to produce N_2 or HN_3 and NH_3 .

Oxidizing agents undergoing reduction in more than two stages (complex delectronators) could manifest the characteristics of mono- and didelectronators, for example:

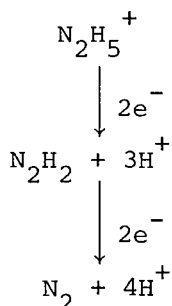


Higginson et al.⁷³ proposed that mono- and didelectronators be distinguished by the following criterion:

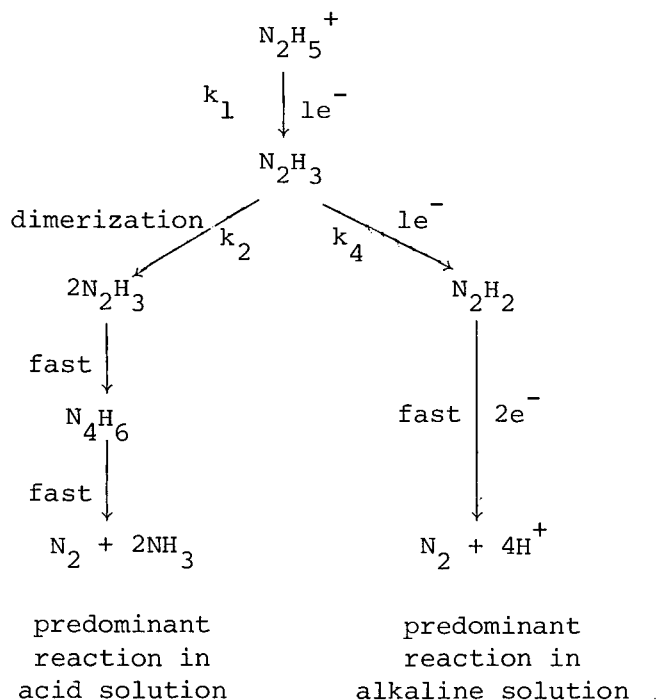
1. Didelectronators were those reagents which oxidized hydrazine at room temperature in acid solution to produce N_2 only.
2. Monodelectronators were those reagents which oxidized hydrazine to NH_4^{+} and N_2 under the same conditions as above with the ratio of $\text{NH}_4^{+}/\text{N}_2$ depending on relative initial concentrations of hydrazine and oxidant.

Simple mechanisms for mono- and didelectronation were proposed:

didelectronation



monodelectronation



The stoichiometry for monodelectronators could lie between $R = 1$ and $R = 4$ depending on the relative rates of the two subsequent reactions of N_2H_3 .

Since in alkaline solutions even monoelectronators produce nitrogen quantitatively the effect of increasing pH was seen as decreasing the rate of dimerization of N_2H_3 relative to its further oxidation.

Subsequently Higginson and Sutton⁷⁴ performed an isotopic study involving the oxidation of ^{15}N enriched hydrazine by excess of various oxidizing agents. The isotopic distribution of the resulting products confirmed the validity of the simple mechanisms proposed. Cahn and Powell⁷⁵ independently performed a similar isotopic study with the same results.

In a subsequent review Higginson⁷⁶ noted that for oxidizing agents in general, yields of ammonia relative to hydrazine consumed are very much smaller in alkaline, neutral, and weakly acid solution than the yields obtained by using monoelectronators in solutions with $pH < 3$. Thus in alkaline solution few, if any, oxidants give values greater than 0.1 for moles NH_3 /mole N_2H_4 whereas for $pH < 3$ most monoelectronators give mole NH_3 /mole $N_2H_4 \geq 0.75$. Use of the equations:

$$\frac{\text{moles } NH_3}{\text{moles } N_2H_4} + \frac{4 \text{ moles } N_2^4}{\text{moles } N_2H_4} = R$$

$$\frac{\text{moles } NH_3}{\text{moles } N_2H_4} + \frac{\text{moles } N_2^4}{\text{moles } N_2H_4} = 1$$

(where N_2^4 is defined as N_2 due to 4 equivalent reduction) shows that this corresponds to $R \geq 3.7$ in alkaline solution and $R \leq 1.75$ for $pH \leq 3$.

Higginson felt it was likely the change from low to high stoichiometry occurred in the pH range 3 to 5 based on the observation that at $pH = 2$

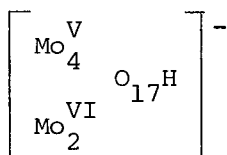
most monoelectronators gave $R < 1.75$ while it was observed that at $\text{pH} = 6$ the monoelectronator ferricyanide reacted with $R = 4$. This prediction was verified for oxidation with manganese trispyrophosphate. For didelectronators Higginson proposed the change to high stoichiometry occurred for $\text{pH} > 0$.

Browne and Shetterly⁷⁰ investigated the reaction of aqueous suspensions of MoO_3 with hydrazine. In alkaline solutions the reaction was very slow and some ammonia was produced. In boiling sulfuric acid solutions with excess MoO_3 appreciable amounts of ammonia and some HN_3 were formed. On the basis of this work Kirk and Browne⁷² considered molybdate ions as didelectronators.

Jakob and Kozlowski⁷⁷ found that molybdate solutions oxidized hydrazine practically completely to N_2 . They were able to prepare mixed $\text{Mo}^{\text{VI}}/\text{Mo}^{\text{V}}$ compounds by reduction in weakly acid solutions. In slightly more acid solutions molybdenum blue was formed while at still higher acidity Mo^{V} was produced directly without intermediate products. In particular they reported preparation of the $\text{Mo}^{\text{V}}/\text{Mo}^{\text{VI}}$ compound $\text{NH}_4 \left[\begin{array}{cc} \text{Mo}_2^{\text{V}}\text{O} & \text{Mo}^{\text{VI}}\text{O}_4 \\ & (\text{OH})_7 \end{array} \right]$ from a solution

containing 0.317 M molybdenum as ammonium paramolybdate and 0.06 M N_2H_4 . This compound has the same $\text{Mo}^{\text{V}}/\text{Mo}^{\text{VI}}$ ratio as the brown species reported by Ostrowetsky⁴² between pH 3 and 4. In fact if the formula given by Jakob and Kozlowski is rewritten to contain six atoms of molybdenum and water is removed it becomes $\left[\begin{array}{c} \text{Mo}_4^{\text{V}} \\ \text{Mo}_2^{\text{n}} \end{array} \text{O}_{17} \right]^{2-}$

and, if it is assumed to be protonated in solution,



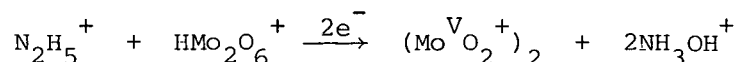
which is the composition found by Ostrowetsky.

Holtje and Geyer³¹ and Rao and Suryanarayana⁷⁸ reported that under no conditions does hydrazine reduce molybdate solutions beyond the Mo^{V} state. It was thus recommended as a method for the preparation of Mo^{V} stock solutions. The latter authors reduced 0.4220 moles of Mo^{VI} in 1 N HCl on the boiling water bath with 0.154 moles of hydrazine. They were interested only in obtaining quantitative yield of Mo^{V} so did not determine the excess hydrazine. These results, however, indicate they obtained $R \geq 2.74$. Since, according to Higginson, a monoelectronator should approach $R = 1$ under such conditions these results suggest Mo^{VI} behaved as a didelectronator.

Fillipov and Nuger⁴⁵ reported that at $\text{pH} > 4$, 0.008 M molybdate solutions were not reduced by 0.02 to 0.04 M hydrazine. At pH 1.3 to 1.4 only molybdenum blue was formed.

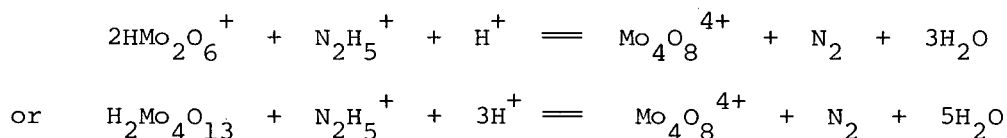
Ostrowetsky and Brinon⁷⁹ studied reduction of molybdate solutions by hydrazine in 0.1 to 10 N acid solutions. In this range of acidity mixed $\text{Mo}^{\text{V}}/\text{Mo}^{\text{VI}}$ compounds did not form and the only product was Mo^{V} . The rate of the reaction increased with increasing temperature and decreased with increasing acidity. Detailed investigations were made in 2 N HCl at 0°C where the reaction was slow enough to follow without difficulty. Spot tests showed that the solutions contained hydroxylamine and polarography in 4 N NaOH allowed determination of the total concentration of $\text{N}_2\text{H}_4 + \text{NH}_3\text{OH}^+$. Mo^{VI} and Mo^{V} were determined by polarography in 2 N HCl.

It was found that the total concentration of $\text{N}_2\text{H}_4 + \text{NH}_3\text{OH}$ did not change during the reaction and that a plot of Mo^{V} vs initial mole ratio $[\text{N}_2\text{H}_4]/[\text{Mo}]$ showed a break at mole ratio 0.5. The reaction proposed was



The species HMo_2O_6^+ had been proposed by Chauveau et al.⁸⁰ as the predominant Mo^{VI} species in 2 N HCl.

In the same conditions of temperature and acidity, however, it was found that for the stoichiometric ratio (according to the above equation) of $[\text{N}_2\text{H}_5^+]/[\text{Mo}^{\text{VI}}] = 0.5$ an increase of initial concentration of Mo^{VI} from 0.02 M to 0.24 M changed the reaction so that N_2 as well as other unidentified products resulted. The reactions proposed in this case were:



It was reasoned that the change in the reaction was due to a change in the degree of polymerization of either Mo^{VI} or Mo^{V} . Chauveau et al.⁸⁰ had reported an equilibrium between HMo_2O_6^+ and $\text{H}_2\text{Mo}_4\text{O}_{13}$ while the work of Viossat and Lamache³⁶ indicated that tetrameric Mo^{V} could exist in equilibrium with a dimeric form. At a given acidity, therefore, an increase in concentration of molybdenum would favour the tetracondensed forms of the Mo^{VI} and Mo^{V} species and hence a four equivalent oxidation of hydrazine.

Ostrowetsky and Brinon's work appears to be the only report of oxidation of hydrazine to hydroxylamine. Audrieth and Ogg⁸¹ in their review of oxidation of hydrazine stated that no evidence had been reported to demonstrate that hydroxylamine is an oxidation product of hydrazine.

Huang and Spence⁸² investigated the reaction of hydrazine and Mo^{VI} at 70°C in phosphate buffers of pH 1.2 to 3.2. The initial mole ratio of N_2H_5^+ to Mo^{VI} was maintained at 0.5 and Mo^{VI} was varied between 5×10^{-4} M and 7×10^{-4} M. The hydrazine was oxidized quantitatively to N_2 and the reaction was first order in each reactant. The rate of reaction increased with increasing pH and exhibited an order in H^+ of 0.25. It was suggested that the fractional dependence on H^+ could be due to changes in polymerization of Mo^{VI} with pH, ionization of a monomeric Mo^{VI} species, or involvement of H^+ in a rate controlling step. N_2H_2 was detected qualitatively by mass spectrometry and trapping with unsaturated acids. The observed stoichiometry and the presence of N_2H_2 indicated Mo^{VI} behaved as a dideelectronator.

Nusgra and Sinha⁸³ observed that in 1 N H_2SO_4 0.025 M hydrazine and 0.01 M Mo^{VI} reacted to yield N_2 quantitatively. They detected both N_2H_3 and N_2H_2 depending on the relative amount of Mo^{VI} added to hydrazine solutions.

The preceding summary indicates that Mo^{VI} tends to oxidize hydrazine to nitrogen with $R \approx 4$. This has been interpreted in terms of predominant dideelectronation to yield N_2H_2 as a first step and also by series of monoelectronation steps. Near quantitative oxidation to N_2 by one electron steps, however, appears to be unlikely except in alkaline solution. Two electron steps require that the molybdate species involved be reduced to Mo^{IV} if they are monomeric. Mechanisms based on the assumed chemistry of Mo^{IV} must, however, be open to question until more is known about the chemistry of Mo^{IV} . Since Mo^{VI} tends to polymerize it seems reasonable to assume that the nature of the reaction could depend on the particular Mo^{VI} species involved.

As has been seen this concept was used by Ostrowetsky and Brinon to explain a change in the nature of the reaction with increasing molybdenum concentration in acid solution. There have been no detailed studies of the reaction under condition of concentration and pH where molybdate polyanions predominate in solution and where formation of mixed $\text{Mo}^{\text{V}}/\text{Mo}^{\text{VI}}$ species might be expected to occur. The work of Jakob and Kozlowski does, however, suggest that four electron stoichiometry and at least intermediate formation of $\text{Mo}^{\text{V}}/\text{Mo}^{\text{VI}}$ species are to be expected.

2.4 Reduction with SO₂ and H₂S

Holtje and Geyer³¹ reported that SO₂ reduces weakly acid molybdate solutions to give light green or blue solutions in which only 0.5% of the molybdenum is present as Mo^V. In more concentrated acid no noticeable reaction occurred. Wardlaw⁸⁸ made similar observations for both SO₂ and H₂S. Thus at best it appears that neither of these reductants can take molybdate past the mixed valent molybdenum blue stage.

2.5 Summary

The work reported in the literature indicates that reductive precipitation of molybdenum oxides with hydrogen or hydrazine might be technically feasible. Hydrogen and hydrazine, as a four electron reductant, are clean reductants thus they offer the potential of producing a pure oxide product. Most of the work reported, however, has been performed in acid solutions and the action of these reductants on neutral or alkaline molybdate solutions is not well documented.

In the neutral pH range it is apparent that polymerization of molybdate ions might be a factor in any reduction reaction. In addition mixed-valent $\text{Mo}^{\text{VI}}/\text{Mo}^{\text{V}}$ compounds might be expected to form in this range and these could influence the course of the reduction reaction. In the case of reduction with hydrazine the reaction might be able to follow different paths depending on pH and degree of polymerization of molybdate.

It has been seen that Mo^{III} , Mo^{IV} , and Mo^{V} hydrated oxides as well as mixed valent oxides can be precipitated in neutral solution. There is also a possibility that the Mo^{V} precipitate may act as an ion exchanger.

3. SCOPE OF PRESENT WORK

The present work was undertaken to investigate the use of hydrogen and hydrazine for reductive precipitation of molybdenum oxides from solutions produced by a sodium hypochlorite leach of Cu-Mo rougher concentrates. The specific objectives were to define the pH range in which reduction could be achieved, the kinetics of the reduction reactions, and the nature of the oxide products.

The procedure adopted was first to determine the behaviour of the reactions using sodium molybdate solutions then to investigate the effects of other components of the actual leach solutions, in particular copper and sodium chloride.

4. EXPERIMENTAL

Molybdate solutions for reduction by both hydrogen and hydrazine were made up with Mallinckrodt analytical reagent sodium molybdate ($\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$). The manufacturer's assay was 99.5% sodium molybdate minimum and the chemical was used without further purification. The molybdate solutions were standardized by flame atomic absorption spectrophotometry and gravimetric analysis for molybdenum.

Mo^{V} stock solutions for polarographic calibration curves and neutralization experiments were produced by reducing 3.5 N HCl sodium molybdate solutions by shaking in a flask with metallic mercury. The solutions were standardized by titration with ceric sulfate using ferroin as an indicator.^{46,84}

Hydrazine solutions were made up by dilution of BDH 99-100% hydrazine hydrate or Eastman Kodak 64% hydrazine in distilled water. The hydrazine solutions were standardized by potassium iodate titration in 5 N HCl.⁸⁵ Commercial tank hydrogen was used for hydrogen reduction experiments.

Hydrogen reduction was performed in a Parr 2 litre autoclave. A glass liner was used for all runs. All parts of the bomb contacting the solution were titanium. The resistance heater surrounding the bomb was controlled by a Yellowsprings Instrument Company Thermistemp Temperature Controller Model 71 and a Variac. The Variac was set to give the approximate temperature desired and the Thermistemp maintained the desired temperature by operating a relay which reduced the power input to the heater by about 15% in the cooling cycles. It was found that on pressurizing the bomb with hydrogen there was a significant temperature increase (e.g. pressurizing to 30 atm H_2 at 180°C led to a temperature increase of around 30°C). To

reduce this effect additional cooling was provided by a jet of compressed air or nitrogen introduced at the base of the bomb. The gas flow was controlled by a solenoid valve which opened on the cooling cycle of the Thermistemp. In all runs stirring was maintained at 600 rpm.

In a typical run one litre of sodium molybdate solution adjusted to the desired pH was added to the glass liner and the bomb was sealed. Nitrogen was bubbled through the solution for about five minutes and the bomb was pressurized to 50 psig with nitrogen. The bomb was brought rapidly to just below the desired temperature using full power input to the furnace. The Variac setting was then reduced and the temperature of the run controlled by the Thermistemp. Once the temperature was stable hydrogen was admitted to the bomb. The hydrogen pressure was increased to that desired and maintained throughout the run. The variation in temperature during a run was $\pm 5^{\circ}\text{C}$ and pressure ± 5 psig.

Samples were taken at appropriate times throughout each run. The sampling system was cleared before each sample by discharging at least 20 ml of solution. Agitation was maintained during sampling. Samples were cooled either by standing at room temperature or holding under cold tap water.

After each run the apparatus was cleaned by running for one hour at 100°C with 50% nitric acid in the glass liner.

Hydrazine experiments were performed in a 420 ml pyrex vessel. The reactor was maintained at the desired temperature by immersion in a water bath. Temperature control was $\pm 0.3^{\circ}\text{C}$.

In a typical run 200 ml of sodium molybdate solution adjusted to the desired pH with HCl was brought to temperature in the reactor. An equal

volume of hydrazine solution adjusted to the same pH was preheated in a separate flask. At zero time the hydrazine solution was added to the molybdate solution. Stirring was maintained at 300 rpm for each run. The pH was controlled by additions of 1:1 HCl as required during the run.

Samples were taken by pipetting 15 to 30 ml of the reacting slurry from the reactor. Various methods were used to freeze the reaction to permit determination of the concentrations of molybdenum and hydrazine as functions of time.

Since preliminary runs had shown that the reduction reaction did not occur above pH 6.5 the first method adopted was to discharge the sample into a centrifuge tube containing enough concentrated NaOH to raise the pH to between 8 and 12. It was hoped this would also precipitate all of the Mo^{V} formed.

The second method used was to discharge the sample into a porcelain filter crucible and collect the filtrate in a centrifuge tube again containing enough NaOH to raise the pH to 8 to 12. This method of analysis gave significantly different results.

The third procedure was to discharge the sample into a small beaker and quickly titrate it with 0.1 to 1 N NaOH to obtain a particular pH. The resulting slurry was then filtered and the filtrate analyzed for molybdenum and hydrazine.

A fourth procedure was simply to discharge the sample into a beaker containing an equal volume of water at about 0°C. Preliminary runs had shown the reaction was very slow at room temperature so it was felt this procedure would permit time for subsequent filtration.

The fifth technique used was to discharge the sample into a filter

crucible then dilute the filtrate to a concentration suitable for determination of molybdenum by atomic absorption ($\approx 10 \mu\text{g/ml}$).

A few runs were performed to follow the evolution of nitrogen gas during reaction. The reaction was carried out in a sealed flask and the gas evolved collected over mercury. These runs were carried out at room temperature. To begin a run a hydrazine solution adjusted to $\text{pH} = 4.5$ was added to a molybdate solution of the same pH in the flask. The flask was quickly stoppered and stirring begun. The pH was not controlled during these runs.

Molybdenum in solution was determined both by flame atomic absorption spectrophotometry using a Perkin Elmer Model 306 spectrophotometer and by polarography using a Sargent Model XXI polarograph. Solutions for polarography were diluted to contain between 0.05 and 0.15 g/l Mo while those for atomic absorption were diluted to contain between 0.01 and 0.04 g/l Mo. Dilution for atomic absorption was performed with a 10% AlCl_3 , 5% NH_4Cl solution which was found by Ismay⁸⁶ to eliminate interferences. Polarography was performed in 2 N HCl where the waves of Mo^{V} and Mo^{VI} are distinct.⁷⁹

Atomic absorption gave total molybdenum regardless of the proportions of Mo^{V} and Mo^{VI} in the sample and hydrazine did not interfere. Polarography of $\text{Mo}^{\text{VI}}/\text{Mo}^{\text{V}}$ mixtures in the presence of hydrazine was unsuitable for separate determination of Mo^{V} and Mo^{VI} because at the acidity required (2 N HCl) the reduction of Mo^{VI} by hydrazine proceeded at a rate sufficient to make the determination of Mo^{V} of doubtful accuracy. Total molybdenum could be determined. Atomic absorption and polarography agreed within 2%.

Hydrazine in sample filtrates was determined by titration with 0.1 N KIO_3 in 5 N HCl. The end point was marked by the disappearance of the pink iodine colour from a CCl_4 layer in the titration flask.⁸⁵ Ammonia,

hydroxylamine, and Mo^{VI} did not interfere. When appreciable hydroxylamine was present in the titration solution, however, a faint pink colour returned to the CCl_4 layer on standing for a few hours. Mo^{V} did interfere in the titration but in general the amount of Mo^{V} present in the reaction filtrates was small enough to render a correction unnecessary.

Ammonia in sample filtrates was determined by a method described by DeVries and Gantz.⁸⁷ Hydrazine was first oxidized by 0.4 N KIO_3 as previously described. The I^+ and excess IO_3^- were reduced to I^- by excess Na_2SO_3 . The excess sulfite was then removed by bubbling air for 15 minutes. Ammonia was then determined by distillation into 0.1 N HCl after making the solution basic. Hydroxylamine did not interfere.

Precipitates produced by hydrazine reduction were analyzed for total molybdenum gravimetrically by precipitation of molybdenum as PbMoO_4 .⁸⁹ The mean oxidation state of molybdenum was determined by oxidation with excess ceric sulfate and back titration with ferrous ammonium sulfate using ferroin as an indicator.⁴⁶ Water was determined using a Dupont 950 thermogravimetric analyzer. Chlorine was determined by dissolving a sample of the precipitate in 3 M HNO_3 , addition of excess AgNO_3 , and back titration with HCl using a silver electrode and a potassium sulfate reference electrode.⁵¹ Sodium was determined by flame emission photometry.

Precipitates resulting from hydrogen reduction were characterized by X-ray diffraction and thermogravimetric analysis.

5. RESULTS

5.1 Hydrogen Reduction

Hydrogen reduction experiments were performed at 200° to 220°C with 30 atm pressure of H_2 . The initial concentration of molybdenum and the initial pH were 17 g/l and 2, respectively. For times up to 7 hours reduction proceeded only to the molybdenum blue stage and no precipitation occurred.

An experiment was then performed in the presence of a platinum clad expanded niobium mesh. In this case the solution passed through the molybdenum blue stage in 30 minutes and later samples were only slightly coloured. Figure 8 shows a plot of percent reduction vs time. The final pH was 8. The black precipitate formed only slightly plated the apparatus and was easily filterable. It gave an X-ray diffraction pattern identical to ASTM 5-0452 for MoO_2 . Thermogravimetric analysis showed the precipitate was anhydrous. Experiments with the mesh were not continued because the niobium substrate suffered extreme hydrogen damage and broke under its own weight.

The run with the mesh resulted in some precipitation on the stirrer and other fixtures as well as the glass liner. A further run performed without cleaning the apparatus resulted in formation of a blue precipitate giving an X-ray powder diffraction pattern indicating the presence of MoO_2 and MoO_3 (ASTM 21-569). Ceric sulfate titration⁹⁰ indicated the average oxidation state of molybdenum in this precipitate was 5.53. Only a small amount of precipitate was formed after 12 hours. The dark blue solution contained 16 g/l molybdenum with an average oxidation state of 5.67.

The apparatus was then cleaned to remove all deposits and the run was

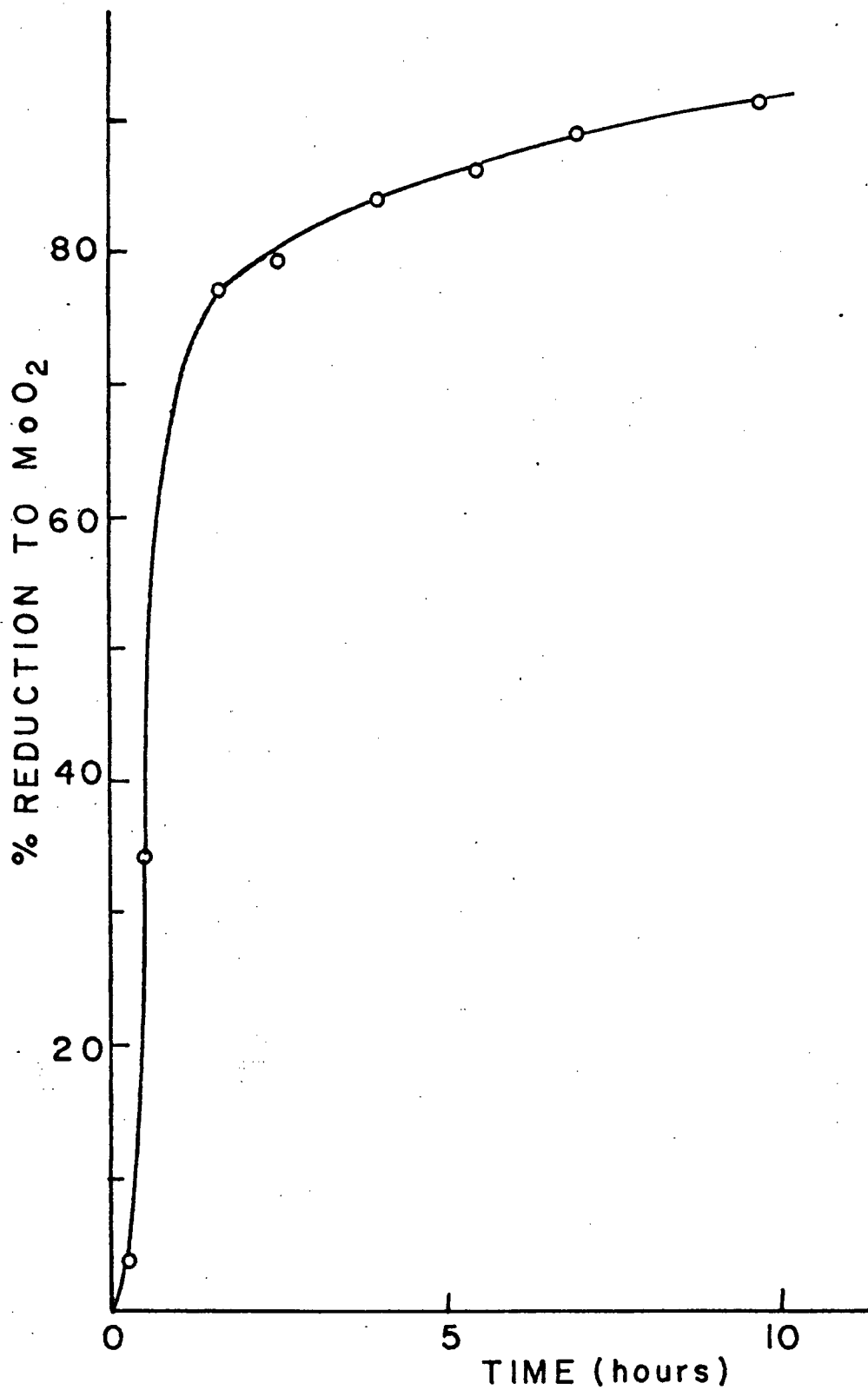


Figure 8: Reduction of 17 g/l sodium molybdate solution by hydrogen at 200°C and 30 atm H₂ in the presence of Pt clad niobium mesh.

repeated. Almost no reduction occurred. The solution was coloured light blue and there was no precipitate.

Three runs were performed in 3 M NaCl to simulate solutions from the proposed sodium hypochlorite leach. Minimal reduction was obtained even when using metallic molybdenum powder as a catalyst.

Hydrogen reduction experiments were discontinued when it was observed that the liquid condensing between the glass liner and the bomb severely corroded the titanium bomb.

5.2 Reduction with Hydrazine

Preliminary runs were carried out at 50°C using 5 g/l molybdenum solutions and various hydrazine concentrations. For pH \approx 5 reaction occurred almost immediately on mixing the reactants. The solution underwent a series of colour changes. It first became blue, then green, and finally an opaque brown. A brown precipitate formed during the green stage but not during the initial blue one.

The effect of pH was investigated at 50°C, 5 g/l initial molybdenum concentration, and an initial hydrazine to molybdenum mole ratio of 4:1. For pH > 6.5 no reaction occurred. As the pH was decreased below 6.5 the rate of precipitation increased but for pH < 3 the nature of the reaction changed. The initial blue colour remained throughout the reaction and the rate of precipitation decreased. The precipitate formed was blue rather than brown.

More detailed investigations were performed at pH = 4.5, 50°C and 4:1 initial mole ratio of hydrazine to molybdenum. These conditions gave a convenient reaction rate for analysis. The results obtained, however, were found to depend markedly on the sampling method employed.

Figure 9 curve a is a plot of the concentration of molybdenum remaining in solution vs time obtained by neutralizing 20 ml samples of the reacting slurry with 8 N NaOH and then centrifuging to obtain a supernatant solution for analysis. Curves b through e were obtained by neutralizing 20 ml samples of the slurry by titration to the pH's indicated followed by filtration through porcelain filter crucibles. Curve f was obtained by discharging the sample of slurry into 20 ml of cold water followed by

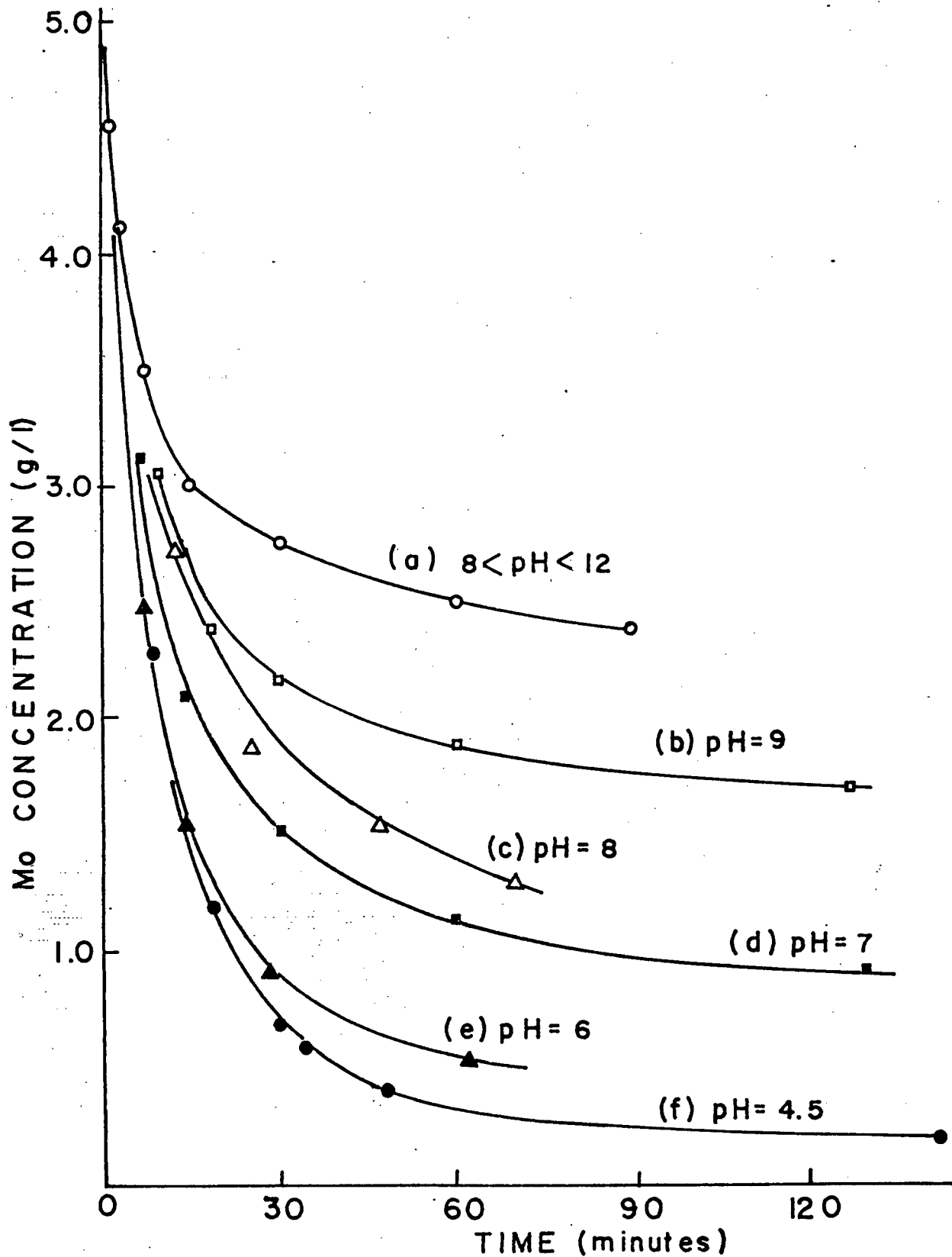


Figure 9: Effect of sampling technique on concentration of molybdenum remaining in solution vs time at 50°C with pH = 4.5, initial molybdenum concentration ≈ 5 g/l, and initial hydrazine to molybdenum mole ratio $\approx 4:1$.

filtration.

Figure 10 compares the results obtained using methods involving direct filtration of the slurry samples with those obtained by first discharging the slurry into an equal volume of cold water. The open circles represent the latter technique. The triangles represent points obtained by direct filtration of the slurry and dilution of an aliquot of the filtrate for atomic absorption analysis of molybdenum. The crosses represent points obtained by direct filtration of the slurry samples into centrifuge tubes containing 1 ml of 8 N NaOH. All three of these methods gave similar results for molybdenum remaining in solution.

When sampling was performed by filtration into centrifuge tubes containing 8 N NaOH it was observed that the clear light brown filtrate formed a brown or blue-green precipitate on mixing with the caustic. Figure 11 shows the dry weight of precipitate retained on filtering 25 ml samples of slurry through a porcelain filter crucible, the dry weight of the precipitate formed in the centrifuge tube, and the concentration of molybdenum remaining in solution in the centrifuged filtrate. Figure 12 shows the results obtained under the same conditions (50°C, pH = 4.5, initial molybdenum concentration = 5 g/l) but with a 2:1 initial mole ratio of hydrazine to molybdenum instead of 4:1.

Since the above sampling method was rather tedious it was decided to use the simpler procedure of direct analysis of the sample filtrate for molybdenum remaining in solution in order to investigate the effects of temperature and initial hydrazine concentration on the rate of the precipitation reaction. The initial molybdenum concentration was ≈ 5 g/l and the pH = 4.5 for each run. Figures 13 and 14 show the results obtained.

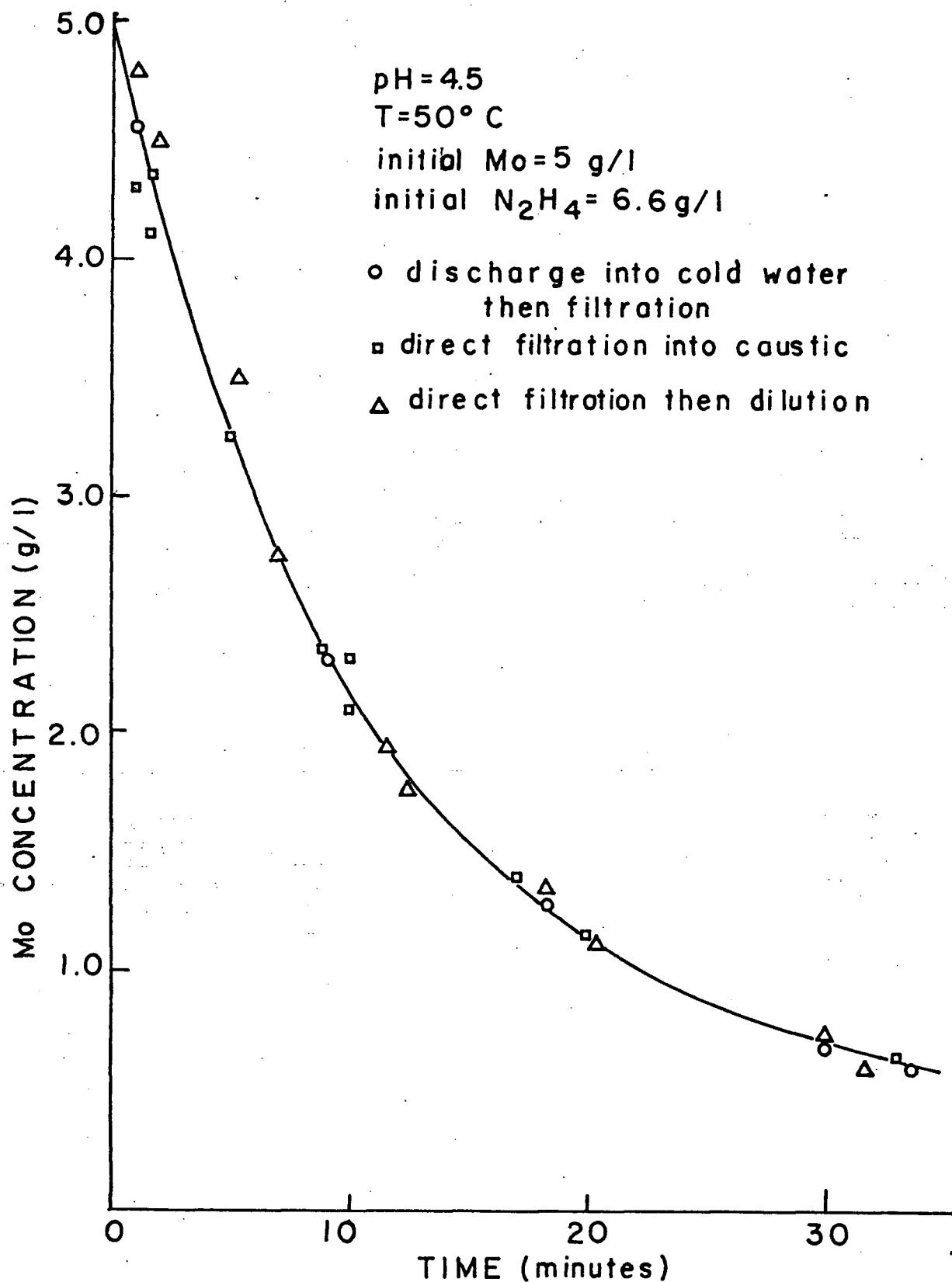


Figure 10: Comparison of results obtained by direct filtration of slurry samples with those obtained by previous dilution of samples with an equal volume of cold water.

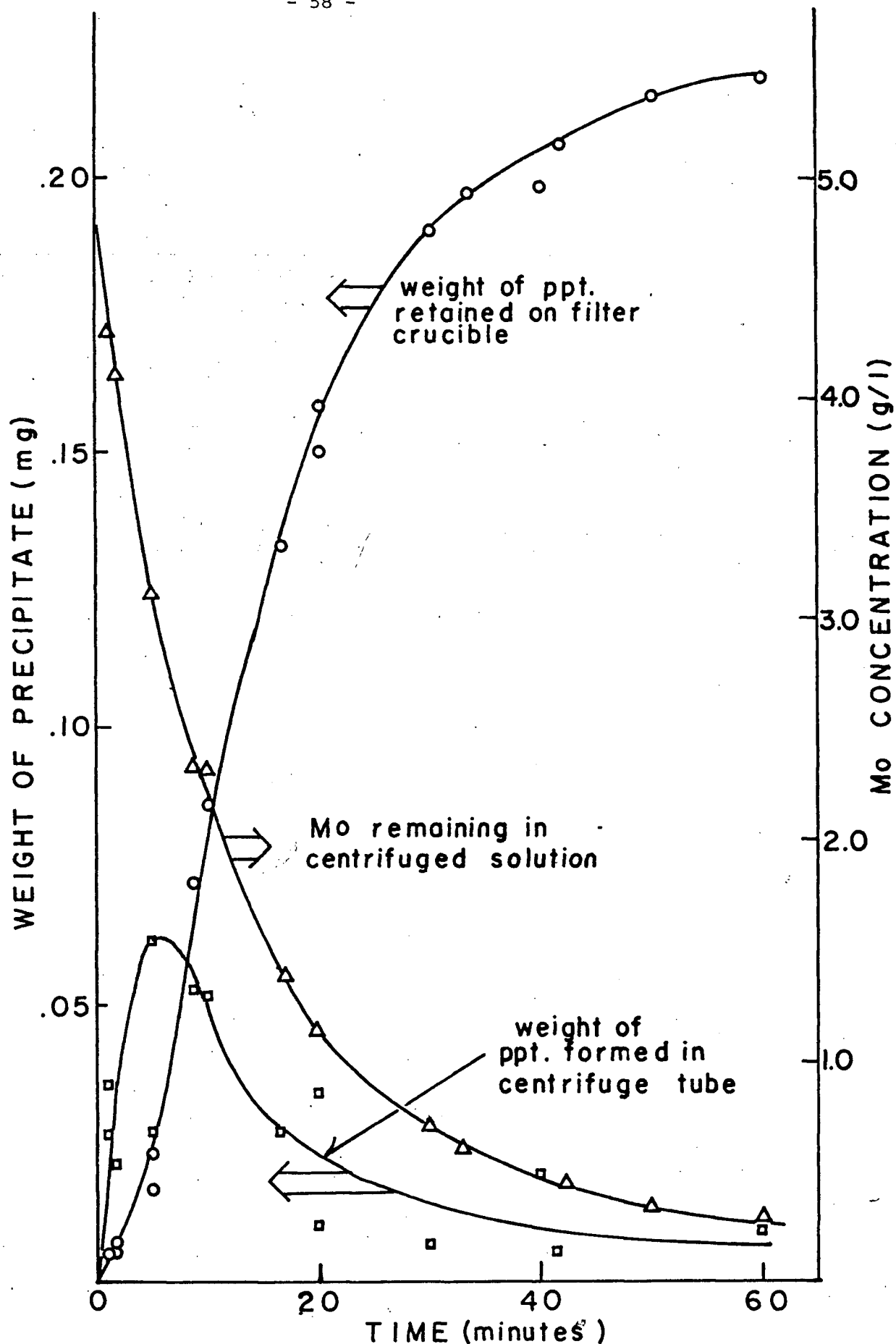


Figure 11: Distribution of molybdenum between solution and precipitates as a function of time at 50° C with pH=4.5, initial molybdenum concentration ≈ 5 g/l, and initial hydrazine to molybdenum mole ratio $\approx 4:1$.

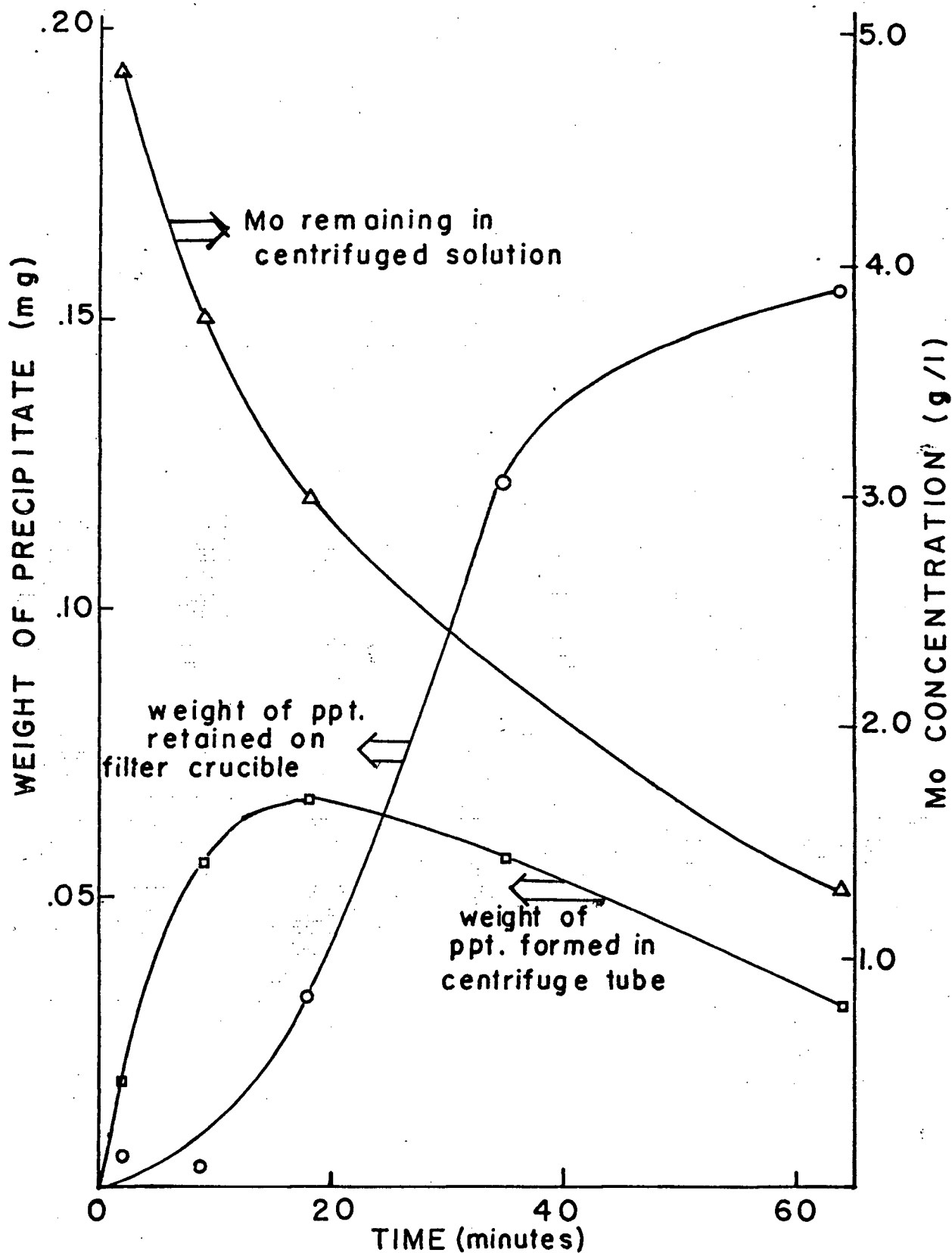


Figure 12: Distribution of molybdenum between solution and precipitates as a function of time at 50°C with pH = 4.5, initial molybdenum concentration ≈ 5 g/l, and initial mole ratio of hydrazine to molybdenum $\approx 2:1$.

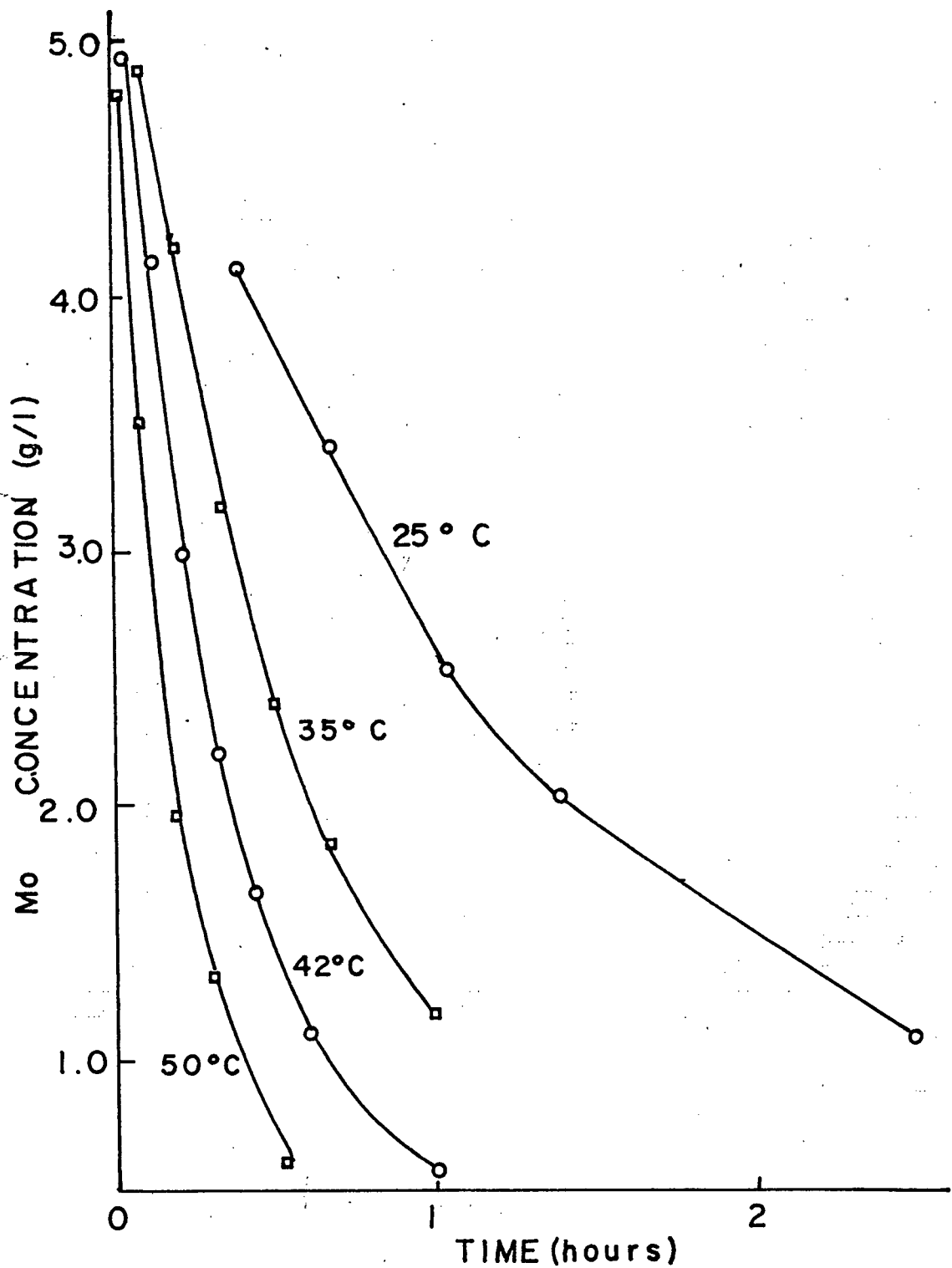


Figure 13: Effect of temperature on rate of precipitation for pH = 4.5, initial molybdenum concentration ≈ 5 g/l, and initial mole ratio of hydrazine to molybdenum $\approx 4:1$.

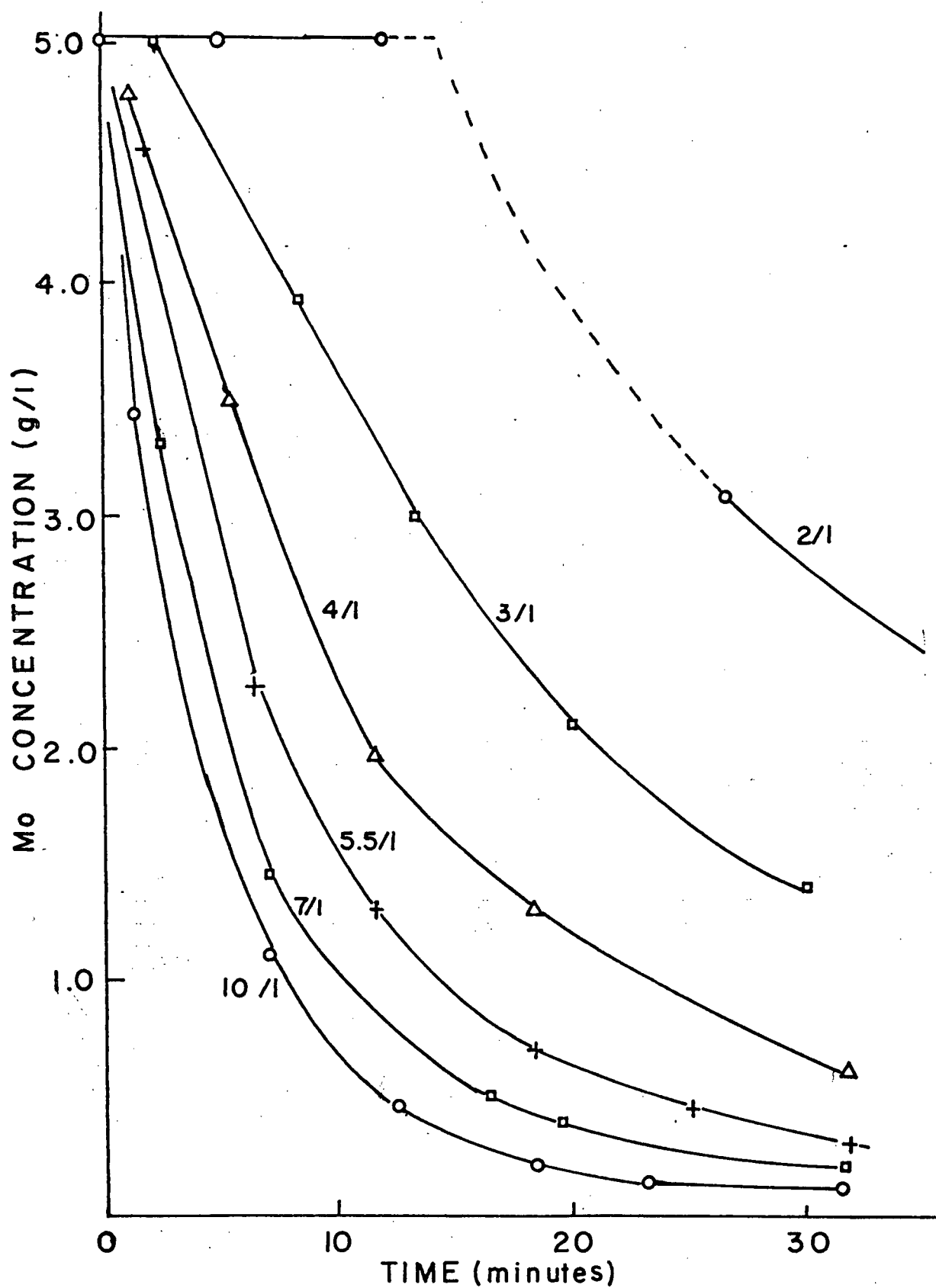


Figure 14: Effect of initial mole ratio of hydrazine to molybdenum on rate of precipitation at 50°C with pH = 4.5 and initial concentration of molybdenum ≈ 5 g/l.

In order to simulate the conditions expected in treating solutions from the sodium hypochlorite leach a run was carried out in 3 M NaCl. Figure 15 compares the results of this run with one performed under the same conditions but without NaCl addition.

The effect of copper on the reaction is shown in Figure 16. The presence of copper did not affect the rate of precipitation of molybdenum. Some of the copper was also precipitated. The precipitate itself changed from the normal brown colour to deep blue on drying for a few minutes in air.

It can be seen from Figures 14 and 15 that for low initial mole ratios of hydrazine to molybdenum and in the presence of 3 M NaCl there was a significant time before precipitation began. In each case, however, reaction began immediately on mixing the reactants as evidenced by the appearance of the colours characteristic of the mixed valent molybdenum blue species. In the extreme case of a 1:1 initial mole ratio of reactants no precipitate was formed in 1 hour at 50°C and pH 4.5 even though some reduction had occurred.

The apparent reaction order in molybdenum was 1.5 as shown in Figure 17 which was plotted using the data of Figure 14. The slopes of the lines in Figure 17 were used to determine the order in N_2H_4 . Figure 18 is a plot of \ln slope vs $\ln [N_2H_4]$. From Figure 18 the order in N_2H_4 was 1.64. Writing the precipitation reaction as $\frac{-d[Mo]}{dt} = k[Mo]^{1.5} [N_2H_4]^{1.64}$ allowed determination of the rate constant k from the slopes of Figure 17. The values of k so obtained are given in Table III. The value obtained for initial hydrazine concentration = 0.522 mole/l

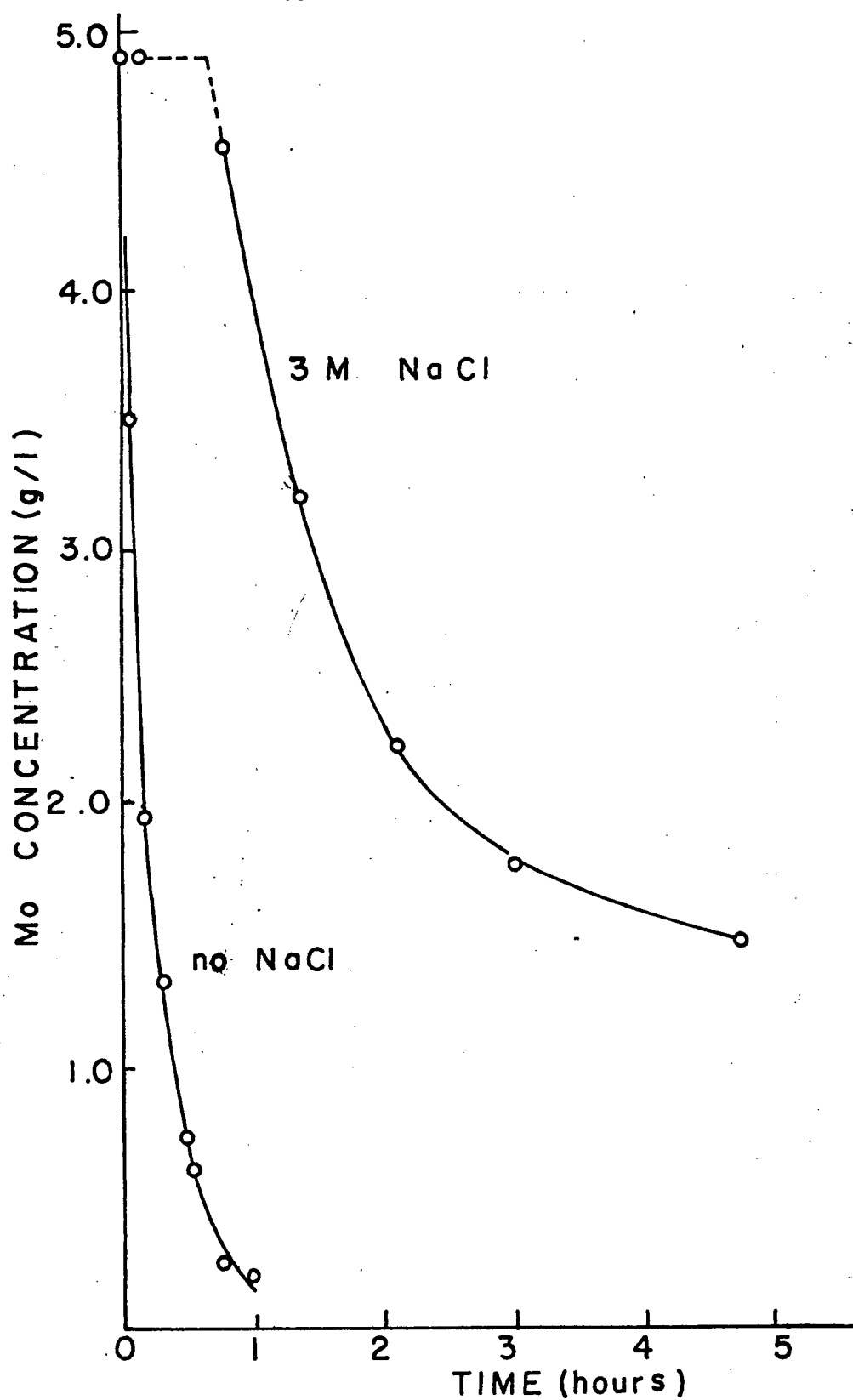


Figure 15: Effect of 3 M NaCl on rate of precipitation at 50°C for pH = 4.5, initial molybdenum concentration \approx 5 g/l, and initial mole ratio of hydrazine to molybdenum \approx 4:1.

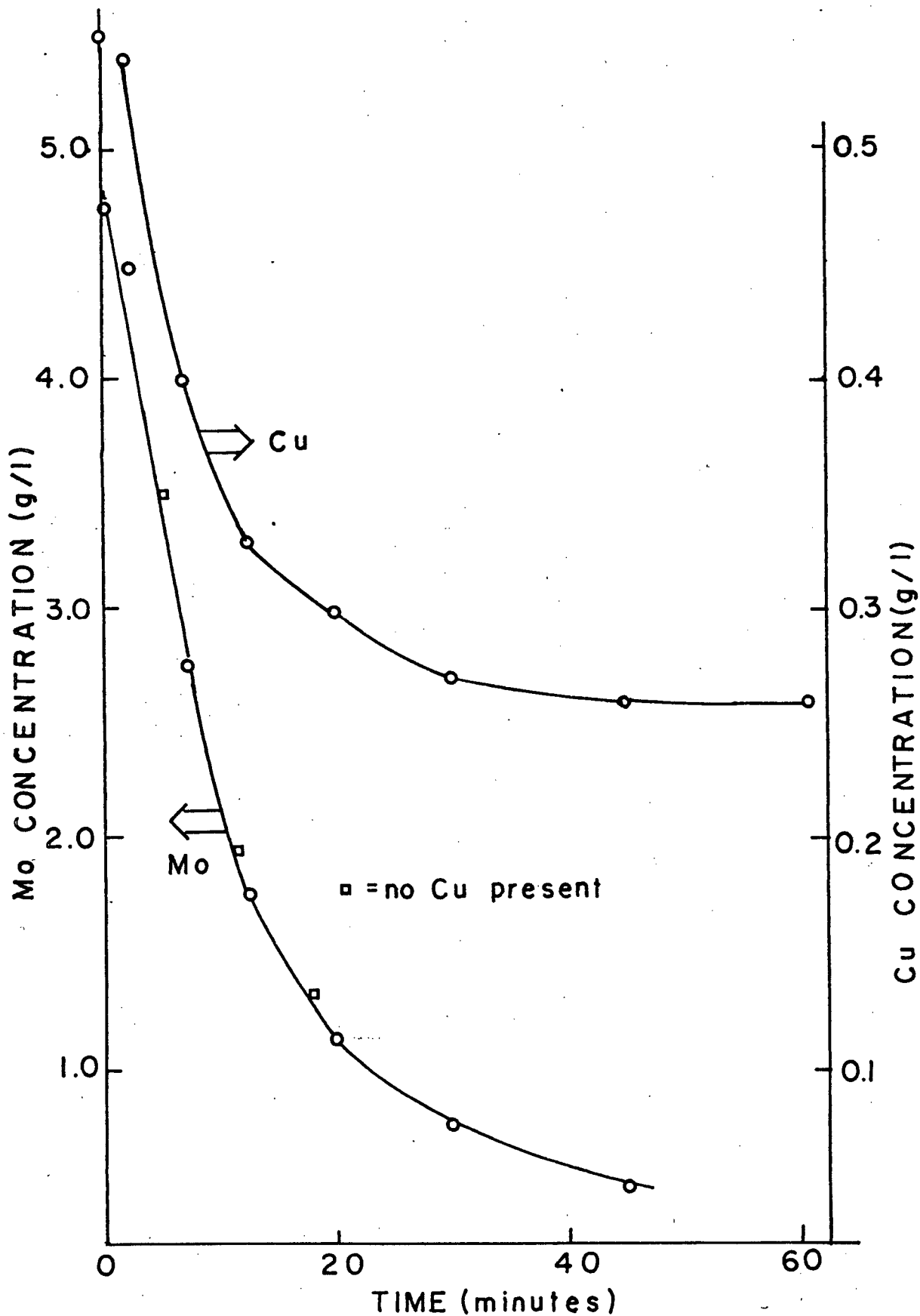


Figure 16: Effect of addition of 0.55 g/l Cu as copper sulfate on the rate of precipitation of molybdenum at 50°C for pH = 4.5, initial molybdenum concentration ≈ 5 g/l, and initial hydrazine to molybdenum mole ratio $\approx 4:1$.

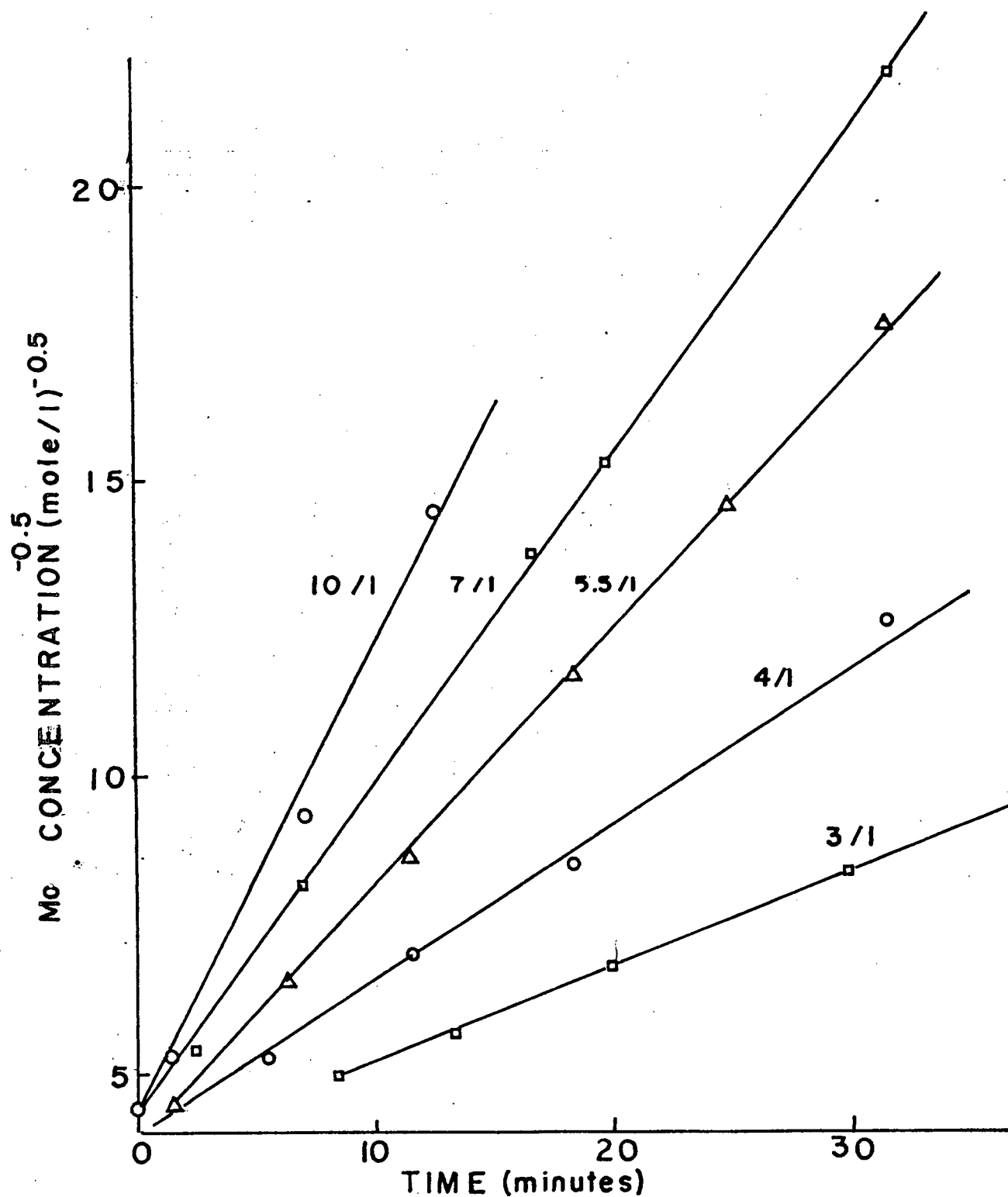


Figure 17: 1.5 order in molybdenum plots for $T = 50^{\circ}\text{C}$, $\text{pH} = 4.5$, and initial molybdenum concentration $\approx 5 \text{ g/l}$.

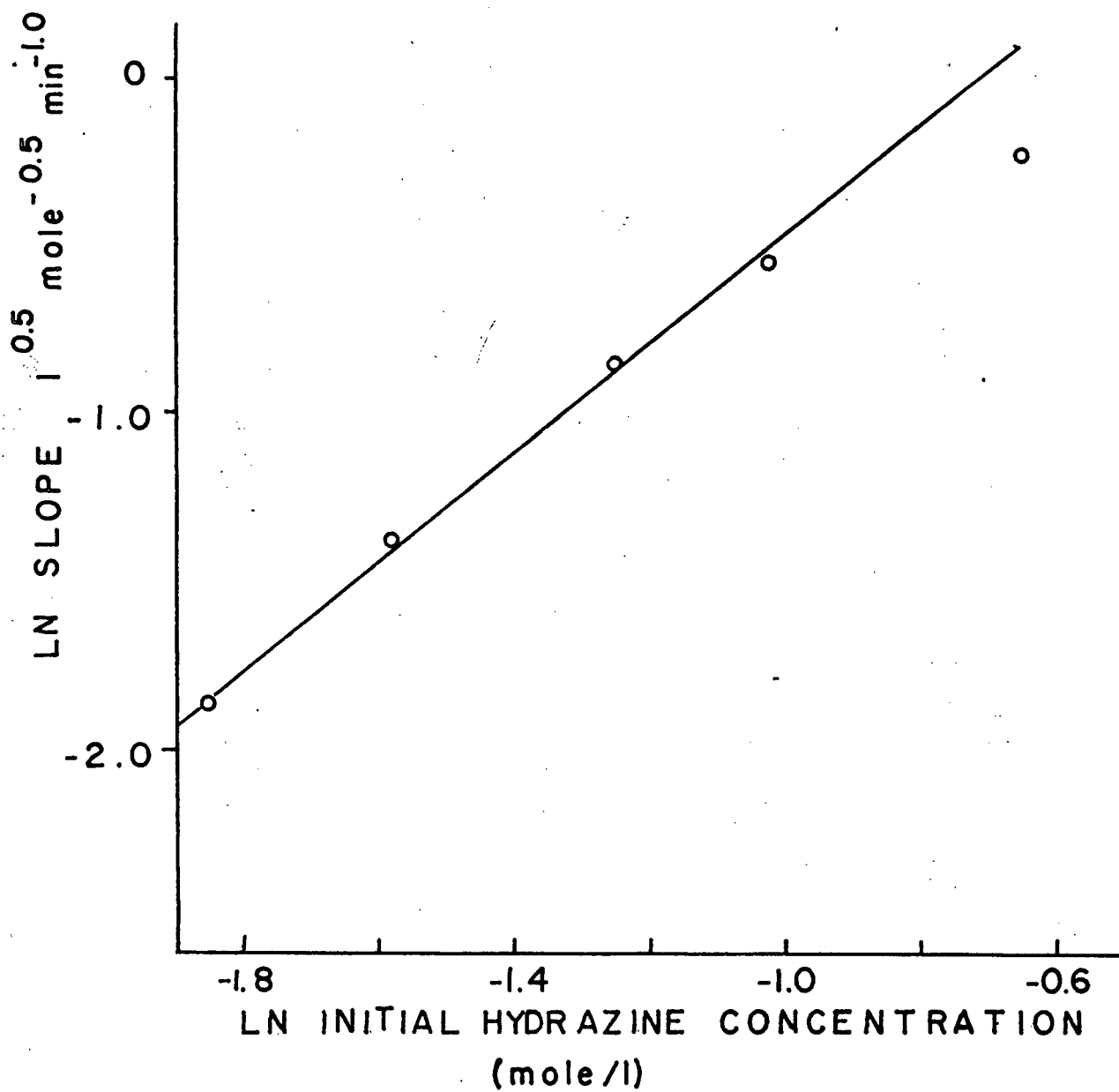


Figure 18: Order in N_2H_4 based on 1.5 order in molybdenum.

initial hydrazine to molybdenum mole ratio	$k \text{ mole}^{-2.14} \text{ l}^{2.14} \text{ min}^{-1}$
3:1	3.35
4:1	3.55
5.5:1	3.32
7:1	3.07

Table III Rate Constants Obtained for Different Values
of Initial Hydrazine to Molybdenum Mole Ratio

(10:1 initial mole ratio of hydrazine to molybdenum) has not been included because the reaction was more rapid than could be followed accurately with the sampling procedure used.

The temperature dependence data of Figure 13 is plotted in Figure 19 assuming 1.5 order in molybdenum concentration. In each case pH = 4.5, initial molybdenum concentration ≈ 5 g/l, and initial mole ratio of hydrazine to molybdenum $\approx 4:1$. Figure 20 is an Arrhenius plot based on the slopes of the lines from Figure 19. The activation energy obtained is 14.1 kcal/mole.

Gravimetric analysis of the brown precipitate after drying overnight in an evacuated dessicator yielded 57.5% and 56.5% molybdenum (expected for $\text{MoO}(\text{OH})_3$ 58.9%). Ceric sulfate titrations assuming all molybdenum was present as Mo^{V} yielded 54.0% and 52.0% molybdenum.

The thermogravimetric weight loss curve obtained in a helium atmosphere is shown in Figure 21. The observed weight loss was 15.8%, compared to 16.57% expected for loss of water by $\text{MoO}(\text{OH})_3$.

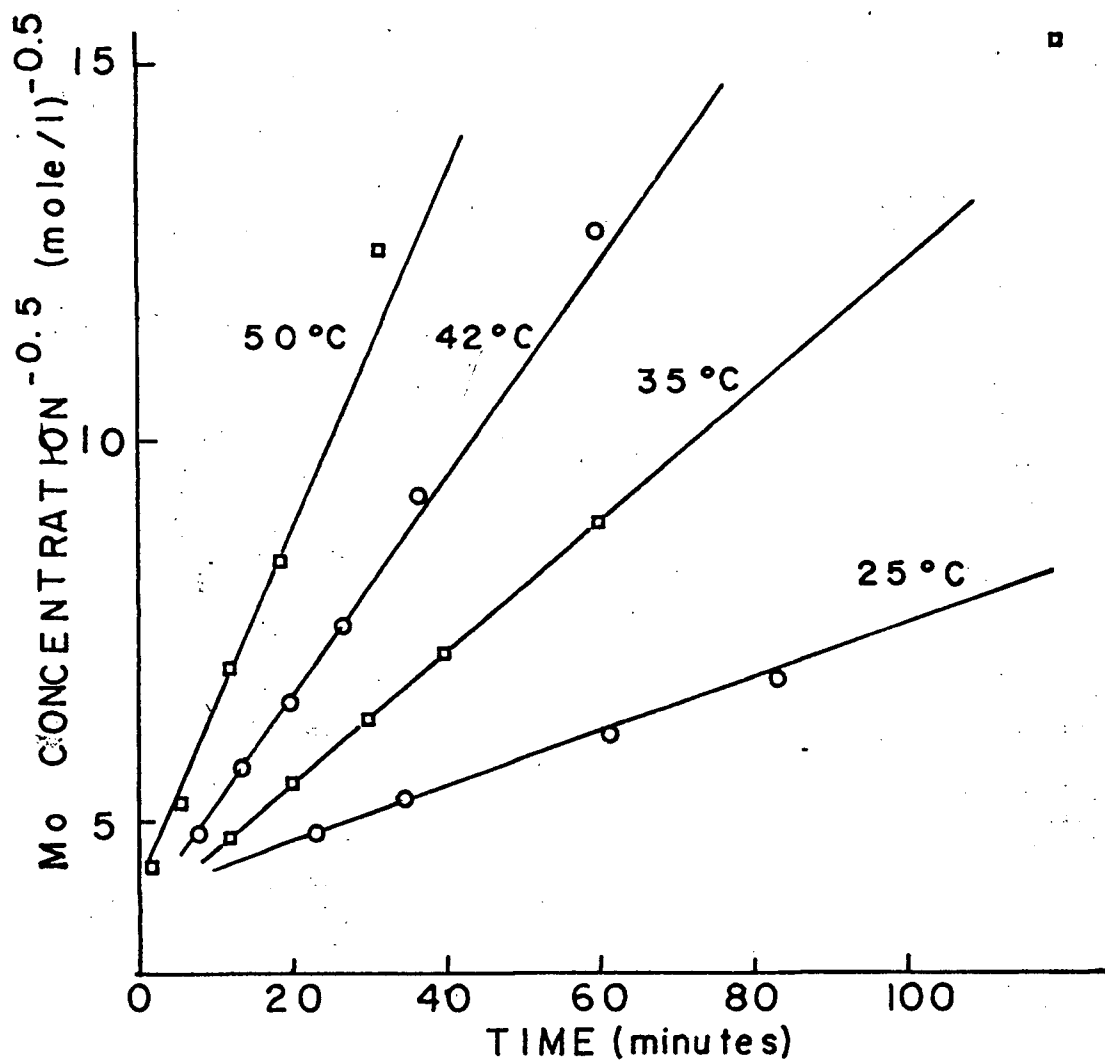


Figure 19: Effect of temperature on rate assuming 1.5 order in molybdenum for pH = 4.5, initial molybdenum concentration ≈ 4 g/l, and initial mole ratio of hydrazine to molybdenum $\approx 4:1$.

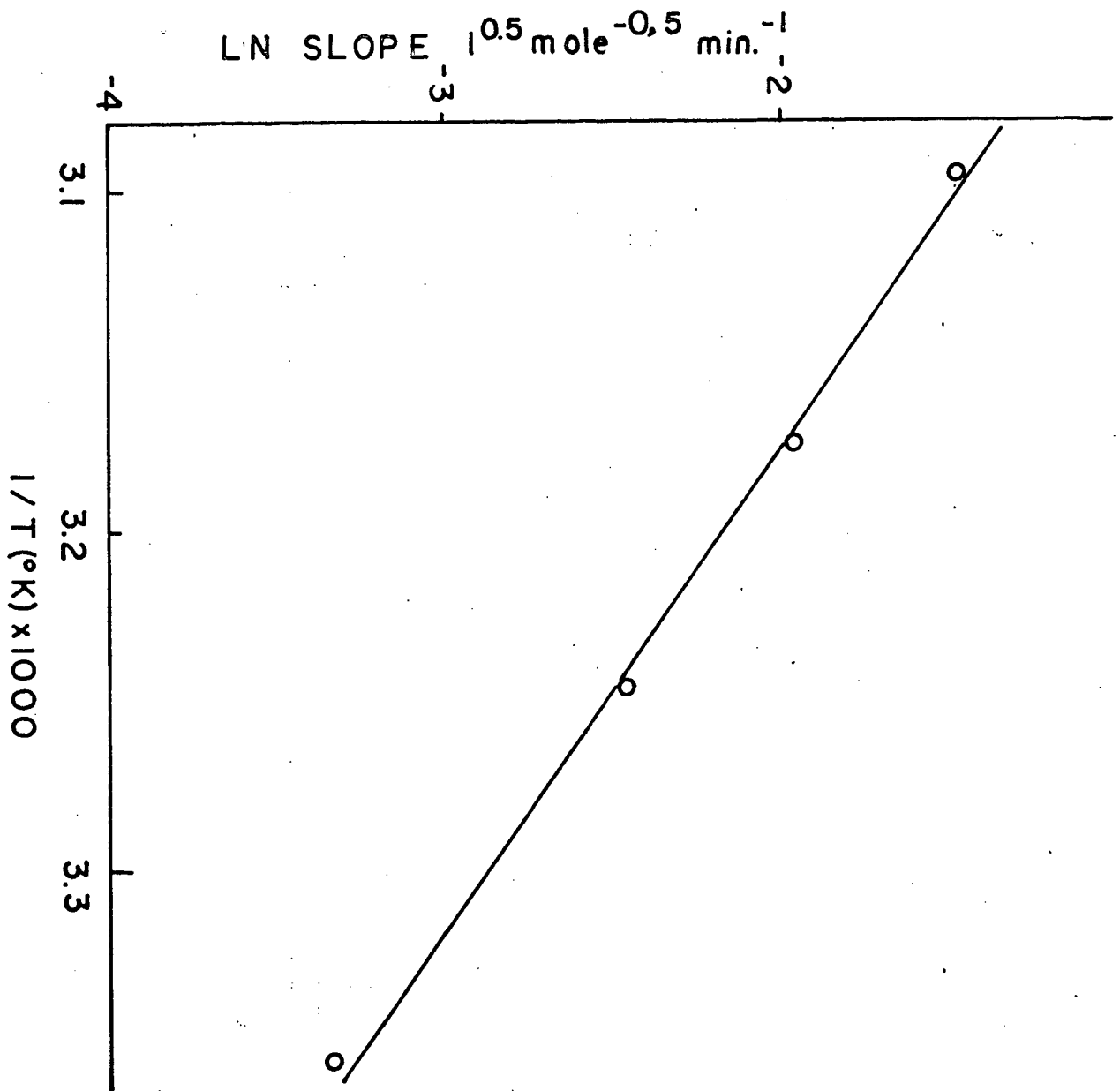


Figure 20: Arrhenius plot based on 1.5 order in molybdenum.

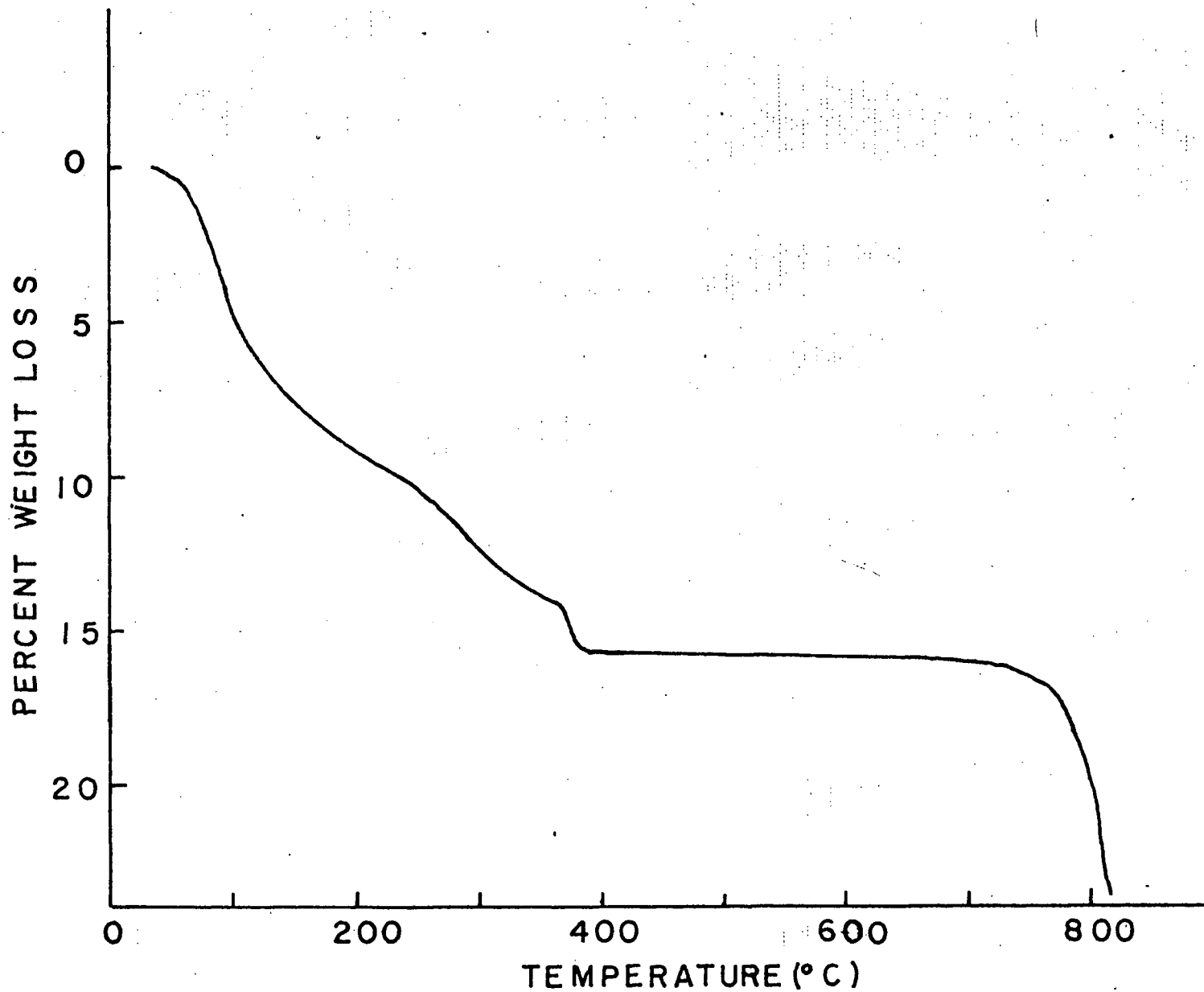


Figure 21: Thermogravimetric weight loss curve for brown precipitate produced by reduction with hydrazine.

Precipitate formed at pH = 4.5 and 50°C was found to contain 0.42 ± 0.09 percent sodium. Neutralization of the reactor slurry to pH = 7 with NaOH after completion of a run at pH = 4.5 and 50°C gave a precipitate containing 0.61 ± 0.03 percent sodium while neutralization to pH = 8 resulted in 1 percent sodium content. Precipitate formed at 50°C and pH = 4.5 in 3 M NaCl solution contained 3.3 percent sodium. No chloride ion was found in any of the precipitates.

Figure 22 shows the concentrations of molybdenum and hydrazine remaining in solution vs time at 50°C with pH = 4.5 and initial mole ratio of hydrazine to molybdenum of 4:1. Although the hydrazine concentration remained constant after about one hour the molybdenum concentration continued to fall. After standing overnight at room temperature the molybdenum concentration in solution reached 0.053 g/l. This compares to 0.041 g/l obtained by neutralizing a stock Mo^{V} solution to pH = 4.5 at 50°C. Similar behaviour was observed in other runs.

This behaviour introduced some uncertainty into the computation of the stoichiometry of the reaction. The method finally adopted was simply to use the hydrazine concentration remaining at the end of each run when the molybdenum concentration was reduced to less than 0.4 g/l. Complete reduction of Mo^{VI} to Mo^{V} was assumed even though, as will be discussed, the molybdenum remaining in solution was present as mixed valent $\text{Mo}^{\text{VI}}/\text{Mo}^{\text{V}}$ species. Since very little molybdenum actually remained in solution this procedure did not make much difference to the stoichiometry obtained. The average stoichiometry based on nine runs was 1.55 moles molybdenum reduced per mole hydrazine consumed. The extreme values were 1.47 and 1.77.

This stoichiometry suggested that molybdenum was acting as a

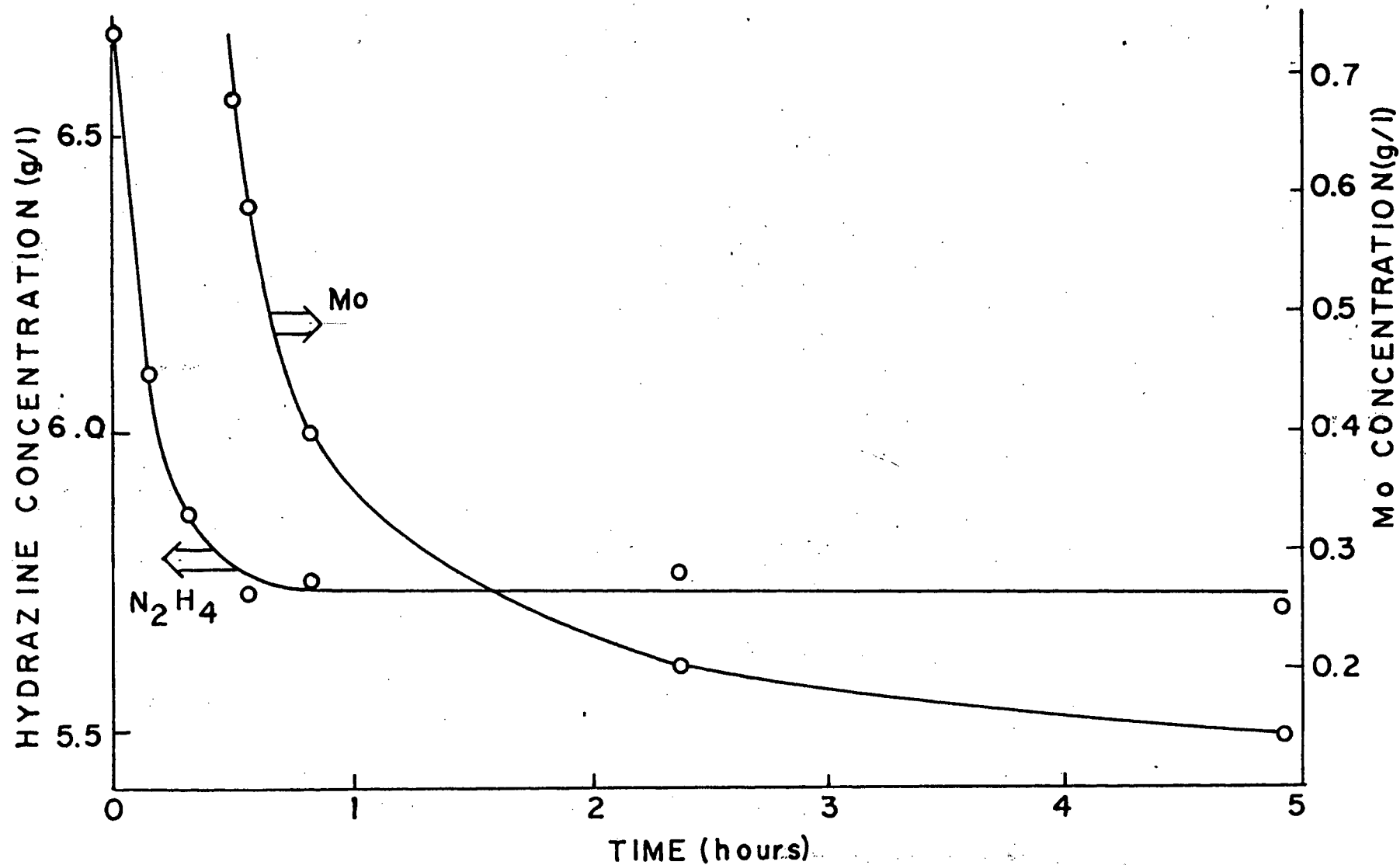


Figure 22: Concentrations of hydrazine and molybdenum remaining in solution vs time at 50°C with pH = 4.5, initial molybdenum concentration ≈ 5 g/l, and initial hydrazine to molybdenum mole ratio $\approx 4:1$.

monoelectronator. Based on the literature the expected reaction products from monoelectronation of hydrazine are nitrogen and ammonia. To verify the stoichiometry a run was performed in which the evolved gas was collected and the filtrate analyzed for hydrazine, molybdenum, and ammonia. The volume of solution used was 200 ml atm 6.95×10^{-3} moles N_2H_4 were consumed generating 1.616×10^{-3} moles of nitrogen. Only a trace of ammonia was found and the pink colour did not return to the CCl_4 layer in the hydrazine titration solution on standing. Gas chromatography of the collected gas did not detect hydrogen.

In every run the end filtrate was coloured indicating the presence of mixed valent Mo^V/Mo^{VI} species. This was verified by polarography in 2 N HCl and in 5 N NaOH. In 2 N HCl the waves of Mo^V and Mo^{VI} were distinct but quantitative determination of the ratio of Mo^V to Mo^{VI} was not possible because in 2 N HCl the excess hydrazine present reduced the remaining Mo^{VI} at a significant rate. Polarography in 2 N HCl, therefore, served only to confirm that Mo^{VI} was indeed present in coloured filtrates. Polarography in 5 N NaOH made use of the observation by Souchay et al.⁵¹ that Mo^V dismutates into Mo^{VI} and Mo^{IV} in such solutions. Since Mo^{VI} does not give any polarographic wave in basic solution the observation of a reduction wave indicated the presence of Mo^{IV} resulting from the dismutation. This technique showed that the Mo^V observed on polarography in 2 N HCl was not due simply to the reduction of Mo^{VI} by hydrazine in 2 N HCl. Polarography in 5 N NaOH did not prove suitable for quantitative determination of Mo^V . The height of the Mo^{IV} wave observed was sensitive to time before polarography and the solutions tended to drop out a grey-green precipitate on standing.

6. DISCUSSION

The hydrogen reduction experiments confirmed the importance of heterogeneous catalysis and pH in attainment of reasonable rate of reduction. The only run in which significant reduction was obtained was that performed in the presence of the platinum clad niobium mesh catalyst with a solution acidified to pH = 2. The rate of reduction was similar to that obtained by Lyapina and Zelikman¹⁰ using metallic molybdenum as a catalyst (Figure 7 curve d). Even in this run, however, complete precipitation of molybdenum was not obtained. The failure to obtain complete reduction was probably due to the increase of pH to 8 and depolymerization of the molybdenum remaining in solution. This depolymerization would result in a decrease of the rate of reduction like that found by Paal and Buttner⁶⁸ and shown in Figure 5. The results of the present study and those reported in the literature cast some doubt on Wagenmann's claims. It seems probable the walls of his apparatus were involved in the reaction.

Satisfactory performance of hydrogen reduction would thus require sufficient acidification to maintain polymerization of Mo^{VI} species. In a batch process this could be accomplished by initial addition of acid beyond the H_2MoO_4 point or by pH control during the reduction. In addition a catalyst and an autoclave material resistant to the conditions encountered in hydrogen reduction of high temperature chloride solutions would be required.

The experiments using hydrazine as a reductant again reflect the importance of polymeric molybdenum species, and hence pH and total molybdenum concentration, in the reduction and precipitation reactions. Above

pH \approx 6.5 monomeric Mo^{VI} predominates and no reduction is observed. On decreasing pH reduction occurs and the rate of precipitation reaches a maximum at about pH = 4.5. This can be attributed to formation of reducible polymolybdates. Below pH \approx 4.5 the rate of precipitation decreases because in this pH range intermediate mixed valent $\text{Mo}^{\text{VI}}/\text{Mo}^{\text{V}}$ compounds are stable.

At pH = 4.5 the sequence of colour change observed during reduction is consistent with that described in the literature³⁷ and interpreted by Ostrowetsky.⁴² Thus on reduction of polymolybdates the initial reaction products are coloured mixed valent $\text{Mo}^{\text{VI}}/\text{Mo}^{\text{V}}$ species. At pH = 4.5, however, these species are not stable and may be reactive towards further reduction to yield a Mo^{V} precipitate or tend to hydrolyse yielding a Mo^{V} precipitate and Mo^{VI} in solution. At pH = 3 where mixed $\text{Mo}^{\text{V}}/\text{Mo}^{\text{VI}}$ species are more stable the rate of precipitation decreases.

The curves of Figures 11 and 12 illustrate qualitatively the importance of mixed valent species in the precipitation reaction. The curves showing the weight of precipitate formed in the centrifuge tubes represent Mo^{V} present in mixed valent species. That is, when the sample filtrate mixed with the caustic in the centrifuge tubes the mixed valent species were made unstable by the increase of pH and decomposed to yield Mo^{V} precipitate and Mo^{VI} in solution. (The pH in fact was likely high enough to cause some disproportionation of Mo^{V} to give Mo^{IV} in the precipitate and additional Mo^{VI} in solution. This phenomenon rendered the results of qualitative value only.)

It can be seen in Figures 11 and 12 that the maximum rate of precipitation approximately coincides with the maximum concentration of mixed

valent species. This suggests that precipitation occurs through further reduction of these species to yield a Mo^{V} precipitate. Polarography indeed confirmed that the slightly coloured solutions at the end of each run contained both Mo^{V} and Mo^{VI} . Complete reduction of Mo^{VI} is never obtained because as the total molybdenum in solution reaches a low enough value the equilibrium between polymeric and monomeric Mo^{VI} ensures that a residual concentration of irreducible MoO_4^{2-} always exists. The minimum residual concentration of molybdenum remaining in solution obtained in this work was 0.053 g/l (5.5×10^{-4} M). This is of the same order as the concentration of MoO_4^{2-} in equilibrium with polymeric molybdate species at pH = 4.5 (Figure 4).

The formation of mixed valent species also explains the observation of a significant time lag between beginning of reduction and beginning of precipitation for low initial mole ratios of hydrazine to molybdenum and at low temperature and in the presence of 3 M NaCl. (Figures 13, 14, 15). In the first two cases no precipitation occurs until reduction has proceeded far enough to yield an appreciable concentration of the mixed valent ion that is ultimately reduced to yield Mo^{V} precipitate. Lower mole ratios of reactants and lower temperatures delay the attainment of this concentration. The effect of NaCl may be due either to stabilization of mixed valent species of lower degrees of reduction than the species that is reducible to Mo^{V} , or to stabilization of this ion itself.

The properties of mixed valent $\text{Mo}^{\text{V}}/\text{Mo}^{\text{VI}}$ species may also be the reason for the behaviour shown in Figure 22 where reduction, as represented by the curve of hydrazine concentration vs time, stops while precipitation of Mo^{V} continues. Presumably this is due to the slow decomposition of

mixed valent $\text{Mo}^{\text{VI}}/\text{Mo}^{\text{V}}$ species to give Mo^{V} precipitate and Mo^{VI} in solution. As has been mentioned, for the low total concentration of molybdenum present, a significant fraction of this Mo^{VI} would be present as irreducible monomeric MoO_4^{2-} so consumption of hydrazine through further reduction would be negligible.

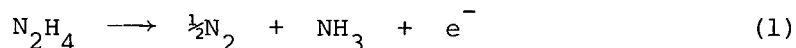
The effect of sampling procedure on the curves of molybdenum vs time as shown in Figures 9 and 10 can be interpreted in terms of the ability of Mo^{V} to disproportionate into insoluble Mo^{IV} and soluble Mo^{VI} . The curves of Figure 9 were generated by neutralizing slurry samples before filtration. As can be seen increasing the pH of neutralization increased the amount of molybdenum found in the filtrate for any given time. Obviously disproportionation occurred at the instant of neutralization as observed by Katsobashvili⁵⁰ and the higher the pH the greater the extent of disproportionation. It is clear that the precipitate itself was disproportionating because filtration before neutralization gave results indistinguishable from those obtained with no neutralization followed by filtration (Figure 10).

It is apparent that the kinetic results obtained can be qualitatively explained in terms of the known chemistry of Mo^{VI} , Mo^{V} , and Mo^{IV} . Quantitative investigation would be difficult, however, because of the complexity of the phenomena involved. The empirical rate law obtained, for example, was based simply on determining total molybdenum remaining in solution after filtration of slurry samples. It is of fractional order in both reactants and reflects the behaviour at one pH only. The overall process of reduction and precipitation probably involves a combination of consecutive and parallel reactions as well as the complex equilibria attendant with the

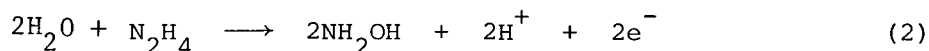
involvement of polymeric molybdate and mixed valent species. The activation energy obtained of 14.1 kcal/mole represents that of the overall reduction and precipitation process. It does indicate at least that chemical processes are rate controlling.

The gravimetric, oxidimetric, and thermogravimetric results are in fair agreement with those expected if the Mo^V precipitate was $\text{MoO}(\text{OH})_3$. It was found that on storage in a dessicator the precipitate oxidized slightly and this may explain the low oxidimetric results. The difference of the gravimetric and thermogravimetric results from the expected values is probably due to variations of the storage and drying procedure before weighing samples for analysis. Since no chloride ion was found in the precipitates analyzed it is concluded that the sodium present was the result of the ion exchange process described by Souchay et al.⁵¹ The increase of sodium content for precipitation carried out in 3 M NaCl is consistent with this interpretation.

The observed stoichiometry can be interpreted in terms of the production of nitrogen and ammonia according to the reaction



and the production of hydroxylamine according to the reaction



It was found that consumption of 6.95×10^{-3} moles of hydrazine generated 1.616×10^{-3} moles of nitrogen. Assuming all the nitrogen was generated according to equation 1 and that the balance of the hydrazine reacted according to equation 2 yields the following results:

$$\text{NH}_3 \text{ produced} = 3.232 \times 10^{-3} \text{ moles}$$

$$\text{NH}_2\text{OH produced} = 7.436 \times 10^{-3} \text{ moles}$$

$$\text{electrons generated} = 10.668 \times 10^{-3} \text{ moles}$$

The stoichiometry with respect to reduction of Mo^{VI} to Mo^{V} obtained is thus 1.53 which is in good agreement with the average stoichiometry found of 1.55. Since the volume of solution used was 200 ml the resultant concentrations of ammonia and hydroxylamine would be 0.016 M and 0.037 M respectively. Both of these concentrations are small enough to escape detection by the analytical techniques used.

The stoichiometry observed in the present work is lower than that reported in the literature which varies between 2⁷⁹ and 4.^{77,82,83} None of the results reported in the literature, however, were obtained under conditions of pH, concentration, and mole ratio of reactants similar to those of the present work. Given the variable nature of the proposed hydrazine oxidation reactions and the possibility of different molybdenum species acting as oxidants it is difficult to relate results obtained under one set of conditions to those obtained under another. There does not seem to be any reason not to suppose that hydrazine could react to produce hydroxylamine in a 2 electron path and ammonia and nitrogen in a 1 electron path. It thus seems likely that one of the unidentified reaction products mentioned by Ostrowetsky and Brinon was ammonia. From the point of view of the present study, however, the important fact is that the economically favourable 4 electron stoichiometry is not obtained in the conditions of interest.

7. CONCLUSION

It is apparent that neither hydrogen reduction nor reduction with hydrazine is an ideal method for recovery of molybdenum from hypochlorite leach solutions. Both reductants require acidification of the solution to be treated so there is no advantage to be gained over solvent extraction in this respect. Hydrogen reduction can only be carried out at a reasonable rate in rather severe conditions from a materials standpoint and an efficient catalyst is required.

Reduction with hydrazine involves a low stoichiometry plus the requirement of an appreciable excess of hydrazine over the stoichiometric amount to obtain a reasonable rate of precipitation. The precipitate produced by hydrazine reduction will contain on the order of 3% sodium and copper must be eliminated from the leach solution or it will contaminate the precipitate. In addition the rate of precipitation is significantly decreased in the 3 M NaCl expected in the leach solution. The barren solution from precipitation by hydrazine would contain at least 0.05 g/l molybdenum plus excess hydrazine. Recycle of this solution for hypochlorite regeneration would require investigation of the effect of hydrazine and molybdate on the electrolytic process employed.

Reduction with hydrazine could, however, be carried out at a relatively low temperature and in a simple reactor. One way to perform the reaction would be to add hydrazine and acid to the leach solution in a small stirred tank and then discharge the reacting mixture to a thickener sized to give a suitable residence time. Precipitate could be discharged as a slurry and the overflow recycled for hypochlorite regeneration. The discharge slurry

could be filtered for precipitate recovery.

It is clear that the cost of hydrazine in relation to the price of molybdenum and the marketability of an $\text{MoO}(\text{OH})_3$ product contaminated with sodium are the deciding factors in the feasibility of using hydrazine for molybdenum recovery. On the basis of this study recovery of 1 kg of molybdenum contained in $\text{MoO}(\text{OH})_3$ would require consumption of about 1.2 kg of hydrazine to obtain reasonable kinetics and completeness of precipitation. At the current price for hydrazine of \$3.52/kg in tank car lots it would cost \$4.22 for hydrazine per kg of molybdenum as $\text{MoO}(\text{OH})_3$. Molybdenum oxide is currently selling for approximately \$20/kg contained molybdenum.

At the current price of \$20/kg Mo as molybdic acid and \$3.52/kg hydrazine in tank car lots it would cost \$4.22 for hydrazine per kg Mo contained in $\text{MoO}(\text{OH})_3$.

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