FACTORS INFLUENCING THE RECOVERY

OF MOLYBDENUM

9 1.

DURING THE HYPOCHLORITE LEACHING OF

LOW GRADE MOLYBDENITE-COPPER CONCENTRATES

by

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A THESIS SUBMITTED IN PARTIAL FULFILMENT OF

THE REQUIREMENTS FOR THE DEGREE OF

MASTER OF APPLIED SCIENCE

in

THE FACULTY OF GRADUATE STUDIES

(Department of Metallurgical Engineering)

We accept this thesis as conforming

to the required standard

THE UNIVERSITY OF BRITISH COLUMBIA

September 1979

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Date _1st October 1979_

ABSTRACT

An investigation into the factors influencing the extraction of molybdenum from copper sulphide molybdenite concentrates in alkaline hypochlorite solutions has been carried out.

Sodium carbonate buffer components were found to act as complexing agents for the copper, enabling it to exist in solution as a cupri-carbonate species several orders of magnitude more soluble than the thermodynamically stable copper phase at pH 9.0. Completely selective molybdenum extraction is therefore only possible from solutions containing no carbonate.

The removal of the carbonate produced adverse side effects for the sodium hypochlorite lixiviant as a result of copper hydroxide formation on the mineral surface which led to rapid decomposition of the hypochlorite by heterogeneous catalysis.

This hydroxide salt was found to consist at least partially of tri-valent copper and it was confirmed that sodium hypochlorite has a sufficiently high redox potential at pH 9.0 to enable the oxidation of copper$^{II} \longrightarrow$ copper^{III} to take place. Experiment also showed that a tri-valent copper carbonate compound precipitated from leaching solutions containing copper after a suitable nucleation period. It was thus established that the copper present in carbonate containing hypochlorite solutions exists as the tri-valent complex $Cu(CO_3)_3^{3-}$; that the induction time to precipitation is a function of the total carbonate content of the

system, and that the solid precipitate is also an active catalyst for hypochlorite decomposition.

The leaching of molybdenite - copper concentrates in acid solutions was studied, and results showed that such a process would not be feasible due to the formation and precipitation of copper molybdate, $CuMoO_4$. This compound is very insoluble, but its formation was found to be suppressed by the presence of sodium bicarbonate at pH values greater than 6.0.

Several other insoluble molybdate compounds were found to be capable of forming in both acid and alkaline solutions as a result of hypochlorite dissolution of impurity elements contained in the copper sulphide ores. Potential-pH diagrams constructed to show the thermodynamic stability of the molybdate salts of copper, iron, calcium, zinc, lead and cadmium are included.

Calcium was isolated as being the most detrimental impurity element in this respect, due to its common occurrence in copper porphyry ores as well as its solubility in chloride containing solutions. A limited study was carried out to show that this solubility increased in proportion to the chloride content and hence the hypochlorite concentration of leaching solutions. Calcium carbonate was found to precipitate in preference to calcium molybdate, but the use of silicates and phosphates as calcium suppressants was also considered as a means of avoiding copper - carbonate complexing while maintaining good molybdenum extraction.

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Acknowledgement

The author is greatly indebted to Dr. I.H. Warren for his generous advice, constant interest and invaluable encouragement throughout the period of this study.

The assistance provided by members of Faculty and technical staff of the Department of Metallurgy, and the help and companionship of fellow graduate students have been much appreciated. Thanks are also extended to Dr. F. Weinberg for the many musical interludes which provided respite from, if not inspiration for, the rigours of research.

Financial support in the form of a CIL fellowship is gratefully acknowledged.

CHAPTER ONE

1.1   Introduction

Molybdenite, MoS_2, is the principal source of the molybdenum metal used commercially. It occurs both in primary molybdenum deposits and in more complex ore bodies associated with other sulphide minerals. Powellite, $CaMoO_4$; Wulfenite, $PbMoO_4$ and hydrated ferric molybdate, $FeMo_3O_{12} \cdot 8H_2O$ are the most common secondary molybdenum minerals but they are not considered to be of economic importance at the present time.

Molybdenum is one of the less common elements with an average concentration in the earth's crust of 0.001%.[1] Its principal use is as an alloying element in iron, steel and certain non ferrous metals. Either alone or in the presence of other elements such as nickel, vanadium, manganese and chromium, molybdenum enhances the strength, toughness and hardenability of these materials and can also improve corrosion resistance. Molybdenum compounds have wide application as lubricants, chemical reagents and as catalysts. They are also used extensively in paint and pigment manufacture.

Consumption of molybdenum has increased on a world wide basis at an average rate of about 5% per annum for the past decade, and demand is expected to grow at least at this level to the year 2000 and beyond. Western world production for 1977 amounted to 89,500 metric tons, of which the United States produced 68% and Canada 17%.[2] Current estimates of molybdenum reserves indicate that supplies should be adequate in the foreseeable future. A few high grade deposits containing up to 20% molybdenum as MoS_2 in rich quartz veins exist, but over 95% of current

and previous production has been from low grade porphyry type deposits

and it seems likely that this figure will increase as more of the richer

ores are worked out. Porphyry ores can be characterized into two types:

1) Molybdenum porphyries; where molybdenite is the only contained

mineral of economic importance and averages 0.15 - 0.8% MoS_2.

2) Copper-molybdenum porphyries; from which copper is extracted

as the primary metal value and molybdenum is recovered as a by-product.

The molybdenite content of these ores is much lower and ranges from

0.005 - 0.01% MoS_2. Copper mineralization consists of primary and secon-

dary sulphide ores including chalcopyrite, $CuFeS_2$; covellite, CuS; chal-

cocite, Cu_2S; bornite, Cu_5FeS_4; and enargite, Cu_3AsS_4. There is often a

leached cap associated with the ore body containing secondary and tertiary

oxides such as cuprite, Cu_2O; malachite $Cu_2(OH)_2CO_3$; tenorite, CuO, and

chrysocolla, $Cu_4H_4Si_4O_{10}(OH)_8$. The overall copper content averages 0.8%.[3,4]

By-product molybdenum recovery from porphyry copper ores accounts

for almost 50% of total world production, but the fact that ore grades

involved are so low means high recoveries are difficult to obtain in many

cases. Separation of molybdenite from copper ores is achieved by selective

flotation in almost all cases. The principal aim of production plants

treating these ores is to optimize copper recovery and values of about

80% are typically obtained. The overall molybdenum yield is usually

much lower and averages 50 - 60%. The recent depressed state of the

copper market followed by rapid increases in the price of molybdenum to

a current value of $9/lb, has given by-product recovery a more important

perspective. In cases where copper ores are relatively lean the two

metals are almost equal in terms of end product value. The molybdenum

not recovered is therefore of economic significance and represents a substantial loss of metal resources.

1.2 Current Molybdenum Production

A molybdenite concentrate averaging 90% MoS_2 is the usual product of beneficiation of run of mine ore. This is then converted to technical grade molybdenum tri-oxide, MoO_3, for further processing into ferro-molybdenum and other compounds. The conventional method of obtaining molybdenum tri-oxide follows a flotation-roasting method as outlined in Figure 1.

Molybdenum-bearing copper ores are most often mined by open pit methods, after which the run-of-mine ore is subjected to crushing and wet grinding to give a product yielding 50 - 70% minus 200 mesh material. Beneficiation by flotation is used in all cases, largely due to the good natural flotability of molybdenite, making it the easiest method by which separation from copper can be achieved. Complex copper-molybdenum ores are subjected to a collective rougher flotation to give a rougher concentrate averaging 0.3% Mo and 12.5% Cu with some iron, sulphur and calcium oxide. This concentrate is re-ground and cleaned to give an up-graded copper flotation concentrate averaging 25 - 35% Cu. The molybdenite is then separated by a selective flotation stage, carried out either by depressing the copper and allowing the molybdenite to float, or by the opposite technique of depressing the molybdenite and floating off the other constituents of the copper concentrate. The former method is generally preferred, giving an initial molybdenum rougher concentrate

Run of mine ore

```
CRUSHING & GRINDING
```

```
COLLECTIVE ROUGHER
FLOTATION
```

Rougher concentrate (12.4% Cu, 0.3% MoS_2)

```
REGRINDING, CLEANING
```

Copper flotation concentrate (25-35% Cu)

>0.2% Mo   <0.2% Mo

```
THICKENING                    THICKENING
```

Cu ```SELECTIVE ROUGHER   FILTRATION
       FLOTATION```
Mo   ```DRYING```

Mo rougher conc. (35% MoS_2)   Cu concentrate

```
CLEANING, REGRINDING
```

Mo flotation conc. (80% MoS_2) ≥0.5% Cu
<0.5% Cu
```THICKENING``` ← Mo ← ```LEACH``` Cu →

```
FILTRATION
```

```DRYING``` → Mo concentrate (90% MoS_2)

```
MoO_3 PRODUCTION
```

Figure 1: Conventional flowsheet for the production of molybdenum
trioxide.

which is purified further in a counter-current circuit until a 90%

MoS_2 product, containing less than 0.5% Cu, is obtained. A low tempera-

ture roast is sometimes incorporated into the cleaning circuit to effect

partial oxidation of copper sulphide minerals, thereby retarding their

flotability.

With careful use of the correct flotation reagents for the mineral-

ization present in a specific ore, as well as optimization of pH by the

use of modifiers, and suitable choice of temperature, up to 85% of the

contained molybdenum can be recovered. However, as noted above, condi-

tions are usually selected to give maximum copper recovery, and this

results in a much lower average level of molybdenum recovery. Loss of

molybdenum can occur on account of the following factors:[5,6]

i) The ore is ground to a size suitable for optimum copper

recovery and this is usually coarser than the ideal size for molybdenite.

This problem is often accentuated during periods of depressed copper

prices when an even coarser grind is used to increase throughput.

ii) Molybdenite can be lost from the copper rougher flotation

tailings because it often exists as large flakes which are trapped by

quartz particles.

iii) Finer particles are lost from the overflow of middling

thickeners after production of the molybdenum rougher concentrate, and

this loss is increased by the presence of flocculants.

iv) The presence of varying copper sulphide mineralization in

an ore can necessitate the use of different depressants due to differ-

ences in surface properties, for example between chalcopyrite and

covellite. Certain reagents can also inhibit molybdenite flotation.

Naturally floating materials such as sulphur, talc, graphite and coal can be equally detrimental to molybdenum recovery, and the presence of molybdenum oxides is also undesirable.

v) Porphyry ores often have a non-uniform distribution of molybdenum, resulting in large variations of head values in the feed material to the flotation circuit, which present additional difficulties in maintaining continuous high molybdenum recoveries.

In many cases the final molybdenite concentrate is subjected to a sulphuric acid or sodium cyanide leach after re-cleaning and prior to thickening and filtration. This serves to remove any copper remaining in the concentrate.

Conversion to molybdenum tri-oxide is by means of an oxidizing roast, usually carried out in "Nichols-Herreshoff" type roasters which enable the temperature to be closely monitored and kept between 600 - 700°C. The final MoO_3 product contains 56 - 62% Mo and has maximum allowable sulphur and copper contents of 0.25% and 0.75% respectively.[7]

1.3 Hydrometallurgical Production of Molybdenum

While existing reserves of molybdenite are expected to be adequate to supply an increased demand of up to 5% per annum for some time to come, production of molybdenum on a day-to-day basis is not always adequate. In 1977 there was a production deficit of some 9 million pounds of molybdenum, which had to be supplied from existing stock piles.[2] It would thus seem desirable to research into ways of increasing current molybdenum recovery. As more of the world's higher grade deposits are worked out, molybdenum bearing copper ores typical of those found in British

Columbia will assume an even more important role as a source of the metal. For these types of ores, a hydrometallurgical method for molybdenum recovery has the potential of giving higher metal extraction and better utilization of raw materials than can be obtained by conventional methods. A hydrometallurgical route could also eliminate either or both of the preliminary and final roasting stages. This would be preferable from an environmental point of view by preventing the evolution of SO_2 into the atmosphere.

Molybdenite is generally unreactive chemically and its dissolution in aqueous media entails oxidation to the Mo^{VI} state. Molybdenum will exist in water in oxidation states of +3 to +6, but only the +6 state is stable over a wide range of potential-pH values. The other valence states can be stabilized by certain complexing agents. Oxidation of molybdenite from Mo^{IV} to Mo^{VI} can be effected by dissolution in hot nitric acid, concentrated sulphuric acid, aqua regia and by oxygen under pressure in aqueous solution; as well as by various oxidizing agents such as acid sodium chlorate and sodium hypochlorite. On the alkaline side of neutrality the monomer MoO_4^{2-} is the usual form of Mo^{VI}, but at pH values below 7.0, and with a molybdenum content in excess of 10^{-4} M, this ion is usually polymerized.[8] The molybdate ion readily combines with most metal cations, and with the exception of the alkali metals, an insoluble salt is precipitated. The anion is able to attain rapid equilibrium in aqueous solution which is of considerable advantage when considering a wet method for molybdenum extraction.

Several studies have been carried out in the last two decades to investigate possible methods of extracting molybdenum by leaching

molybdenite. The majority of these suggested the use of nitric acid or

a strong oxidant in alkaline solution as a lixiviant, with subsequent

recovery of molybdenum by means of an ion-exchange or solvent extraction

technique, or by reductive precipitation in acid solutions using metal

(mercury, zinc, cadmium or molybdenum) or gaseous (hydrogen, hydrogen

sulphide, sulphur dioxide) reductants. Investigations into the use of

other reducing agents such as hydrazine and sodium sulphite have recently

been carried out in this department.[9]

The biggest loss of molybdenum in current processes occurs during

the collective rougher flotation stage and amounts to some 36%. Further

losses of about 10% occur between this point and the final molybdenite

product. The most logical hydrometallurgical treatment should therefore

use run of mine ore as the starting material for a leaching circuit,

but this would not be economically practical for many porphyry ores

which contain less than 0.02% Mo. Most of the processes envisaged to

date have thus worked on the basis of a leaching circuit in conjunction

with existing flotation methods, using either molybdenum or copper rougher

concentrates as feed material. Both methods appear to be feasible provid-

ed the leach is sufficiently selective for molybdenum over copper and

other sulphide minerals.

While the treatment of un-beneficiated ores is not generally

acceptable, the possibility of extracting molybdenum by in-situ leaching

or solution mining methods, could have considerable potential value. The

advantages of solution mining in terms of reduced capital and operating

costs and a reduction in materials handling, a more efficient utilization

of resources and less environmental disturbances, as well as the

disadvantages associated with handling and storing large volumes of leaching solutions and careful prediction and control of their underground movements, have been well documented in the literature.[10] Low grade copper-molybdenum ores could be very amenable to this type of leaching provided the lixiviant used gave a sufficiently rapid and selective leach of the contained molybdenum values, and could be economically produced.

1.4 Literature Review

1.4.1 The extraction of molybdenite with sodium hypochlorite solutions

Cox and Schellinger carried out laboratory scale tests in an investigation to determine the feasibility of a leach-ion exchange type process for producing molybdic oxide, in which they used sodium hypochlorite as a lixiviant for three different grades of material containing 0.015%, 1,05% and 63% MoS_2 respectively.[11] Dresher, Wadsworth and Fassel had previously studied the kinetics of dissolution of molybdenite in alkaline solutions with potassium hydroxide at temperatures in excess of 100°C and pressures up to 700 psi, and had found that suitable rates of leaching could be obtained with these conditions.[12] Cox et al. concluded that use of hypochlorite reagents could give a much more economical process than one necessitating a high pressure-high temperature leach, and optimum conditions for molybdenum recovery were obtained with a 3% solution of sodium hypochlorite at room temperature. They put forward the following stoichiometric relationship as being operative during the leach:

$$7NaOCl + MoS_2 + 4e^- \longrightarrow MoO_4^- + S_2O_3^{2-} + 7NaCl \qquad (1)$$
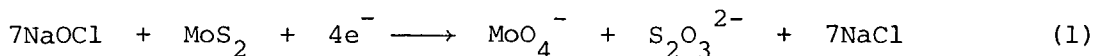
The rate of leaching was found to decrease to zero after about thirty minutes, at which point molybdenum extractions ranging from 91 - 99% had been achieved. Both Cox and Schellinger, and Dresher et al. observed that thiosulphate ions were present in the leaching solutions, but the latter workers concluded that $S_2O_3^{2-}$ was only an intermediate reaction product and that after complete oxidation, only molybdate and sulphate ions would exist in solution:

$$MoS_2 + \frac{9}{2}O_2 + 6OH^- \longrightarrow MoO_4^{2-} + 2SO_4^{2-} + 3H_2O \qquad (2)$$
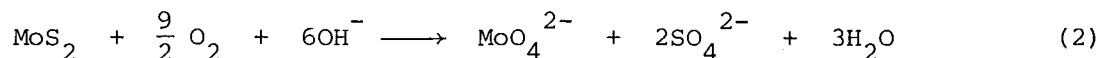
A kinetic study of the oxidation of molybdenite using sodium hypochlorite solutions was reported by Iordinov and Zelikman in 1961.[13] They used a reagent concentration varying from 15 to 60 g/l OCl^- at temperatures of 20 - 80°C and their starting material was pure MoS_2. A detailed description as to the theory of the different stages involved in molybdenite oxidation from a physico-chemical standpoint is given, and the overall reaction was found to be:

$$MoS_2 + 9NaOCl + 6NaOH \longrightarrow Na_2MoO_4 + 2Na_2SO_4 + 9NaCl + H_2O \quad (3)$$
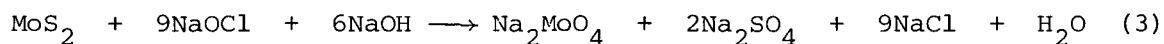
This is in good agreement with the findings of Dresher et al., with 9 moles of oxidant required per mole of molybdenite. Zelikman also found that thiosulphate was present initially but that its concentration went through a maximum value and had reached zero by the end of the reaction. The oxidation of molybdenite to molybdate was found to be first order, with an activation energy of about 5.25 kcal/mole over the temperature range under study. The rate constant increased both with increased

hypochlorite content and with increased temperature.

Shapiro and Kulenkeva carried out tests using a sodium hypochlorite lixiviant to try and obtain efficient molybdenum recovery from intermediate concentrates containing 2 - 6% Mo produced during the processing of disseminated molybdenite or polysulphide ores.[14] Leaching experiments were done in the presence of sodium carbonate and it was found that a 30 g/l solution of hypochlorite gave a maximum rate of molybdenite decomposition at 50°C:

$$MoS_2 \ + \ 9NaOCl \ + \ 3Na_2CO_3 \longrightarrow Na_2MoO_4 \ + \ 2Na_2SO_4 \ + \ 9NaCl \ + \ 3CO_2 \quad (4)$$
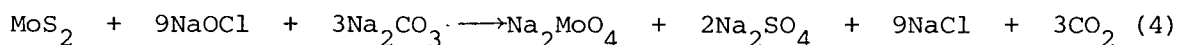
The leach was stated as being selective for molybdenum because any other metal sulphides present would be converted to insoluble carbonates, as represented by the following equation:

$$MeS \ + \ 4NaOCl \ + \ Na_2CO_3 \longrightarrow Na_2SO_4 \ + \ 4NaCl \ + \ MeCO_3 \quad (5)$$
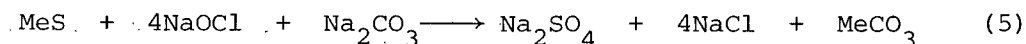
Bhappu, Reynolds and Stahman made a study of the sodium hypochlorite leaching of molybdenite from three different sources: a high grade concentrate containing 96 - 98% MoS_2, low grade ores typical of those found in a waste dump (0.2 - 0.8% MoS_2) and medium grade lumps of molybdenite averaging 60%.[15] They calculated the stoichiometric relationship for hypochlorite consumption to be the same for each test sample, indicating negligible consumption by gangue material, and in agreement with the findings of Iordinov and Zelikman, that nine moles of OCl^- were required to oxidize each mole of MoS_2.

They also confirmed reports by Choppin and Faulkerberry[16] which showed that provided an excess of hypochlorite is present in solution, the

end product of sulphide oxidation is entirely sulphate. Doubt was thus expressed concerning Cox's claim that thiosulphate was present as a final product of hypochlorite oxidation, and Bhappu et al. stressed that any thiosulphate or other intermediate oxidation state of sulphur would, in their opinion, exist only for very short periods of time before being oxidized to sulphate.

These authors concluded that such a hypochlorite process offered considerable potential for molybdenite leaching, especially for the treatment of low grade ores, on account of the seemingly low consumption of reagent by gangue material.

In a later paper however, Bhappu et al.[17] reviewed a number of oxidizing agents for the hydrometallurgical treatment of molybdenite ores and concluded that while alkaline hypochlorite solutions gave rapid and selective molybdenum extraction, the reagent was expensive to manufacture, unstable and corrosive; and the only economically feasible method for its generation in this type of leaching system would be in an electrolytic re-generation circuit from the sodium chloride solution produced by the oxidation reaction. Other reagents considered included sodium chlorate in acid solutions, manganese dioxide-sulphuric acid and nitric acid. The possibilities of bacterial leaching as well as in-situ leaching were also reviewed, especially in the presence of non-sulphide ores such as ferrimolybdate and limonite. For these ores and for those containing mixed oxides and sulphides either an acid-chlorate or a basic hypochlorite-carbonate lixiviant seemed feasible, with the latter being generally preferred because of potential problems with the precipitation of molybdate compounds in acid solutions.

Zelikman reviewed the possibility of leaching molybdenite with hypochlorite again in 1970,[18] particularly from low grade concentrates which would probably also contain copper and iron sulphides. Although such sulphides would be oxidized by hypochlorite in alkaline solution, the oxidation products would be insoluble hydroxides which inhibit the reaction and prevent subsequent dissolution, thus giving a selective molybdenum leach. It was pointed out in this article that the hydroxides of certain transition metal elements, including copper and iron, are also active catalysts for the decomposition of sodium hypochlorite in alkaline media. Catalysis can either be homogeneous or heterogeneous, and it was suggested the latter involves the formation of unstable hydroxides of higher valence states, especially for copper. Optimum conditions for concentrates containing 23% Mo and 9% Cu were found to exist with a hypochlorite content of 30 g/l and 20 - 30 g/l free alkali. Higher temperatures were found to increase the rate of molybdenum extraction, but as this also gave an increased rate of catalyzed hypochlorite decomposition, leaching at room temperature was recommended.

In all the above studies molybdenite leaching has been carried out on the alkaline side of neutrality, with pH 10.0 being stated as optimum in several cases. Sodium hypochlorite is much more stable in alkaline solutions than it is in acid media. A pH range of 5.0 - 7.0 was used in an electrooxidation technique investigated by the United States Bureau of Mines for extracting molybdenum and rhenium from low grade ores,[19] despite this being the region in which decomposition of hypochlorite to chlorate takes place most rapidly. The method was based on in-situ hypochlorite generation by electrolysis in brine ore pulp. Extractions

of 90 – 99% molybdenum were reported and a stoichiometric ratio of MoS_2:
$9OCl^-$ was again found to be operative (equation 3). The required pH
value was maintained by semi-continuous addition of sodium carbonate
and a temperature of 30 – 40°C was used. The overall power consumption
was reported as 9.7 kwh/lb Mo extracted, with a current density of 0.5
amp/in^2.

The study was extended to determine the extractability of molyb-
denum from copper-molybdenum flotation concentrates, averaging 3 – 28% Mo
and 2 – 15% Cu.[20] A maximum extraction of 97% Mo was achieved with a
final pH of 7.0: this value apparently decreased at both lower and higher
pH levels. It was stated that a minimum copper solubility of 1 – 3 ppm
occurred at pH 7.0, and in alkaline solutions copper was dissolved to
the extent of 25 ppm due to formation of the soluble compound $(CuX_2)CO_3$
where X = Cl^- or OH^-. Scheiner et al. suggested copper molybdate com-
pounds could adversely affect molybdenum recovery, but oxidation of copper
sulphides by hypochlorite could be prevented by adding sufficient sodium
carbonate to the system.

In two later papers[21,22] process solutions were treated, and the
technique was demonstrated with a prototype cell. 89 – 98% molybdenum
extraction was obtained from concentrates containing less than 1% Cu
and about 36% Mo. No copper was dissolved in the pH range 5.5 – 7.0,
but large amounts of chlorate were produced in this region and an SO_2
reduction step was therefore incorporated into the process. This pro-
cedure also served to reduce the pH of molybdate solutions for subsequent
molybdenum recovery by solvent extraction. Power consumption for treating
flotation concentrates was 13.7 kwh which is 4% higher than the corresponding

value for higher grade molybdenite concentrates. In the prototype cell demonstration 'off grade' flotation concentrates containing 16 - 35% Mo and 6 - 15% Cu as chalcopyrite and/or chalcocite were treated. It was reported that the molybdenum extraction decreased to only 75% in the presence of higher initial copper contents, and copper molybdate compounds were reportedly found in leaching tails. It was claimed that any chalcopyrite present in the feed material was unaffected by electrolysis, but that chalcocite was oxidized by sodium hypochlorite with subsequent formation of soluble copper compounds. These then reacted with molybdate ions in solution to give insoluble copper molybdates.

All subsequent trials were therefore performed with low copper/ high molybdenum concentrates and no information was given as to how, if at all, the copper molybdate problem could be rectified. In conjunction with these studies, Barr and co-workers investigated the effects of chlorate production on molybdenum recovery during electrooxidation, and concluded that by-product sodium chlorate was detrimental to molybdenum recovery as well as representing a power loss from the system. Both these factors are unfavourable economically. To minimize chlorate production the authors recommended a low temperature-low current density leach in which the pH was also reduced to 4.0 - 5.0. The use of 'flow through' cells was shown to be preferable to lead dioxide anode batch cells.[23,24]

By measuring respective oxidation rates of molybdenite and chalcopyrite in alkaline solutions, Stumpf and Berube concluded that the selective leaching of molybdenum from typical flotation concentrates was unlikely.[25] The unit consumption of oxygen for the two minerals is apparently very similar, and this was taken to mean that both species

would be simultaneously attacked, thereby preventing selective molybdenum dissolution.

These predictions are in direct contrast to the findings of Warren, Ismay and King,[26] who showed that molybdenite could be rapidly and selectively leached in alkaline hypochlorite solutions. The feed material in this case was a copper rougher concentrate containing 12.4% Cu and 0.3% Mo. The use of externally generated hypochlorite was proposed. By consideration of power requirements, sodium chloride consumption and other factors for the production of sodium hypochlorite by this method; and also taking into account the potential reduction in molybdenum losses by the use of a process which eliminated cleaner flotation steps, Warren et al. suggested that dismissal of this type of hypochlorite leaching system on economic grounds was no longer valid; and that it would compare favourably with the electrooxidation techniques outlined above. A study was therefore carried out to determine optimum conditions for molybdenum extraction and these were found to exist at pH 9.0, with an excess of hypochlorite and a temperature range of 30 - 40°C. Selectivity of molybdenum over copper was obtained with a ratio of about 100:1, but the presence of even small amounts of copper in solution at pH 9.0 appeared to contradict solubility data. It was postulated that partially oxidized sulphur species could be complexing the copper and holding it in solution. Excessive hypochlorite consumption over that predicted by the stoichiometry of equation 3 was observed in certain cases, and this was attributed to the formation of surface oxides during the oven-drying of copper sulphide minerals, which subsequently act as catalysts for hypochlorite decomposition. The study includes a proposed flowsheet for the overall process.

1.4.2 The behaviour of copper in alkaline carbonate solutions

Addition of a number of anionic ligands to solutions containing dissolved copper in the form of the aquo-ion $[Cu(H_2O)_6]^{2+}$ leads to the formation of complexes. Because the six water molecules are not equidistant from the central copper atom, successive displacment by other ligands can readily occur. Ammonia, NH_3, is one such complexing agent in alkaline solution and the fact that cupric hydroxide is readily soluble in ammonia solutions has been used to advantage in a number of processes for copper extraction. Ammonium carbonates are used in this respect, but due to the strong complexing action of the ammonia itself, the fact that carbonate also acts as a complexing ligand for copper is generally overlooked. The $[CO_3^{2-}]$ anion forms a stronger complex than do any of the halide ions, for example, in alkaline solutions, but the latter are more often considered to stabilize cupric salts in solution.

It was observed in the middle of the last century that the addition of certain copper salts to sodium carbonate solutions produced intensely blue solutions which subsequently precipitated light blue crystals of some basic copper carbonate salt. Pickering published the most detailed early study on this subject[28] and he confirmed that salts obtained by the above methods reported by Deville[27] and Reynolds[29] were 'double carbonates' with the typical formula $Na_2Cu(CO_3)_2 \cdot 3H_2O$. Pickering noted that the liquid retained negligible amounts of copper after precipitation and assumed that as the liquid and solid were quite different colours, two different substances were involved. He also observed that the solution was much darker than a copper sulphate solution containing an equivalent

amount of copper. He postulated that it contained a 'cupri carbonate' species in which copper formed part of the anion. Cuprammmonium com-pounds with copper displacing the hydrogen atoms of ammonium salts to give a deep purple-blue solution were cited as an analogous case. Reynolds[29] and Wood and Jones[30] had previously shown in independent studies that electrolysis of these blue carbonate solutions liberated copper at both the anode and the cathode.

The two most common copper carbonates are the minerals azurite, $Cu_3(OH)_2(CO_3)_2$, and malachite, $Cu_2CO_3(OH)_2$. Pickering reported isolating several other salts including $5CuO,2CO_2$; $5CuO,3CO_2$ and $8CuO,3CO_2,6H_2O$, by mixing copper sulphate solutions with either sodium carbonate or sodium bi-carbonate. He found all these basic carbonates to be insoluble in water and sodium carbonate solutions, but slightly soluble in carbonic acid and sodium bicarbonate. He also observed that introducing copper sul-phate solutions into alkaline carbonates containing various proportions of $NaHCO_3$:Na_2CO_3 produced a very blue solution with a copper content dependent on the CO_3^{2-}:HCO_3^- ratio (and thus of pH), but which for any mixture was directly proportional to the total carbonate content. It was observed that on allowing these solutions to stand for a couple of days precipitation of either malachite or a 'double salt,' $Na_2Cu(CO_3)_2$ occurred, leaving an almost colourless solution containing very little copper. No clear explanation as to why decomposition should occur after a certain time was given, but Pickering does suggest that the degree of electropositive and electronegative copper present in a given case determined whether malachite or the double salt formed, and that in fact the double carbonate had two isomerides; one (the

cupri-carbonate) containing anionic copper and the other cationic copper. A proposed molecular structure for each substance is given.

Other observations made by Pickering included:

i) A slight increase in temperature produced a small increase in the amount of copper dissolved in a given amount of carbonate, but strong heating of the solution gave black colouration and deposition of a black precipitate, probably copper oxide.

ii) Addition of excess sodium hydroxide to a carbonate containing copper solution removes carbon dioxide causing decomposition of the solution and formation of a blue basic carbonate salt. Dilution wtih excess water also decomposed the solution, with a black precipitate appearing in some cases.

Appleby and Lane[31] also carried out a study of the double carbonates of sodium and potassium with various transition metals including copper. They prepared samples of the salt $Na_2Cu(CO_3)_2 \cdot 3H_2O$ by allowing it to precipitate from copper carbonate solutions: concentrated cupric acetate was added to a sodium carbonate/bicarbonate mixture (100 g Na_2CO_3:40 g $NaHCO_3$) at 50°C and a clear deep blue solution free of any precipitate was immediately formed. On standing overnight, crystals of the double salt were obtained from this solution and it was observed that the mother liquor could be reused after separation of the crystals, in which case a slightly better yield was obtained.

These authors also observed that both crystals and solutions decomposed at higher temperatures giving cupric oxide and sodium carbonate, as a result of loosing water and carbon dioxide. The solution was decomposed by addition of excess water. Appleby and Lane concluded that

crystal deposition was not due to the solution being super-saturated in the normal sense because, although precipitation occurred slowly and only after several hours of standing, addition of previously formed crystals did not speed up the nucleation procedure. It was also shown that crystallization time was unaffected by atmospheric carbon dioxide and was constant for solutions in either open or sealed flasks as well as those in a desiccator connected to a Kipp's apparatus for carbon dioxide. The following reasons were thus put forward to explain the precipitation behaviour:

i) A very slow rate of crystallization is operative and no stable super-saturated solutions exist.

ii) The crystals are precipitated via formation of an intermediate compound which undergoes slow transformation into the final produce.

In agreement with the observations of Pickering this study showed that the equilibrium copper content in solution increased as a function of total carbonate concentration. It was also noted that clear solutions could only be obtained in the presence of both sodium bicarbonate and sodium carbonate. Omission of the bicarbonate led to almost instantaneous precipitation of a basic carbonate salt. The fact that more copper was dissolved by the carbonate/bicarbonate mixture than would be obtained by dissolving $CuCO_3$ in water was attributed to the formation of the complex ion $Cu(CO_3)_2^{2-}$, or even $Cu(CO_3)_4^{6-}$ in the case of a double salt. The possibility of copper being present as a colloidal substance as well as (or instead of) a complex ion, was also discussed.

A number of other studies of these characteristically blue copper carbonate solutions and of the basic salts derived from them have been

made, including a polarographic study by Meites,[32] an investigation into

the effects of altering the Na_2CO_3:$CuSO_4$ on subsequent precipitation by

Hsu,[33] and a determination of the solubility of malachite by Scaife.[34]

In this last study Scaife observed that malachite solubility in sodium

bicarbonate solutions was far greater than would be expected form calcu-

lations for the cupric ion. It was therefore suggested that ionic

association or complex formation occurs between cupric and bicarbonate

ions. An analogy was drawn between this case and that of cupric/

acetate ion complexes. The total concentration of copper in solution

was suggested as being given by the expression

$$[Cu_T] \quad = \quad [CuCO_3] \quad + \quad [CuHCO_3^+] \quad + \quad [Cu^{2+}] \tag{6}$$

which seemed to give good agreement with experimentally determined values

for copper dissolution.

Garrels and Christ,[35] give an Eh-pH diagram for the system

$Cu-O_2-S-CO_2-H_2O$ at 25°C which shows that at atmospheric pressure (P_{CO_2} =

$10^{-3.5}$) malachite has a large zone of stability in a pH range from 7.0 -

13.0 and potentials higher than 0 - 0.2 V. An increase in the dissolved

carbon dioxide content would extend this region of stability (Figure 2).

The solubility constant, K_s, for the reaction

$$Cu_2(OH)_2CO_3 \quad = \quad 2Cu^{2+} \quad + \quad CO_3^{2-} \quad + \quad 2OH^- \tag{7}$$
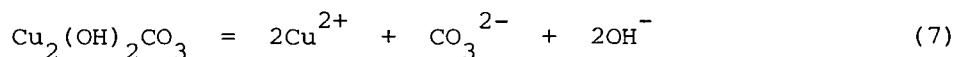
is given as $K_s = 10^{-31.90}$.

De Zoubov et al.[36] investigated the behaviour of copper in sodium

bicarbonate solutions of varying strengths, and found that the corrosion

of copper metal was significantly affected by the carbonate content.
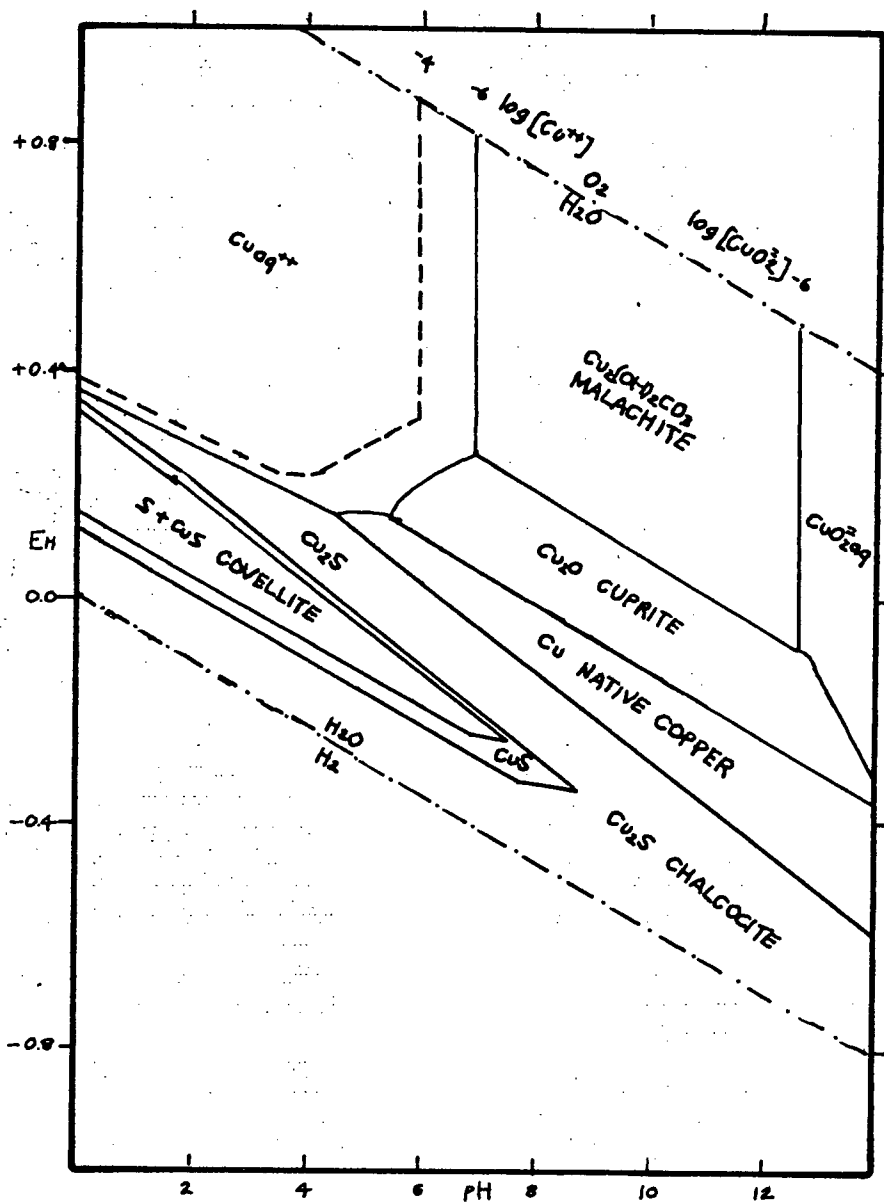
Figure 2: Stability relations for copper compounds in the system $Cu-H_2O-O_2-S-CO_2$.

Experiment showed that solutions containing less than 0.0032 M bicarbonate were mildly corrosive towards copper wire; those with 0.01 - 0.032 M were practically non-corrosive and a further increase of bicarbonate above 0.1 M produced strongly corrosive solutions. Electrochemical equilibrium (Eh-pH) diagrams were drawn to explain these observations. It was found that conditions of stability of the basic copper carbonate malachite corresponded to the passivation effect observed in the region of 0.01 = 0.032 M bicarbonate, but that dissolution of malachite to give stable, complex cupri-carbonate ions could occur in solutions with a very low bicarbonate content, or in those containing more than 0.1 M.

A series of four diagrams are given in which the total dissolved CO_2 content, defined as

$$[H_2CO_3] \quad + \quad [HCO_3^-] \quad + \quad [CO_3^{2-}]$$
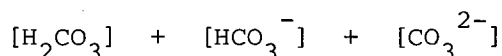
increases from 10^{-3} M to 1 M in concentration (Figure 3). As this value of dissolved CO_2 increases, the region of malachite stability grows to higher pH values causing cuprite and tenorite zones to correspondingly diminish. Azurite, $2CuCO_3Cu(OH)_2$, becomes stable in a pH range of $\approx 3 - 7$ at $[CO_2]$ values greater than 10^{-1} M. The dissolved species which are stabilized by the presence of carbonate include the $CuCO_3$ (aq.) molecule, the cupri dihydroxo carbonate ion, $CuCO_3(OH)_2^{2-}$, and the cupri carbonate ion, $Cu(CO_3)_2^{2-}$. The $CuCO_3$ (aq.) species exists at the lower end of the pH scale, being stable from 6.5 - 10.0 at low carbonate concentrations, and being pushed downwards to 5.0 - 7.0 at higher levels of $[CO_2]$. The cupri-carbonate ion appears in a narrow band of pH (9.0 - 10.5) at CO_2 levels in excess of 10^{-2} M and expands to a much wider band (7.0 -
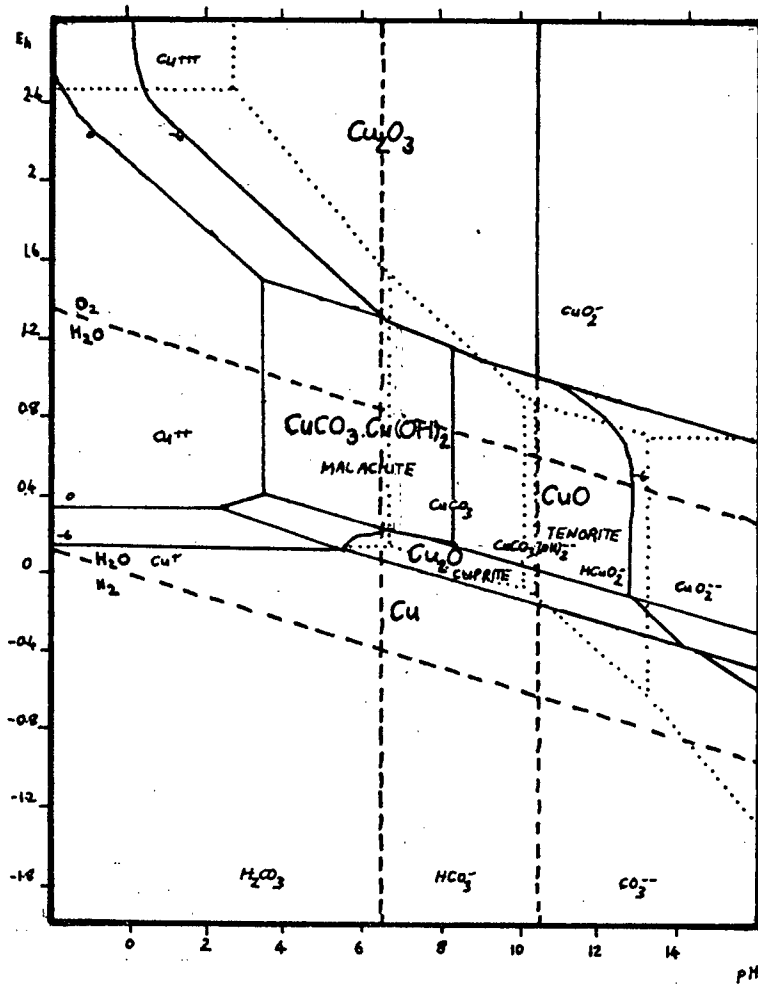
Figure 3 (a): Potential – pH diagram for the system $Cu-CO_2-H_2O$ with $10^{-3}M$ $[CO_3^=]_T$.
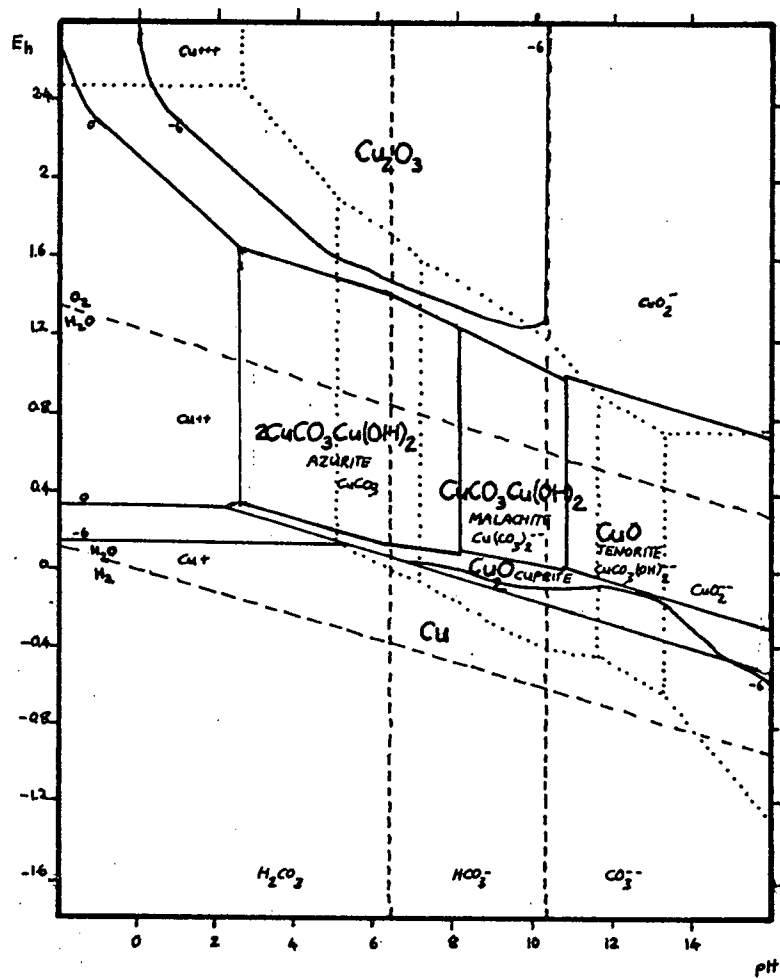
Figure 3 (b): Potential - pH diagram for the system $Cu-CO_2-H_2O$ with 10^{-6} M $[CO_3^=]_T$.

11.5) at the 1 M CO_2 level. These soluble carbonate species also become

stable at increasingly higher potential values for a given pH as the

dissolved CO_2 content goes up. At E values above this, Cu_2O_3 (hydrated)

is shown as the stable species.

Diagrams showing theoretical circumstances of corrosion, passiva-

tion and immunity for copper as a function of pH and carbonate content,

together with solubility diagrams for azurite, tenorite and malachite,

are also given.

Schindler and co-workers[37] also studied the solubilities of azurite

and malachite, and with the help of thermodynamic data produced by

Silman for the $Cu-H_2O-CO_2$ system, stability diagrams showing the zones

of predominance for the various components of this system are given.

The occurrence of the uniquely stable carbonate complexes $CuCO_3$(aq.) and

$Cu(CO_3)_2^{2-}$ is again recognized as causing dissolution of the basic

copper carbonate minerals:

$$\tfrac{1}{2}Cu_2(OH)_2CO_3 \ + \ \tfrac{1}{2}CO_2 \ = \ CuCO_3 \ (aq.) \ + \ \tfrac{1}{2}H_2O \tag{8}$$

$$\tfrac{1}{2}Cu_2(OH)_2CO_3 \ + \ 2HCO_3^- \ = \ Cu(CO_3)_2^{2-} \ + \ \tfrac{1}{2}CO_2 \ + \ \tfrac{3}{2}H_2O \tag{9}$$
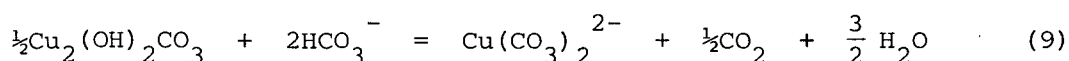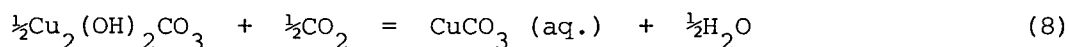
for which the following equilibria apply:

$$Cu^{2+} \ + \ CO_3^{2-} \ \rightleftharpoons \ CuCO_3 \ (aq.)$$

$$\log k = 6.73$$

$$Cu^{2+} \ + \ 2CO_3^{2-} \ \rightleftharpoons \ Cu(CO_3)_2^{2-}$$
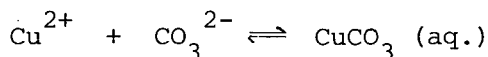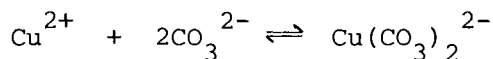
$$\log k = 9.83$$

It was noted that in air-saturated solutions the majority of the copper

is present as Cu^{2+} at pH values below 7.0, and as $Cu(CO_3)_2^{2-}$ in more alkaline solutions.

Stumm and Morgan[38] give both an activity ratio diagram and a solubility diagram for the predominant solid phases and soluble species of the $Cu-H_2O-CO_2$ system. They have been constructed for a total carbonate content of 10^{-2} M for the relevant Cu^{II} equilibria, and show that the important soluble species with increasing pH are Cu^{2+}, $CuCO_3$ (aq.), $Cu(CO_3)_2^{2-}$ and hydroxo-copper[II] anions (Figure 4).

In a paper which considers the corrosion of metallic copper in typical sea water solutions, Bianchi and Longhi[39] give a stability diagram showing predominance areas of the species which can exist as cupric complexes in solutions containing both chloride and carbonate ions. These include $CuCl^-$, $CuCl_2^0$, $CuCl_3^-$, $CuCl_4^{2-}$, $Cu(CO_3)_2^{2-}$, $Cu(CO_3)_3^{4-}$ and $Cu(HCO_3)_5^{3-}$. It is again apparent that the $Cu(CO_3)_2^{2-}$ ion is predominant at pH 9.0, indicating that the carbonate complexes copper more strongly than chloride in alkaline solutions.

The fact that copper-chloride complexes are weak in alkaline solutions, even in the presence of large quantities of Cl^-, is also noted by Van Muylder et al.[40] and it is stated that copper would be precipitated from such solutions as CuO (or $Cu(OH)_2$).

1.4.3 Decomposition of sodium hypochlorite in alkaline solution

Sodium hypochlorite, NaOCl, is a strong oxidant in alkaline solutions and has been shown to be an effective lixiviant for the extraction of molybdenum from molybdenite ores and concentrates, as outlined
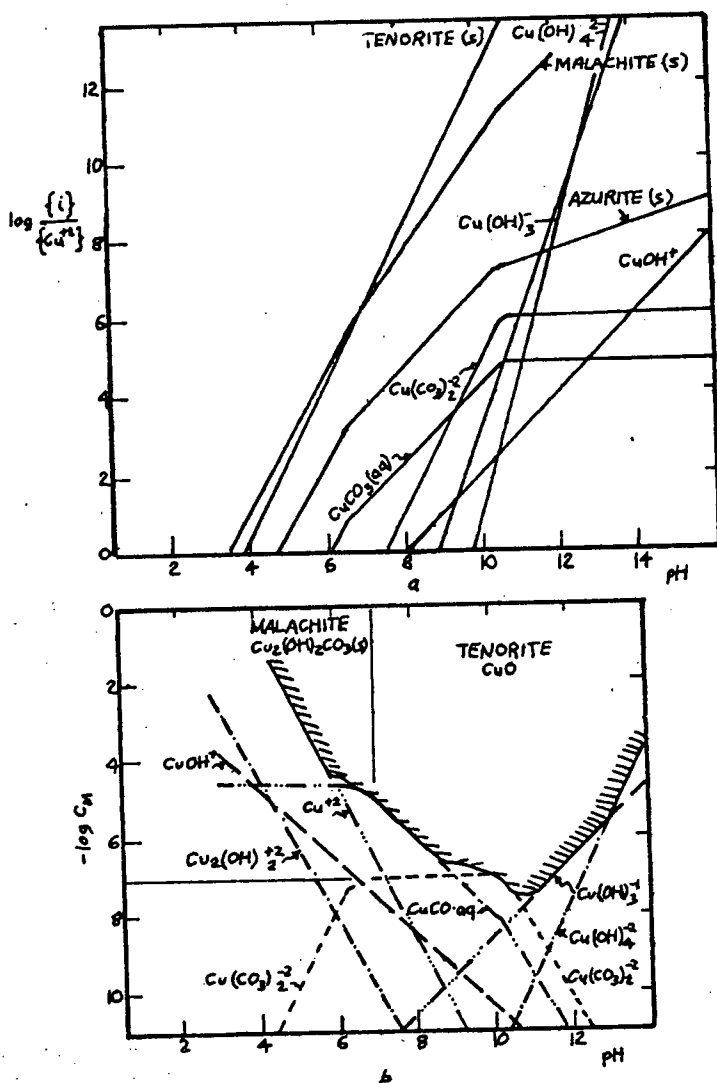
Figure 4: Solubility of Cu (II) in the system Cu-H$_2$O-CO$_2 \cdot$[CO$_2^=$]$_T$ = 10^{-2}M.
    a) activity ratio diagram.
    b) solubility diagram.

above. There are two potential problems associated with the use of this reagent from a commercial standpoint however:

i) It is expensive to generate.

ii) It is unstable and undergoes spontaneous decomposition under certain conditions of pH and ionic strength. This decomposition reaction can be catalyzed, especially by the salts of certain transition metals.

Most early investigators concluded that the costs incurred in hypochlorite generation would be too great to give an economically feasible process for molybdenum extraction. In view of the current strong demand and high price of molybdenum, together with the capabilities of modern electrolytic generators for manufacturing hypochlorite, this type of hydrometallurgical process would now seem to compare favourably with existing technology.

In a process using externally generated hypochlorite, however, any decomposition of the reagent during leaching is detrimental and would necessitate generation of more than the stoichiometric hypochlorite required for the oxidation of molybdenite to molybdate. It is therefore important to appreciate the conditions under which decomposition takes place, and the extent to which it occurs.

Several investigations have reported the results of studies carried out to determine the exact nature of hypochlorite decomposition under varying conditions of pH, temperature, ionic strength etc. It is generally agreed that the products of decomposition are oxygen, chloride and chlorate in varying proportions. The uncatalyzed reaction can be represented as follows:

$$HClO + 2OCl^- \longrightarrow ClO_3^- + 2Cl^- + H^+ \qquad (10)$$

$$2HClO + OCl^- \longrightarrow ClO_3^- + 2Cl^- + 2H^+ \qquad (11)$$

$$HClO + OCl^- \longrightarrow 2Cl^- + O_2 + H_2 \qquad (12)$$
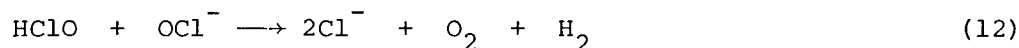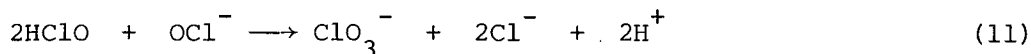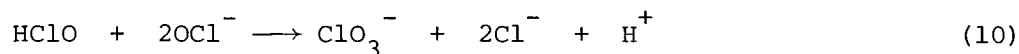
Equations 10 and 11 both represent decomposition to chlorate. The former is generally applicable in alkaline solutions while the latter more often occurs in acidic media. D'ans and Fruend[41] suggested that in very pure hypochlorite solutions chlorate can be the sole decomposition product, but this is more generally accompanied by simultaneous decomposition to oxygen, as shown by Lister.[42]

It is this oxygen forming reaction which is usually thought of as being catalysed by certain transition metal hydroxides and oxides. While detailed consideration of the many mechanisms which have been put forward to explain this behaviour has not been undertaken, a review of some of the relevant work is included as it introduces concepts which are applicable to the present study:

Bell[43] measured the velocity of oxygen evolution from solutions of calcium hypochlorite, $Ca(OCl)_2$, in the presence of a number of salts in both acid and alkaline solution. This velocity increased rapidly in solutions containing $Co(NO_3)_2$ and $NiSO_4$ and was slightly increased by the presence of $BaCl_2$, $CaSO_4$, $AgNO_3$, $HgCl_2$, $FeCl_3$, $K_2Cr_2O_7$ and $FeSO_4$. LiCl, Na_2CO_3, KCN, Na_2S and KNO_2 were reported to retard oxygen evolution.

Hofman and Ritter[44] in a study of the stability and redox potentials of hypochlorites, concluded that decomposition was catalyzed to approximately the same degree by CoO, NiO and IrO, while the oxides of manganese, uranium, bismuth, palladium, tellurium and vanadium had no

effect.

A detailed study of the rate of decomposition of sodium hypochlorite solutions in the presence of cobalt and nickel peroxides, CoO_2 and NiO_2, and oxides of copper, iron and cobalt, was made by Chirnoaga in 1923.[45] He reported that oxygen evolution during decomposition was less than first order and could be represented by the general equation

$$-\frac{dc}{dt} = k_1 c^{1/n} \tag{13}$$

where c = concentration of hypochlorite at time t, and k_1, n are constants.

Chirnoaga postulated that OCl^- ions were adsorbed onto the surface of catalyst particles. Decomposition of these ions would then determine the reaction velocity. The adsorption step would be faster than the subsequent decomposition, and thus the surface layer would be kept in adsorption equilibrium with the bulk of the solution.

Experiment showed that oxygen evolution increased with time and with concentration (and hence surface area) of the catalyst. The oxides under study were found to decrease in order of catalytic activity: Ni > Co > Cu > Fe, and equation 13 was found to be more applicable for the catalysts with higher activities. Chirnoaga noted that a mixed CoO/NiO catalyst was more active than either oxide alone.

This increased catalytic activity of mixed oxides was also reported by Lewis.[46] He suggested less active catalysts could have a promoting influence when combined with a more active one. Fe_2O_3 in the presence of CuO for example, gave a more effective catalytic action than that produced by either catalyst alone.

Lewis suggested a more simple equation to describe the rate of

decomposition:

$$\frac{dc}{dt} = k \qquad (14)$$

representing a linear relationship between evolved oxygen and time. He found the rate to be constant for a wide range of initial hypochlorite concentrations, and that it was directly proportional to catalyst concentration. The mechanism was considered to be one that involved the formation and subsequent decomposition of a hypochlorite-catalyst complex in a continuous cycle. Such a process would occur at a constant rate provided the active centres on the catalytic surface were entirely covered by reactant. Any loss of these due to coagulation, dehydration etc. would lead to decreased catalytic action. Lewis therefore suggested that the 'promoter' effect occurred as a result of the second substance preserving the active centres on the catalyst itself, thus producing a more efficient (and prolonged) reaction.

The first reported study that hypochlorite could be catalytically decomposed to chlorate as well as to oxygen was given in a Russian paper of Glikman and Dain in 1941.[47] They showed that cobalt hydroxide accelerated the reaction

$$ClO^- + \tfrac{1}{2}O_2 \longrightarrow Cl^- + ClO_3^- \qquad (15)$$
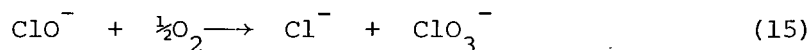
but gave no details of the pH region in which this effect was observed.

Ayres and Booth[48] showed that both oxygen and chlorate are formed as decomposition products in a catalysed reaction. Oxidative decomposition was more predominant in less strongly alkaline solutions and overall decomposition reached a maximum around pH = 9.0. It was also observed

that where the initial pH had a value below 10, decomposition was accompanied by acidification of the solutions, giving a final value of 3 - 4. Chlorine evolution was also observed in such cases. Equations representing this observation were cited as:

$$2HClO \longrightarrow O_2 + 2Cl^- + 2H^+ \tag{16}$$

$$3HClO \longrightarrow ClO_3^- + 2Cl^- + 3H^+ \tag{17}$$

$$HClO + Cl^- + H^+ \longrightarrow Cl_2 + H_2O \tag{18}$$
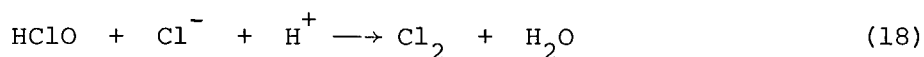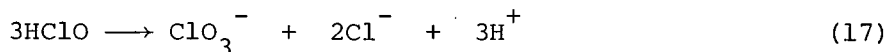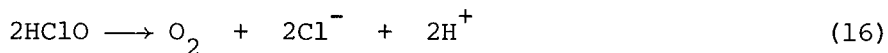
The catalyst used in this study was iridium oxide and Ayres and Booth proposed an overall mechanism involving the formation of an intermediate active complex allowing the production of molecular oxygen which can then recombine with more hypochlorite to give chlorate:

$$ClO^- + c^- \rightleftharpoons x^- + Cl^- \tag{19}$$

$$x^- \rightleftharpoons c^- + O \tag{20}$$
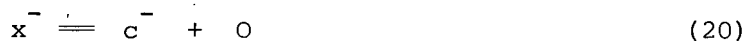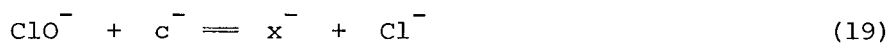
where c = catalyst and x = active complex

$$ClO^- + O \longrightarrow ClO_2^- \tag{21}$$

$$ClO^- + O \longrightarrow ClO_3 \tag{22}$$

Lister, on the other hand, concluded after carrying out an extensive study of both uncatalysed and catalysed reactions of sodium hypochlorite decomposition, that chlorative decomposition was not catalysed.[42,49]

In the former study he confirmed the findings of Foerster et al.[50] that the uncatalysed reaction produces mainly chlorate, is second order and occurs in a two stage process:

$$2NaOCl \longrightarrow NaClO_2 + NaCl \tag{23}$$

$$NaOCl + NaClO_2 \longrightarrow NaClO_3 + NaCl \tag{24}$$

The first, chlorite forming step is the slower of the two. Lister found that a small part of the decomposition reaction produced oxygen:

$$NaOCl \longrightarrow NaCl + \tfrac{1}{2}O_2 \tag{25}$$

and that this was a first order reaction. He noted that it could not be concluded with certainty that absolutely no catalysts were present during his experiments.

In his study of the catalysed decomposition reaction[49] Lister used manganese, iron, cobalt, nickel and copper oxides and determined that none of these increased the rate of formation of chlorate from hypochlorite, but that the oxygen reaction was catalysed to a different extent by each metal oxide. For cobalt and nickel this was found to be a zero order reaction and for copper it was almost first order. The previously made proposal that this heterogeneous catalysis involves oxidation of the metal to a higher oxide with subsequent loss of oxygen, followed by reoxidation, was considered by Lister to be quite feasible. The fact that iron and manganese showed only very weak catalytic activity could then be explained by the stability of the higher oxidation states of these metals, in contrast to the cases of cobalt, nickel and copper all of which exist as 'higher oxides' in relatively unstable conditions. This mechanism would not result in increased chlorate production and this was also in agreement with experimental observations. However, more oxygen was evolved than could be accounted for by this type of oxidation-reduction

cycle so an alternative mechanism was suggested. This still involved
the formation of higher valence oxides, but it was proposed that this
oxide formed an adsorbed metal-hypochlorite complex on the catalytic
surface, and subsequently decomposed:

$$2MO + ClO^- \longrightarrow M_2O_3 + Cl^- \tag{26}$$

$$M_2O_3 + ClO^- \longrightarrow M_2O_3ClO^- \text{ (ads.)} \tag{27}$$

$$M_2O_3ClO^- \longrightarrow 2MO + Cl^- + O_2 \tag{28}$$
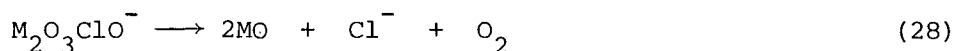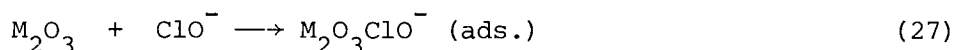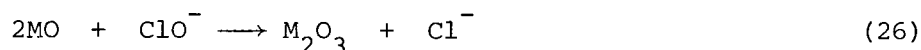
Prokopchik[51] dismissed this mechanism of Lister as being experi-
mentally unfounded. He concluded from his own work that higher oxides
were formed as intermediate compounds and that these were actually the
catalysts for hypochlorite decomposition. It was found that both oxida-
tive and chlorative decomposition were catalysed, with the latter occurring
as a result of partial hypochlorite oxidation to chlorate during the
decomposition of the higher valence oxide. Thus in his study of both
homogeneous and heterogeneous hypochlorite decomposition in the presence
of copper, Prokopchik determined that an important role was played by
copper[III] compounds. When in solution these existed as anionic cuprates,
for example, $NaCu(OH)_4$, while solid compounds such as Cu_2O_3 produced
heterogeneous catalysis.

The tri-valent cuprate was found to be unstable in solution and
its formation in the presence of hypochlorite was followed by rapid decom-
position to bi-valent cuprite:

$$4Cu(OH)_4^- + 4OH^- \longrightarrow 4Cu(OH)_4^{2-} + O_2 + H_2O \tag{29}$$
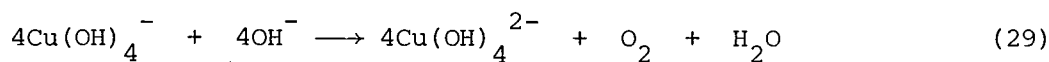
with a reaction rate given by

$$- \frac{d\ (Cu(OH)_4^-)}{dt} = k_2\ (Cu(OH)_4^-)\cdot(OH^-) \quad (30)$$

$$\simeq k_2'\ (Cu(OH)_4^-),$$

since hydroxyl ion concentration is always greater than that of cuprate anions.

The decomposition of hypochlorite occurred simultaneously:

$$2Cu(OH)_4^{2-} + ClO^- + H_2O \longrightarrow 2Cu(OH)_4^- + Cl^- + OH^- \quad (31)$$

$$2Cu(OH)_4^- + 2OH^- \longrightarrow 2Cu(OH)_4^{2-} + H_2O + \tfrac{1}{2}O_2 \quad (32)$$

$$ClO^- \rightleftharpoons Cl^- + \tfrac{1}{2}O_2 \quad (33)$$
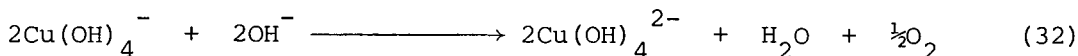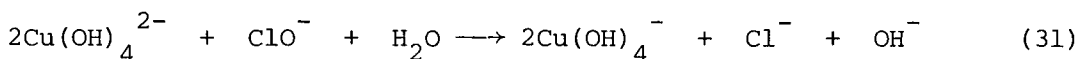
The rate of reaction was found to be first order for hypochlorite concentrations up to 0.1 M, above which it deviated towards zero order.

In the case of heterogeneous decomposition it was observed that the action of sodium and calcium hypochlorites on blue cupric hydroxide caused rapid transformation to a brownish-black compound accompanied by catalysed decomposition of the hypochlorite solution. The nature of the catalyst was considered, and Prokopchik concluded that while a copper peroxide compound could be produced by this method, the observed decomposition data suggested formation of cuprates at high pH values, and the tri-valent hydroxide at lower levels of alkalinity, as being more likely. Formation of a red compound was noted at the end of some experiments, and this was taken to be a deactivated cuprate which no longer had catalytic properties.

A certain amount of confusion appears to exist concerning the compound responsible for hypochlorite decomposition at pH levels below 11.0. Prokopchik states firstly, as noted above, that cuprates cannot exist at low alkalinity and that oxidation of bi-valent to tri-valent hydroxide thus occurs. He later states, however, that it is impossible to obtain a tri-valent hydroxide, and that in fact no oxidation of bi-valent copper will occur below pH 11.5, so that dehydrated cupric hydroxide is responsible for catalytic action at lower pHs. Since it is emphasized that no hypochlorite decomposition can occur in the absence of copper[III], these statements appear to be self-contradictory.

In the proposed mechanism for heterogeneous decomposition, however, both the hydroxide and cuprate are considered:

i) at lower alkalinities:

$$Cu(OH)_2 + OH^- \longrightarrow Cu(OH)_3^- + e^- \tag{34}$$

$$ClO^- + 2Cu(OH)_2 + H_2O \longrightarrow Cl^- + 2Cu(OH)_3 \tag{35}$$

$$4Cu(OH)_3 \longrightarrow 4Cu(OH)_2 + O_2 + H_2O \tag{36}$$

$$4Cu(OH)_3 + ClO^- \longrightarrow 4Cu(OH)_2 + ClO_3^- + 2H_2O \tag{37}$$
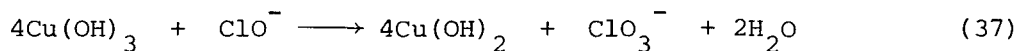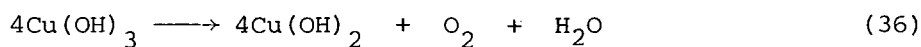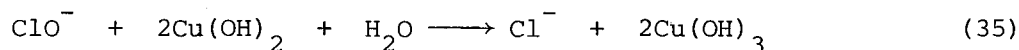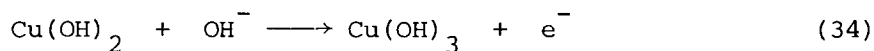
ii) higher alkalinity (pH > 12.0):

$$Cu(OH)_2 + 2OH^- \longrightarrow Cu(OH)_4^- + e^- \tag{38}$$

$$2Cu(OH)_2 + ClO^- + H_2O + 2OH^- \longrightarrow Cl^- + 2Cu(OH)_4^- \tag{39}$$

$$4Cu(OH)_4^- \longrightarrow 4Cu(OH)_2 + O_2 + 2H_2O + 4OH^- \tag{40}$$

$$4Cu(OH)_4^- + ClO^- \longrightarrow 4Cu(OH)_2 + ClO_3^- + 2H_2O + 4OH^- \tag{41}$$
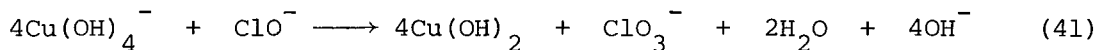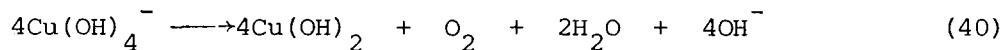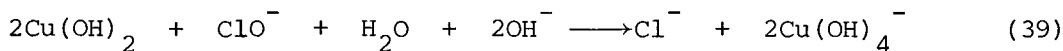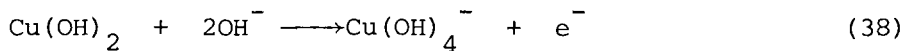
Consideration of the redox potential for reactions[34-41] confirmed that oxidation to the tri-valent state by hypochlorite solutions was thermodynamically possible.

A further ambiguity exists regarding the chlorate forming reaction: the above equations suggest this occurs only at higher pH values, and Prokopchik in fact states that chlorative decomposition becomes more pronounced as alkalinity increases, and may even predominate. Considerable discussion previously however had led to the conclusion that in strong alkaline solutions hypochlorite decomposes to oxygen, while at pH 11.0 and below copper hydroxide significantly accelerated the decomposition to chlorate. At pH 9.0 the mole ratio of $ClO_3:O_2$ attained a value of 3. Graphical representation based on experimental data is given to illustrate this point.

By consideration of the catalytic action of cobalt, iron, and nickel under similar conditions, Prokopchik concluded that catalytic activity decreased in the order Co > Ni > Cu > Fe. The generalized mechanism for any metal Me was given as:

$$ClO^- + Me(OH)_n \longrightarrow Cl^- + Me(OH)_{n+1} \tag{42}$$

$$Me(OH)_{n+1} \longrightarrow Me(OH)_n + \tfrac{1}{2}O_2 \tag{43}$$

$$Me(OH)_{n+1} + ClO^- \longrightarrow ClO_3^- + Me(OH)_n \tag{44}$$
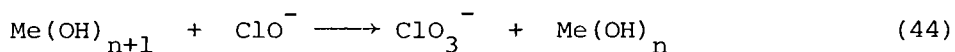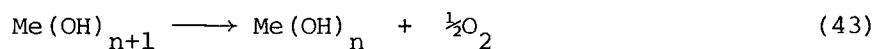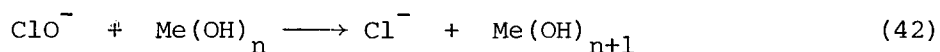
1.4.4 Copper[III] compounds

Copper exists in the tri-valent state as a result of 4s and 3d electrons being removed from the copper atom to give a $1s^2$, $2s^2$ $2p^6$, $3s^2$ $3p^6$ $3d^8$ configuration. This is iso-electronic with the nickel[II] structure, and tri-valent copper compounds are generally diamagnetic as a result of all electrons being paired. Although this is a relatively rare oxidation state for copper, its existence has been acknowledged since the middle of the last century, and several workers have studied the formation and stability of copper[III] compounds:

Crum, in 1845, obtained what he described as a cuprate by the action of an acidic solution of "bleaching powder" on copper nitrate. This occurred as a red powder and was assigned the formula $H_2Cu_2O_4$ corresponding to the hydrated form of the sesquioxide, Cu_2O_3.[55]

Moser used hydrogen peroxide to oxidize copper hydroxide and obtained a compound approaching the formula $CuO_2 \cdot H_2O$. Tests with chlorine and bromine produced no oxidation.[56]

Scagliarni and Torelli[57] produced an amaranth red compound by the action of potassium persulphate, $K_2S_2O_8$, on copper hydroxide solutions. The compound evolved oxygen when treated with dilute H_2SO_4, decolourised $KMnO_4$, and did not contain a peroxide group. It was thus taken to be trivalent copper oxide, Cu_2O_3.

The earliest report of oxidation of copper[II] by hypochlorite solutions is one by Muller and Spitzer[60] in which it was shown that tri-valent copper could be produced in strongly basic solutions (>3N) of copper hydroxide by oxidation with hypochlorite. Hypobromite, chlorine and bromine produced similar effects. The colour of the resultant solution

apparently varied from red and violet to brown and black, dependent on the degree of alkalinity.

The same authors carried out electrochemical tests to produce tri-valent copper oxide, and suggested its formation to be caused by

i) oxidation of metal ions contained within the copper anode, or

ii) oxidation of metal ions contained in the electrolyte solution, with subsequent oxide precipitation.

Aldridge and Appleby in 1922[59] did a number of experiments to investigate the peroxidic compounds of copper. Hydrogen peroxide was added to copper containing carbonate solutions and a yellow-brown compound was rapidly precipitated. Analysis showed this precipitate to contain more oxygen than would correspond to Cu_2O_3, but insufficient to give CuO_2. It was assumed, however, that a peroxide had been produced, but that its separation in a pure state was not possible.

Lepore reported obtaining the compound Cu_6O_4 (or $Cu \cdot Cu_5O_4$) by treating Fehling's solution with hydrogen peroxide.[60] He also claimed that the addition of copper nitrate solutions to barium hydroxide gave the compound $Cu_2O_3 \cdot 3H_2O$ or $Cu_2(OH)_6$.

More recent studies regarding the existence of alkaline and alkaline earth metal cuprates have been made by Scholder and Voelskow,[61] Prokopchik,[62] and Magee and Wood.[63] Crystalline barium cuprate, $Ba(CuO_2)_2 \cdot H_2O$ was obtained by the addition of potassium hypobromite solutions to cupric hydroxide in the presence of barium salts such as $BaCl_2$ or $BaCO_3$ in alkaline solution, in experiments carried out by Scholder in 1951. The sodium salt, $NaCuO_2$, was produced in a similar manner by the action of hypobromite, $NaOBr$, and sodium bromate, $NaBrO_3$.

Calcium and strontium cuprates could not be obtained by this method.

Calcium cuprate was produced by Prokopchik who used calcium hypochlorite to oxidize cupric chloride, $CuCl_2$, at a pH value of 12.2. A red-purple precipitate was observed, having a Cu:O ratio of 1:0.5. Similar oxidation was effected by the use of an equivalent amount of sodium hypochlorite (0.2 M).

Magee and Wood carried out an investigation of sodium cuprate[III] stability in alkaline solutions of varying strength. They concluded that the salt was very unstable in all cases and estimated that the CuO_2^- ion had a half life of only 25 seconds. Copper[III] was thus assumed to exist in solution only when complexed. The fact that Scholder and Voelskow found tri-valent copper solutions to be stable in the presence of excess base and hypobromite was suggested to be caused by a hypobromite-copper[III] complex. A number of workers have, in fact, shown that copper[III] can be complexed and hence stabilized either in solution or as a solid compound, by the presence of certain complexing ions. Periodates and tellurates are the commonest such groups:

Malatesta, in 1941[64] obtained a stable periodate copper[III] complex with both chemical oxidation of cupric hydroxide using persulphate, and electrolytic oxidation of copper, followed by addition of periodite. The resultant compound was diamagnetic and was analysed chemically to be tri-valent. Malaprade[65] also stabilized the tri-valent state by the presence of potassium periodate, KIO_4. He produced firstly a cuprate, $KCu(OH)_4$ by oxidizing copper hydroxide with a $KOH/K_2S_2O_8$ mixture, and then added periodate to give a stable complex compound.

Lister[66] made essentially the same compound, $Na_7Cu(IO_6)_2 \cdot 16H_2O$, as

well as the corresponding tellurate, $Na_9Cu(TeO_6)$, using sodium hypo-
chlorite as oxidant. A cupric chloride/sodium hydroxide mixture was
added to a 1.5 M NaOCl solution and the blue precipitate which formed
initially, turned rapidly black, giving what Lister presumed to be
either a tri-valent oxide, Cu_2O_3, or hydroxide, $Cu(OH)_3$. Addition of
an acidified sodium periodate solution, NaH_3IO_6, gave a brown compound
after standing for a short time. Both this precipitate and the complex
tellurate were found to contain tri-valent copper by iodide titration
and by use of their oxidation equivalent weights. It was observed that
oxygen was evolved on acidification of each precipitate and in some cases
a scarlet colour was briefly visible. This was therefore suggested to
be the colour of the Cu^{3+} ion.

To determine the amount of copper present in these compounds in
an uncomplexed state, Lister measured oxygen evolution as a result of
NaOCl decomposition both before and after addition of the complexing
agent. In the former case he found the reaction to be catalyzed by
copper, presumably as the $Cu(OH)_4^-$ ion. The rate of reaction was first
order with respect to copper. After addition of either periodate or
tellurate anions the rate of oxygen evolution was found to drop consider-
ably, and to correspond to a rate representing uncatalyzed hypochlorite
decomposition. It was therefore assumed that when virtually all the
copper existed in a complex state it was no longer an active catalyst
for the reaction.

Jensovsky prepared complex cuprates by anodic oxidation of copper
in alkaline solutions containing periodate and tellurate ions. The
maximum yield was obtained at pH 10.2, and increased with temperature.

The compounds were found to be diamagnetic, and thermal decomposition curves showed loss of water caused decomposition of the copper^{III} complex.[67]

On account of their relative stability and strong oxidative powers, complexes of tri-valent copper with periodates and tellurates can be used for the oxidimetric determination of a number of inorganic and organic compounds.[68] Titrations using standard solutions of copper^{III} are carried out in alkaline media and applications include the determination of antimony, calcium, thallium, cyanide and thiosulphate salts. Most other copper^{III} complexes which have been isolated are organic in nature. These include salts made from carborane ions, $Cu(B_{10}H_{10}CH)_2^{3-}$, a potassium bis (birueto) cuprate^{III} prepared by peroxodisulphate oxidation of $[Cu(-NHCON-)]$, and a number of peptide complexes.[52,69]

Meyerstein[70] carried out a study of the chemical properties of a tri-valent copper 'aquo' complex by radiolytic means. He reported that Cu^{III} exists in neutral solution as a $CuOH^{2+}$ (aq.) or $Cu(OH)_2^+$ (aq.) ion and decomposes by the mechanism

$$2CuOH^{2+} \longrightarrow 2Cu^{2+} + H_2O_2 \qquad (45)$$
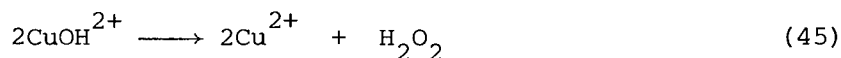
Such ions were made by the reaction

$$Cu^{2+} + OH \longrightarrow Cu^{III} \qquad (46)$$

in radiolyzed solutions, followed by a tri-valent copper oxidation of water:

$$Cu^{3+} + H_2O \longrightarrow CuOH^{2+} + H^+ \qquad (47)$$
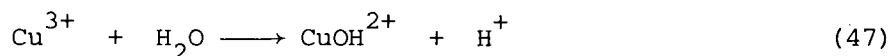
It was stated that Cu^{III} will be formed by any oxidant which can lower

the redox potential of the couple $Cu^{III} - Cu^{2+}$ in the presence of various ligands.

The potential for the reaction

$$Cu^{2+} \longrightarrow Cu^{3+} + e^- \tag{48}$$

is quoted by Latimer to be 1.8 V in alkaline medium at 25°C.[75]

Shams El Din and co-workers[71] reported the formation of the sequioxide Cu_2O_3 by alternate anodic/cathodic polarization of a copper electrode in 0.1 N sodium hydroxide solutions, at oxygen evolution potentials, i.e. at 0.76 V. The reaction involved was thought to be:

$$2Cu(OH)_2 + 2OH^- \longrightarrow Cu_2O_3 + 3H_2O + 2e^- \tag{49}$$
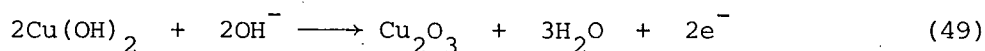
In an extensive study to investigate the formation of the sesquioxide by various wet and dry chemical methods and electrochemically, Delhez[72] calculated the redox potential for Cu^{3+} formation as 2.3 V. This was derived from the equation:

$$Cu(OH)_3 + e^- + H^+ \rightleftharpoons Cu(OH)_2 + H_2O \tag{50}$$
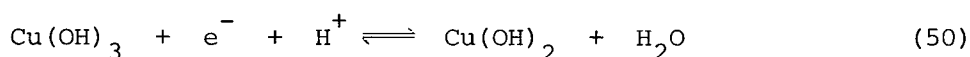
for which E = 1.57 - 0.054 pH (pH < 13.9).
Approximate Eh-pH diagrams for the Cu^{2+}/Cu^{3+} oxidation-reduction system are given, and this study was later used as a basis for the extension of existing diagrams of the $Cu-H_2O$ system given by Pourbaix and co-workers[73] to take account of tri-valent copper and its derivatives.[74]

Delhez concluded from his work that the only feasible method of preparing Cu_2O_3 was by oxidation of cupric hydroxide in alkaline solution using either hypochlorite or peroxodisulphate ions as oxidant. While

electrochemical methods may produce Cu_2O_3 in some cases, the yield is usually insufficient to carry out meaningful analysis. He thus suggested that all previous workers who had used oxidants including hydrogen peroxide, peroxomonosulphuric acid, chlorine or bromine, had actually produced either copper peroxide, CuO_2 or cuprous oxide, Cu_2O, which in many cases had been confused with the sesquioxide.

Using a method of potassium persulphate oxidation of cupric sulphate in alkaline solutions (pH 12.0 - 13.0) similar to that outlined by Scagliarni and Torelli[57] Delhez produced a red amaranth precipitate which contained, but was not exclusively, tri-valent copper oxide. It was therefore presumed to be a mixture of $Cu(OH)_2$ and $Cu_2O_3/Cu(OH)_3$, with a ratio of $Cu^{II}:Cu^{III}$ dependent on the rates of the relevant reactions:

$$2Cu(OH)_2 + 2OH^- + S_2O_8^{2-} \longrightarrow 2Cu(OH)_3 + 2SO_4^{2-} \qquad (51)$$

$$4Cu(OH)_3 \longrightarrow 4Cu(OH)_2 + O_2 + H_2O \qquad (52)$$
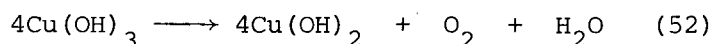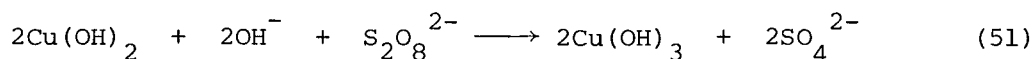
The reaction forming copper^{III} was catalyzed by the presence of Ba^{2+} ions, in agreement with the previous findings of Scholder and Voelskow.[61] It was also found that the compound existed in an unidentified state of hydration, fluctuating between Cu_2O_3 and $Cu(OH)_3$, apparently at random.

For the case of Cu^{II} oxidation with hypohalogen solutions, Delhez found the results of previous studies to be confusing. Several workers gave strong evidence to show Cu^{III} had been produced, but it was often difficult to ascertain whether it was Cu_2O_3, or a tri-valent cuprate. Scholder and Voelskow, for example, had found that oxidation of a bi-valent cuprate with hypobromite produced a copper^{III} compound which they assumed to be a cuprate. Delhez concluded it was probably Cu_2O_3. In

less alkaline solutions, using cupric hydroxide as a starting material they obtained a different product, having a maximum Cu:available O_2 ratio of 1:0.3, but in his own work Delhez never produced more than 35% Cu^{III} by any method.

Consideration of the potentials of OI^-, OBr^- and OCl^- ions showed that only the latter has a sufficiently high value to give a good yield of Cu^{III}. Barium ions also catalyzed this hypochlorite reaction and a mechanism similar to that given by Prokopchik (equations 34 - 37) was thought to be operative. The catalytic action of Ba^{2+} ions was due to an increase in the redox potential of the oxidizing solution in which they were present.

CHAPTER TWO

Experimental

2.1 Scope of the Present Investigation

A number of studies have been made to investigate the leaching characteristics of molybdenite in alkaline solutions of sodium hypochlorite, as outlined above; but very little work has been done to determine the oxidation behaviour of copper sulphide minerals when exposed to similar solutions. As one of the principal objectives of finding a hydrometallurgical process suitable for treating molybdenite concentrates is to enhance by-product molybdenum recovery from porphyry ores, it would seem to be of prime importance to gain an understanding of any reactions occurring between copper and the lixiviant, and hence to delineate any steps necessary to prevent copper dissolution. This would ensure optimum conditions for a selective molybdenum leach, and at the same time prevent copper losses, both of which are fundamental to an economically feasible process.

Previous work in this department was carried out by Ismay,[76] to research the possibilities of extracting molybdenum from copper-molybdenum sulphide rougher concentrates, by means of a sodium hypochlorite leach. A proposed process flowsheet was drawn up on the basis of successful molybdenite leaching; and although molybdenum recoveries were high, it was found that some copper was also extracted by the hypochlorite.

The object of the present work at its inception was thus to determine the extent of the reaction between various copper sulphide minerals

and sodium hypochlorite under similar conditions to those found by Ismay to be optimum for molybdenum extraction, with a view either to preventing copper from entering solution, or to finding a suitable method for its removal:

1) Initial experiments revealed that the dissolution of copper in hypochlorite solutions at pH 9.0 only occurred in the presence of carbonate buffer reagents but that removal of the carbonate had undesirable side effects.

2) This led to an investigation of the kinetics of copper catalysed hypochlorite decomposition reactions. The nature of decomposition products was also considered.

3) The mechanism of reaction between sodium hypochlorite and copper was studied on a general basis, with and without the presence of carbonate, to increase an understanding of the effects observed during leaching.

4) As the study progressed it became apparent that the presence of copper sulphide minerals adversely affected molybdenum extraction at pH 9.0. A number of experiments were thus carried out at pH levels of 5.5 - 6.0, which had previously been suggested to be optimum for molybdenum recovery in an investigation by the U.S. Bureau of Mines.

5) Further work in alkaline solutions was done using synthetic minerals and this highlighted the fact that certain elements normally present as impurities were detrimental to high levels of molybdenum extraction. A thermodynamic study of the stability of various molybdate compounds in aqueous solution was thus carried out and several Eh-pH diagrams were constructed.

6) It was then necessary to determine the leaching characteristics of certain calcium minerals in hypochlorite and other chloride-containing solutions.

7) Consideration of all the above factors led finally to establishing the necessary conditions for maximum molybdenum extraction while minimizing hypochlorite decomposition and copper dissolution.

2.2 Materials

2.2.1 Natural minerals

Chalcocite, Cu_2S, and covellite, CuS, were obtained as massive samples from Butte, Montana. Chalcopyrite, $CuFeS_2$, was purchased in massive form from Ward's Natural Science Establishemnt, and obtained as a ground concentrate from the Phoenix mine, British Columbia. Large pieces of ore were crushed in rod and ball mills and wet ground to pass a -200 mesh sieve in preparation for leaching as powdered samples. Small pieces of broken ore were polished on a 'Texamat' 5μ diamond polishing wheel for surface examination before and after leaching. In some cases samples were mounted in epoxy resin (Epon 828/DETA) prior to polishing.

Molybdenite, MoS_2, was obtained as a high grade concentrate from Alice Arm, British Columbia, ground to pass a -325 mesh sieve.

Calcite, $CaCO_3$ was obtained in powdered form from the Micro-ionized company (Texas) Ltd.

Mineral Analysis

Wet chemical analysis gave the following results:

i) Covellite:

Element	Weight %
Cu	58.80
Fe	3.00
Ca	0.16
Zn,Ni	Trace (<0.05%)

This indicates a CuS content of 88.3%.

ii) Chalcocite:

Element	Weight %
Cu	64.50
Fe	4.80
Ca	0.12
Pb	0.06
Zn	Trace

This gives a Cu_2S content of 81.0%.

iii) Chalcopyrite:

Element	Weight %
Cu	31.6
Fe	29.20
Ca	1.51
Zn,Ni	Trace

This gives a $CuFeS_2$ content of 93.3%.

Qualitative X-ray analysis using the Scanning Electron Microscope showed that the covellite and chalcocite samples also contained significant amounts of silicon, and traces of sodium and potassium. X-ray diffraction studies gave good agreement with literature values. Silica, SiO_2 and

pyrite, FeS_2 were the only other major peaks obtained (Tables 1-3).

(All diffraction studies reported for copper k_α radiation)

| d Å | I/I$_o$ - species identified | | | d Å | I/I$_o$ - CuS |
	CuS	FeS$_2$	SiO$_2$		(Reported)
8.11	7			8.18	7
4.26			36		
3.33			100		
3.28	9			3.29	14
3.21	27			3.22	28
3.04	64			3.05	67
2.80	83			2.81	100
2.72	100			2.72	56
2.70		84			
2.31	10			2.32	10
2.04	13			2.04	7
1.90	28			1.90	25
1.89	68			1.89	75
1.73	33			1.74	34
1.63		100		1.63	3
1.55	31			1.55	37
1.46	6			1.46	6
1.35	8			1.35	7
1.27	6			1.28	9
				1.09	10

Table 1: X-ray Diffraction Pattern for Covellite Sample

| dÅ | I/I$_o$ - species identified | | dÅ | I/I$_o$ - Cu$_2$S |
	Cu$_2$S	SiO$_2$		(Reported)
4.25		35	3.77	10
3.35		100	3.60	10
			3.39	30
			3.31	10
			3.26	20
			3.05	20
2.86	30		2.88	20
2.74	15		2.73	10
2.63	12		2.67	10
			2.54	10
			2.47	20
2.39	60		2.40	70
2.28	21		2.20	20
1.96	79		1.97	80
1.87	100		1.87	100
1.82		17	1.69	40
1.70	36		1.64	20

Table 2: X-ray Diffraction Pattern for Chalcocite Sample

dÅ	I/I$_o$ - species identified		dÅ I/I$_o$ CuFeS$_2$	
	CuFeS$_2$	SiO$_2$	(Reported)	
3.35		100		
3.03	100		3.03	100
1.90	50		1.87	40
1.87	78		1.86	80
1.59	49		1.59	60
1.57	19		1.57	20
			1.32	10
1.23	26		1.20	30
1.10	43		1.08	60

Table 3: X-ray Diffraction Pattern for Chalcopyrite Sample

iv) Qualitative spectrographic analysis of the molybdenite showed it to have the following analysis:

Element	Weight %	Element	Weight %
Al	0.10	Mg	0.01
Bi	0.05	Mn	0.001
Ca	0.50	Mo	58.52
Cr	0.01	S	39.02
Cu	0.05	Si	1.00
Fe	0.50	Sn	0.20
Pb	0.01	Ti	0.03

Traces (<0.001%) of gold, silver and strontium were also detected.

2.2.2 Synthetic minerals

i) Cupric sulphide analyzing 99.9% CuS was purchased from the Rocky Mountain Research Co., Denver, Colorado.

ii) Cuprous sulphide, analyzing 99% + Cu_2S was obtained from Matheson, Coleman & Bell, East Rutherford, N.J. Small amounts of these materials were crushed in a pestle and mortar, and screened to give 100% -200 mesh material.

iii) Reagent grade molybdenum disulphide from BDH Chemicals, Poole England was used. This analyzed as:

Element	Weight %
Mo	53.4
S	35.6
Si	$\simeq 10$

iv) Molybdenum disulphide analyzing >98% MoS_2 was purchased from the Venton Company, Danvers, Mass.

2.2.3 Sodium hypochlorite

The source of hypochlorite used in all experiments was a household bleach sold under the trade name 'JAVEX,' and containing 50 - 60 g/l in the as-purchased condition. Suitable dilutions with water were made to this stock solution to obtain the desired concentration for leaching experiments.

2.2.4 Chemical reagents

All other chemicals used were reagent grade.

2.3 Apparatus

The majority of leaching experiments were carried out in a 1 litre glass vessel fitted with 4 Teflon baffles at equi-distant points around its inner surface. Solution agitation was effected using a turbine type titanium stirrer coated with a thin layer of 'MICROSTOP' paint. Agitator and vessel dimensions together conformed to a 'standard tank' configuration. The stirrer was mechanically powered with a Fisher-Dyna mix motor, and the agitation rate was measured for each experiment using a Tecklock chronometric hand tachometer.

The leaching vessel was placed in an open water bath which contained a Micro-set thermo-regulator manufactured by the Precision Scientific Company. After setting a desired temperature, this unit was capable of maintaining it to $\pm 0.1°C$.

The pH of leaching solutions was monitored during each run by placing electrodes inside the glass vessel. In initial experiments a Beckman Expandomatic pH meter was used; this was later replaced with a Chemtrix pH controller (Horizon Ecology Co., Chicago, Ill.) In combination with an ASCO 2-way teflon coated solenoid valve, this controlled the pH automatically to within ± 0.2 pH units.

The experimental apparatus is outlined schematically in Figure 5.
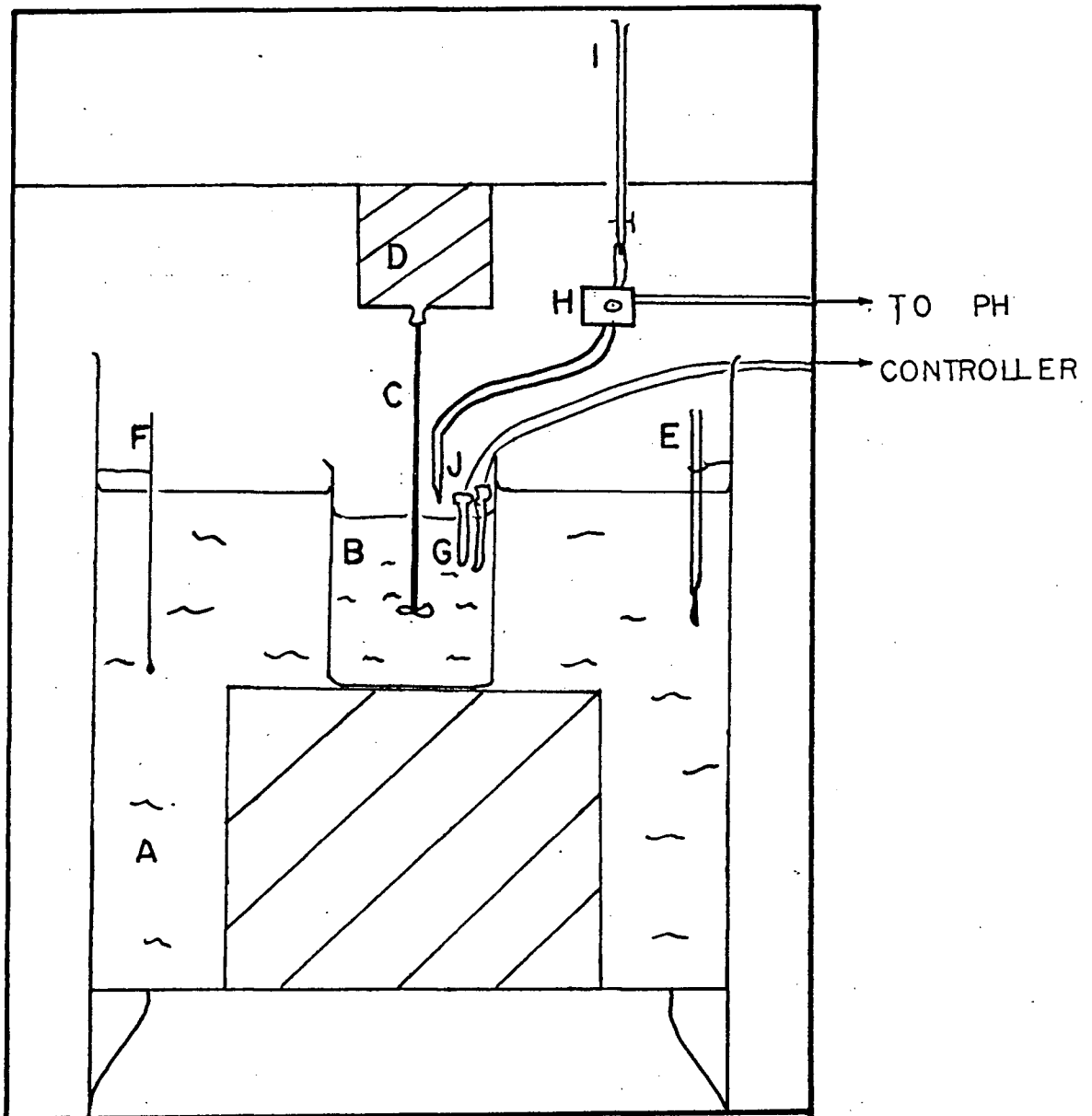
A Water bath

B Glass leaching vessel

C Ti mechanical stirrer

D Fisher Dyna Mix

E Thermo-regulator

.F. Thermometer

G pH electrodes

H 2 way solenoid valve controlling addition of buffering solution from

I burette, to leaching vessel via

J capillary tube

Figure 5: Experimental leaching apparatus.

2.4 Experimental Procedure

2.4.1 Leaching experiments

Experiments leaching copper minerals, and copper sulphides and molybdenite together, were carried out in the following way:

A required amount of JAVEX reagent was added to 700-800 ml distilled water and the resultant pH ($\simeq$12.5) was lowered to the required value by addition of 1 N HCl. In cases where carbonate buffering was employed, Na_2CO_3 and $NaHCO_3$ were added in ratios calculated from pka values to buffer the solution at the necessary pH level. The solution was made up to 1 litre, transferred to the leaching vessel and placed in the water bath. Slow agitation was imparted until the solution had attained the temperature of the surrounding water, then 'blank' samples were taken for hypochlorite and metal analyses. Agitation was stopped while mineral samples were introduced: where copper sulphides and molybdenite were leached simultaneously they were added as two separate powders, and in some cases addition of one sample was not made until the reaction with the other had proceeded for several minutes. The agitation was then increased. Samples were taken at timed intervals by solution with-drawal through a pipette, and filtered using either filter paper or Gooch filter crucibles.

In experiments where no carbonate buffering was used the required pH was maintained by dropwise addition of 2 N NaOH from a burette, or, in later experiments by using the pH controller.

2.4.2 Copper^{III} preparation

Samples of copper^{III} were made by the action of sodium hypochlorite on cupric chloride using two methods:

i) A sodium hypochlorite solution of the required concentration was made up as outlined above, the pH adjusted to 9.0, and heated to 35°C. 8 g of $CuCl_2 \cdot 2H_2O$ (equivalent to 3 g/l Cu) were then added, and the pH maintained by NaOH addition.

ii) 8 g of $CuCl_2 \cdot 2H_2O$ were dissolved in water and the pH raised to 9.0 with NaOH, to give a blue precipitate of cupric hydroxide. A measured volume of stock hypochlorite solution was then added. After an initial rapid rise in pH this dropped, and had to be maintained at a value of 9.0 as before.

After about 5 minutes agitation the solution was completely black, and after a period of brief standing to allow some settling of the contained precipitate this was filtered, collected and dried in a desiccator.

Samples made in the presence of sodium carbonate required a longer period of agitation to give complete precipitation of the copper, but the method used was essentially the same (method (i) was found to be preferable).

2.5 Analysis

2.5.1 Chemical analysis

i) Copper: The amount of copper contained in leaching solutions was determined using a Perkin Elmer 306 spectrophotometer with an air-acetylene flame and a wavelength of 324.7 nm, after suitable dilutions with

distilled water, and by comparison with a calibration curve from known standards. To determine any effect caused by the presence of large amounts of chloride in these solutions, test analyses were done using standard solutions swamped with excess NaCl, but no differences were detected.

Copper in ore samples was determined by atomic absorption analysis after dissolution in a warm mixture of concentrated hydrochloric and nitric acids, and subsequent digestion with bromine, Br_2.

ii) Molybdenum: molybdenum in leaching solutions was determined by atomic absorption spectrophotometry with a nitrous oxide-acetylene flame at a wavelength of 313.3 nm. Dilutions prior to analysis were made with a solution containing 10% aluminum chloride and 5% ammonium chloride.

iii) Calcium: $[Ca^{2+}]$ in solution was similarly determined at a wavelength of 422.7 nm using an air-acetylene flame.

iv) Sodium Hypochlorite: the hypochlorite concentration of each batch of 'JAVEX' used was accurately determined by potassium iodide-sodium thiosulphate titration as outlined in ASTM D2022-64.[77] A small sample was diluted with water, then added to an acidified potassium iodide solution and titrated against standardized thiosulphate. Starch indicator solution was added and the disappearance of its characteristic blue colour marked the end point.

Sodium hypochlorite concentrations of samples taken during leaching runs were determined by the same method, usually undiluted.

v) Sodium chlorate: the $[ClO_3^-]$ content of leaching solutions was determined by a related method, also outlined in ASTM D2022-64.[77]

The chlorate was reduced by addition of sodium bromide, NaBr, and concentrated hydrochloric acid. After dilution and addition of potassium iodide, the released iodine was titrated against standard thiosulphate as before. This gives the total concentration of (OCl^- + ClO_3) so the actual chlorate content was determined from the difference between this value and that for hypochlorite in the same sample.

vi) Chloride: the total chloride content of hypochlorite solutions both before and after leaching was found:

a) by silver nitrate/potassium thiocyanate titration, as outlined in ASTM D2022-64.[77] All the hypochlorite and any chlorate present are reduced to chloride by sodium bisulphate in the presence of dilute HNO_3. The total chloride content is then determined using a standard Volhard titration.

b) potentiometrically: this method is essentially the same as a) above, but the endpoint of the silver nitrate titration was more accurately determined by immersion of a platinum electrode into the solution, and making a graphical plot of potential vs. [$AgNO_3$].

2.5.2 Instrumental analysis

i) Minerals. Qualitative analysis for powdered samples and massive mineral pieces was carried out using the X-ray energy analyzing facility of the scanning electron microscope. Quantitative X-ray analysis for the ground concentrates was obtained with a Philips X-ray diffractometer, and for surface analysis of massive samples the electron probe micro-analyzer was used.

ii) Copper^{III}.

a) Infra-red spectrophotometry: samples of the black compound were prepared in mull form with fluorolube oil, and run through a Perkin Elmer 621 grating infra-red spectrophotometer.

b) Magnetic susceptibility: a small sample was weighed on a 'Gouy' magnetic balance, both in and out of a magnetic field. More detailed measurements of the gram magnetic susceptibility were also made.

c) Ultra-violet visible spectrophotometry: leaching solutions were examined in the UV/visible regions using a Perkin Elmer ultra-violet spectrophotometer with a path length of 2 - 10 nm.

d) X-ray diffraction patterns were obtained using the diffractometer.

CHAPTER THREE

Results and Observations

3.1 Sodium Hypochlorite Leaching of Copper Sulphide Minerals

Experiments were carried out to determine the oxidation behaviour

of certain copper sulphide minerals in solutions of alkaline sodium

hypochlorite. The selected minerals were covellite, CuS, chalcocite,

Cu_2S, and chalcopyrite, $CuFeS_2$. These are three of the most commonly

occurring copper ores associated with molybdenum bearing porphyries.

3.1.1 Leaching of ground concentrates in the presence of carbonate

10 g samples of each mineral, previously ground to pass a -200

mesh sieve were agitated in solutions containing 7 - 8 g/l hypochlorite

at a temperature of 35°C and a pH value of 9.0, buffered with a sodium

carbonate/bicarbonate mixture. The ratio of $HCO_3^-:CO_3^{2-}$ was 14:1 and

10.7 g/l total carbonate were used initially.

A small amount of copper was found to be rapidly dissolved in

each case. Small variations were observed between the three minerals,

but the copper content of solution averaged 100 - 130 ppm and represented

2 - 3% of the copper introduced into the system (Figure 6, Tables I - III).

Copper concentration did not maintain a constant value with respect to

time, and after attaining a maximum initial value it fluctuated in an

apparently random manner. Leaching solution separated from the mineral
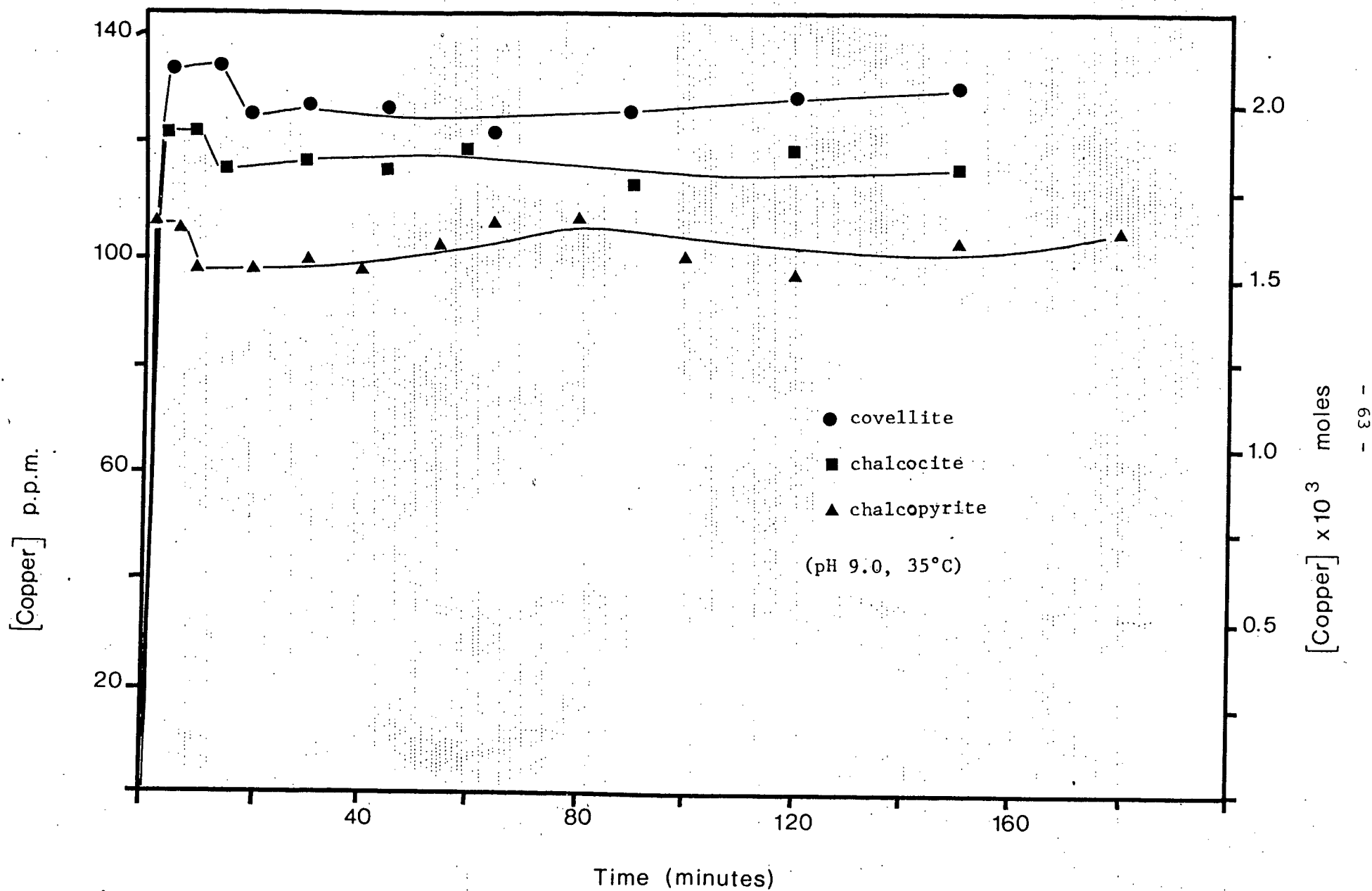
Figure 6: Oxidation of copper sulphide minerals by NaOCl.

slurry in the early stages of agitation maintained an almost constant

copper content (Figure 7, Tables IV, V). All solutions showed deep blue

colouration: significantly more so than standard copper sulphate solutions

containing an equivalent amount of copper. Solutions left to stand over-

night were observed to deposit a black precipitate which, after a further

time period of 1 - 3 days, was accompanied by loss of the characteristic

blue colouration of the solution. Subsequent analysis revealed these

clear solutions to contain negligible amounts of copper. Heating to

50 - 60°C also produced a black precipitate and this was found to be

copper oxide by analysis using the Debye Scherrer powder method for X-ray

diffraction. Insufficient of the material put down from filtered leach-

ing samples could be collected to carry out meaningful analysis. Dilution

of samples with water also produced a black precipitate in some cases.

Sodium hypochlorite consumption was found to vary slightly for

each of the three minerals: equal samples of $CuFeS_2$, CuS and Cu_2S con-

sumed 10%, 27% and 18% of the initial hypochlorite present respectively.

One mole of copper thus consumed 0.28 M, 0.4 M and 0.22 M OCl^- in the

respective minerals (Figure 8, Tables I - III).

3.1.2 Effect of carbonate removal

Experiments were carried out in which no carbonate/bicarbonate

reagents were added to the leaching solution, to determine the effect, if

any, on copper solubility. The pH was maintained instead with a sodium

hydroxide buffer, added dropwise from a burette, to counteract the

observed drop in pH. All other conditions were identical to those of
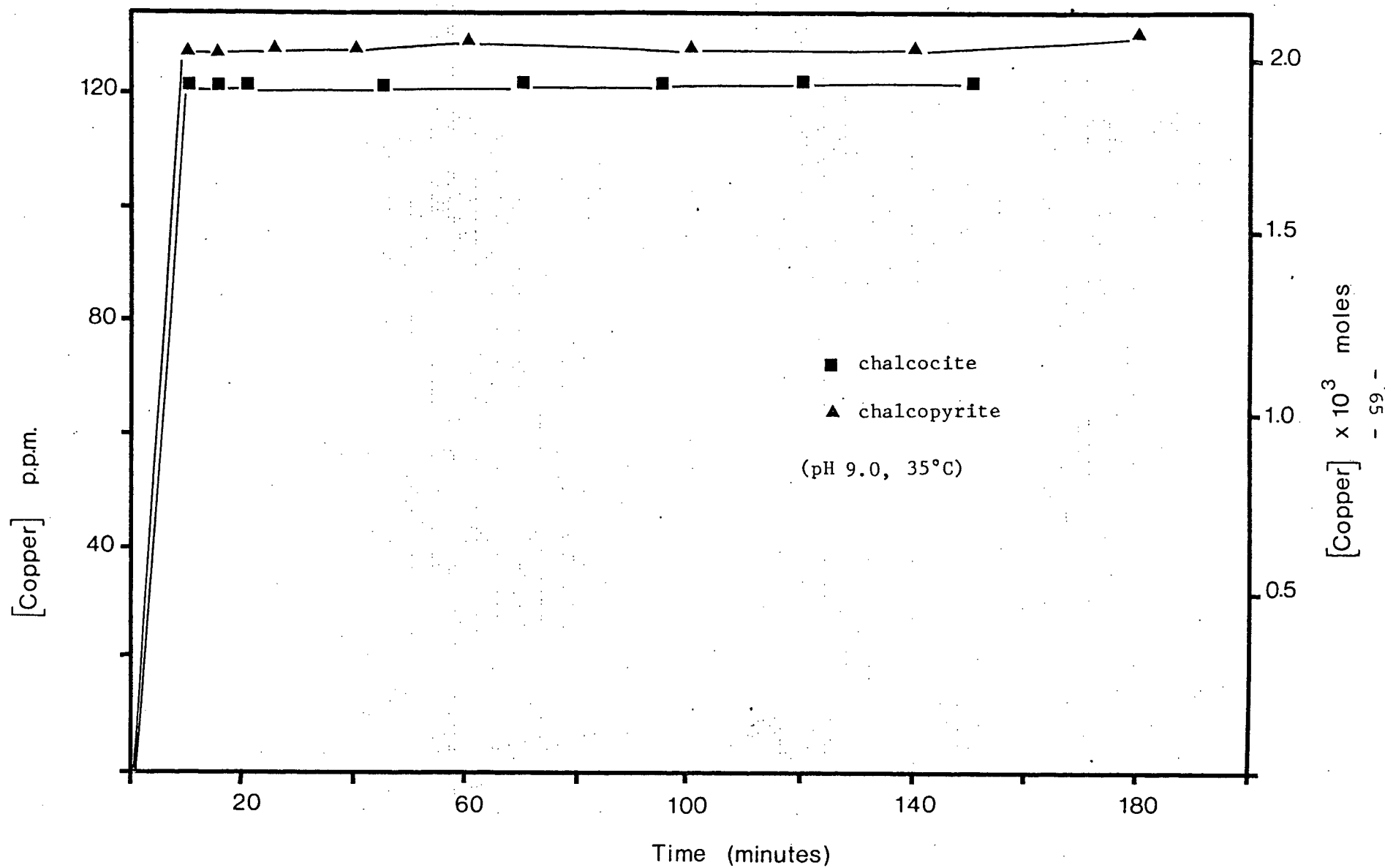
Figure 7:   Effect of separating leaching solution from mineral slurry.
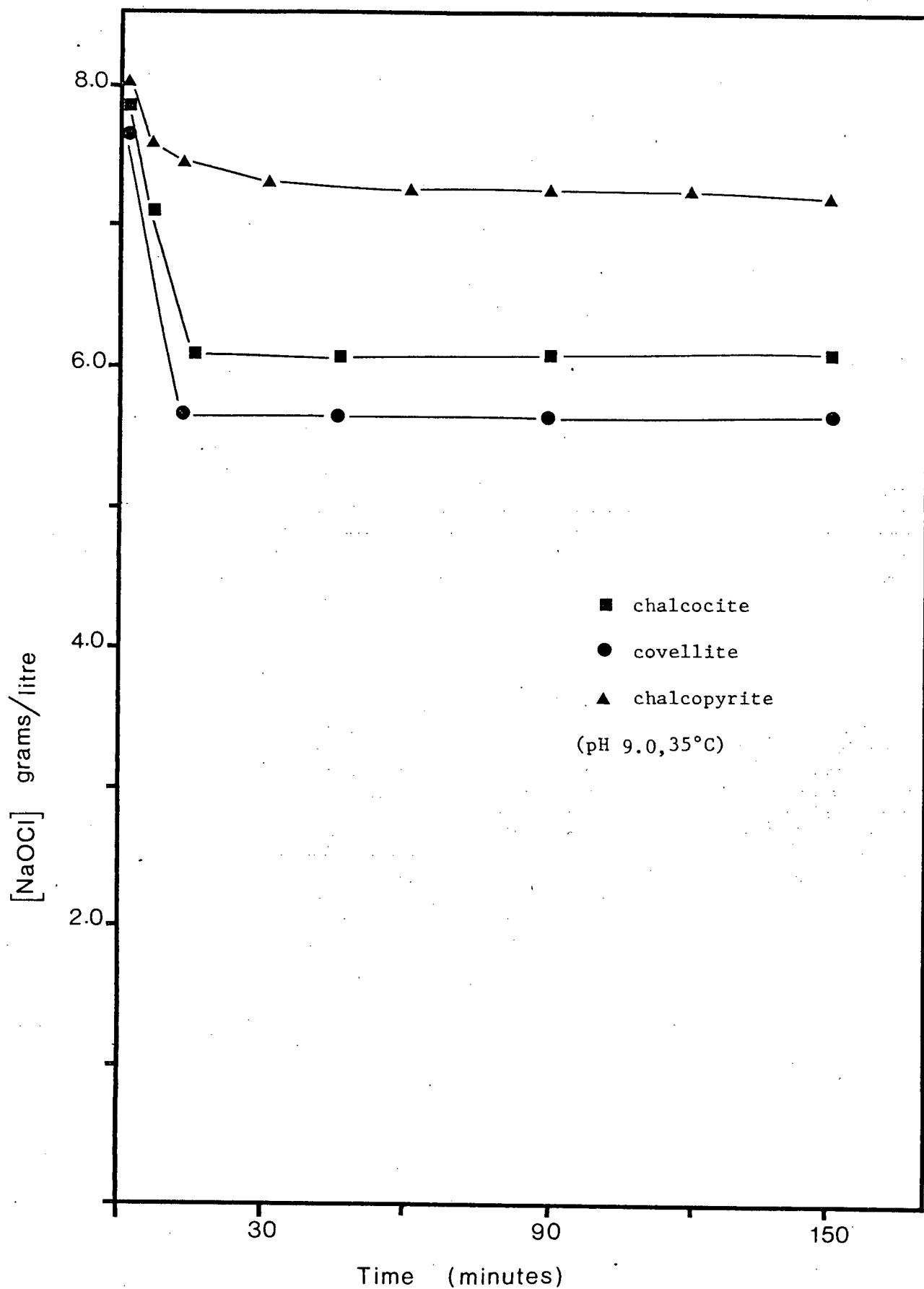
Figure 8: NaOCl Consumption during copper sulphide leaching.

previous runs.

The analytical results showed this carbonate removal from the system to have a very significant effect:

i) Less than 1 ppm copper was dissolved from a 10 g sample of each mineral.

ii) The solution pH was found to drop rapidly as agitation commenced, and this was accompanied by sodium hypochlorite decomposition. The actual rate of decomposition was a function of the particular copper mineral being leached:

CuS produced 50% decomposition in 9 minutes

$CuFeS_2$ produced 50% decomposition in 12.5 minutes

Cu_2S produced 50% decomposition in 82 minutes.

Total decomposition occurred in all three cases, but the rate of decomposition was not linear (Figure 9, Tables VI - VIII).

3.1.3 Leaching of synthetic copper sulphides

Decomposition was presumed to be caused by catalytic action of copper at the mineral surface. To determine whether the observed differences in the rate of reaction were attributable to copper alone, samples of cuprous and cupric sulphide powder were leached under identical conditions to those used for the natural minerals. In the presence of carbonate results were almost identical to those of covellite and chalcocite with respect to both copper dissolution and hypochlorite consumption. In the absence of carbonate no copper was detected in solution and the
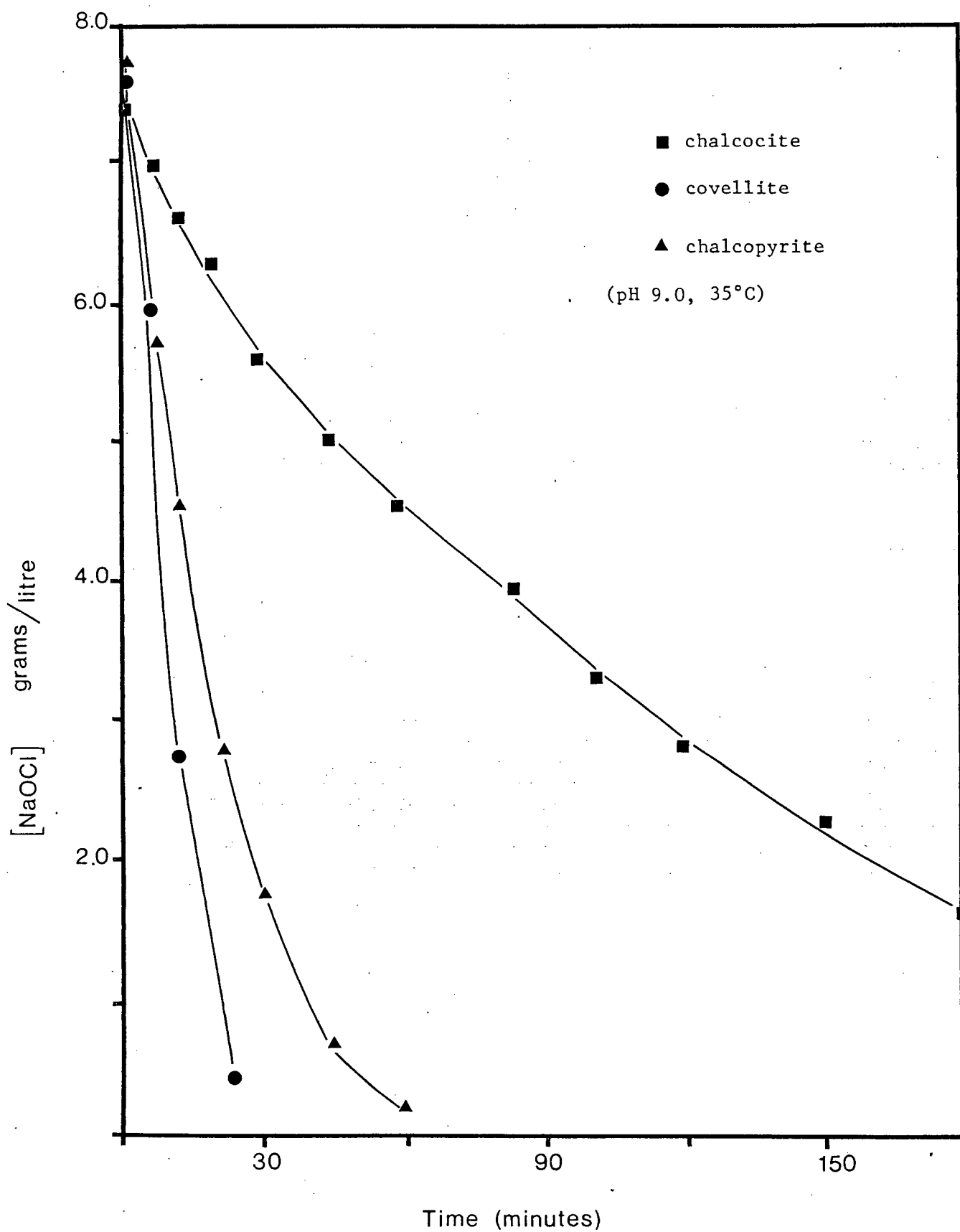
Figure 9: Effect of carbonate removal on NaOCl decomposition.

rate of hypochlorite decomposition was constant in each case (Tables XI, XII; Figure 10). This was linear and gave 50% of the initial OCl^- content remaining after 52 and 54 minutes for Cu_2S and CuS respectively.

3.1.4 Determination of decomposition products

Leaching solutions were analysed for sodium chlorate content to determine whether this was a decomposition product, as given by the equation:

$$3OCl^- \longrightarrow ClO_3^- + 2Cl^- \tag{53}$$
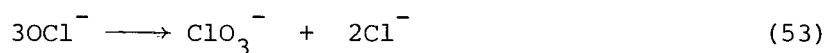
or whether oxygen was the only product:

$$2OCl^- \longrightarrow O_2 + 2Cl^- \tag{54}$$

It was found that some chlorate was produced in all three cases, but that the results for the different minerals were very variable: covellite and chalcopyrite both showed a decrease in the percentage chlorate present in solution as hypochlorite decomposition progressed, being 13.7% and 36.15% respectively after 5 minutes, and decreasing to 9.57% after 45 minutes for covellite and 20.22% after 90 minutes for chalcopyrite (Figure 11, Tables VI - VIII). Chalcocite on the other hand, which produced a much slower rate of catalyzed decomposition, showed the reverse trend in that 8.7% of the decomposition product was chlorate after 5 minutes, and this increased to over 23% after 150 minutes leaching. These general patterns were observed in several different runs, although the absolute values varied slightly in each experiment.
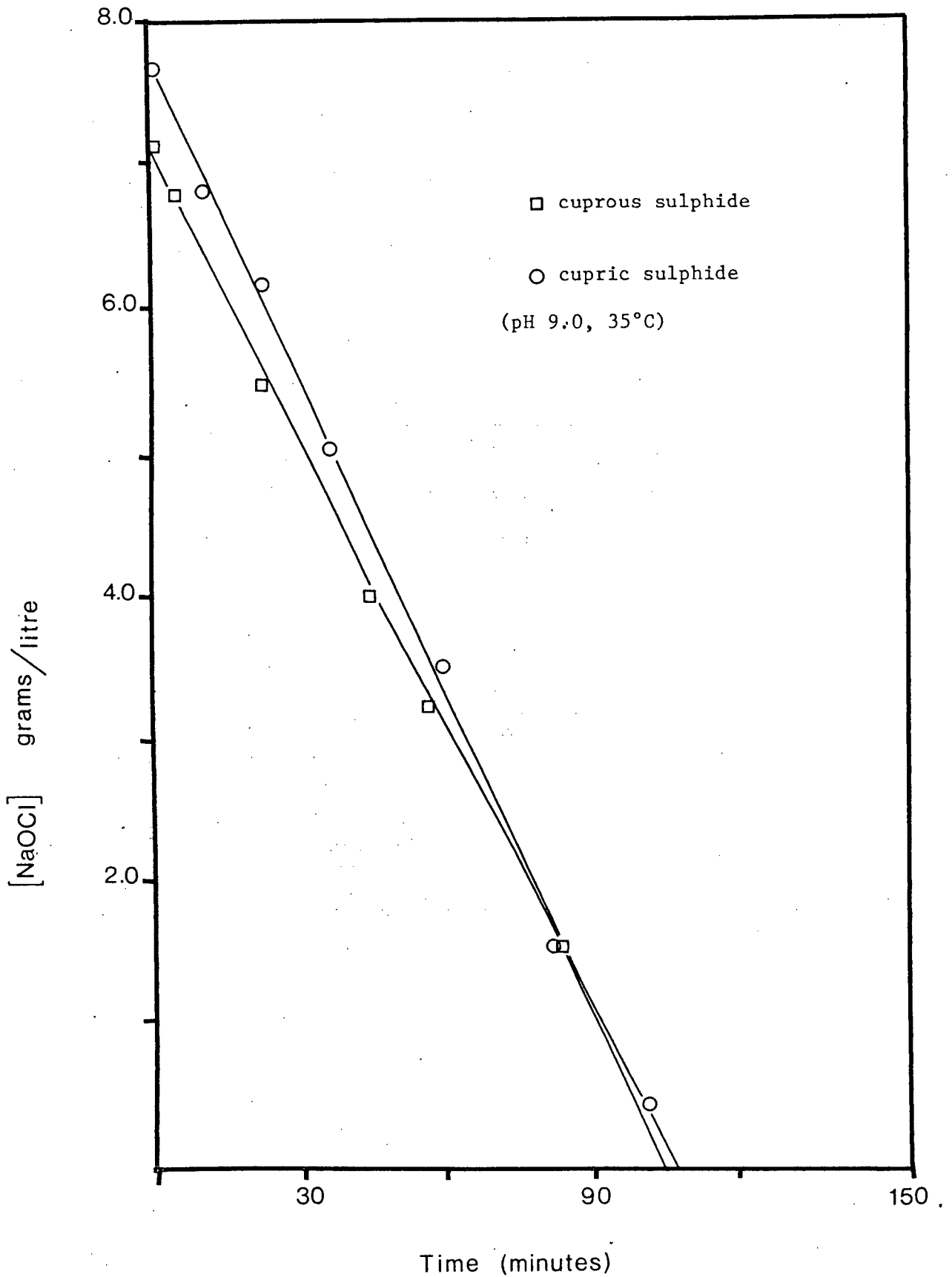
Figure 10: NaOCl decomposition during leaching of synthetic copper Sulphides.
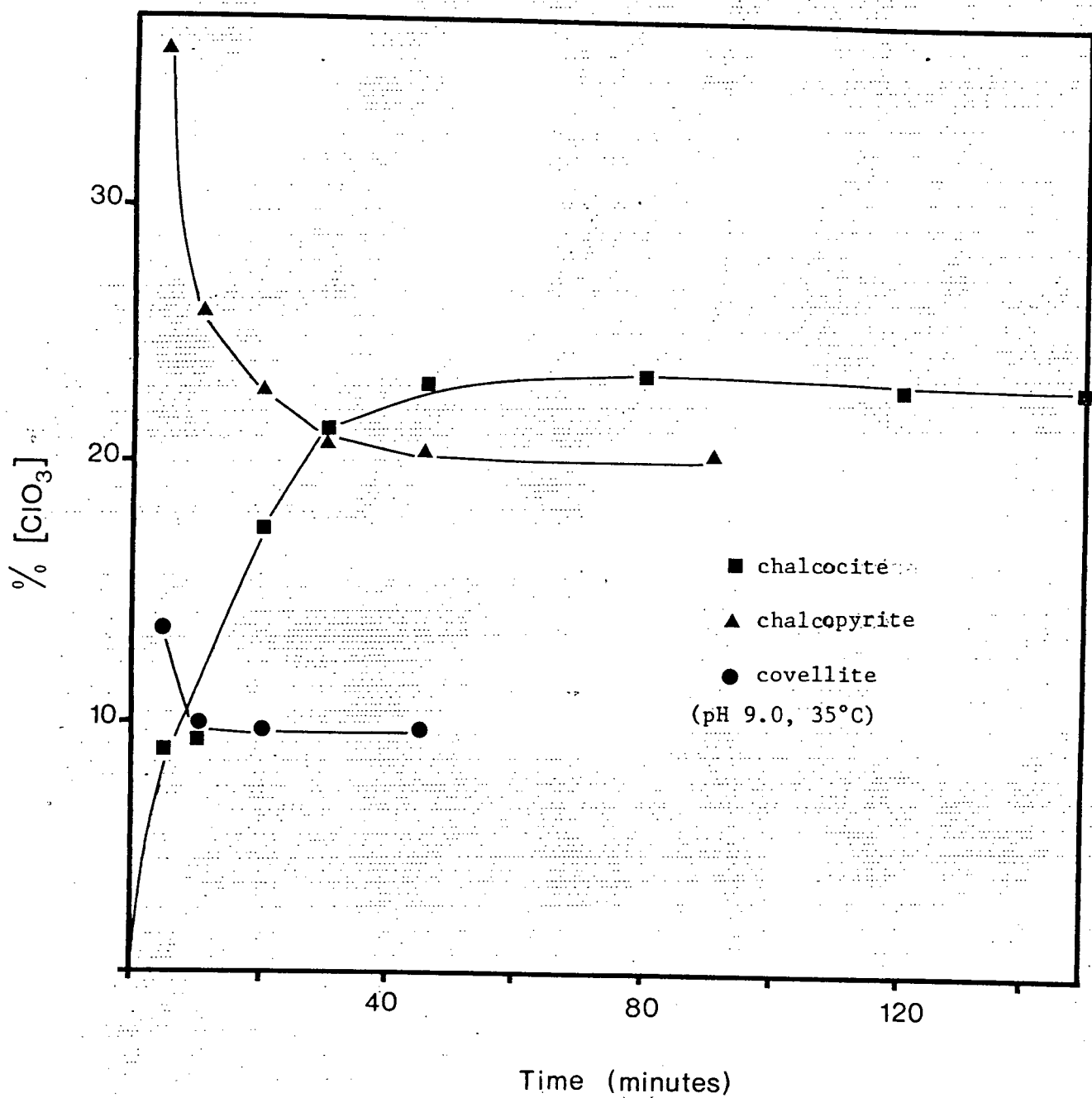
Figure 11: NaClO$_3$ production during NaOCl decomposition.

3.1.5 Sodium hypochlorite leaching of massive samples of copper sulphide minerals

Small pieces of chalcocite, covellite and chalcopyrite were polished on one face and immersed in solutions of sodium hypochlorite at pH 9.0 for varying amounts of time. Slow agitation was maintained in most cases and the experiments were carried out with and without the presence of carbonate. Mineral surfaces were examined before and after leaching using the scanning electron microscope, the electron microprobe and optical microscopy; and to this end specific areas were marked so that quantitative analysis could be carried out:

i) Chalcocite. Immersion in carbonate solutions at pH 9.0 for periods of up to 3 hours produced little difference to the polished surface, although some tarnishing was observed. Approximately 0.003 g/l copper were detected in solution (3 ppm) from a total surface area of about 6 cm^2. Electron microprobe examination of marked areas revealed that in most cases both the copper and sulphur content at the surface had decreased, with an overall increase in the Cu:S ratio. In a few small areas an increased sulphur content was observed giving a decreased Cu:S ratio (Table IX).

Samples immersed into carbonate containing hypochlorite solutions for longer periods, in excess of fifteen hours, began to form dark green areas on the surface. These areas grew in magnitude with time and after one week the mineral was entirely covered with a green deposit, which analysis showed to have a significantly increased copper content. The deposit was not water soluble, and resembled malachite, $Cu_2(OH)_2CO_3$.
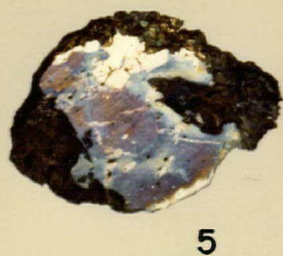
PLATE 1

1) Cu_2S, unleached

2) after 3 hours in hypochlorite/carbonate solution

3) after 24 hours in hypochlorite/carbonate solution

4) after 3 weeks in hypochlorite/carbonate solution

5) after 12 hours in hypochlorite solution (no carbonate)

6) after 3 days in hypochlorite solution (no carbonate)

7) after 1 week in hypochlorite solution (no carbonate)

Effect of NaOCl $\pm$ Na_2CO_3/$NaHCO_3$ on massive chalcocite samples at pH 9.0, 35°C.

(Plate I). After 3 weeks immersion in hypochlorite solution, small black patches were observed on the green coating covering the chalcocite sur-face.

Agitation of solutions containing 7 - 8 g/l hypochlorite, but no carbonate, produced similar tarnishing of the chalcocite surface, and after about 12 hours a powdery green deposit formed in certain areas. Within 3 days the entire surface was green, and after 1 week a black deposit covered most of the sample.

ii) Covellite. CuS was observed to have a more rapid reaction than Cu_2S when exposed to both carbonate-containing solutions and hypo-chlorite alone. In the former case the polished surface lost its shine within 10 minutes and white patchy areas were visible. After 4 hours agitation the surface was covered by a white deposit. Probe analysis showed areas with different leaching characteristics to be present:

a) areas with an increased Cu:S ratio caused by a large decrease in sulphur content and a relatively small decrease in copper,

b) areas with a significantly increased sulphur content and hence a decreased Cu:S ratio. Subsequent washing in carbon tetra-chloride, CCl_4, removed this 'excess' sulphur and suggested it was an elemental sulphur deposit (Table X).

After exposure to carbonate solutions for longer periods, the entire covellite surface was covered by a dark green deposit similar to that formed on the chalcocite. Gradual dissolution of copper occurred to give a deep blue solution containing up to 100 ppm Cu. After 2 - 3 weeks standing this solution lost its characteristic blue colour within a 24 hour period and the mineral surface was simultaneously coated with
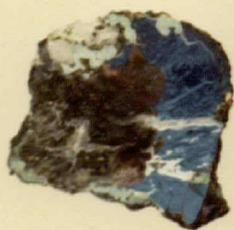
PLATE II

1) CuS, unleached.

2) after 10 minutes in hypochlorite/carbonate solution.

3) after 15 hours in hypochlorite/carbonate solution.

4) after 1 week in hypochlorite/carbonate solution.

5) after 3 weeks in hypochlorite/carbonate solution.

6) after 5 minutes in hypochlorite solution (no carbonate).

7) after 15 hours in hypochlorite solution (no carbonate).

8) after 1 week in hypochlorite solution (no carbonate).

Effect of $NaOCl \pm Na_2CO_3/NaHCO_3$ on massive covellite samples at pH 9.0, 35°C.

a very black deposit (Plate II). This phenomenon was found to be quite reproducible, although the time to precipitation varied slightly for different samples.

Covellite samples were rapidly tarnished by sodium hypochlorite solutions containing no carbonate, with the appearance of brown patches within 10 minutes. A powdery green deposit developed within 12 hours and covered the entire surface after about 15 hours exposure. This substance was found to have a significantly increased copper count (Table X) and was similar in appearance to cupric hydroxide.

After 1 week a dark brown/black deposit had developed on top of the green. It was 'flaky,' and easily removable, unlike the precipitate produced by carbonate solutions. The copper contents of both black deposits were similar to those of the green layers which they superceded.

iii) <u>Chalcopyrite</u>. Immersion into 'unbuffered' hypochlorite solutions produced a tarnishing of the $CuFeS_2$ surface, and several brown patches were observed to form. The entire sample was covered by a brown coating after 2 weeks standing.

Samples exposed to carbonate solutions underwent little change: some tarnishing of the polished surface was observed and several dark brown patches appeared after long standing.

SEM examination showed that both treatments produced a similar surface coating. Probe analysis indicated a slight increase in copper and a corresponding decrease in sulphur at the surface. No green material appeared on samples left in either solution for periods of up to 4 weeks.

3.1.6 Variation of total carbonate content during the leaching of ground copper sulphide minerals

The surface studies reported above, together with the observed dependence of copper dissolution and hypochlorite decomposition on the presence of $Na_2CO_3/NaHCO_3$ in the leaching system, indicated that these reagents played a significantly more important role than had been initially supposed when a carbonate mixture was added as a buffer component. Several experiments were thus carried out in which the total carbonate content of the system was varied from 0.55 g/l $[CO_3^{2-}]$ to 10.0 g/l $[CO_3^{2-}]$ during the leaching of covellite.

This was found to have a rather remarkable effect on the behaviour of both copper and hypochlorite. As $[CO_3^{2-}]_T$ increased, the amount of copper initially taken into solution increased in an almost linear manner and varied from 6 ppm with 0.55 g/l $[CO_3^{2-}]$ to 125 ppm with 10 g/l $[CO_3^{2-}]$ as shown in Figure 12 a,b and Table XIII. This value of dissolved copper represented a peak concentration which occurred within the first five minutes of leaching and then dropped to a slightly lower level. The second value was maintained for a finite period of time and was apparently a function of the amount of added carbonate. It was followed by a further rapid drop in the copper concentration, accompanied by equally rapid decomposition of the hypochlorite, which had previously maintained a constant value (Figure 13, Table XIII). In experiments using 5 g/l $[CO_3^{2-}]$ and above, the copper content remained at a second 'plateau' level after hypochlorite decomposition, but those cases containing 0.5, 1.0 and 2.0 g/l $[CO_3^{2-}]$ showed zero copper in solution after this point.
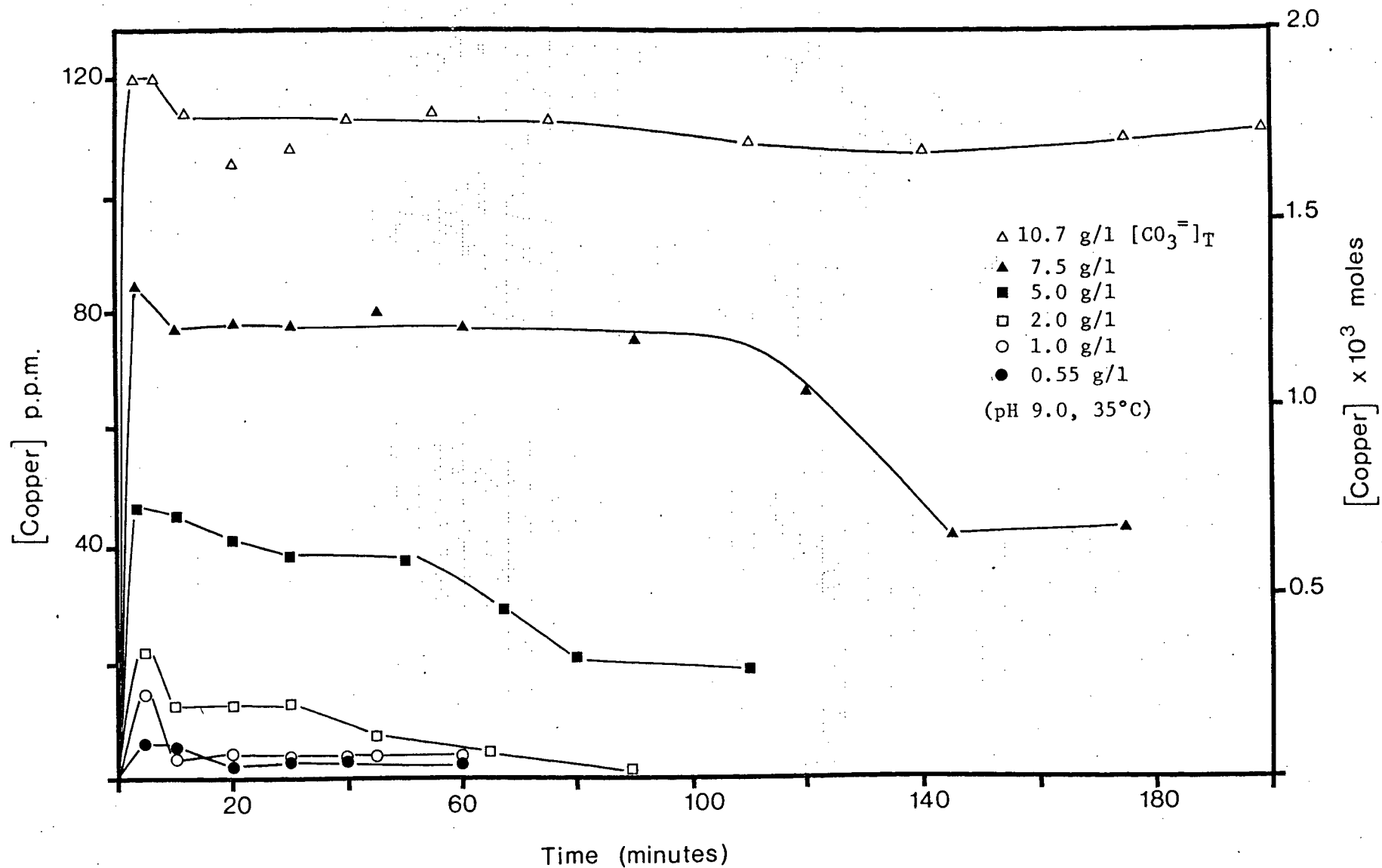
Figure 12(a): Effect of varied carbonate content on Cu dissolution from Covellite.

- 76 -
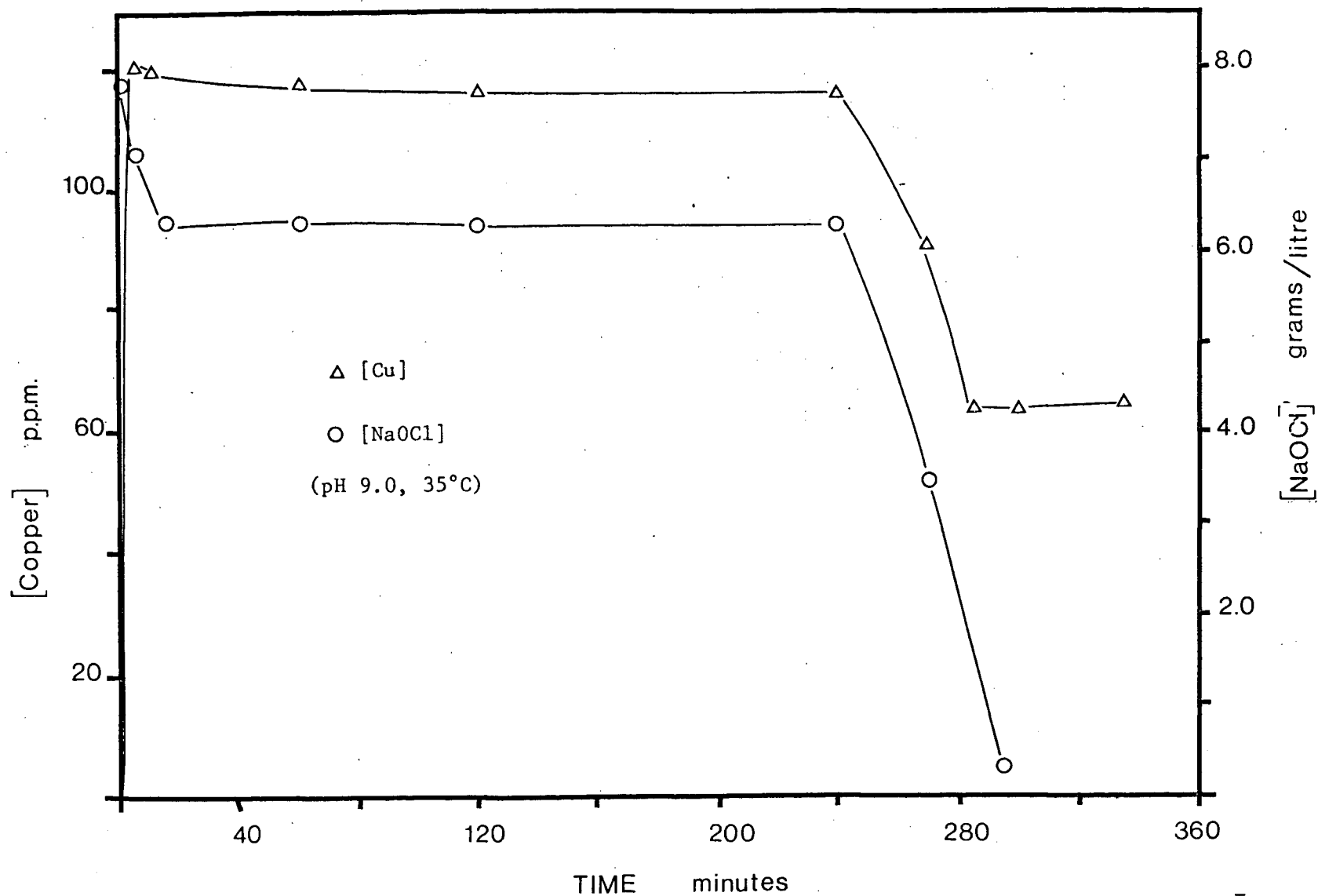
Figure 12(b): Cu dissolution and NaOCl decomposition for Covellite leaching with 10 g/l $[CO_3^=]_T$

Figure 13: Effect of varied carbonate content on [NaOCl] decomposition.
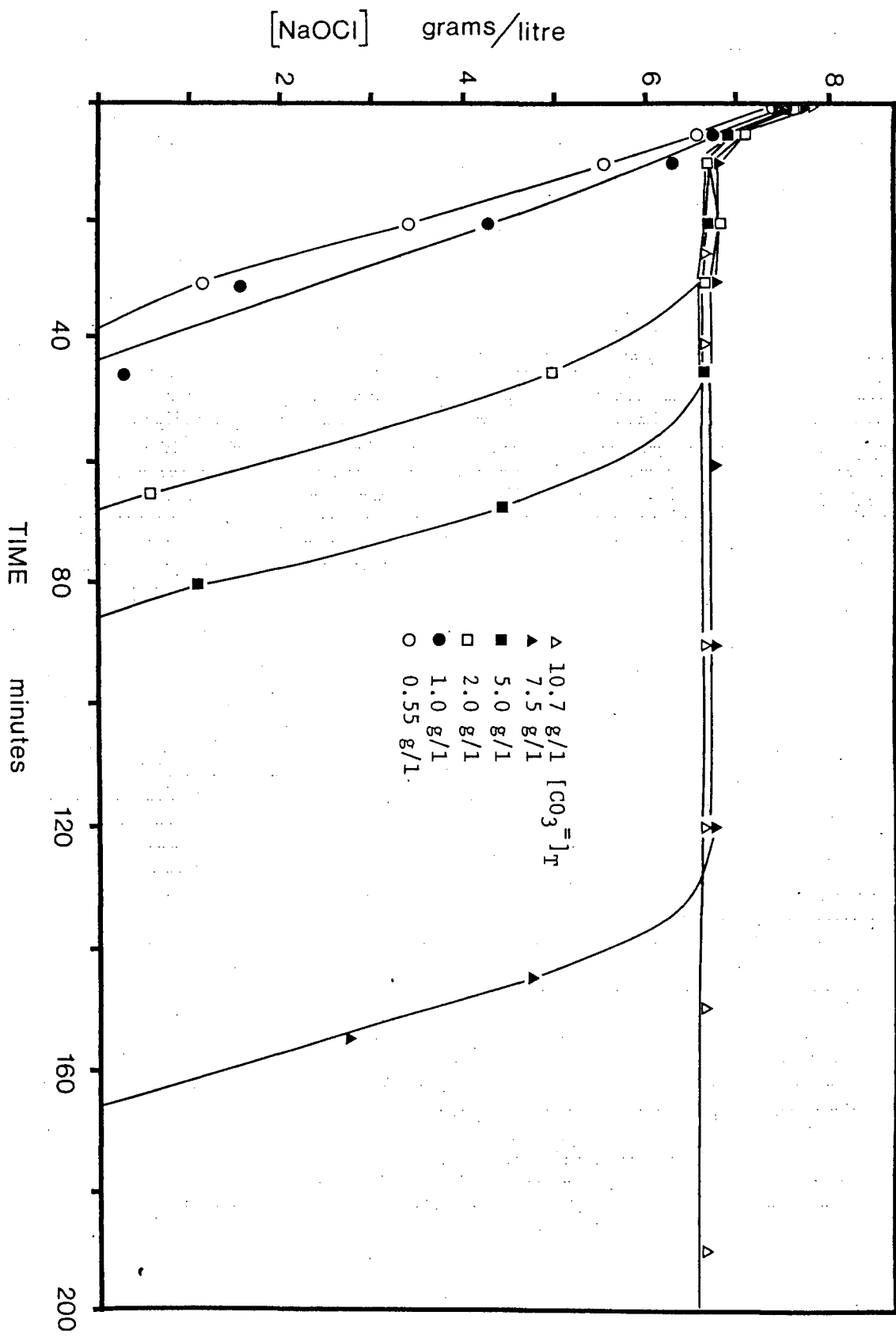
It was observed that the rate of sodium hypochlorite decomposition was constant, and not therefore a function of dissolved copper or initial carbonate concentration. In all cases the rate was almost identical to that produced during the leaching of covellite in the absence of carbonate.

To determine whether or not similar effects occurred with the other copper sulphide minerals, identical runs were carried out using chalcocite and synthetic cupric and cuprous sulphide powders. All three samples showed the dissolved copper content to pass through a rapidly attained maximum value and then to maintain a constant value for an amount of time dependent on the carbonate content of the system. This was again followed by rapid loss of copper and simultaneous hypochlorite decomposition (Figures 14 - 17, Tables XIV, XV). The necessary induction period to copper precipitation was almost identical to the analogous case for covellite being 10, 25 and 65 minutes for 1.0, 2.0 and 5.0 g/l carbonate respectively. The amounts of copper dissolved from each sample were also very similar, but the observed rates of hypochlorite decomposition were not constant. They were however consistent with the rates obtained in each case during leaching without carbonate.

3.1.7 Effect of varying the hypochlorite concentration

To determine whether an increase of hypochlorite strength had any effect on copper dissolution, a covellite sample was leached in a solution containing 20 g/l $[OCl^-]$, rather than 7 - 8 g/l concentration used previously, and in the presence of 5 g/l carbonate.

Results showed that the copper extracted had increased from
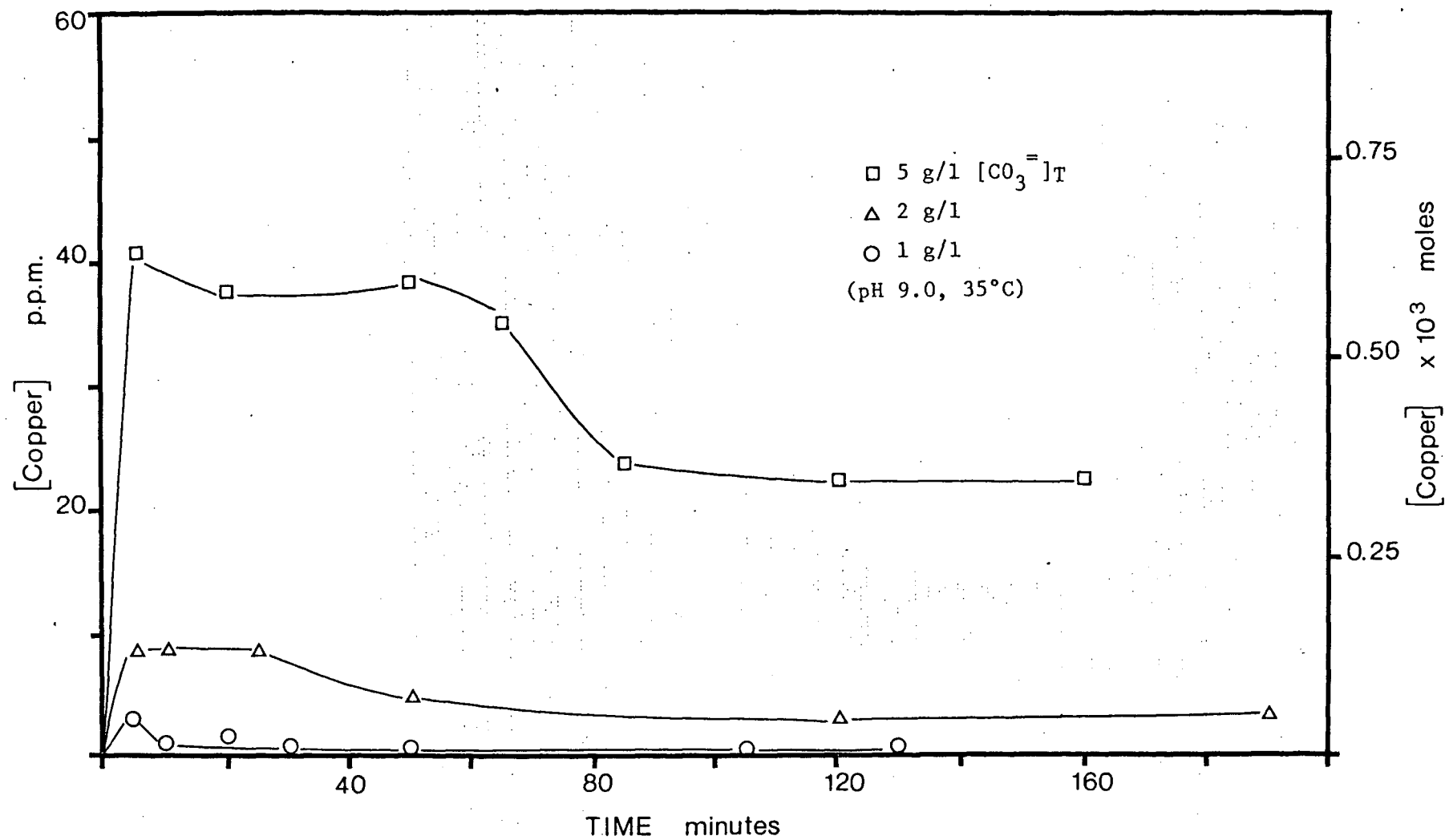
Figure 14: Effect of varied carbonate content on Cu dissolution from Chalcocite.
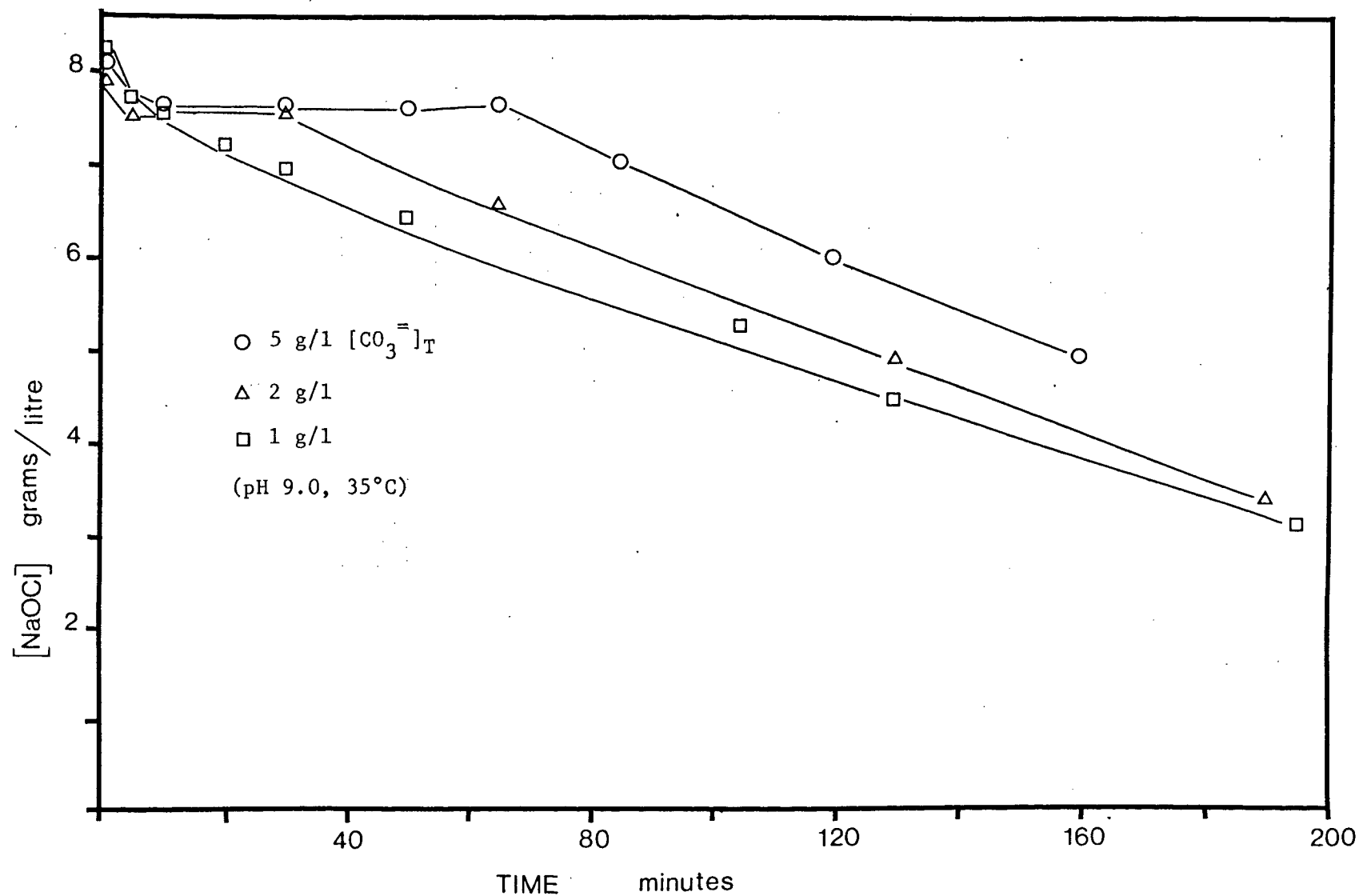
Figure 15: Effect of varied carbonate content on NaOCl decomposition during Chalcocite leaching.
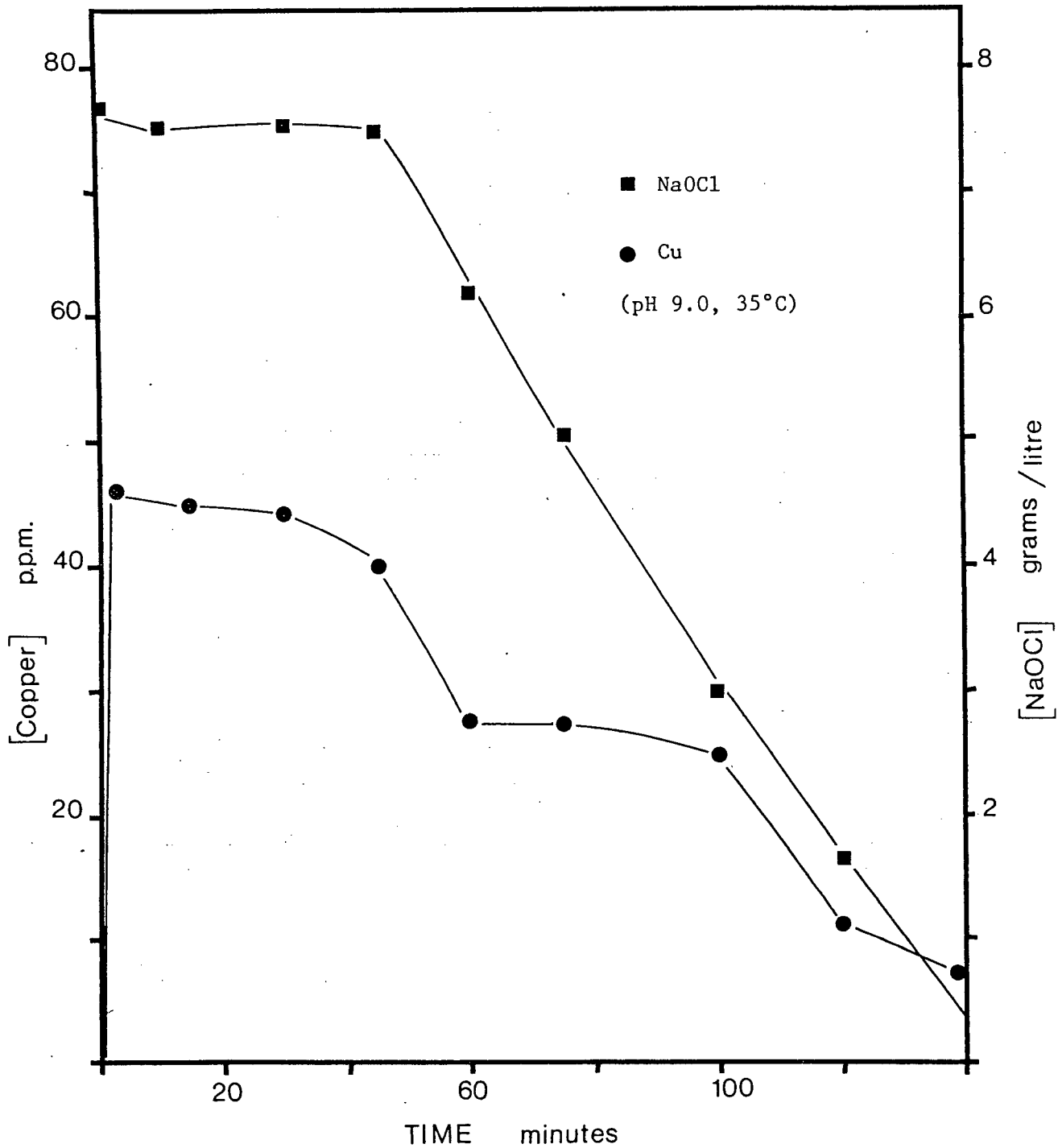
Figure 16: Cu dissolution and NaOCl decomposition for cupric sulphide leaching with 5 g/l $[CO_3^=]_T$.
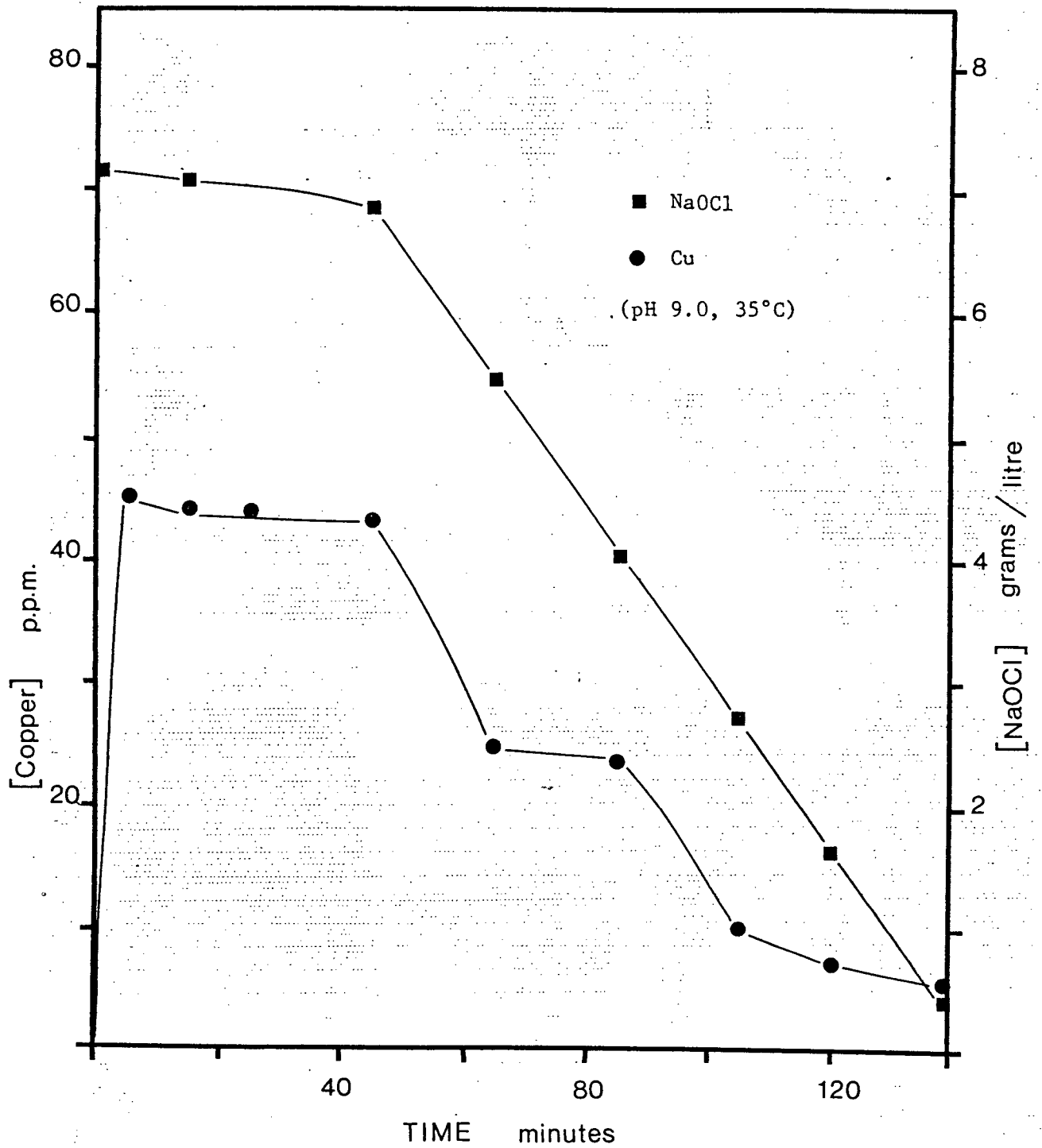
Figure 17: Cu dissolution and NaOCl decomposition for cuprous sulphide leaching with 5 g/l $[CO_3^=]_T$.

0.045 g/l to 0.1 g/l, and that this copper was held in solution for a longer period before both it and the hypochlorite concentration rapidly decreased. The rate of OCl^- decomposition was consistent with that obtained in all previous runs using covellite, and the copper remaining in solution after decomposition was the same as in all other runs using 5 g/l carbonate (Figure 18, Table XVI).

3.1.8 Effect of hypochlorite removal

Samples of covellite were agitated in sodium carbonate solutions in the absence of hypochlorite to gain a better insight into the precise role played by the oxidant.

Copper was dissolved to a level of 0.06 g/l in the presence of 10 g/l total carbonate. This gradually decreased to zero after 70 minutes agitation in cases where sodium chloride was also present, or after 30 minutes in 'carbonate only' solutions (Figure 19, Table XVII). Filtered samples taken for analysis were observed to precipitate a green powder after standing overnight. These solutions had lost their blue colouration and contained negligible amounts of copper.

As noted earlier, both in the present study and in previous work carried out by Ismay[76] filtered solutions from experiments leaching copper sulphide minerals in hypochlorite deposited a black precipitate after standing for a short time. Ismay postulated that complexing between copper and a partially oxidized sulphur species could occur, with slow transformation into sulphate in the presence of hypochlorite, causing precipitation of copper from solution as copper oxide, CuO.
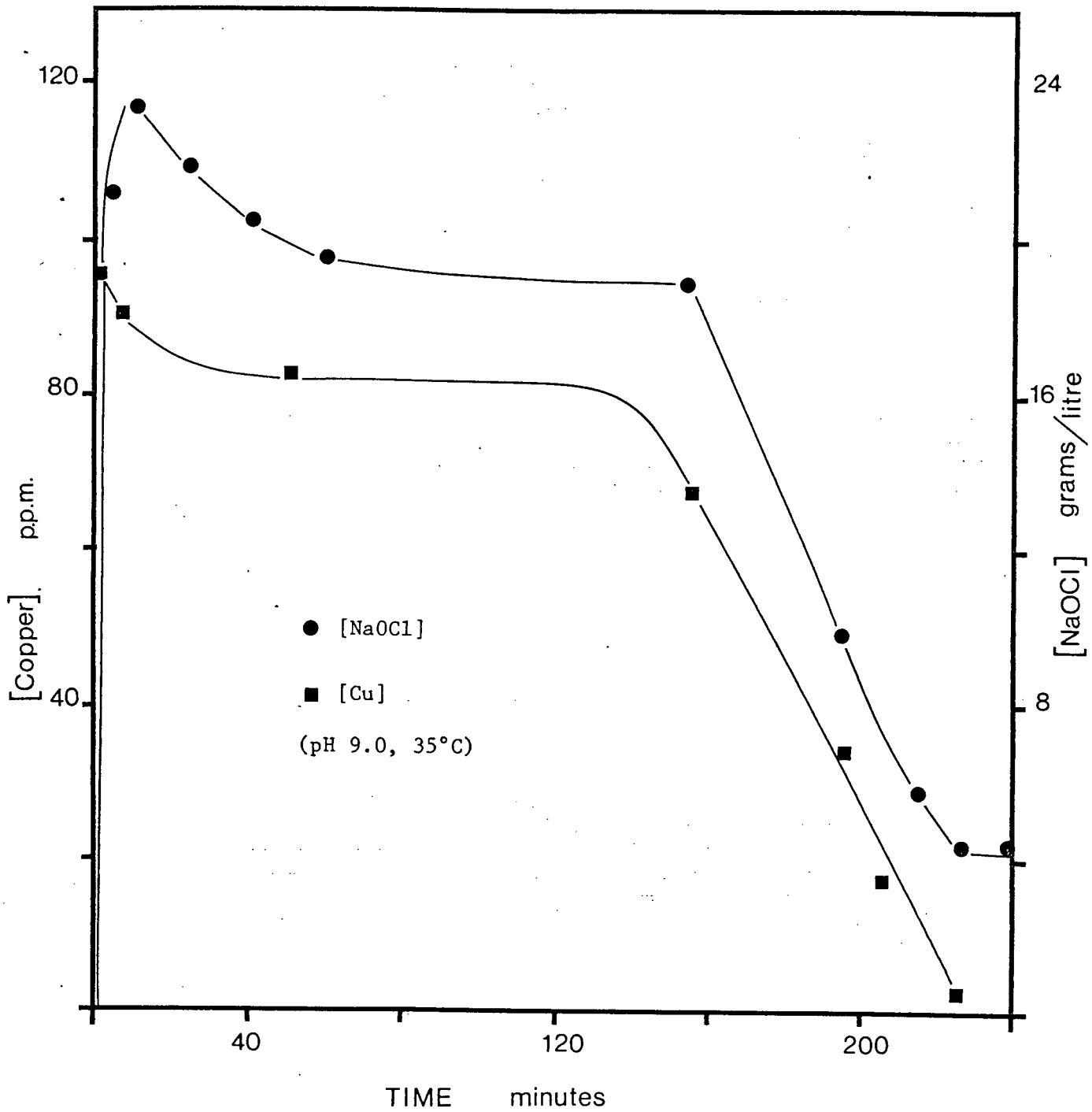
Figure 18: Cu dissolution and NaOCl decomposition from Covellite leaching with 20 g/l [NaOcl] and 5 g/l [$CO_3^=$]$_T$
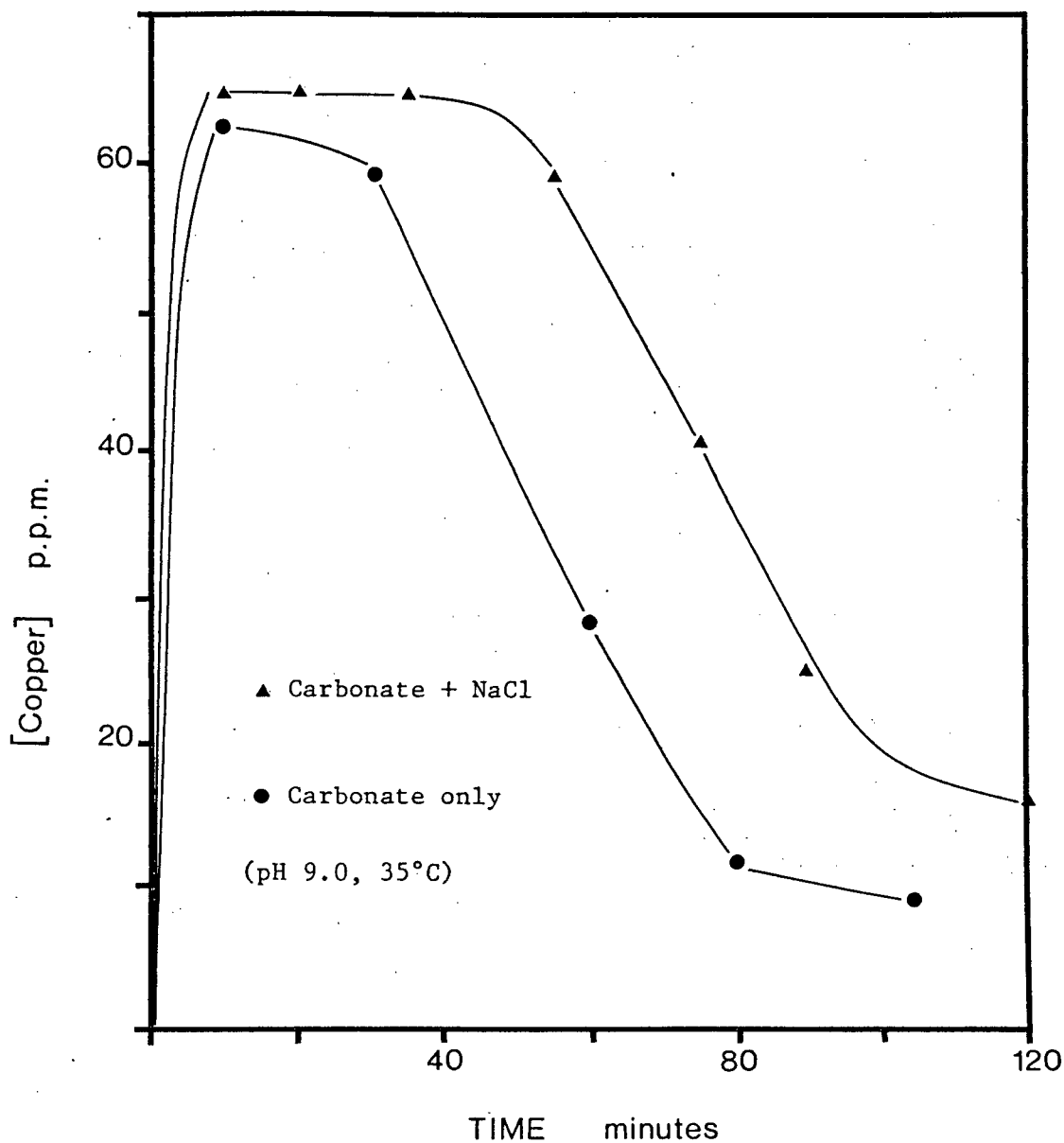
Figure 19: Agitation of Covellite in $Na_2CO_3/NaHCO_3$ solution $\pm$ NaCl.

To test this hypothesis, copper sulphate was agitated in a solu-
tion containing 7 g/l [OCl^-] and 10 g/l Na_2CO_3/$NaHCO_3$ at pH 9.0, in
sufficient amounts to give 0.1 g/l copper in solution. If less than
this dissolved it could be taken as an indication that the carbonate
could not hold this much copper in solution in the presence of fully
oxidized sulphur, i.e. as SO_4^{2-}.

It was found however that all the copper was taken into solution,
giving the same deep blue colour observed in leaching solutions.
Further experiment showed a maximum of 0.127 g/l Cu to be dissolved
under these conditions. Removal of hypochlorite from this system enabled
only 0.065 g/l of the copper to be dissolved giving a less intensely blue
solution. Samples left to stand again produced a solid precipitate:
black in the former case, and green in the latter where no hypochlorite
was present. It was also observed that this precipitation effect could
be "seeded," and addition of a small amount of this green precipitate
to freshly made copper - carbonate solutions produced complete precipita-
tion of the dissolved copper, as more green powder, within one hour.

3.2 Copper^{III}

From the above observations it is evident that hypochlorite has a
direct effect on the solubility of copper in sodium carbonate solutions,
and on the nature and colour of substances precipitated from them. The
resemblances between copper sulphide leaching and copper sulphate dissolu-
tion and the subsequent behaviour of solutions with and without hypo-
chlorite were found to be significant:

i) The copper dissolved by a given $OCl^-/[CO_3^{2-}]$ solution is constant whether the starting material is a copper sulphide mineral, or copper sulphate reagent.

ii) A lesser amount of copper is held in carbonate solutions containing no hypochlorite. This amount is identical to that found during copper sulphide leaching after hypochlorite decomposition and loss of some of the initially dissolved copper (Figures 12b, 19).

iii) The copper carbonate complex decomposes after a certain time period. Copper is thus precipitated as a solid compound which is black in hypochlorite containing solutions and green otherwise.

These factors led to the conclusion that oxidation of copper sulphides in the system under study occurs in a "two stage" process. After due consideration of the redox potentials involved, together with consultation of relevant literature, particularly studies of Lister, Prokopchik and Delhez[66,62,72] it was postulated that the observed leaching behaviour involves oxidation of copper to a tri-valent state. Thus the initial, higher copper content of the leaching solution is caused by a copper[III]-carbonate complex which subsequently decomposes precipitating a black copper[III] solid and causes simultaneous catalytic decomposition of the hypochlorite. The same cycle is then repeated for a copper[II]-carbonate complex. This also decomposes after a certain time, precipitating the remaining copper as a green powder which is presumably malachite, $Cu_2(OH)_2CO_3$ (Figure 20, Table XVII).
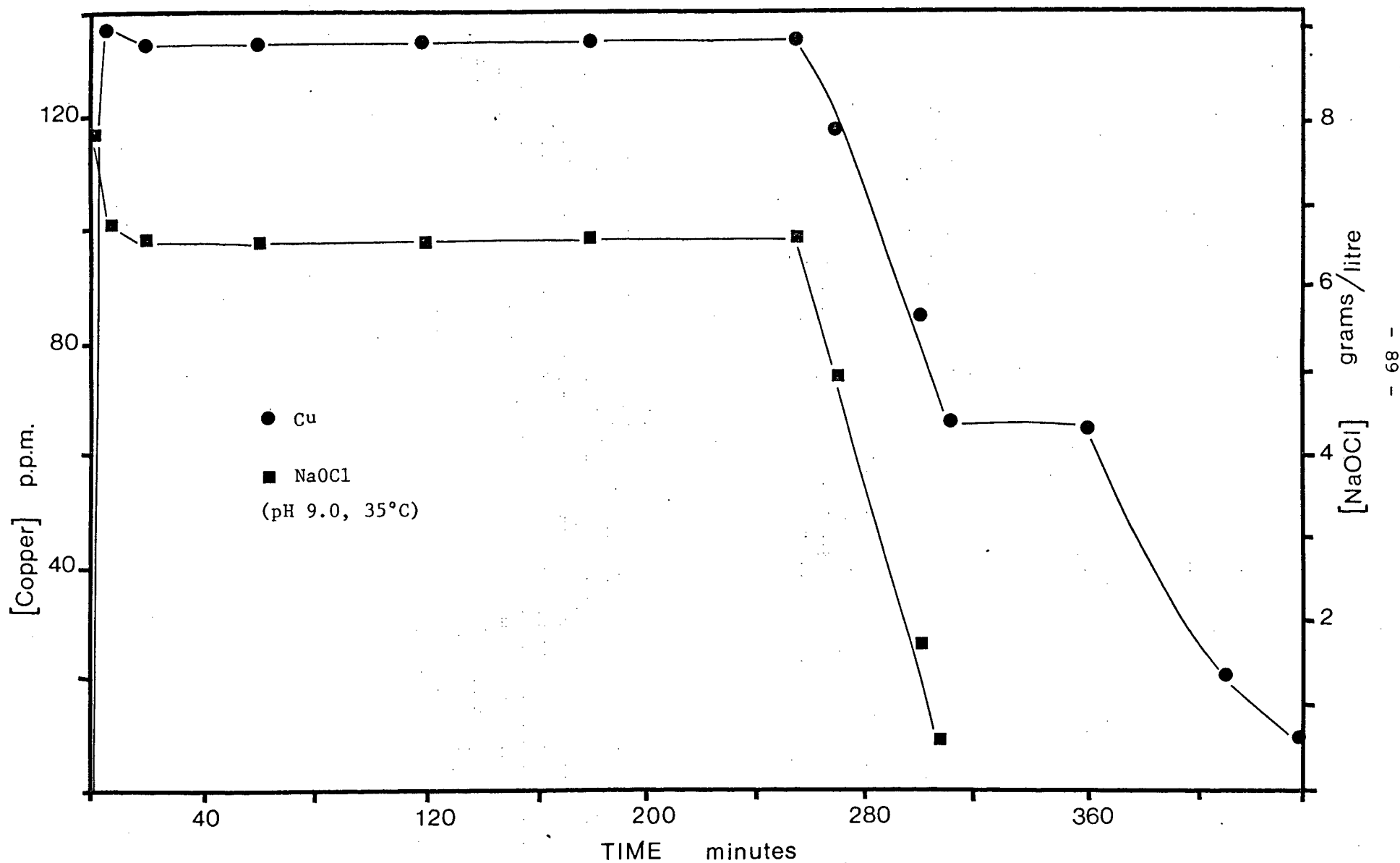
Figure 20:   Covellite leaching with 10 g/1 [CO$_3^=$]   for over 6 hours.

3.2.1 Analysis of copper[III]

A black compound similar in appearance to that precipitated from filtered leaching solutions was produced by the action of sodium hypochlorite on copper hydroxide, as outlined in Section 2.4.2. The following tests were then carried out (initially on samples made in the absence of carbonate).

3.2.1.1 Effect of acidification

A small amount of the substance was added to a solution of 5 N hydrochloric acid. This produced rapid dissolution of the powder giving a pale blue solution, accompanied by vigorous gas evolution. Passage of this gas through a calcium hydroxide solution ("limewater test") showed no cloudiness whatsoever, indicating that no carbon dioxide was present.

3.2.1.2 Evaluation of oxidation state by idometric titration

The amount of excess oxygen contained in the sample was determined from the formula

$$2Cu \equiv I_2 \equiv 2Na_2S_2O_3$$

$$\implies 1 \; ml \; N \; Na_2S_2O_3 \equiv 0.0635 \; g \; Cu$$
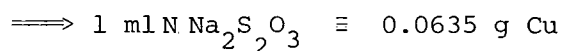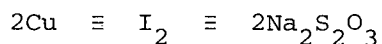
using the following method:

Iodide will reduce both Cu^{3+} and Cu^{2+} to the +1 oxidation state

with formation of a CuI precipitate. Thus a difference in the quantity

of thiosulphate titrant required in cases a) and b) below allows the

amount of Cu^{3+} to be calculated:

a) A weighed sample of the compound was added to an acidified

potassium iodide solution and the liberated iodine titrated against

standardized sodium thiosulphate.

b) An identical sample was added to dilute sulphuric acid, 2 g

of crystalline KI were dissolved and the solution was then titrated

against $Na_2S_2O_3$ as before.

Table 4: Determination of Copper^{III} by Idometric Titration

		Sample (g)	$Na_2S_2O_3$ (0.1 N) (ml)		Cu (g)		Cu %
a)	1)	0.5	47.5		0.302		60.3
	2)	0.5	47.5		0.303		60.6
	3)	0.5	47.5		0.302		60.3
				Excess $S_2O_3^{2-}$	Cu (g)	O_2 (g)	O_2 Moles
b)	1)	0.5	90.47	42.97	0.302	0.034	0.0021
	2)	0.5	91.53	44.03	0.302	0.035	0.0022
	3)	0.5	89.50	42.00	0.302	0.034	0.0021
							Av.=0.00214 M

Therefore, 0.0021 M of oxygen are present as Cu^{3+}, presumably Cu_2O_3.   Cu associated with this is 0.002 x 2/3 M = 0.00143 M or 0.091 g.

Therefore Cu_2O_3 = 0.034 g O + 0.091 g Cu = 0.125 g total, equivalent to 25% of the sample.

For comparison, the same test was done using a standard CuO sample and no difference was observed between cases a) and b).

3.2.1.3 Measurement of oxygen evolution using a mercury column

A Hg resevoir

B Hg column in graduated tube

C Sample powder

D 5N HNO_3

E Capillary tube

F Connecting tube
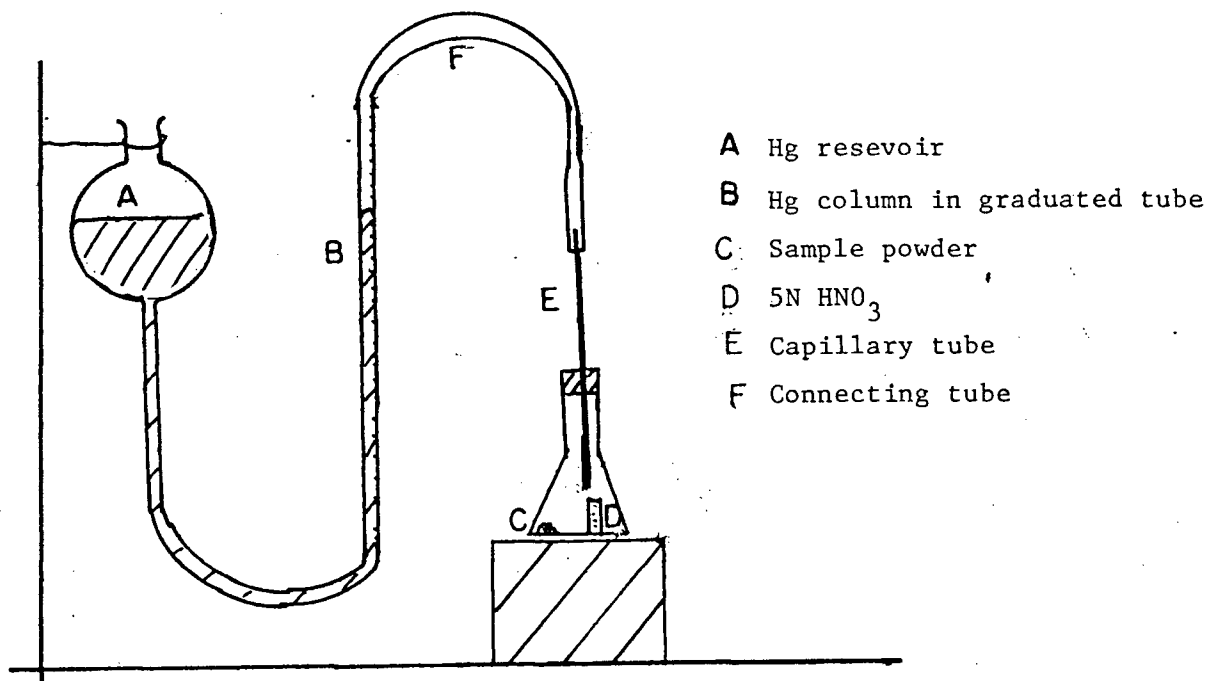
Figure 50: Apparatus for Measuring Gas Evolution

The gas evolved on acidification of a weighed sample of the black substance was measured using a mercury column connected to a mercury reservoir in a device resembling a Lunge apparatus outlined above (Figure 50). The mercury column was attached to a flask containing dilute nitric acid and the specimen sample. Evolution of gas on dissolution of each sample caused a depression of the mercury level. This was assumed to be oxygen and its volume determined by reduction to STP.

$$\text{Sample} \quad : \quad 2 \text{ g}$$

$$\text{Depression of Hg column} \quad : \quad 23.4 \text{ cm}$$

$$\text{Barometric pressure} \quad : \quad 755 \text{ mm Hg}$$

$$\text{Temperature} \quad : \quad 18°C$$

Reducing to STP:

$$V_o \;=\; 234 \times \frac{755}{760} \times \frac{273}{294} \;=\; 21.56 \text{ cm Oxygen}$$

1 mole gas at STP occupies 22.4 l

$$\text{Therefore, 215.6 mm} \quad \frac{215.6}{22400} \;=\; 0.0096 \text{ M Oxygen}$$

Copper associated with this as Cu_2O_3:

$$2/3 \times 0.0096 \;=\; 0.064 \text{ M Cu or 0.4064 g}$$

Therefore, percentage of sample which is Cu_2O_3 = 0.154 g O + 0.406 g Cu = 0.56 g or 28% of sample.

This is in reasonable agreement with the result obtained titrametrically.

Atomic absorption analysis showed the amount of copper contained in a solution obtained by acid dissolution of the black compound to vary between 60 - 64% copper. This is insufficient to account for 70 - 75% of the sample being present as pure cupric oxide, CuO, and it is likely

that some water is also present, either as adsorbed H_2O or as a hydroxy group.

3.2.1.4 Gas chromatography

Further confirmation of the presence of available oxygen in the sample was obtained using the gas chromatograph. A sample of gas evolved by acid dissolution of the black compound was passed through the chromatograph and peaks obtained had a $N_2:O_2$ ratio of 71:46 or 1.54:1. This compares to a ratio of 78:40, or 1.95:1, for a standard air sample. The former case thus showed an oxygen enrichment of about 22%.

Replications of the above analyses produced variations in the amount of excess oxygen present, but the value was always between 20 - 30%. The variations appeared to be fairly random, but two distinct trends were observed:

i) An increase in pH during the preparation of the sample gave slightly more copper^{III}. No change in the nature of the substance was observed however, and even at pH values of 12 - 14 no more than 30% available oxygen was obtained.

ii) An increase in the time period between precipitation of the black solid to the end of filtration seemed to decrease the percentage yield of copper^{III}.

3.2.1.5 Instrumental analysis

i) Magnetic susceptibility

The above results indicate the presence of copper^{III} in the

substance produced by hypochlorite oxidation of cupric salts, but it
was evident that the compound did not consist entirely of a tri-valent
copper oxide. Tests to determine its magnetic susceptibility were
therefore carried out: as noted previously the d^8 configuration of
copper^{III} salts produces diamagnetic substances.

Initial weighing of samples on a magnetic balance both in and
out of a field however, indicated that the compound was paramagnetic.
More detailed measurements of the gram magnetic susceptibility were
then made, and a value for $10^6 \chi g$ equal to 6.93±0.03 cgs units was obtained.

Using suitable corrections for the diamagnetism of copper and
oxygen and a value for total copper content of the sample from atomic
absorption analysis gave:

$$10^6 \chi \; Cu \; = \; 753 \; cm^3 \; mol^{-1}$$

or magnetic moment, $\mu eff \; = \; 1.33$ B.M.

Considering that Cu^{II} compounds normally have $10^6 \chi$ Cu values of
over 1500 cm^3 mol^{-1} and a $\mu eff.$ of $\simeq 1.98$ M, it can be assumed that this
compound contains 30 - 40% copper^{III} and 60 - 70% copper^{II}.[78]

ii) Infra-red spectra

To try and determine the nature of the compound more precisely,
and especially whether the copper was present as an oxide or a hydroxide,
a sample prepared in mull form with Fluorolube oil was run in the infra-
red spectrophotometer.

The results obtained were far from being consistent: in some cases
a distinct absorbance peak was obtained in the 2700 - 3000 cm^{-1} wavenumber

band, indicating the presence of a hydroxy, OH group, while other samples gave no peaks at all. Drying the compound at 110°C overnight and re-running through the I.R. spectrum caused the disappearance of a previously obtained hydroxide peak in about 80% of all samples.

iii) <u>X-ray diffraction</u>

Small samples were analyzed in the X-ray diffractometer, and the resultant diffraction pattern was compared with one obtained from a standard CuO sample:

Cu^{III} Sample		CuO Sample		CuO (Reported)	
d$\overset{\circ}{A}$	I/I_1	d$\overset{\circ}{A}$	I/I_1	d$\overset{\circ}{A}$	I/I_1
2.77	9	2.75	12	2.75	12
2.54	100	2.52	100	2.52	100
2.34	96	2.32	96	2.32	96
1.87	28	1.87	25	1.87	25
1.71	9	1.71	9	1.71	8
1.59	14	1.58	14	1.58	14
1.51	19	1.51	21	1.51	20
1.41	21	1.42	14	1.42	12
1.38	17	1.41	16	1.41	15
		1.38	18	1.38	19
		1.30	6	1.304	7
				1.27	6
				1.19	2

Table 5: <u>X-ray Diffraction Patterns for Copper^{III} and Copper^{II} Oxides</u>

These results are strongly indicative that the substance consists primarily of CuO.

3.2.2 Precipitation of copper^{III} in the presence of carbonate

Samples made by the action of sodium hypochlorite on cupric hydroxide at pH 9.0 in solutions which also contained sodium carbonate and bicarbonate salts were very similar to those made in the absence of carbonate, but there was a 'nucleation period' before any precipitation occurred. This was a similar effect to that observed during copper sulphide leaching, before hypochlorite decomposition:

$[CO_3^{2-}]_T$	Time to precipitation
0.5 g/l	30 seconds
2.0 g/l	5 minutes
5.0 g/l	165 minutes
10.0 g/l	12 hours

3.2.2.1 Effect of seeding

Addition of a small amount of the filtered precipitate to a carbonate-hypochlorite solution containing dissolved copper caused instantaneous blackening of the blue solution with subsequent precipitation of more black material. This occurred in all cases, regardless of the initial carbonate concentration.

3.2.2.2 Effect of acidification

Addition of dilute nitric acid to the sample produced a clear blue solution. Rapid gas evolution was observed and a limewater test indicated a certain amount of carbon dioxide, CO_2, was present. Some excess oxygen was also detected by passage of a gas sample through the chromatograph and comparison of the observed retention times with those of a standard air sample.

3.2.2.3 I.R. spectra

Analysis of the infra-red spectra produced by samples of this black precipitate gave a consistent peak in the 950 - 1000 cm^{-1} wavenumber band. This indicates the presence of an HCO_3^- or CO_3^{2-} group. Peaks in the 2500 - 3000 cm^{-1} band, corresponding to a hydroxy group, were again found to be rather random in appearance.

3.2.2.4 X-ray analysis

X-ray diffraction studies gave the following diffraction pattern:

d$\overset{\circ}{A}$	I/I_1 - species identified		d$\overset{\circ}{A}$	I/I_0 - malachite
	Malachite	CuO		(Reported)
7.43	16		7.41	11
			5.99	55
5.02	64		5.06	75
3.68	80		4.07	13
3.25	unidentified		3.69	85
			3.02	
			2.98	
			2.86	100
2.81	100		2.81	
2.52		100	2.52	45
2.51	41			
2.32		96	2.47	
			2.46	35
			2.43	20
			2.32	17
1.99	10		1.99	11
1.87		25		

Table 6: X-ray Diffraction Pattern for Copper^{III} Carbonate

It is thus apparent that the substance made by the oxidation of cupric hydroxide in the presence of carbonate is a mixture of copper^{III} carbonate (essentially an oxidized form of malachite) and copper^{II} oxide, and that it is this compound which is precipitated from leaching solutions on long standing.

A similar black compound was produced by the action of undiluted 'JAVEX' (50 - 60 g/l OCl$^-$) on malachite, but solutions containing only 7 - 8 g/l gave no visible change to the green powder.

3.2.3 Hypochlorite decomposition studies

2 g samples of each precipitate, i.e. the oxide/hydroxide and carbonate, were agitated in hypochlorite solutions at pH 9.0 and 35°C, to determine the rate of hypochlorite decomposition. Graphical plots of the results suggested this rate to be very similar to that observed during covellite leaching, and considerably more rapid than that produced by the analogous case of cupric oxide agitation in hypochlorite (Figure 21, Table XIX).

3.2.4 Analysis of leaching solutions

It was postulated that if copper^{III} exists in hypochlorite solutions as a relatively stable carbonate complex, then the spectrum obtained from an ultra-violet-visible spectrophotometric scan should be different from that produced by a copper^{II} carbonate complex, the colour of which is much less intensely blue.

However, the only detectable difference between the two solutions
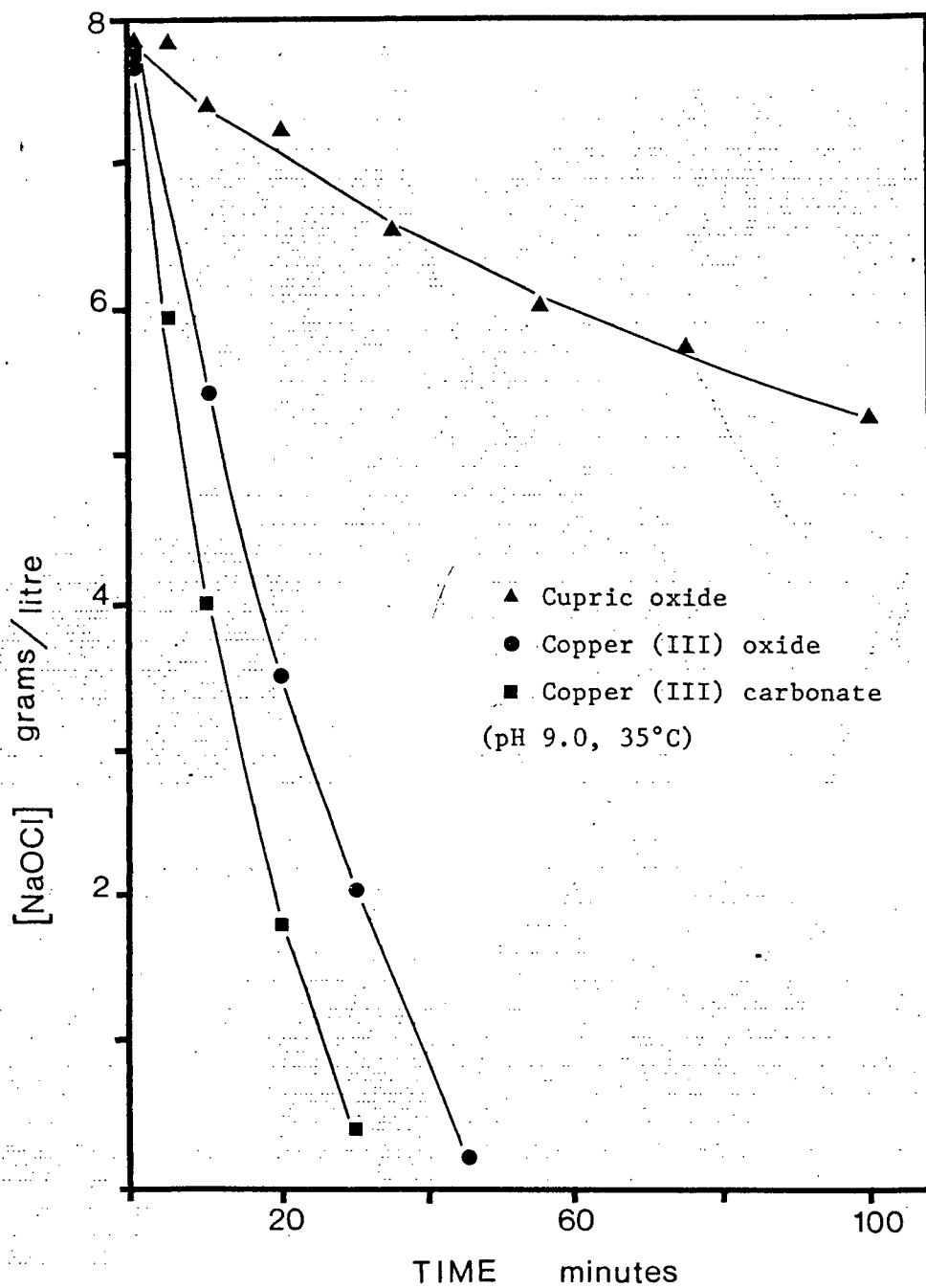
Figure 21: Decomposition of Sodium Hypochlorite in the presence of trivalent Copper Salts.

was a strong hypochlorite peak in the UV region of the darker sample. No

sensible peaks were obtained in the visible region whatsoever, despite

the blue colouration of the samples. A cupric choride sample significantly

more concentrated in copper than the carbonate solutions was then run as

a standard, and a very broad peak appeared in the 440 - 650 μm region.

It was thus assumed that the carbonate complexes were too dilute to give

any meaningful peaks ([Cu] $\simeq 1.6 \times 10^{-3}$ M).

3.3 Sodium Hypochlorite Oxidation of Molybdenite

0.3 g samples of natural molybdenite, MoS_2, were leached in

solutions containing 7 - 8 g/l OCl^- ± carbonate at pH 9.0 and 35°C. A

value of 0.3 g/l was chosen because it represents the typical concentra-

tion of molybdenum found in copper rougher concentrates after flotation.

Extractions of the order of 93 - 94% Mo were obtained within 5

minutes of the commencement of leaching. Hypochlorite consumption

amounted to about 12% of the initial value (Figure 22, Table XX), corres-

ponding to the use of 1.69×10^{-2} moles OCl^- to oxidize 0.17 g/l Mo

(1.77×10^{-3} moles) from $MoS_2 \longrightarrow NaMoO_4$.

These results therefore confirmed the findings of Ismay, that

hypochlorite is a rapid and efficient lixiviant for molybdenite oxidation;

but the fact that greater than 94% molybdenum extraction was not obtained

was not entirely satisfactory. The amount of molybdenite sample used was

thus increased to produce sufficient residue after leaching to enable

X-ray analysis to be carried out:
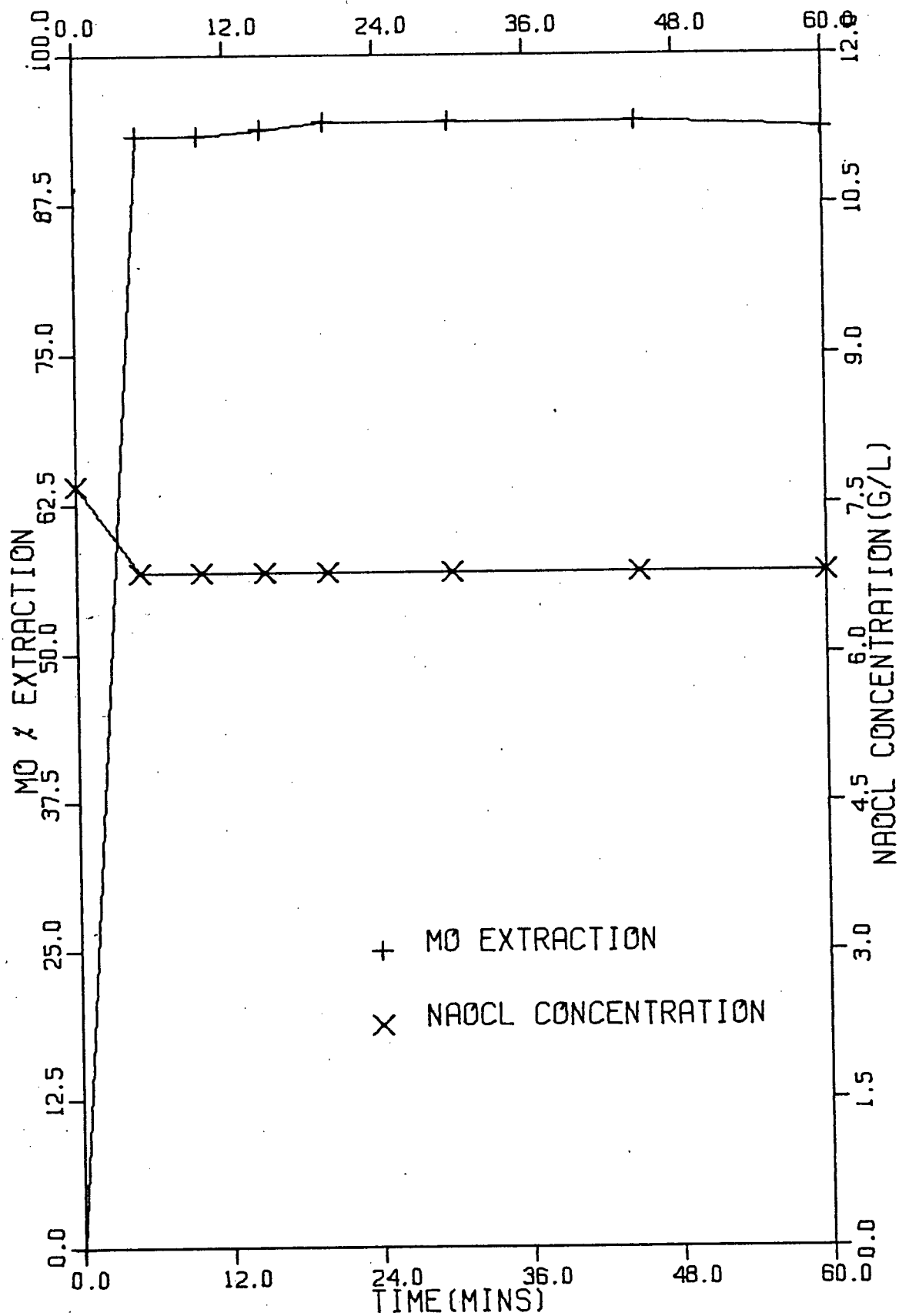
Figure 22: NaOCl oxidation of molybdenite at pH 9.0.

i) X-ray fluorescence indicated the following elements to be present in decreasing order of magnitude:

$$Fe > Pb > Cu, Mo > Zn$$

ii) X-ray diffraction studies identified two lead molybdate species, Pb_2MoO_5 and $PbMoO_4$ as being present. Both of these were assumed to be insoluble, since re-leaching of about 0.2 g of residue produced no detectable molybdenum in solution.

Spectroscopic analysis confirmed that the concentrate did not contain 100% MoS_2 (Section 2.2.1.1 (iv)), and that at least 3% of impurities were present. The level of extraction obtained therefore represented more than the apparent 94%.

Samples of reagent grade molybdenum disulphide were subsequently used, but gave no better results (Figure 23). This material was shown by X-ray analysis (SEM) to contain significant amounts of silicon. Leaching tests were finally carried out with material guaranteed to contain over 98% MoS_2. Extractions of nearly 98% were then obtained (Figure 24). Hypochlorite consumption was slightly higher than for the oxidation of an equivalent amount of the natural mineral (Table XXI).

The presence or otherwise of carbonate buffer reagents was found to have no effect on molybdenum extraction.

3.3.1 Sodium hypochlorite leaching of molybdenite and copper sulphide minerals at pH 9.0

In order to determine the selectivity of molybdenum extraction from molybdenite-copper sulphide mixtures, samples of both minerals were
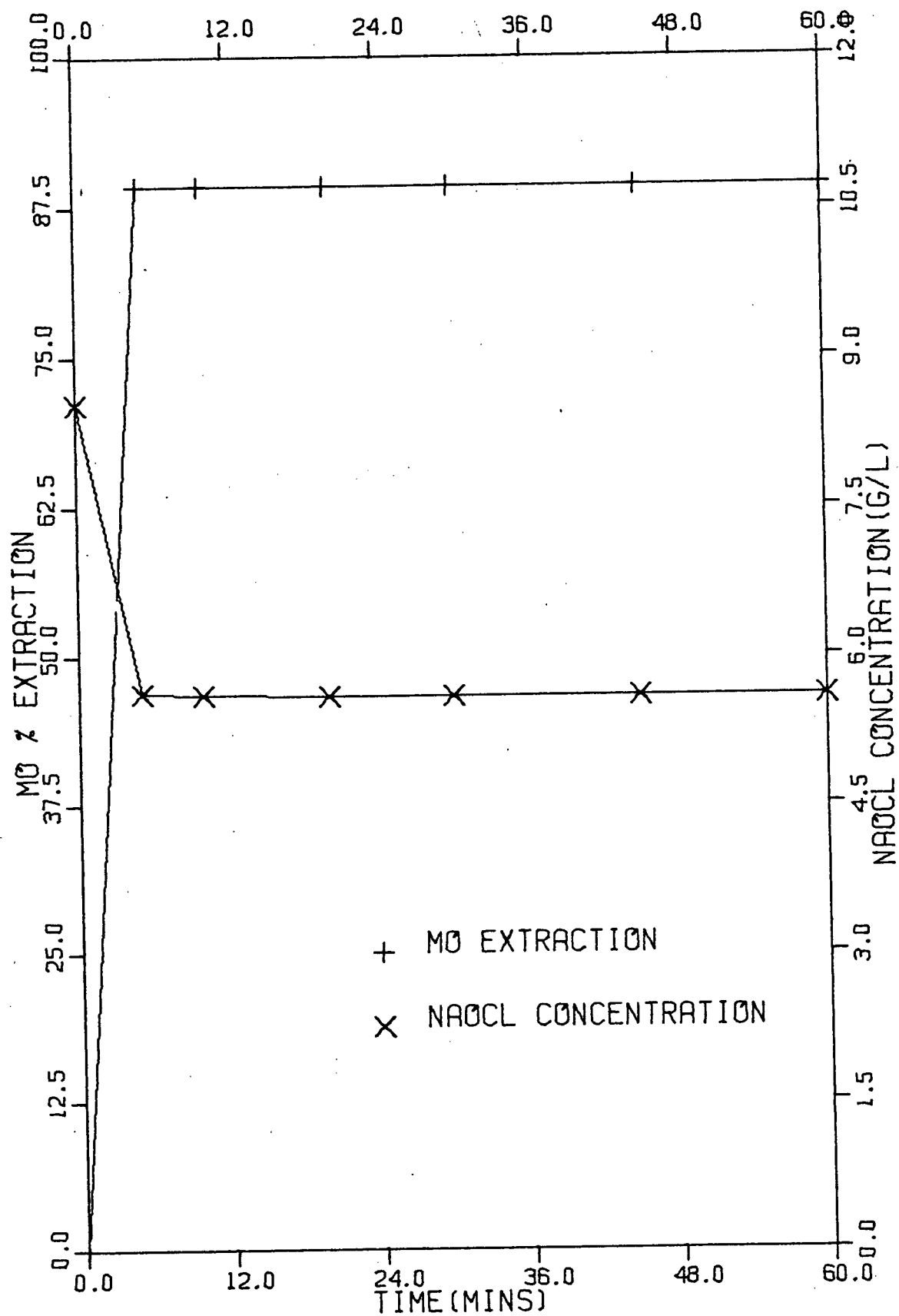
Figure 23: NaOCl oxidation of reagent grade molybdenum disulphide.
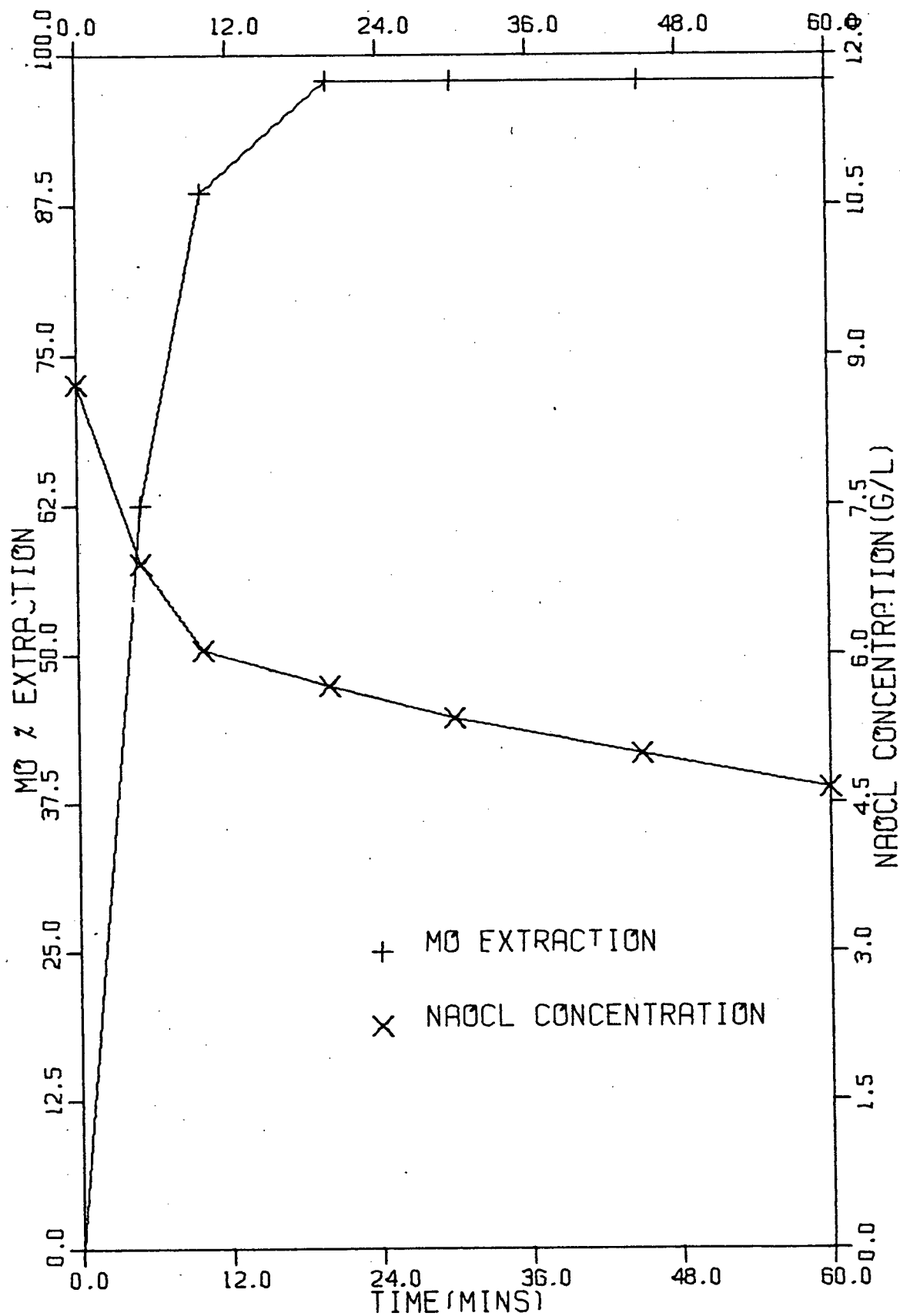
Figure 24:   NaOCl oxidation of 98% molybdenum disulphide.

leached simultaneously. In the presence of carbonate, 89% Mo extraction was obtained, accompanied by dissolution of 2 - 3% of the copper ($\approx$0.12 g/l). Hypochlorite consumption in the presence of all three copper minerals was virtually the same as for oxidation of molybdenite alone (Figures 25a, 26a, 27a, Tables XXII - XXIV).

Removal of carbonate from the system resulted in negligible amounts of copper being dissolved, but also produced a significant decrease in the level of molybdenum extraction: 74% Mo dissolution was obtained in the presence of covellite, 77% in the presence of chalcocite and 79% with chalcopyrite (Figures 25b, 26b, 27b, Tables XXII - XXIV).

To confirm that this was a real effect, and not caused by the small amount of MoS_2 sample used giving unrepresentative results, 10 g of chalcopyrite were leached with 5 g 'reagent grade' MoS_2 under otherwise identical conditions. A 2% loss of molybdenum occurred in the presence of carbonate and a 4 - 5% loss in the absence of carbonate (Table XXV).

Scheiner et al. stated that copper molybdate compounds were found to be detrimental to good molybdenum recovery in the U.S. Bureau of Mines process.[20,22] Experiments were therefore carried out to see if copper molybdate formation could be induced, although in the present study it appeared that the greater molybdenum loss was occurring from solutions containing no dissolved copper:

i) Copper sulphate solution was added dropwise from a burette during molybdenite leaching.

ii) Sodium molybdate solution was added to a covellite leach under similar conditions.
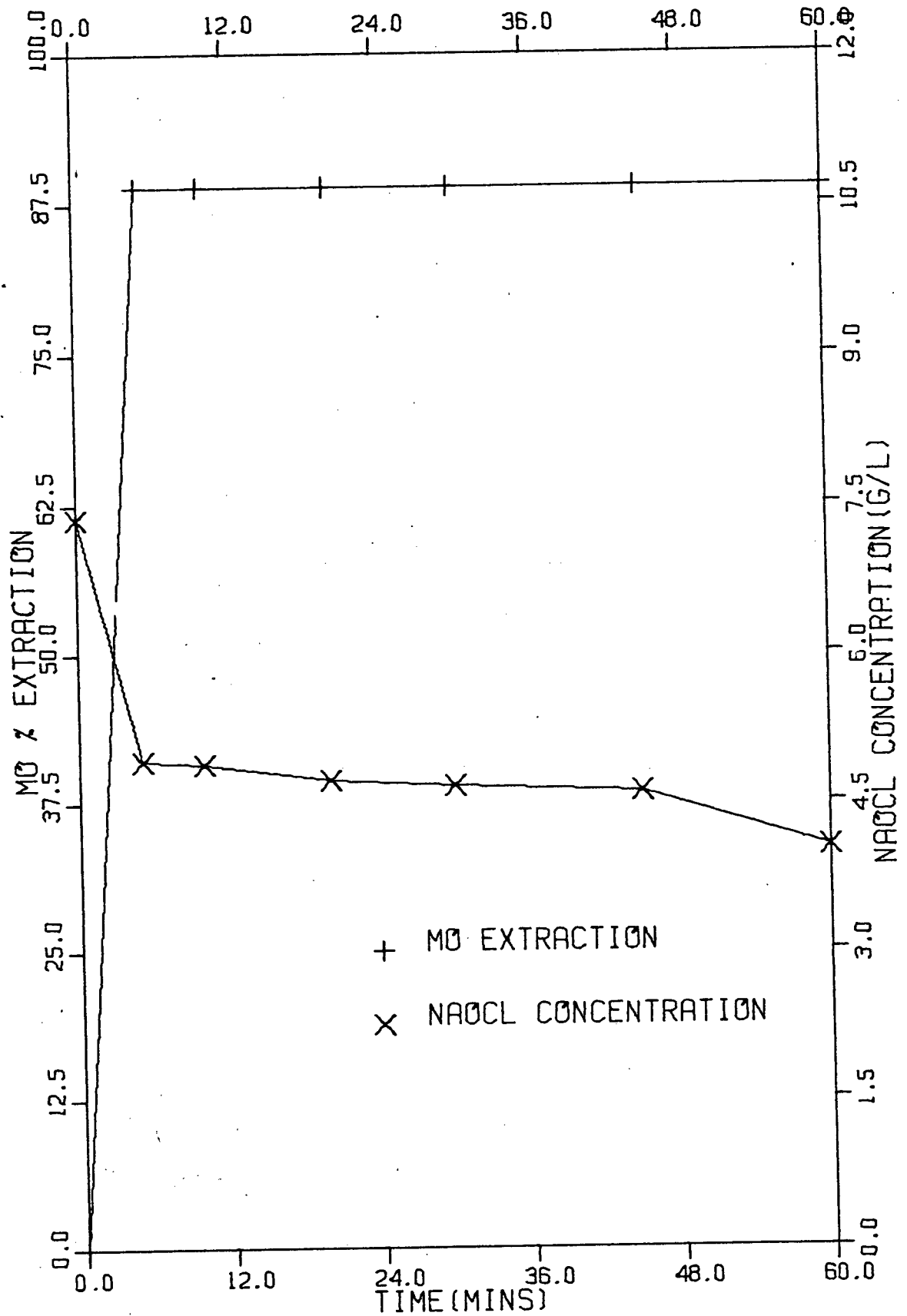
Figure 25 (a): NaOCl oxidation of molybdenite and covellite in the presence of carbonate buffer.
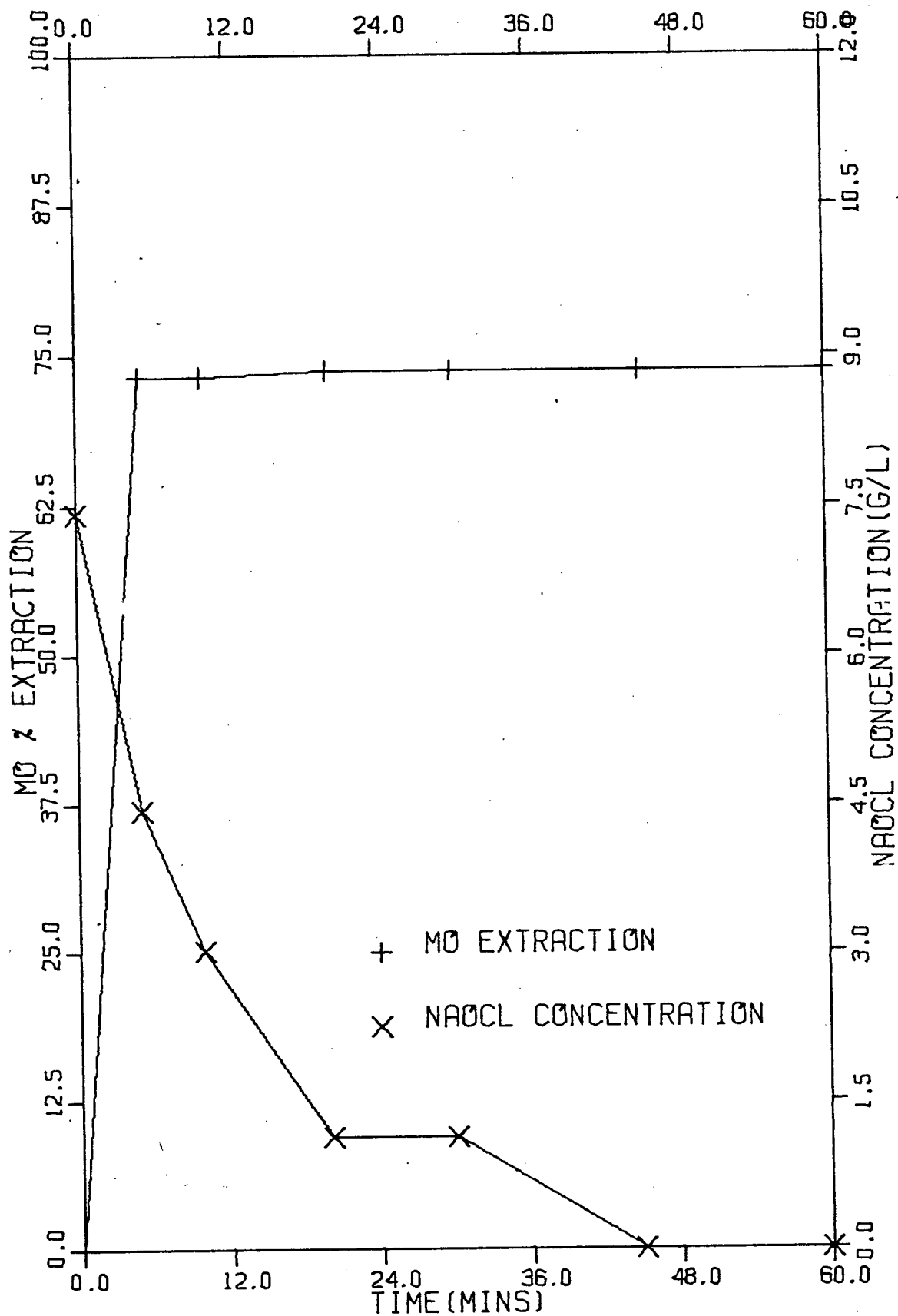
Figure 25 (b): NaOCl oxidation of molybdenite and covellite in the absence of carbonate buffer.
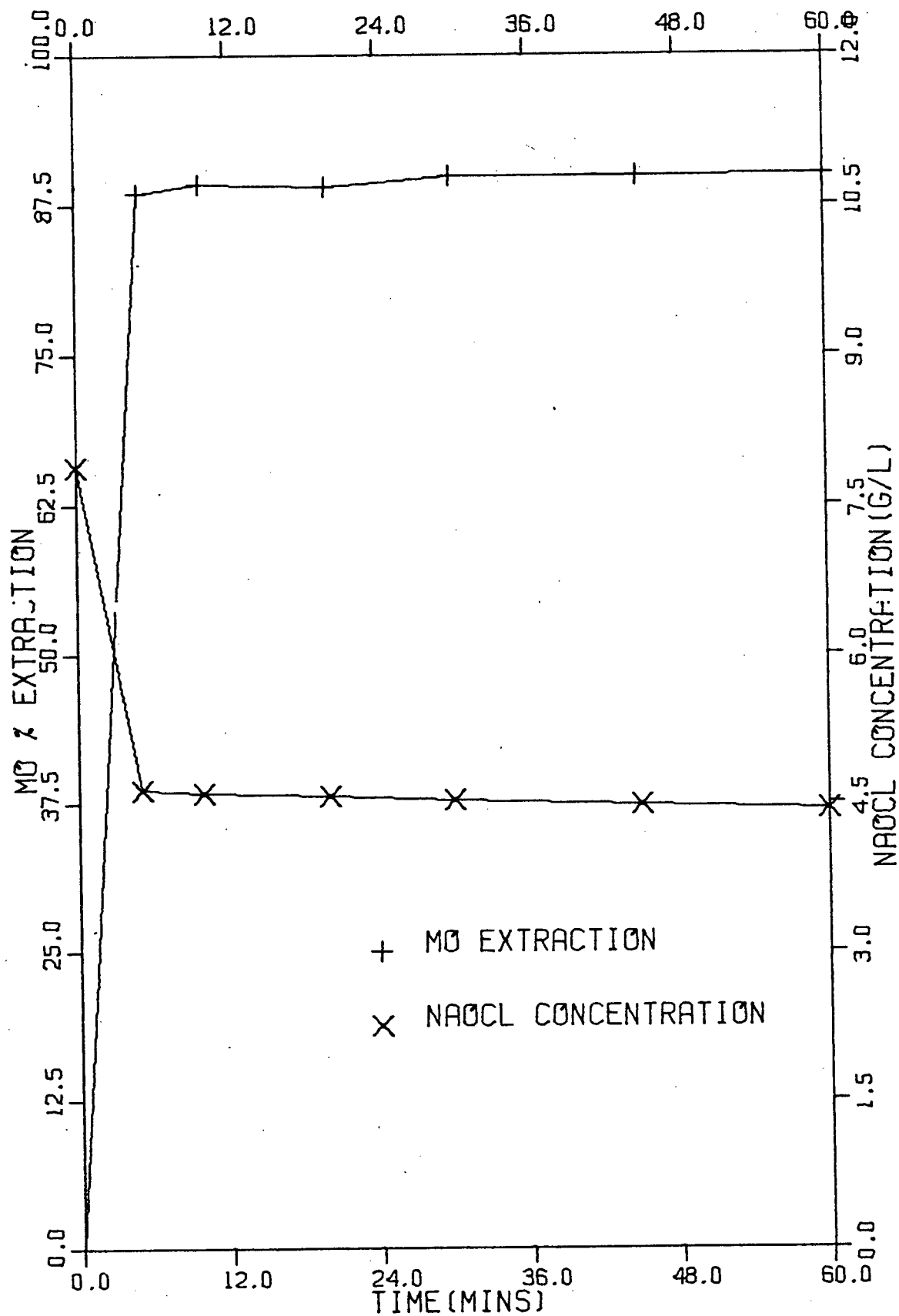
Figure 26 (a):   NaOCl oxidation of molybdenite and chalcocite in
the presence of carbonate buffer.

Figure 26 (b):   NaOCl oxidation of molybdenite and chalcocite in
the absence of carbonate buffer.

Figure 27 (a): NaOCl oxidation of molybdenite and chalcopyrite
in the presence of carbonate buffer.
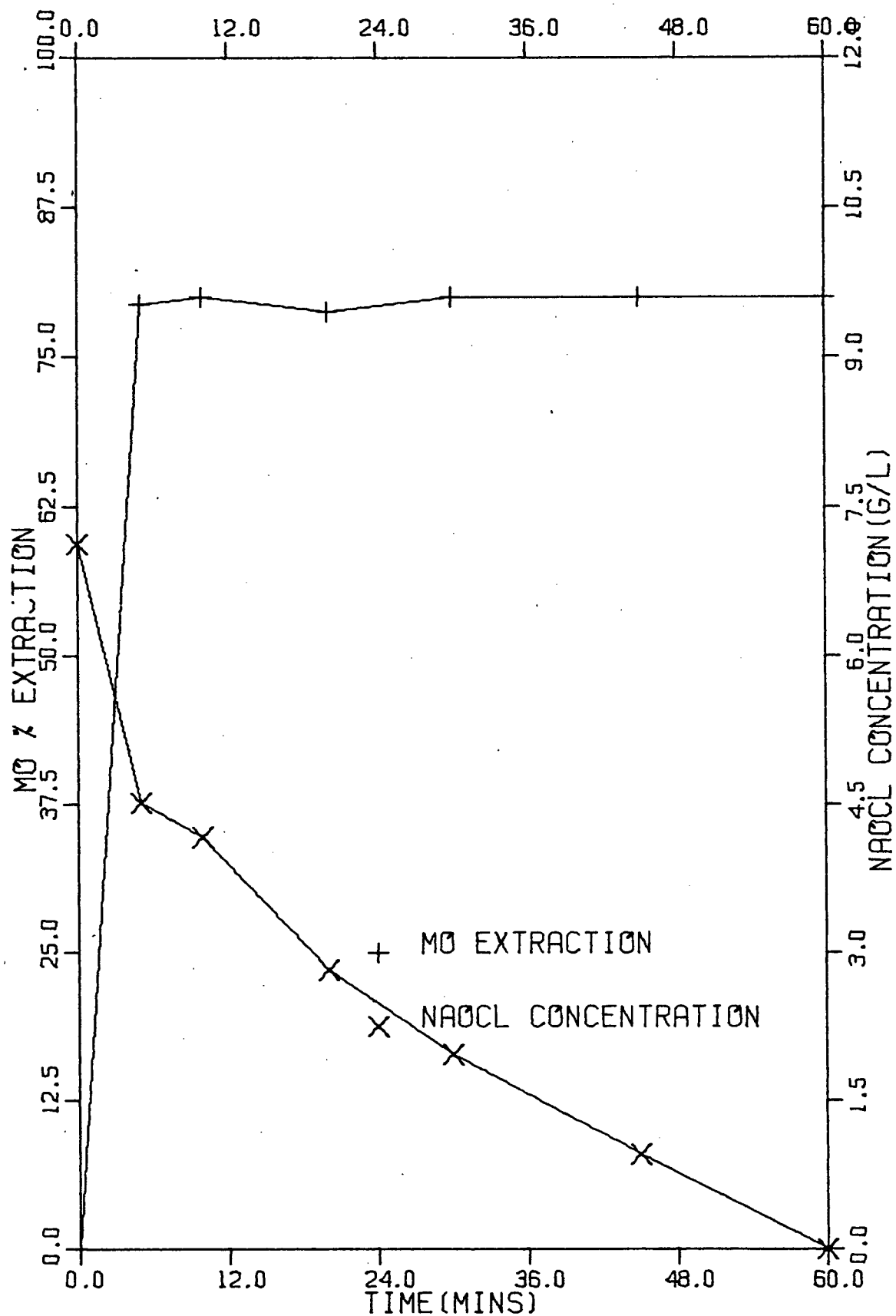
Figure 27 (b):   NaOCl oxidation of molybdenite and chalcopyrite
in the absence of carbonate buffer.

In both runs copper and molybdenum contents were monitored with respect to time. In the former case no copper was detected in solution, but significant amounts of molybdenum were removed. The presence of copper was also detected on the molybdenite surface after leaching. In the second case with no carbonate present and hence no copper dissolution, nearly 20% of the molybdenum added to the system was lost from solution after 60 minutes agitation (Tables XXVI, XXVII).

3.3.2 Leaching of molybdenite and copper sulphides at pH 5.5

A pH value of 9.0 had been maintained in all experiments reported to date, largely because this was previously found to be beneficial by Ismay for two reasons:

i) pH 9.0 is the point at which a maximum rate of molybdenite oxidation occurs in sodium hypochlorite solutions.

ii) It is coincidently the pH value at which chlorate production is minimized during hypochlorite decomposition.

In view of the adverse effects apparently caused by introduction of copper minerals into the system however, the leaching of molybdenite on the acid side of neutrality was investigated. A pH value of 5.5 was chosen because this is below the region in which chlorate production is most rapid (6.0 - 7.0).

In most cases molybdenite was leached for 5 - 10 minutes before any copper samples were added to the system.

Sodium bicarbonate was added one gram at a time, after copper sulphide addition, and this maintained the desired pH value initially.

After 10 g of reagent had been added, and in cases where no carbonate was used, sodium hydroxide was used as a buffer reagent, as before. The results clearly showed that an even greater loss of molybdenum occurred under these conditions. Leaching of molybdenite alone gave over 90% recovery, but the introduction of covellite, chalcocite or chalcopyrite reduced the level of molybdenum in solution to about 10% (Figures 28 - 30a, Tables XVIII - XXX). The amount of copper dissolved was also much lower than that found leaching $CuFeS_2$ or CuS alone at pH 5.5.

Addition of sodium bicarbonate to the system increased this value slightly (Table XXXII), but did nothing to prevent the precipitation of molybdenum (Figures 28 - 30b). It was thus presumed that copper molybdate readily formed at this pH level. Furthermore this substance acted as a catalyst for hypochlorite decomposition as shown by the very rapid loss of OCl^- accompanying molybdenum precipitation. The consumption of the lixiviant was higher in experiments leaching only molybdenite at pH 5.5 than for the corresponding case at pH 9.0 (8.3×10^{-2} M OCl^- for 5.72×10^{-3} M Mo which is higher than the stoichiometric requirement of 9 moles OCl^- per mole MoS_2).

A number of runs were carried out at slightly higher pH values: 6.0, 6.5 and 7.0, to determine the effect on molybdenum recovery. Considerable losses of both molybdenum and $[OCl^-]$ again occurred in the presence of copper minerals with no carbonate in the system, but recovery was significantly increased on addition of $NaHCO_3$. A chalcocite/ molybdenite leach at pH 6.5 with bicarbonate in the system gave 89% Mo extraction and the copper and hypochlorite concentrations in solution maintained a constant value for the duration of the experiment. In an
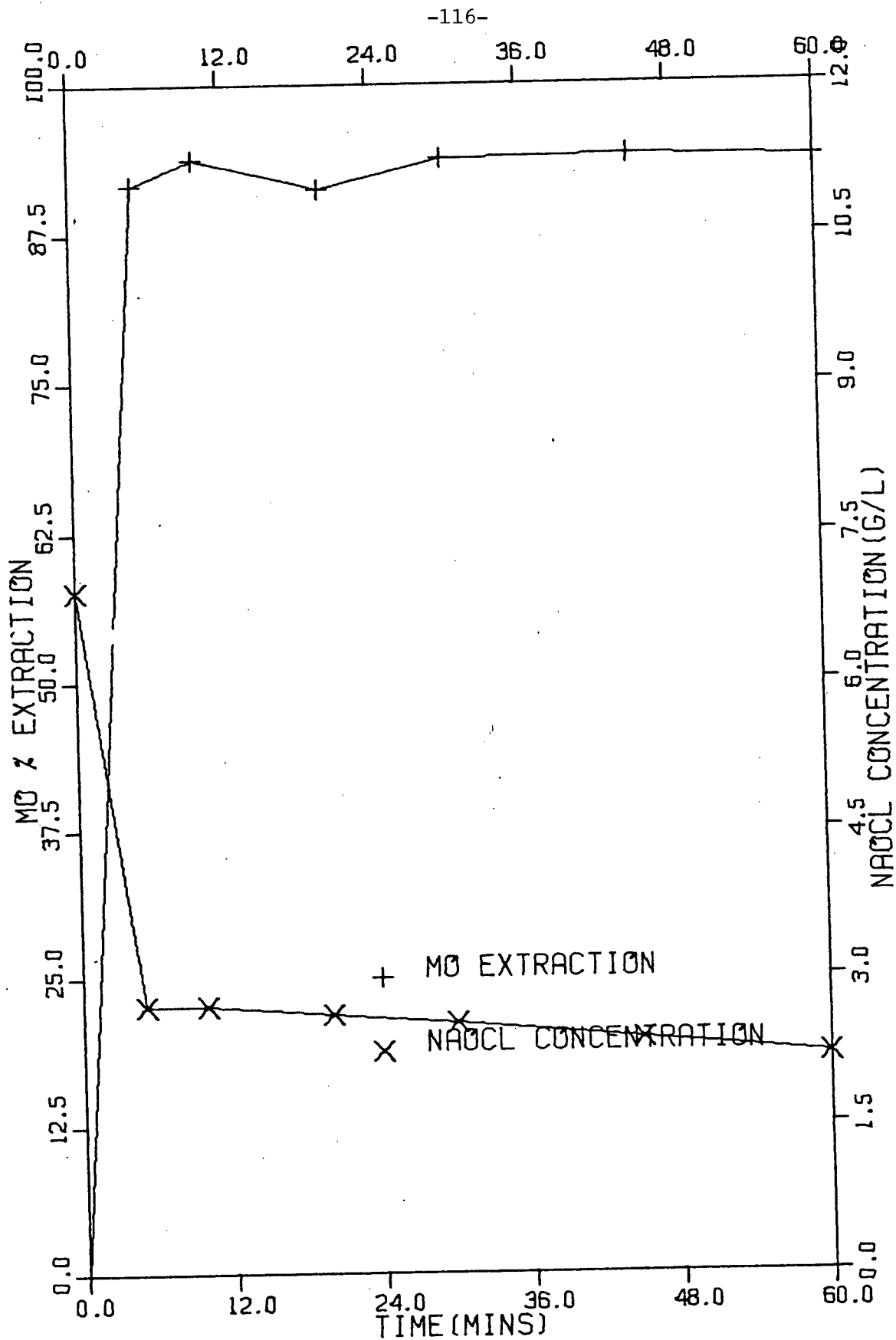
Figure 28: NaOCl oxidation of molybdenite at pH 5.5.
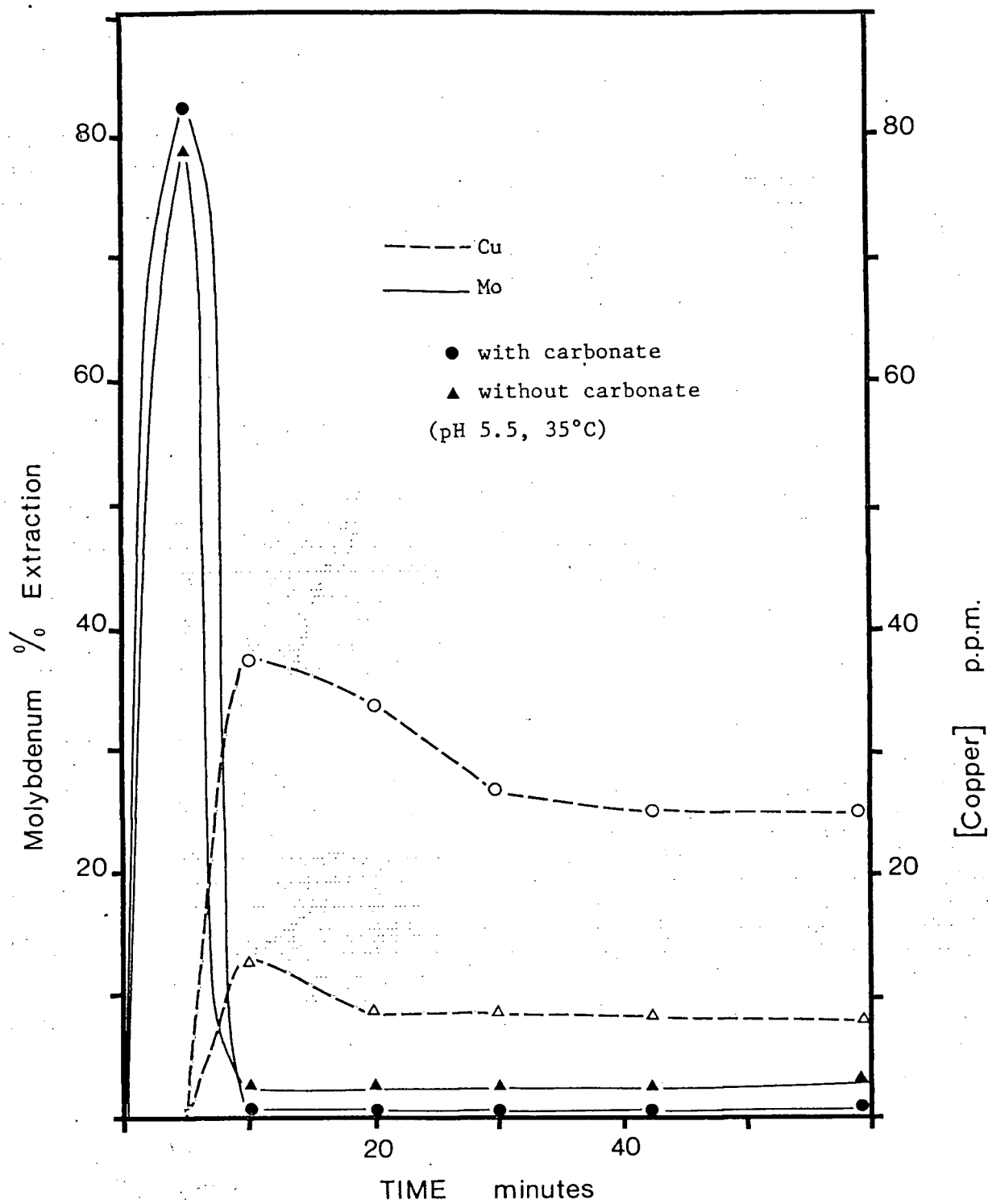
Figure 29: NaOCl leaching of Chalcopyrite/Molybdenite at pH 5.5.
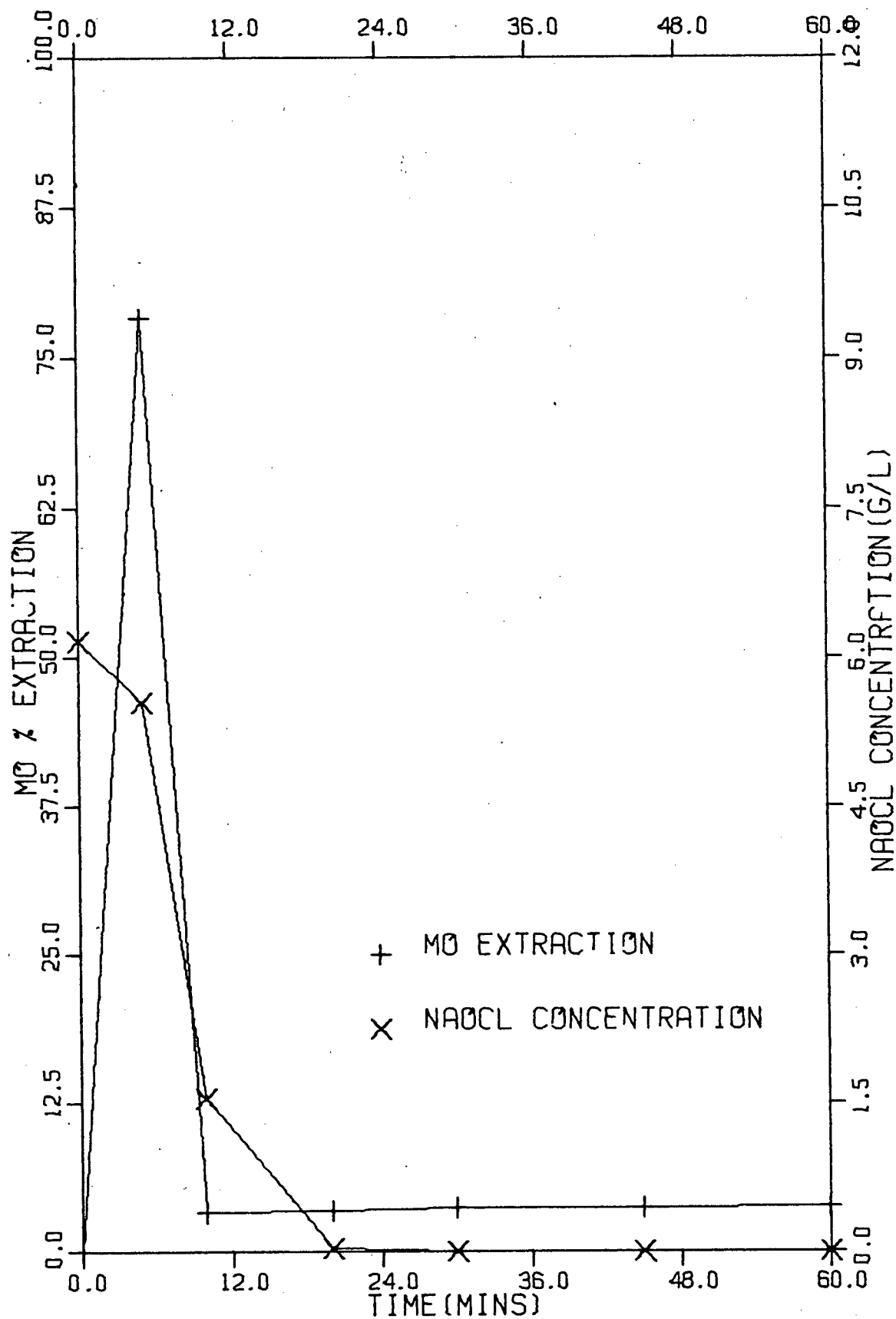
Figure 30 (a): NaOCl oxidation of molybdenite and covellite at
pH 5.5 in the absence of $NaHCO_3$.
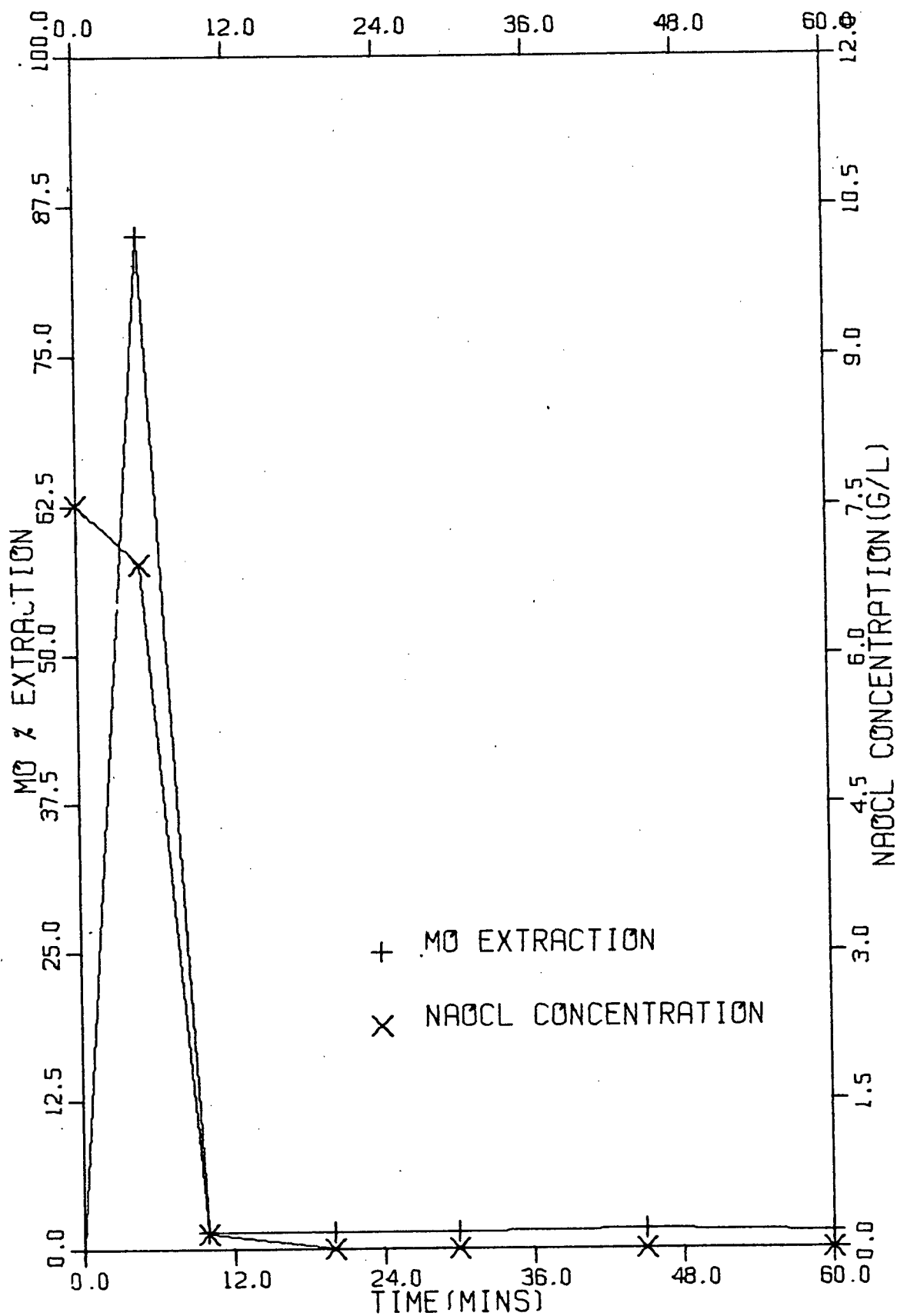
Figure 30 (b): NaOCl oxidation of molybdenite and covellite at pH 5.5 in the presence NaHCO₃.

identical run carried out in the absence of bicarbonate, introduction of
the chalcocite sample reduced the molybdenum in solution from 80% to
15% within 30 minutes (Figure 31a,b, Tables XXXIII, XXXIV). The copper
dissolved initially also decreased with respect to time, and there was
a rapid loss of hypochlorite.

The fact that copper was entirely responsible for molybdenum
precipitation was confirmed by a similar experiment using synthetic CuS
at pH 6.0. Results showed the same molybdenum losses occurred without
bicarbonate in the system, and that this was prevented by leaching with
$NaHCO_3$ present (Figure 32a,b, Tables XXXV, XXXVI).

Molybdenum depression lessened slightly as the pH was further
increased: a $CuFeS_2/MoS_2$ leach at pH 7.0 with no carbonate gave 30% Mo
extraction. Subsequent addition of sodium bicarbonate in a similar run
increased this to over 95%. The hypochlorite decomposed more rapidly in
the latter case (Figure 33a,b, Table XXXVII, XXXVIII).

3.3.3 Copper molybdate

To determine more about the conditions of formation of this sub-
stance, especially with respect to pH, experiments were carried out in
both acid and alkaline solutions in which equi-molecular solutions of
sodium molybdate, Na_2MoO_4 and copper sulphate, $CuSO_4$ were mixed. At pH
9.0 a fine blue-green precipitate was observed while at pH 5.3 a darker
green gelatinous precipitate was visible. Analysis of each solution
both before and after mixing revealed that:

i) at pH 5.3 copper and molybdenum were lost from solution in a
stoichiometric ratio of 1:1.
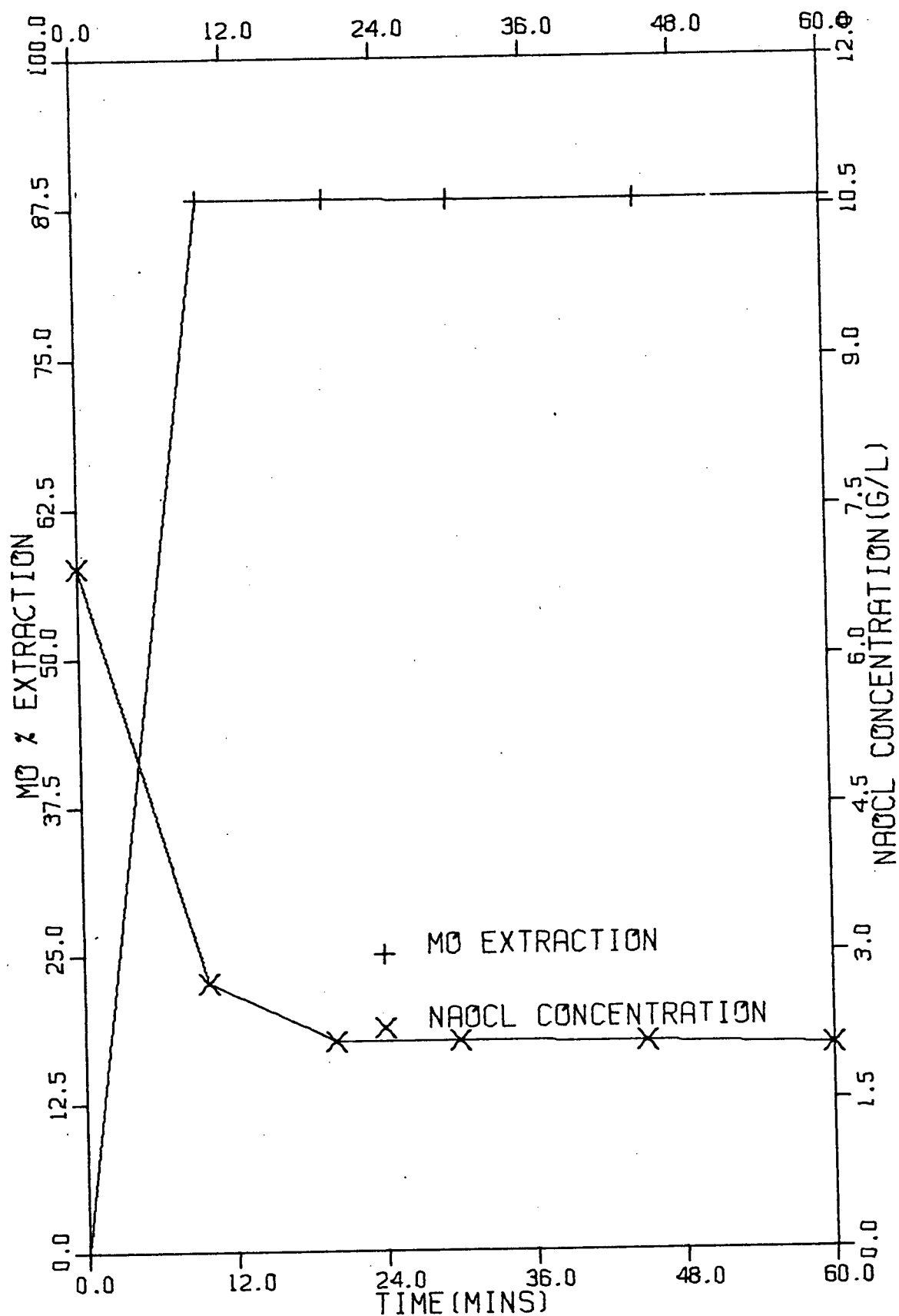
Figure 31 (a): NaOCl oxidation of molybdenite and chalcocite at pH 6.5 in the presence of $NaHCO_3$.
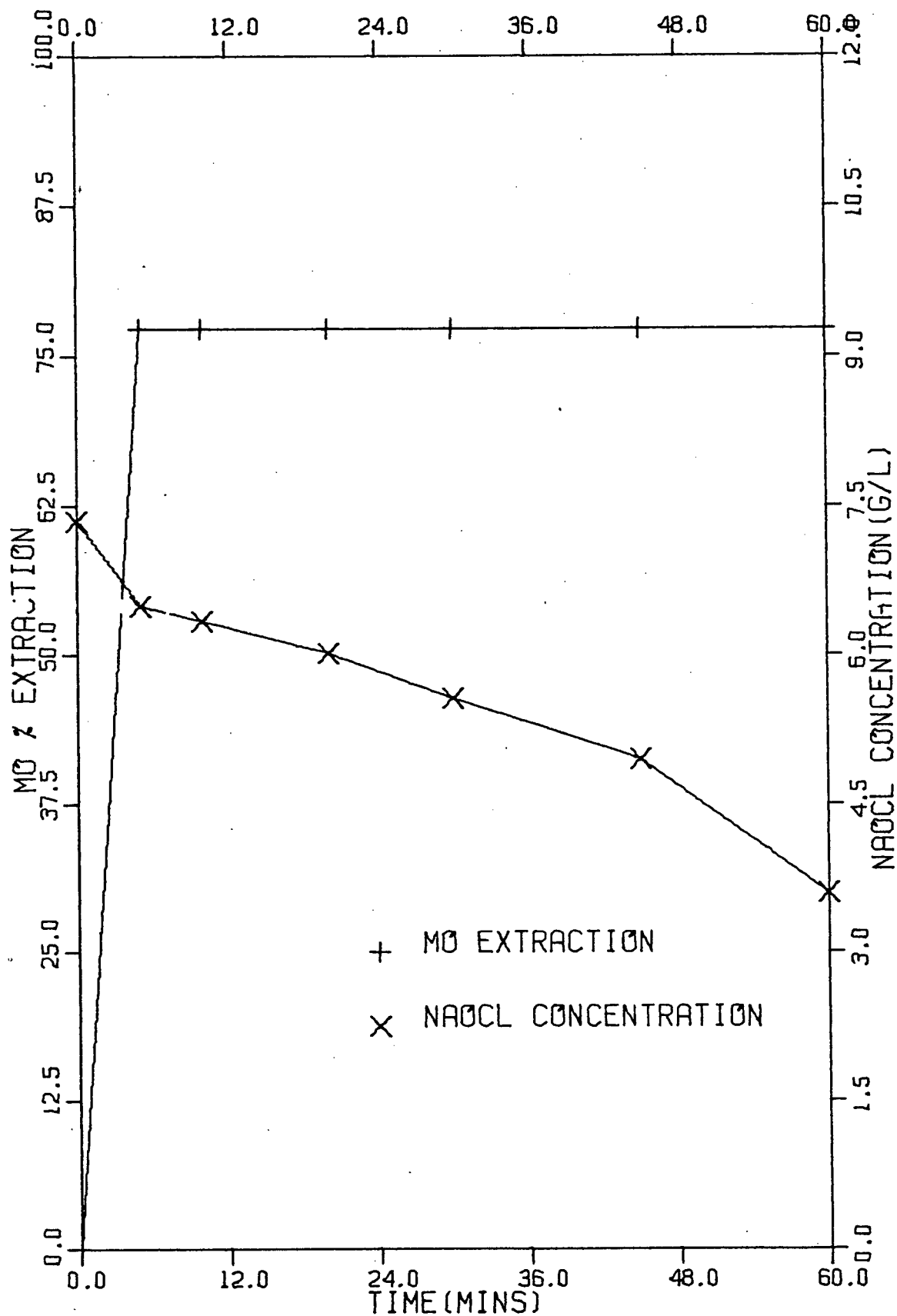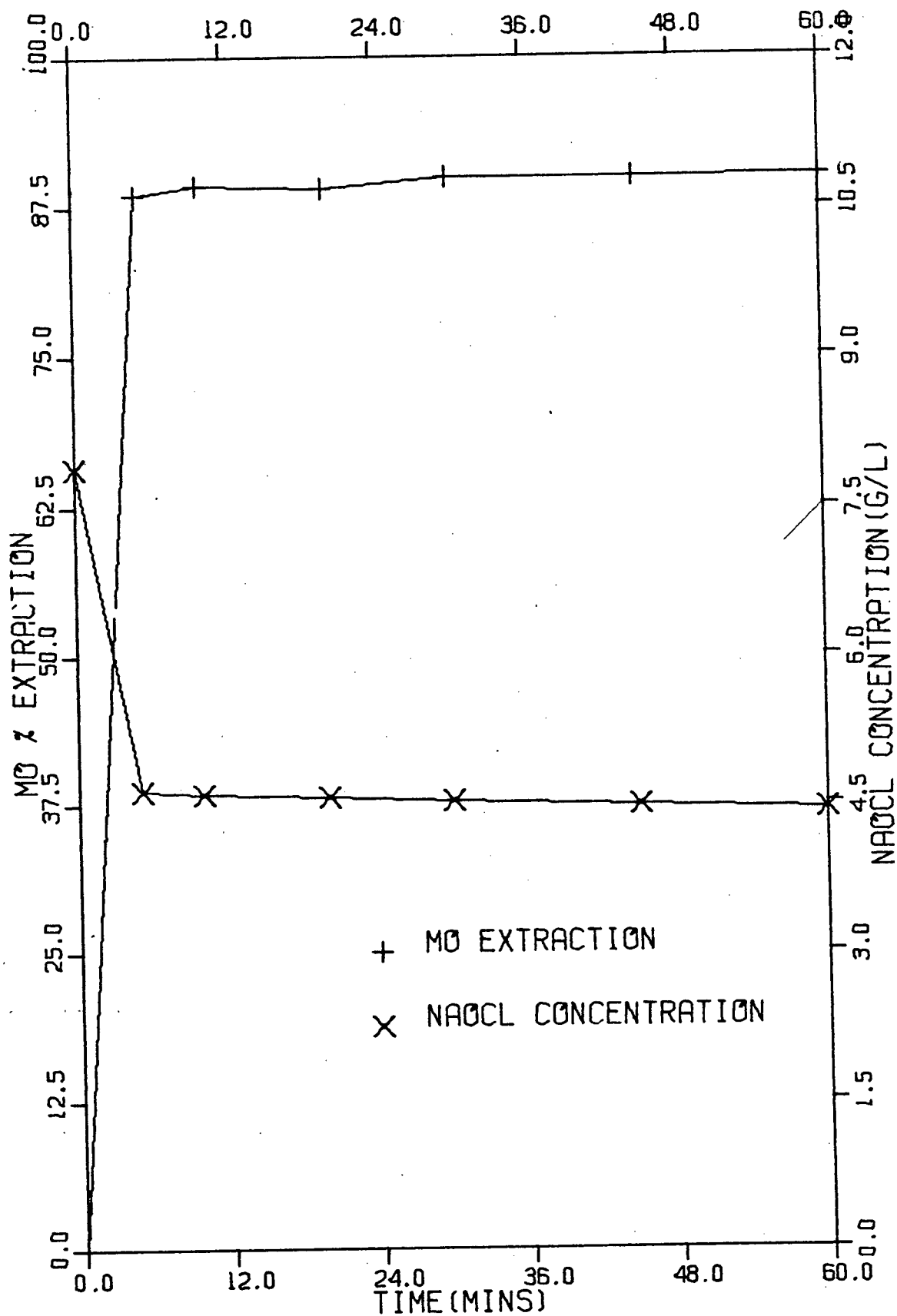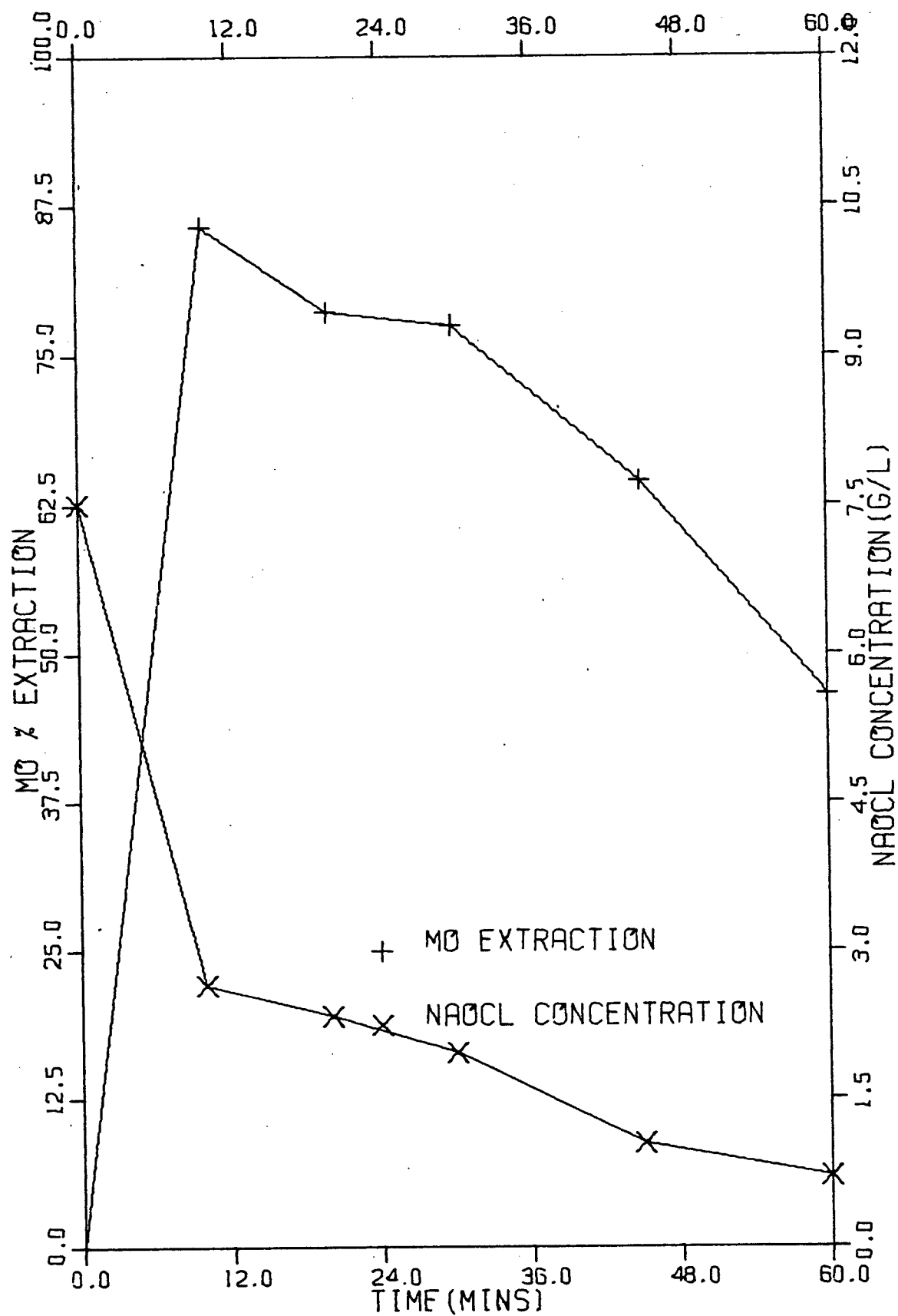
Figure 31 (b): NaOCl oxidation of molybdenite and chalcocite at pH 6.5 in the absence of $NaHCO_3$.

Figure 32 (a): NaOCl oxidation of molybdenite and cupric sulphide at pH 6.0 in the presence of bicarbonate.

Figure 32 (b): NaOCl oxidation of molybdenite and cupric sulphide
at pH 6.0 in the absence of bicarbonate.
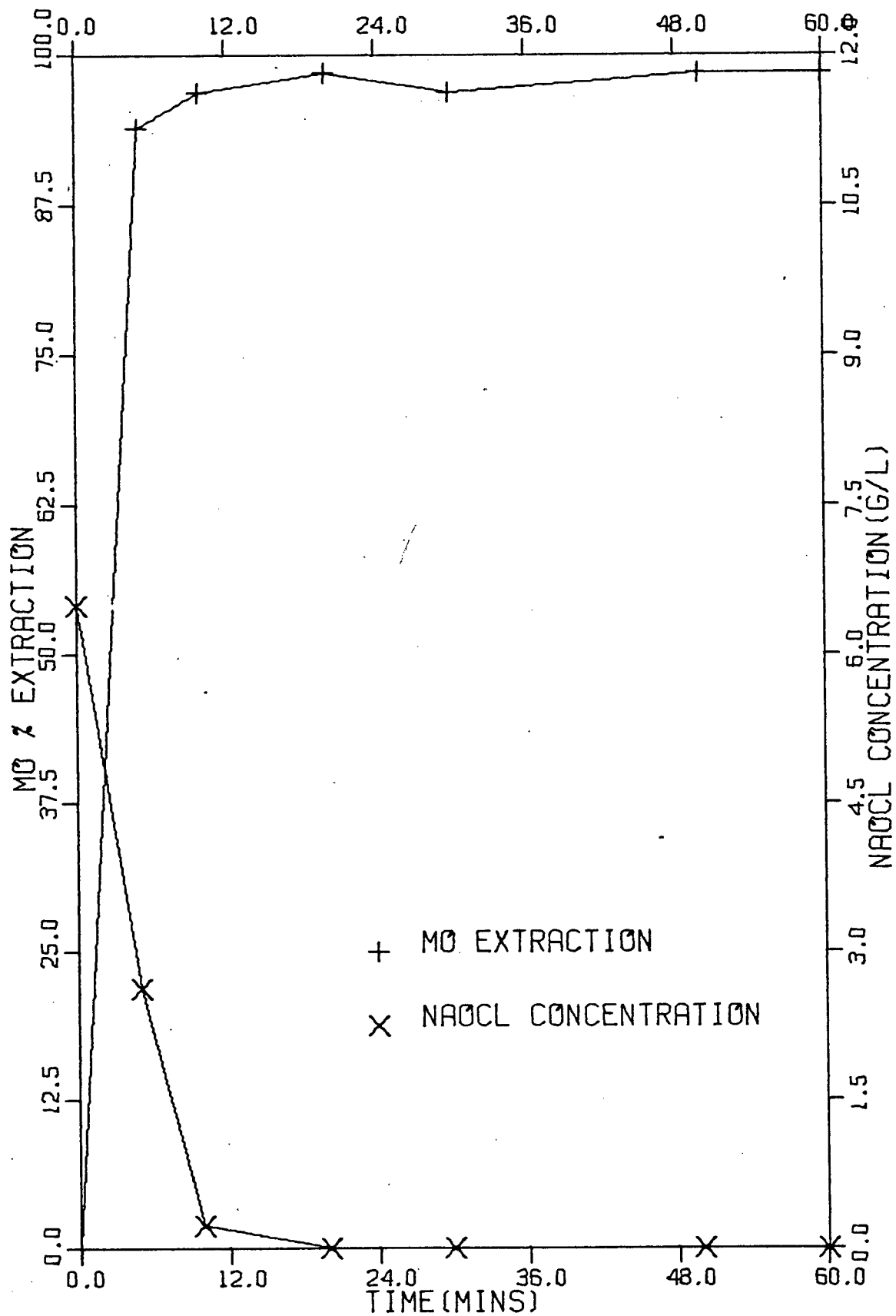
Figure 33 (a): NaOCl oxidation of molybdenite and chalcopyrite
at pH 7.0 in the presence of $NaHCO_3$.
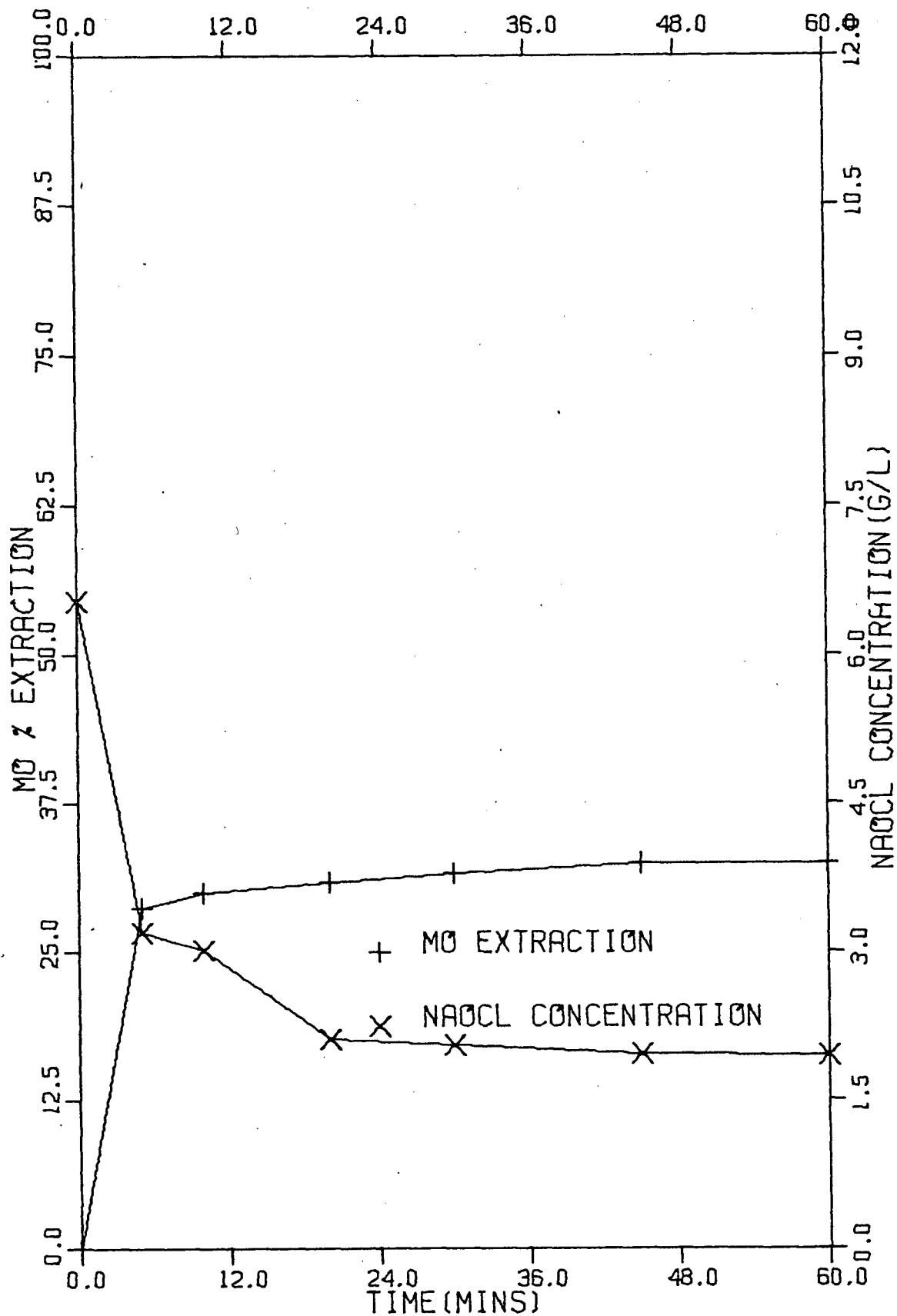
Figure 33 (b):   NaOCl oxidation of molybdenite and chalcopyrite
at pH 7.0 in the absence of $NaHCO_3$.

ii) at pH 9.0 all the copper precipitated and a small fraction of the molybdenum was also lost from solution.

Each precipitate was left to stand overnight and then heated over a steam bath at 60°C for 1 hour. The solutions were then reanalyzed.

i) At pH 5.3: On standing, slightly more copper and molybdenum had dropped out of solution, again in an approximate Cu:Mo ratio of 1:1.

ii) pH 9.0: Conversely at the higher pH, aging had a negligible effect on the copper content of solution (which remained virtually zero) but the molybdenum content increased after standing overnight, and again on heating (Table 7).

3.3.3.1 Solubility of copper molybdate

Addition of Na_2MoO_4 solution to $CuSO_4$ of an equal concentration (10^{-2} M) was made dropwise from a burette at pH 5.4. It was observed that about 0.8 g/l molybdenum could be added before any precipitation occurred. Copper was also removed from solution at this point, after which the molybdenum content remained constant even with the addition of more molybdate solution:

$$840 \text{ ppm Mo} \equiv 0.00875 \text{ M}$$

$$0.00875 \text{ M CuMoO}_4 \equiv 1.4 \text{ g/l (Table XL, Figure 34)}$$

A further test of solubility was carried out by adding some of the filtered, green $CuMoO_4$ precipitate to 100 ml water and leaving it to stand for several weeks, during which time the Cu and Mo contents of the solution were periodically monitored. Maximum values of 0.75 g/l Mo and 0.49 g/l Cu were detected. This corresponds to a copper molybdate
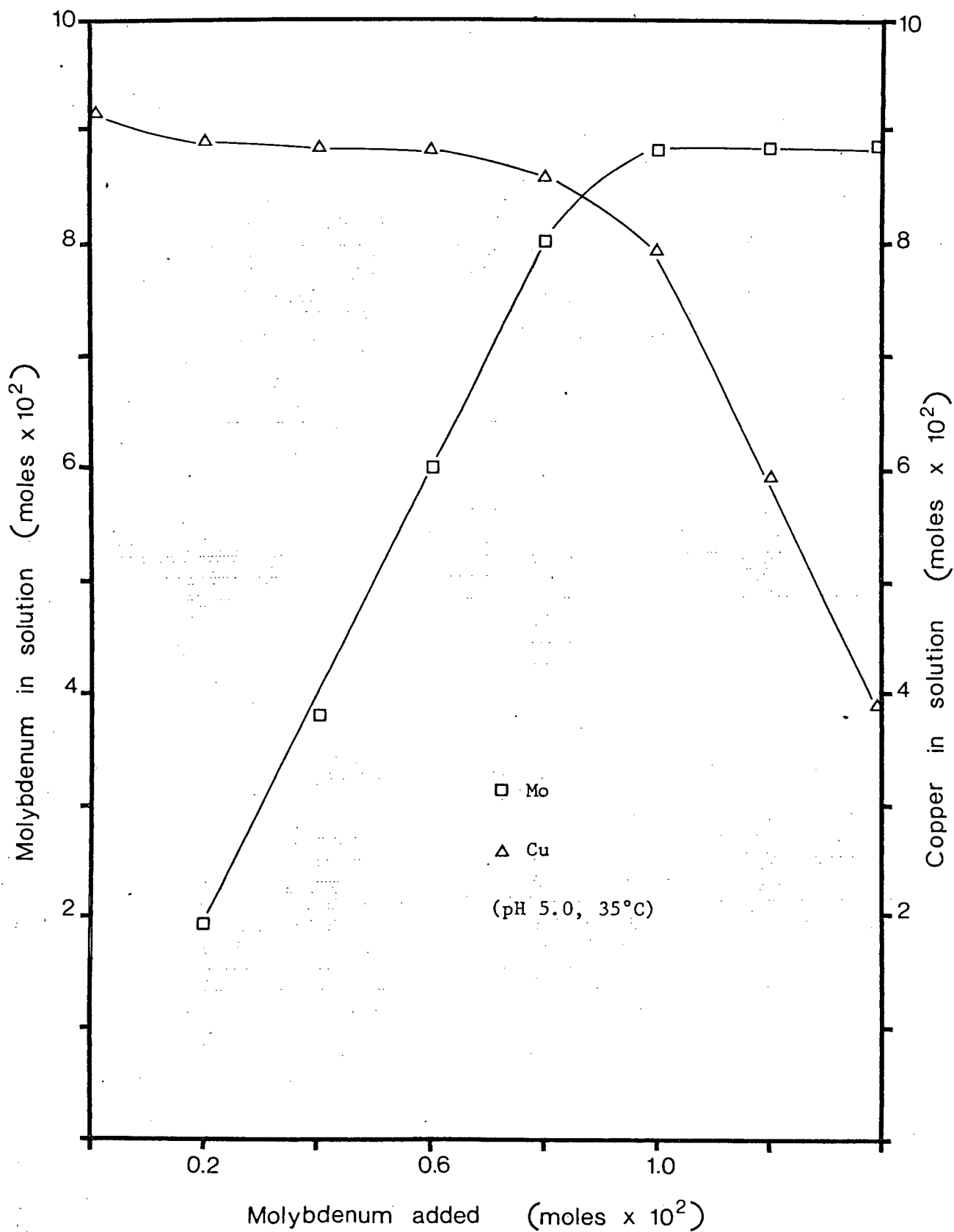
Figure 34: Solubility of Copper Molybdate at pH 5.0, 35°C.

pH	Condition	[Mo] M	[Cu] M	Mo ppt M	Cu ppt M
5.3	Before Mixing	0.00979	0.00913	--	--
	After Mixing	0.00875	0.00813	0.00104	0.00100
	24 Hours Stand	0.00792	0.00740	0.00188	0.00173
	30 Min at 60°C	0.00396	0.00252	0.00583	0.00661
9.0	Before Mixing	0.00979	0.00913	--	--
	After Mixing	0.007192	1.57×10^{-5}	0.00260	0.00911
	24 Hours Stand	0.00792	5.12×10^{-5}	0.00187	0.00908
	30 Min at 60°C	0.00849	7.08×10^{-5}	0.00130	0.00906

Table 7: Effect of Mixing and Ageing Equi-molecular Volumes of Na_2MoO_4 and $CuSO_4$ at pH 5.3 and pH 9.0

solubility of 1.24 g/l, or 7.83 x 10^{-3} M which is in reasonable agreement

with the above value. To confirm the effects observed during leaching,

sodium bicarbonate was added to one or other solution prior to mixing.

At pH 5.3 this had no effect on either copper or molybdenum precipitation.

At pH 9.0 1.57 x 10^{-3} moles Cu (100 ppm) were held in solution and only

slight lowering of the initial Mo content was observed.

3.3.3.2 Catalyzed decomposition of hypochlorite in the presence of copper molybdate

A 2 g sample of copper molybdate was agitated in a solution

containing 7.0 g/l hypochlorite at pH 5.0 and 35°C. Samples were taken

at timed intervals and analysis showed that 50% of the initial hypo-

chlorite decomposed within 35 minutes and that the rate was almost

linear. About 4% of this decomposition was to sodium chlorate, the rest

presumably being to oxygen and chloride (Figure 35, Table IXL). No

detailed investigation of the effects of varying surface area, pH,

temperature etc. during copper molybdate catalysis was undertaken.
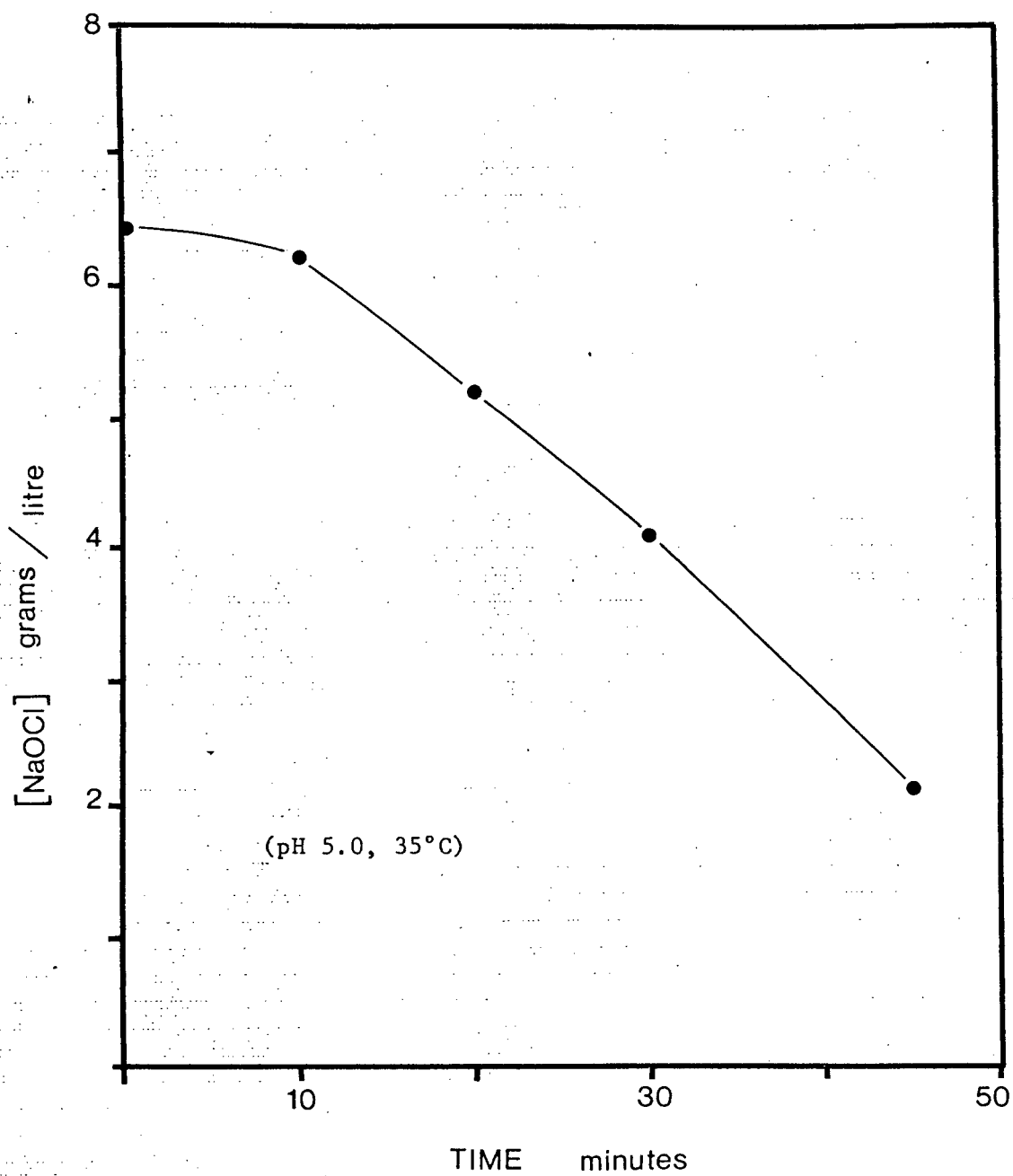
Figure 35: Effect of Copper Molybdate on NaOCl decomposition at pH 5.0, 35°C.

3.3.3.3 X-ray analysis

X-ray diffraction studies of a copper molybdate sample gave the following diffraction pattern:

This Study		Reported	
d$\overset{\circ}{A}$	I/I_o	d$\overset{\circ}{A}$	I/I_o - $2CuMoO_4 \cdot Cu(OH)_2$
7.155	10	7.01	20
4.392	20	4.34	35
4.207	50	4.15	55
3.517	100	3.50	100
2.979	10	2.96	20
2.794	18	2.76	20
2.699	8	2.72	20
2.531	36	2.67	40
2.416	22	2.50	25
2.313	12	2.40	20
1.728	10	2.29	25

Table 8: X-ray Diffraction Pattern for Copper Molybdate

3.3.4 Solubility of calcium in hypochlorite solutions

The fact that copper and molybdenum apparently do not combine at pH 9.0 to form a stoichiometric $CuMoO_4$ compound, together with the observations made during leaching that solutions containing copper as a soluble carbonate species were not those in which molybdenum extraction was adversely affected, raised the question that other elements contained in the copper sulphide minerals as impurities could be precipitating insoluble molybdate salts.

An Eh-pH diagram for the $Cu-H_2O-MoO_4$ was constructed (Figure 51) and this confirmed that copper molybdate exists as a stable compound at pH levels below about 9.2. Further evidence that copper was not primarily responsible for the molybdenum losses at pH 9.0 was then obtained by

i) leaching reagent grade molybdenum disulphide and synthetic cuprous or cupric sulphides together and obtaining >95% molybdenum extraction whether or not carbonate (and hence copper) was present in solution (Figure 36); and

ii) leaching covellite and molybdenite at pH 10.0, which should be well outside the zone of stability of $CuMoO_4$. In the presence of carbonate ≈91% of the molybdenum was recovered, but this dropped to only 78% in a leach with no carbonate (Figure 37, Tables XLI, XLII).

X-ray and chemical analysis of the ores indicated that iron, zinc, calcium and lead were the major metallic impurities. Leaching in hypochlorite solutions produced no dissolution of lead or iron, and only negligible amounts of zinc. However, 0.067 g/l, 0.058 g/l and 0.004 g/l calcium were detected in solution during the leaching of 10 g samples of
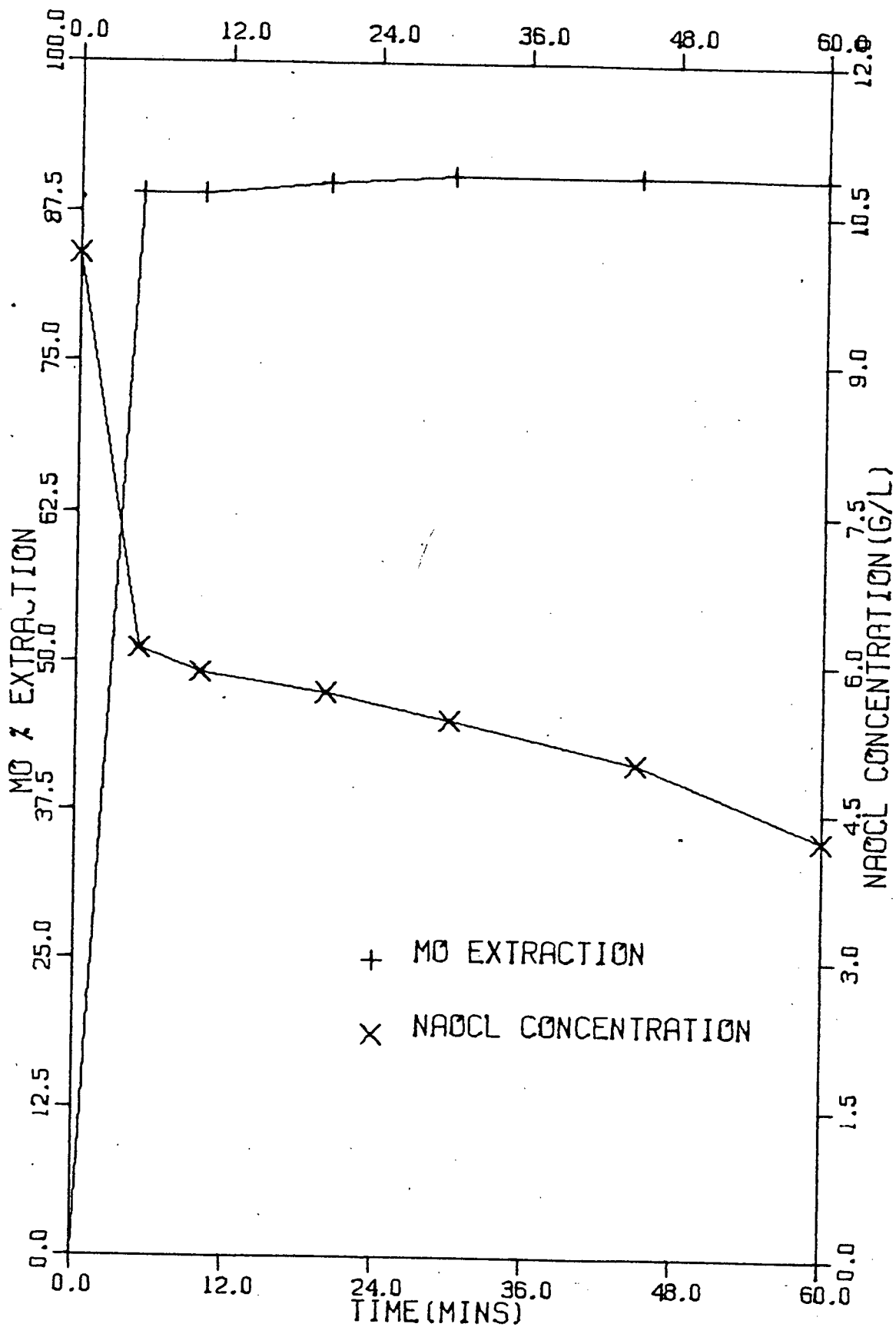
Figure 36: NaOCl oxidation of molybdenum disulphide and cuprous sulphide at pH 9.0 ± carbonate.
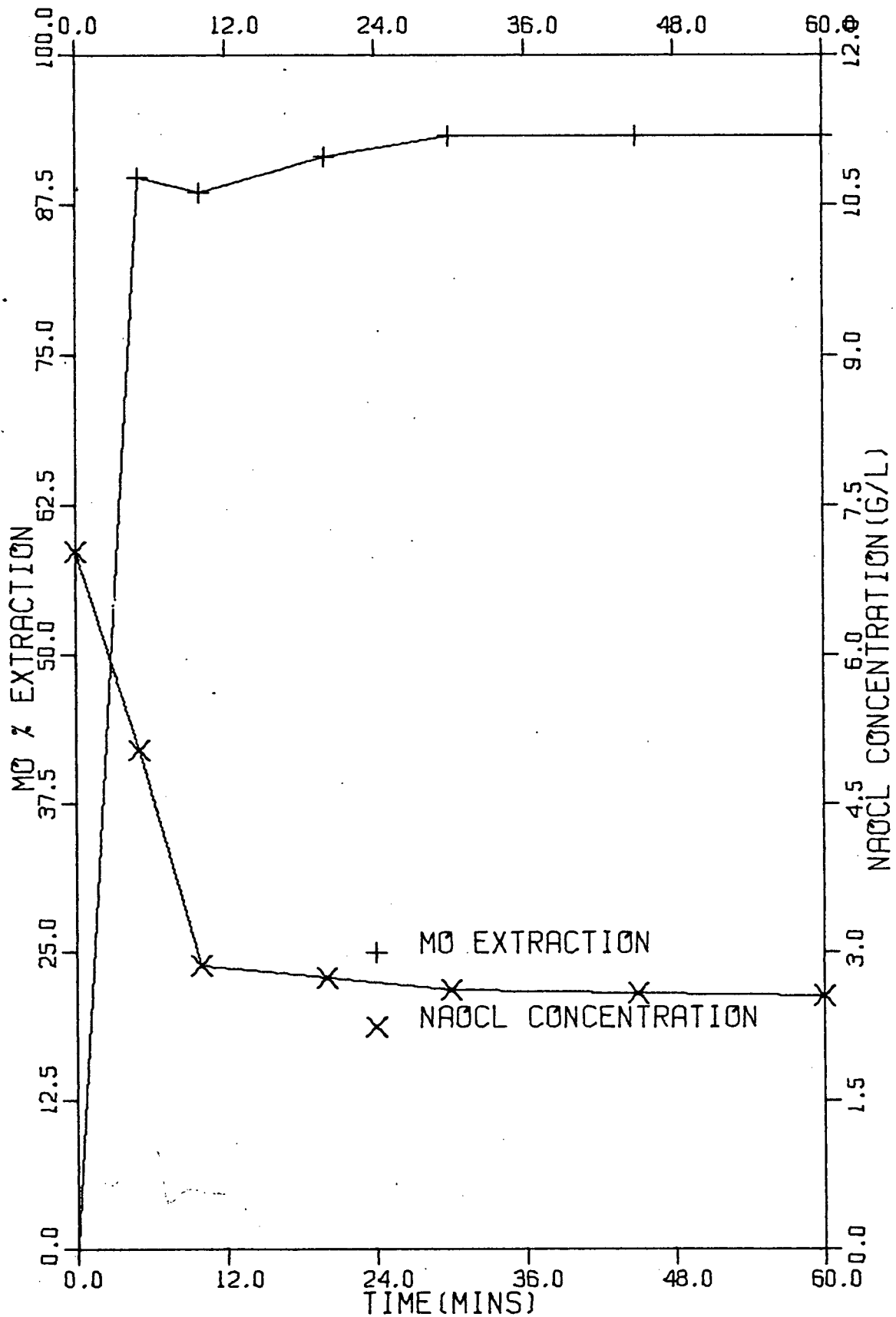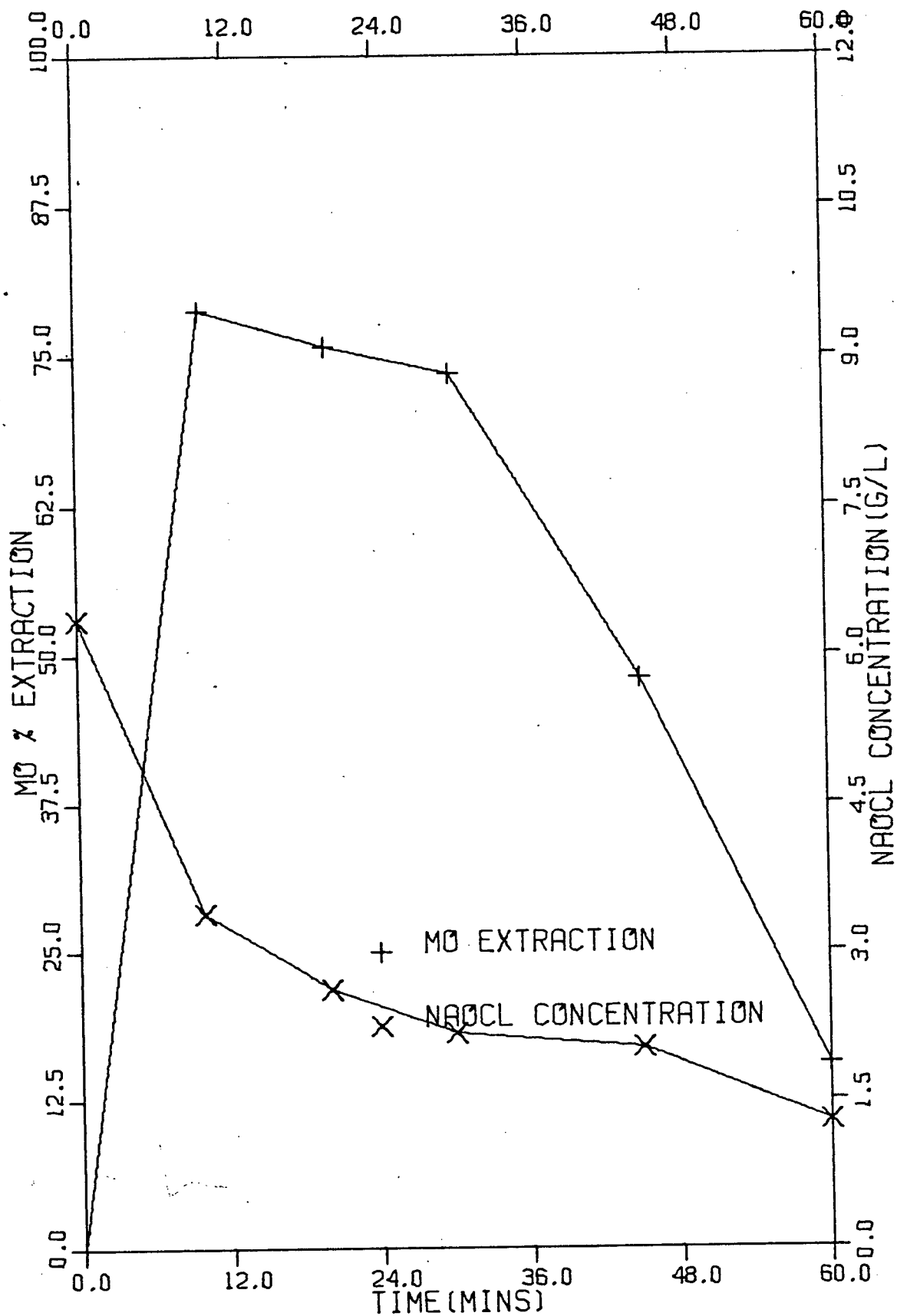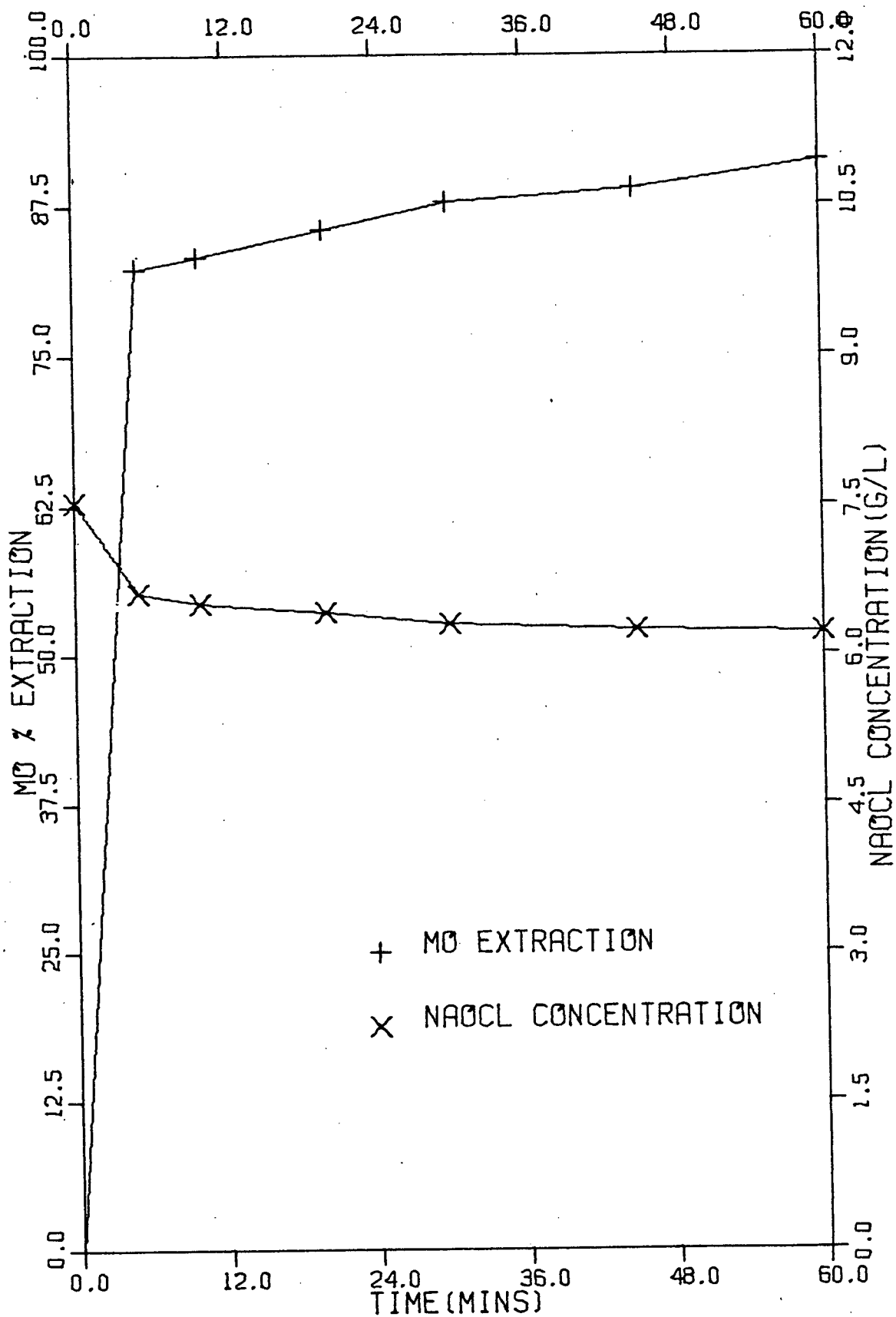
Figure 37 (a): NaOCl oxidation of molybdenite and covellite
at pH 10.0 in the presence of carbonate buffers.
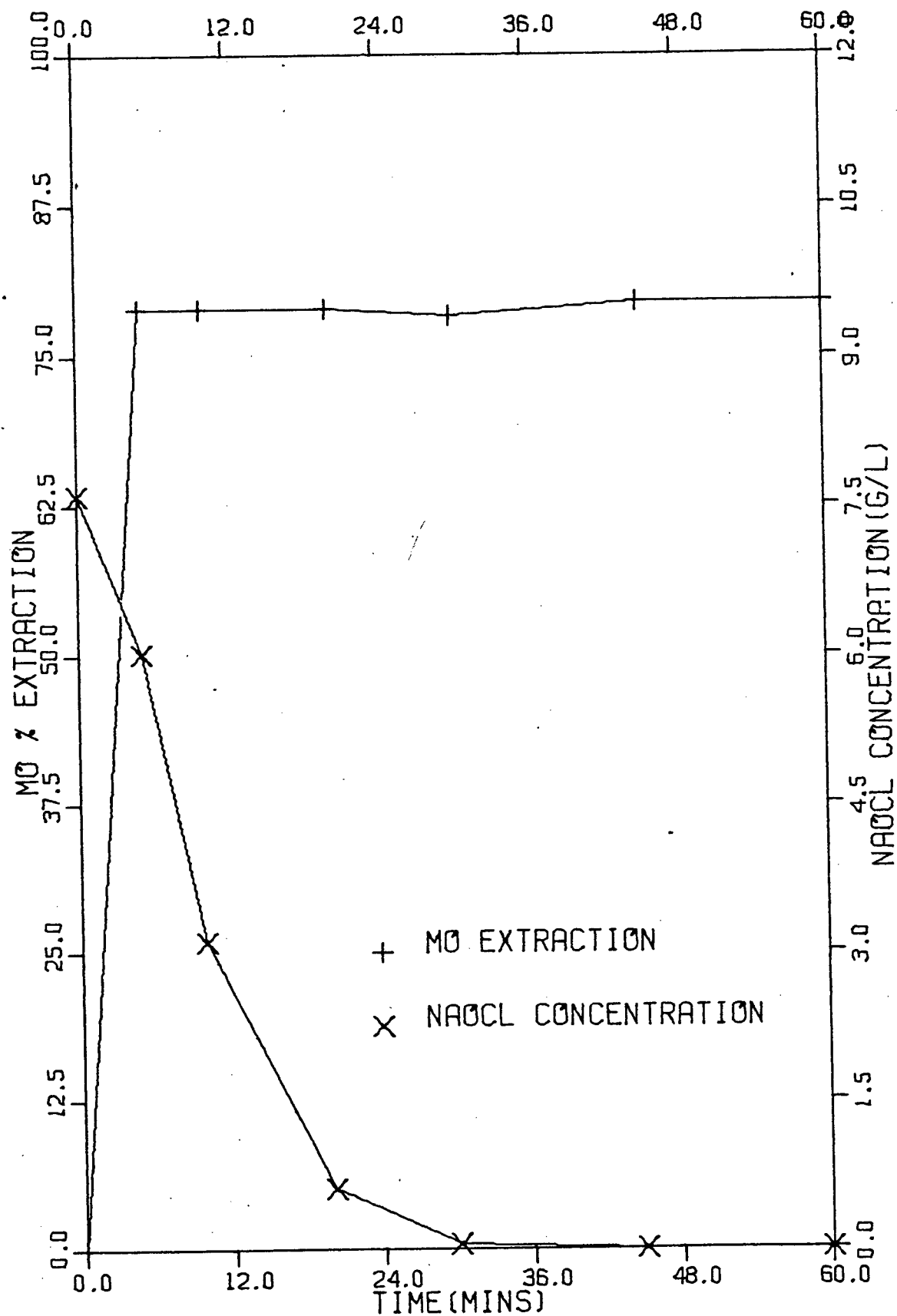
Figure 37 (b): NaOCl oxidation of molybdenite and covellite at
pH 10.0 in the absence of carbonate buffers.

of chalcopyrite, covellite and chalcocite respectively (Figure 38, Table XLV). It is well known that calcium molybdate and calcium carbonate are both insoluble salts.

The fact that calcium will remove molybdenum from hypochlorite solutions at pH 9.0, except in the presence of carbonate reagents, was illustrated by adding a calcium chloride solution to a molybdenite leach. Loss of 1.25×10^{-4} moles of both calcium and molybdenum was observed when no carbonate was added, but virtually all the calcium was removed and 98% molybdenum maintained in solutions which also contained sodium carbonate/bicarbonate buffers (Tables XLVI, XLVII).

3.3.4.1 Sodium hypochlorite leaching of calcium sulphate/calcium carbonate minerals

The most commonly occurring calcium minerals are calcite, $CaCO_3$, and gypsum, $CaSo_4 \cdot 2H_2O$. With the assumption that either or both of these form the principal source of calcium impurity in the copper sulphide minerals under study, samples of each mineral were leached under identical conditions to those used for copper/molybdenum:

10 g of $CaCO_3$ containing 4 g calcium yielded ≈ 0.016 g Ca^{2+} in solution, amounting to 0.4% extraction.

10 g of $CaSO_4 \cdot \frac{1}{2}H_2O$ ("Plaster of Paris") gave 2 g/l dissolved calcium which is equivalent to 64.5% extraction (Figure 39, Tables IL, L).

That the small amount of calcium dissolved by the action of a 7 g/l solution of sodium hypochlorite on calcite was sufficient to adversely affect molybdenum recovery was confirmed by a combined calcite/molybdenite leach. This gave only 80% molybdenum extraction. The same
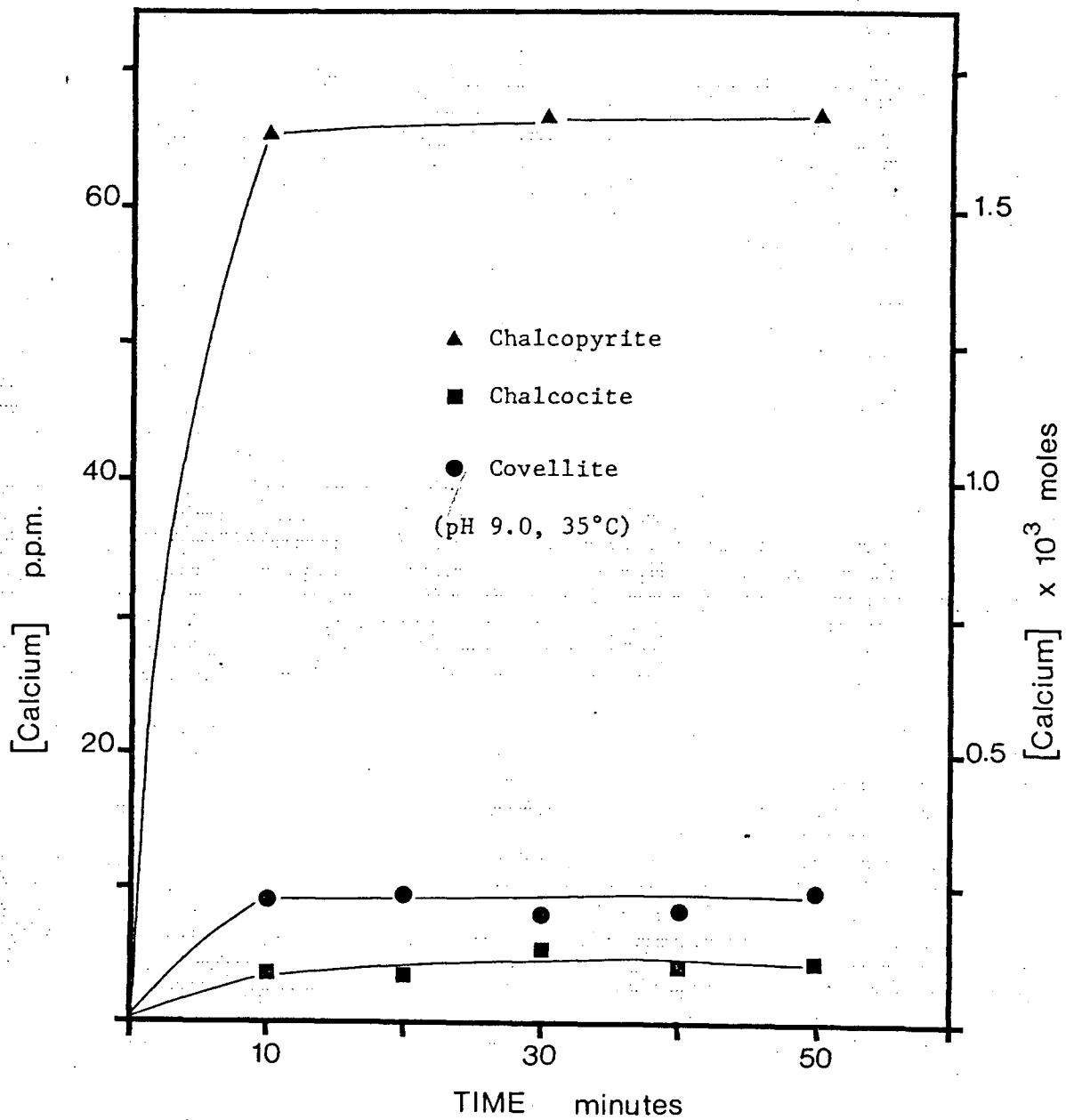
Figure 38: Calcium dissolution during NaOCl leaching of Copper Sulphide Minerals.
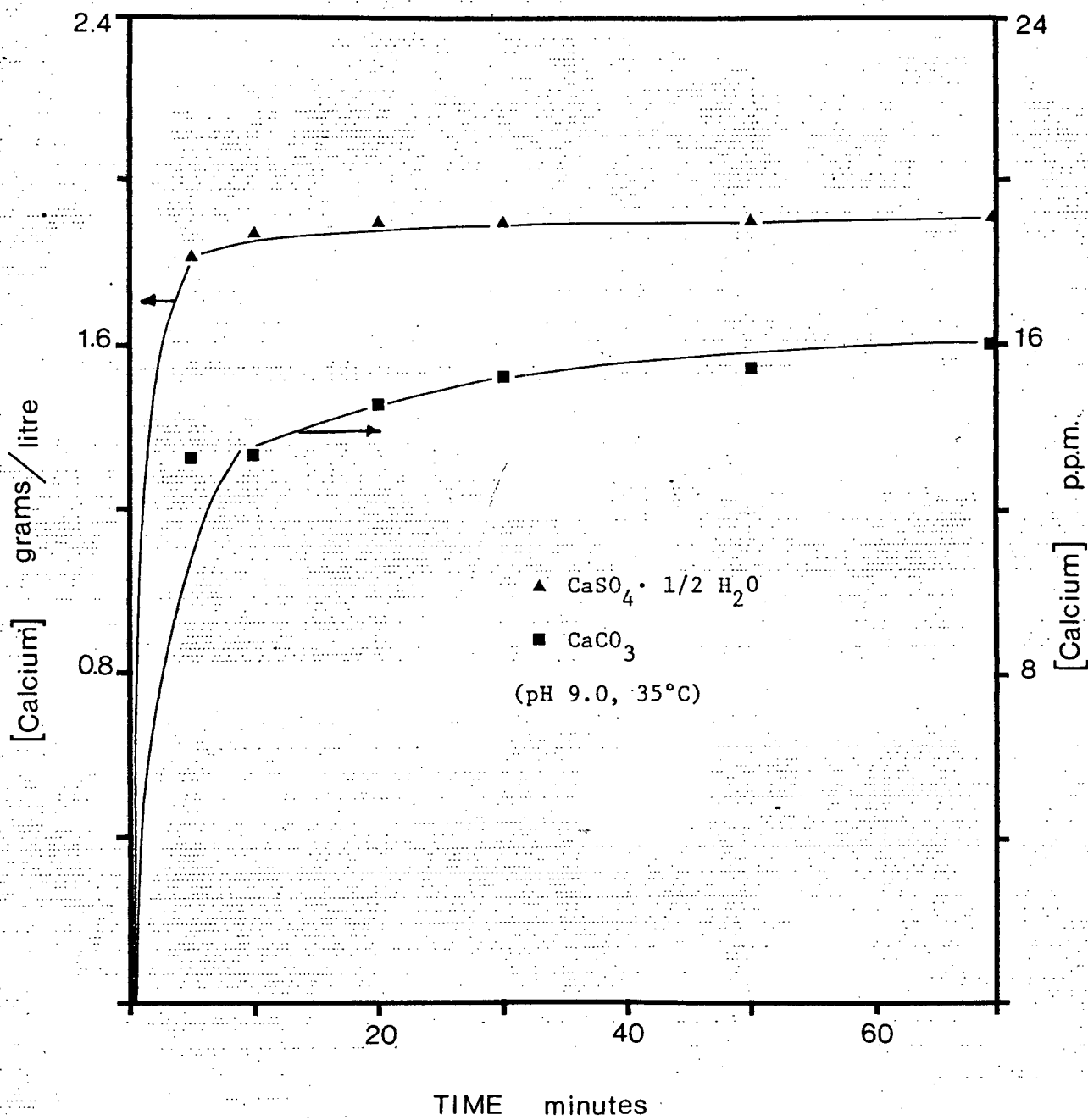
Figure 39:   NaOCl leaching of Calcium Minerals at pH 9.0.

experiment in the presence of carbonate produced over 95% extraction (Figure 40, Table XLVIII).

3.3.4.2 Effect of chloride concentration on calcium solubility

Calcium solubility increases in the presence of chloride solutions. A number of experiments were carried out to determine whether the solubility observed during the leaching of calcium minerals in hypochlorite solutions prepared from a commercial bleach, was in line with that expected from sodium chloride solutions of equivalent strength. The total chloride content was varied from zero to 2 M and it was found:

i)   The amount of calcium dissolved from 10 g samples of both calcite and gypsum increased as a function of the total chloride content. (Figures 41, 43, Tables LI, LII). The absolute amounts were higher in the latter case.

ii)   Identical results were obtained whether the chloride was present as NaCl only, NaOCl made from 'JAVEX', or as a mixture of both.

iii)   The results were in good agreement with values reported in the literature for calcium solubility in chloride solutions (Figures 42, 44).

iv)   The rate of extraction was fast in all cases and there was a slight increase as the chloride content was increased.

3.3.4.3 Removal of calcium from solution

It is evident that leaching molybdenite in the presence of soluble calcium salts is undesirable. It was therefore necessary to find a method
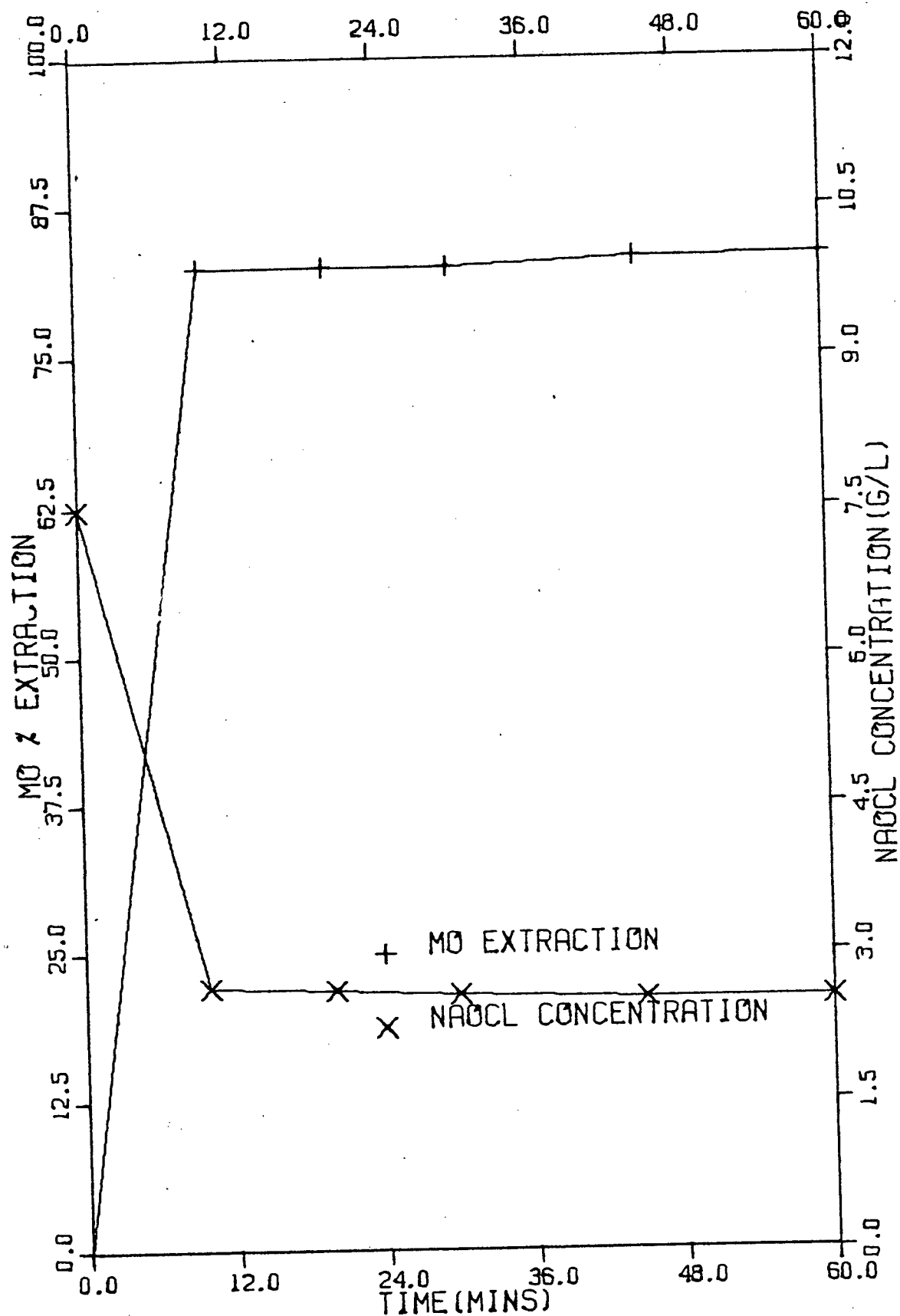
Figure 40: NaOCl oxidation of molybdenite and calcite at pH 9.0, in the absence of carbonate.
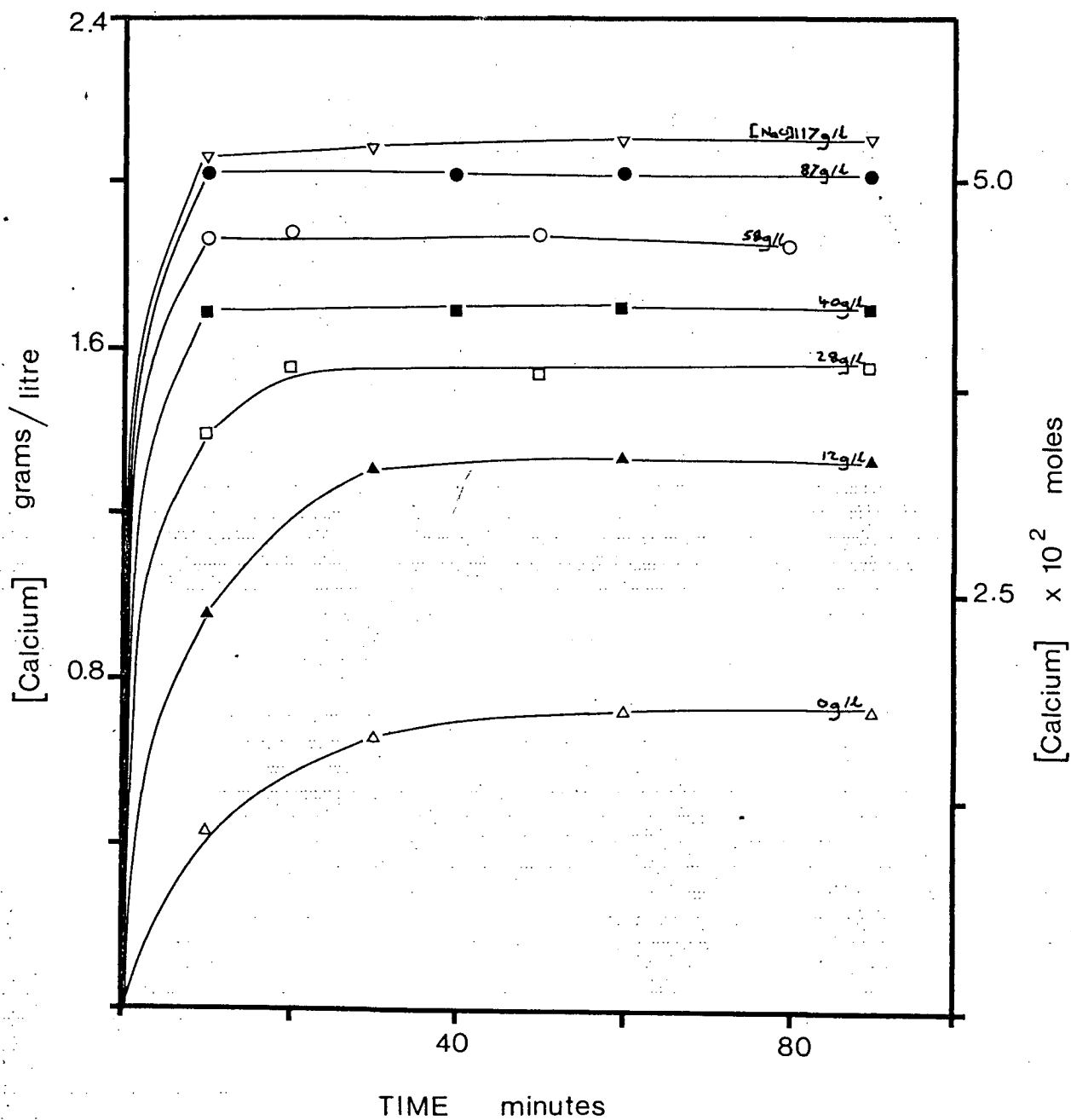
Figure 41: Effect of Chloride Concentration on Ca dissolution from $CaSO_4 \cdot 1/2\ H_2O$.
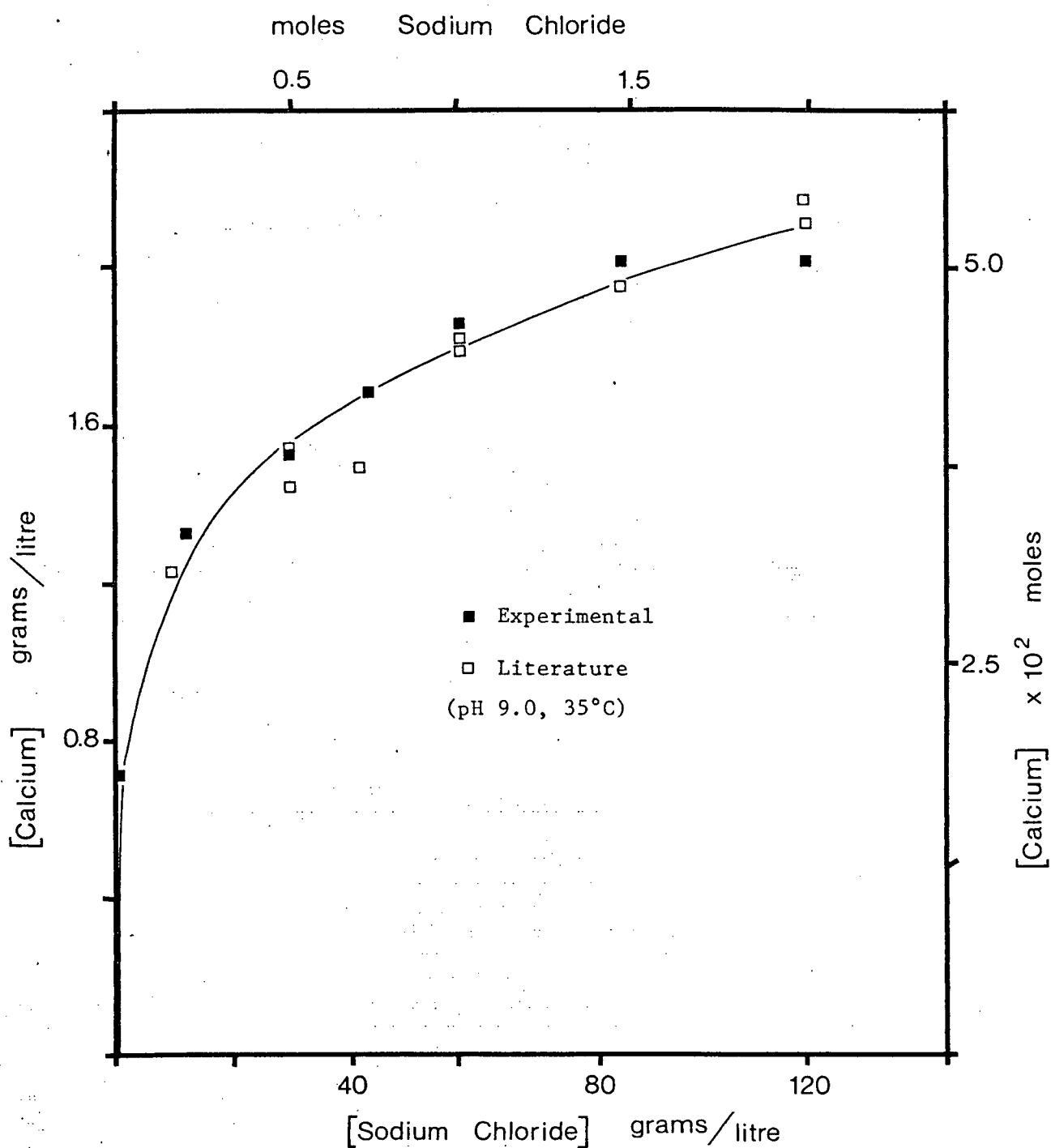
Figure 42: Calcium Sulphate Solubility as a Function of Chloride Content.
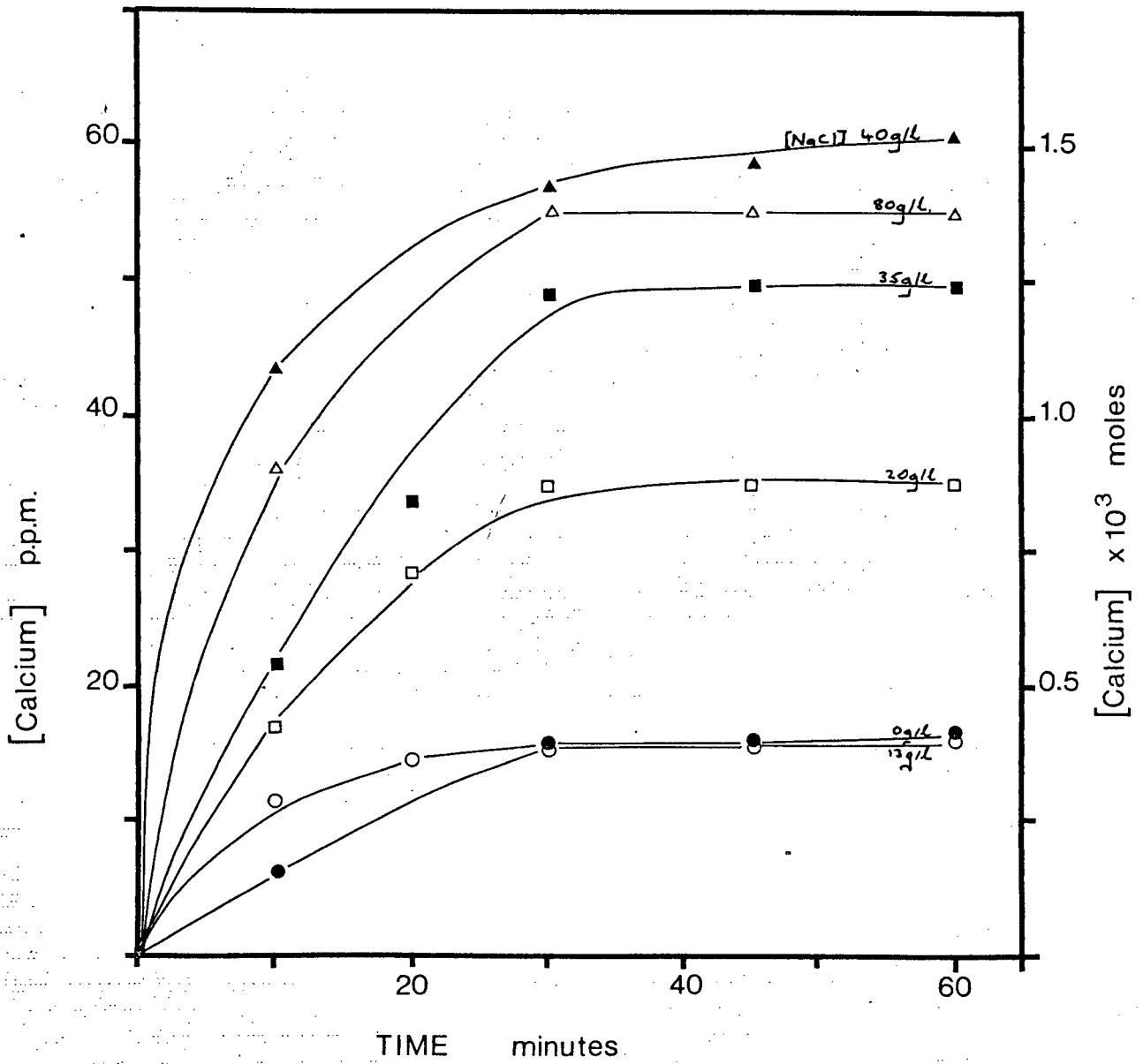
Figure 43: Effect of Chloride Concentration on Ca dissolution from $CaCO_3$.
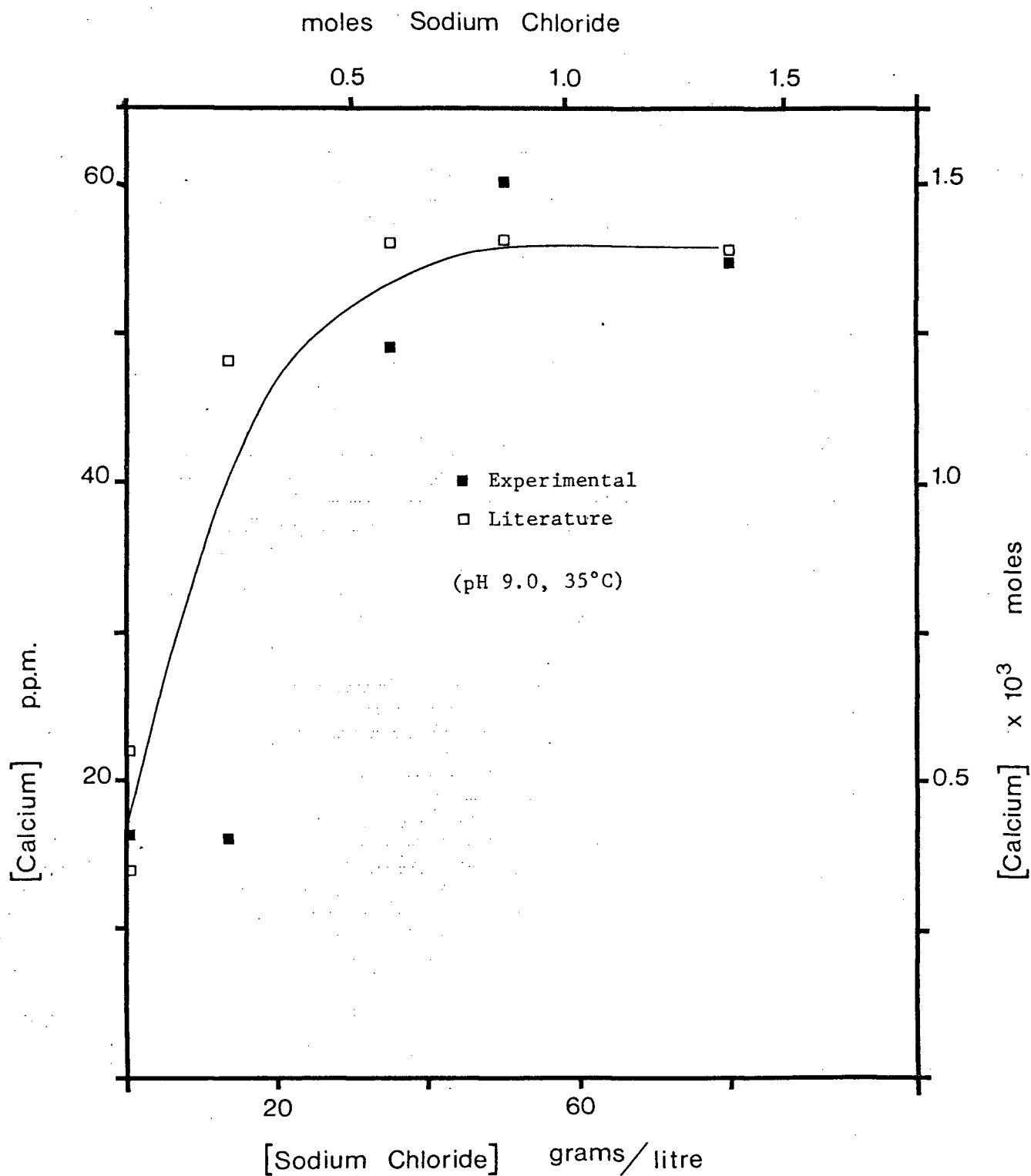
Figure 44: Calcium Carbonate Solubility as a Function of Chloride Concentration.

of removing Ca^{2+} from the leaching solution, without detriment to the molybdenum. Despite the fact that calcite is slightly soluble in hypochlorite solutions, experiment showed that the presence of excess carbonate in the system suppressed formation of $CaMoO_4$. Further tests indicated that a minimum of 3.19 M CO_3^{2-} per mole Ca were required to ensure complete precipitation as $CaCO_3$ (Figure 45, Table LIII).

In practice however, it appeared that the quantity of carbonate required by the system may be dictated by factors other than for calcium suppression. It was noted in Section 3.1.6 that low carbonate concentractions produced a loss of hypochlorite more quickly than higher concentrations during the leaching of Cu_2S, CuS and $CuFeS_2$. Experiments in which molybdenite and copper sulphides were leached together showed this nucleation time decreased further for a given $[CO_3^{2-}]_T$ concentration. This was apparently due to the presence of molybdenite. CuS/MoS_2 runs at the 5 g/l and 10 g/l carbonate level showed hypochlorite decomposition to occur after 45 and 110 minutes respectively, representing a decrease of 30 - 50% over the nucleation time for CuS alone. Copper dissolution was also slightly lower (Figure 46, Tables LIV, LV). A similar effect was observed with Cu_2S/MoS_2 and 10 g/l carbonate (Figure 47, Table LVII).

At the 5 g/l $[CO_3^{2-}]_T$ level it was also found that a gradual loss of hypochlorite occurred continuously from the beginning of agitation and before the rapid loss caused by copper[III] catalysis. Leaching CuS in the presence of sodium molybdate confirmed this trend and showed loss of both copper and molybdenum from solution in a 1:1 ratio suggesting that some $CuMoO_4$ forms even in the presence of carbonate. This then causes catalyzed hypochlorite decomposition before Cu^{III} precipitation
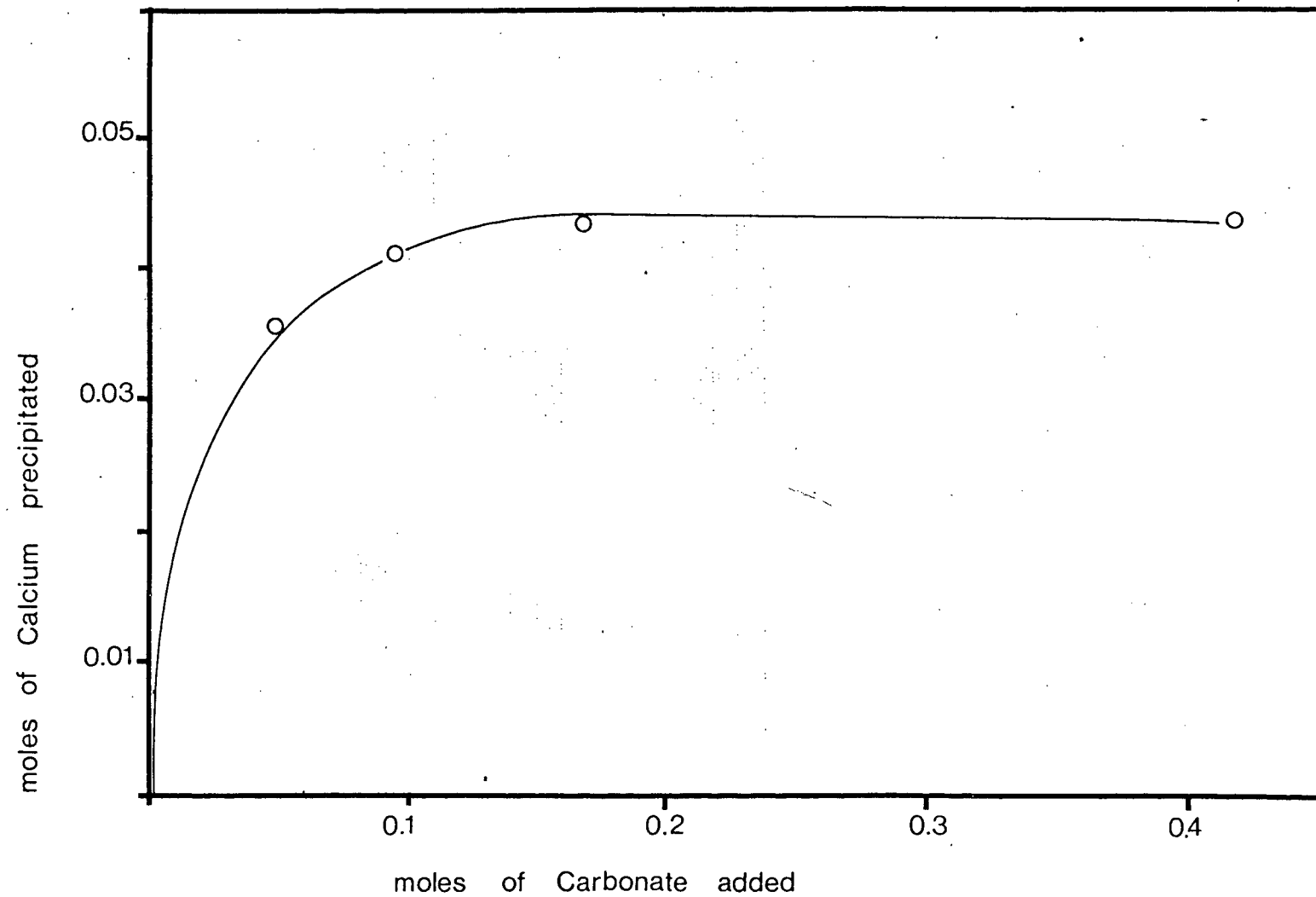
Figure 45:   Effect of Carbonate Addition on Calcium Precipitation from Solution.
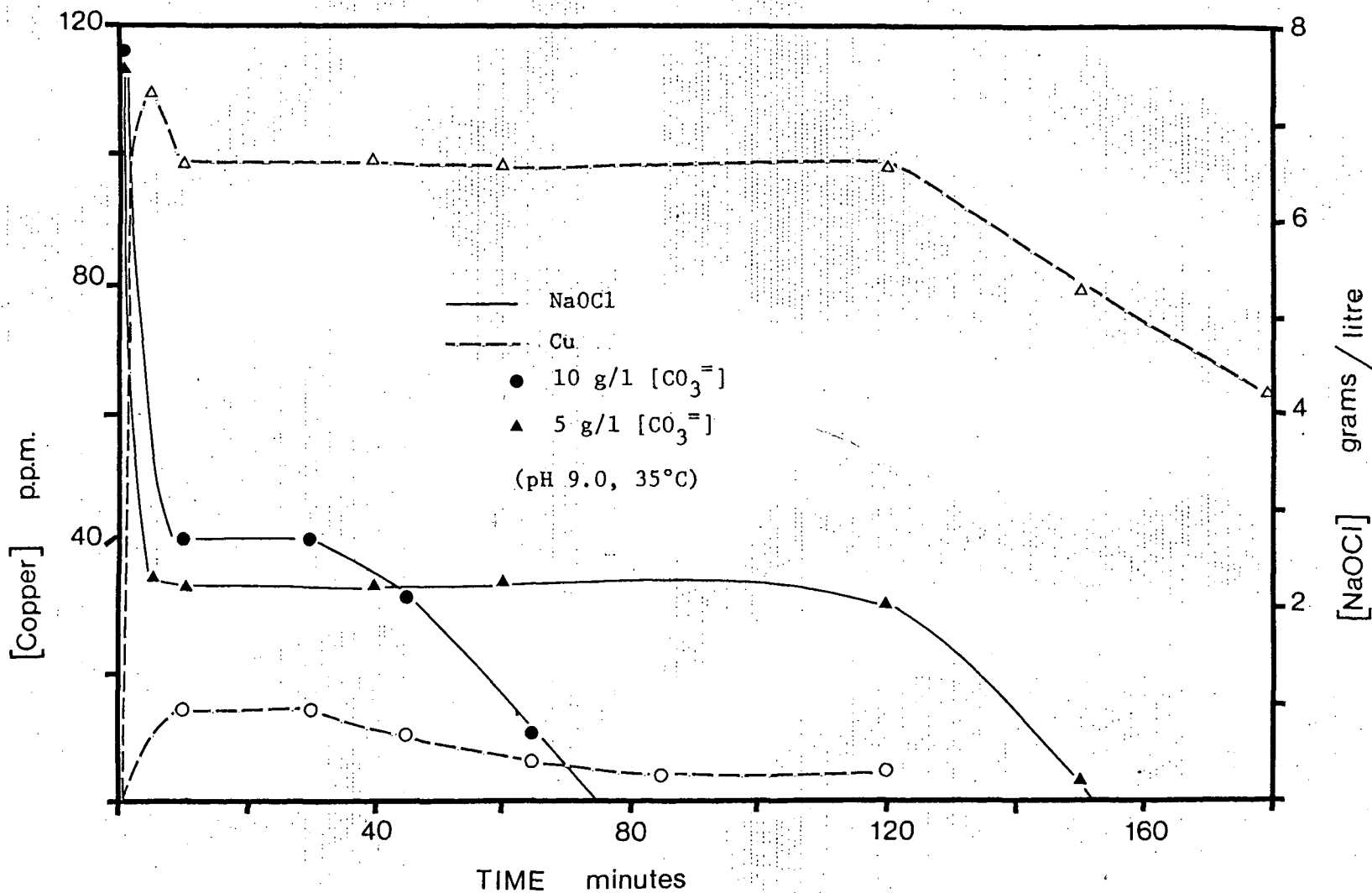
Figure 46: Copper dissolution and NaOCl Decomposition during Covellite/Molybdenite leaching at pH 9.0, with varied $[CO_3^=]_T$.
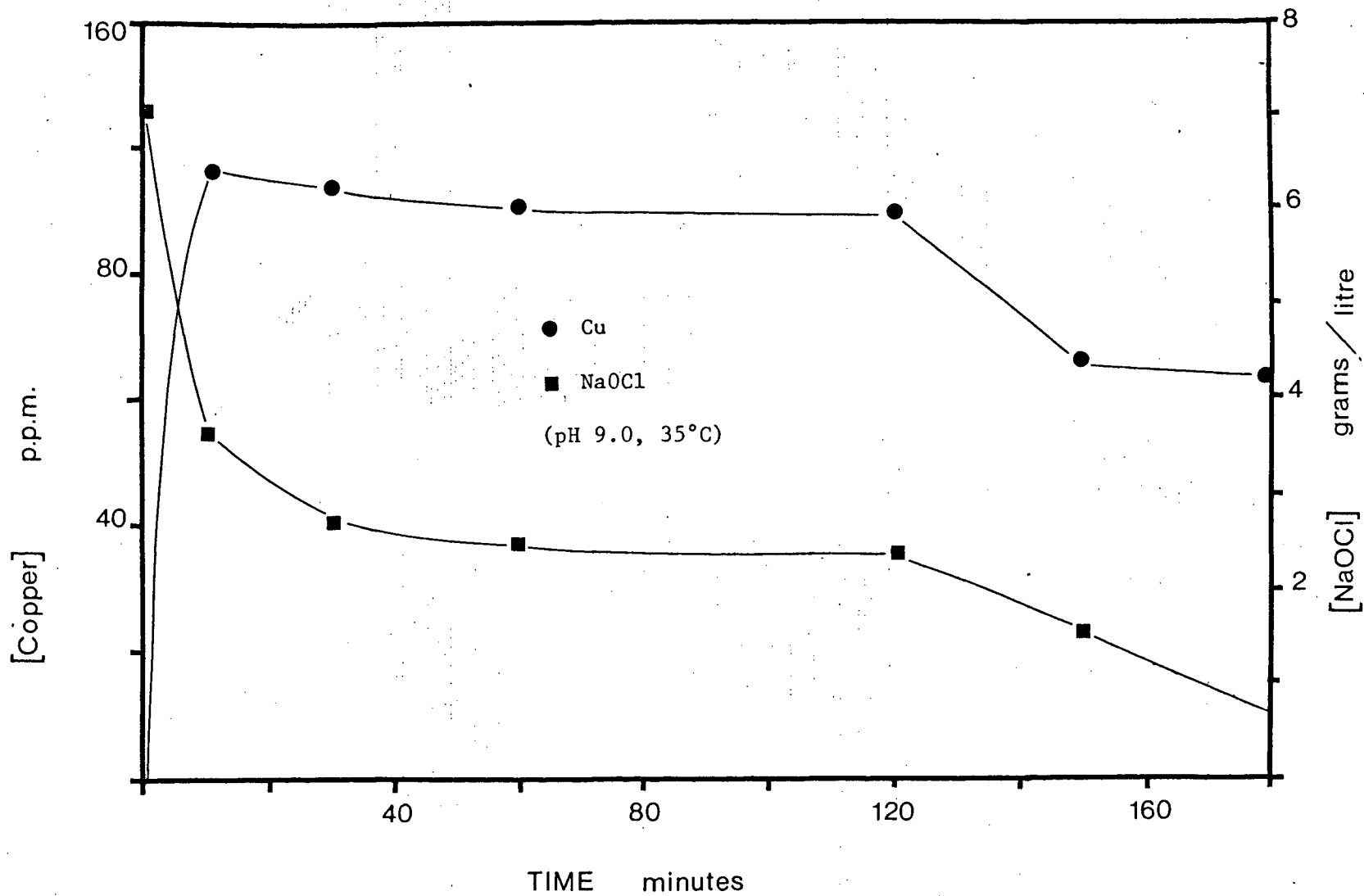
Figure 47: Copper Dissolution and NaOCl Decomposition during Chalcocite/Molybdenite Leaching at pH 9.0 (10 g/l [$CO_3^=$]).

(Figure 48, Table LVI). A similar run with double the amount of carbonate produced no loss of copper or molybdenum and no hypochlorite decomposition for over 4 hours (Figure 12b, Table XVIII).

Leaching in the presence of larger amounts of carbonate would thus extend the period of maximum molybdenum extraction prior to copper^{III} precipitation and OCl^- decomposition, as well as preventing $CuMoO_4$ and $CaMoO_4$ formation.

Silicates and phosphates also have insoluble calcium salts. Various beaker experiments were done to investigate the effectiveness of these reagents in precipitating calcium, as an alternative to carbonate, thereby preventing copper dissolution. Sodium meta silicate, $Na_2SiO_3 \cdot 5H_2O$ was found to be most efficient in this respect (Table 9).

A molybdenite/chalcopyrite leach was subsequently carried out in the presence of 1 g/l SiO_3^{2-}. Almost 99% Mo recovery was obtained (Figure 49, Table LVII). No copper was detected in solution and the hypochlorite maintained a constant value for the duration of leaching.
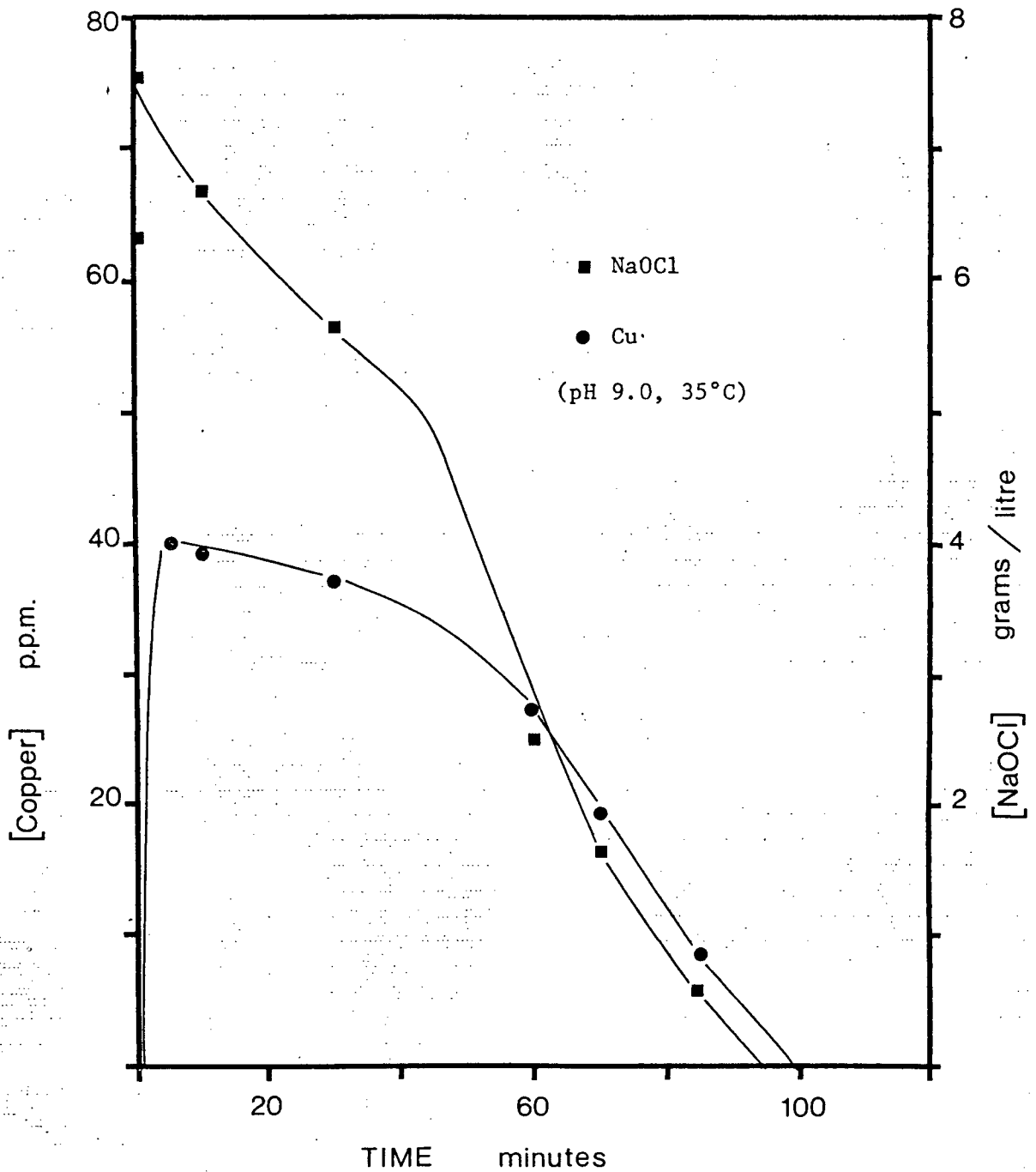
Figure 48: NaOCl Leach of Covellite with 5 g/l $[CO_3^=]_T$ in the Presence of Na_2MoO_4.
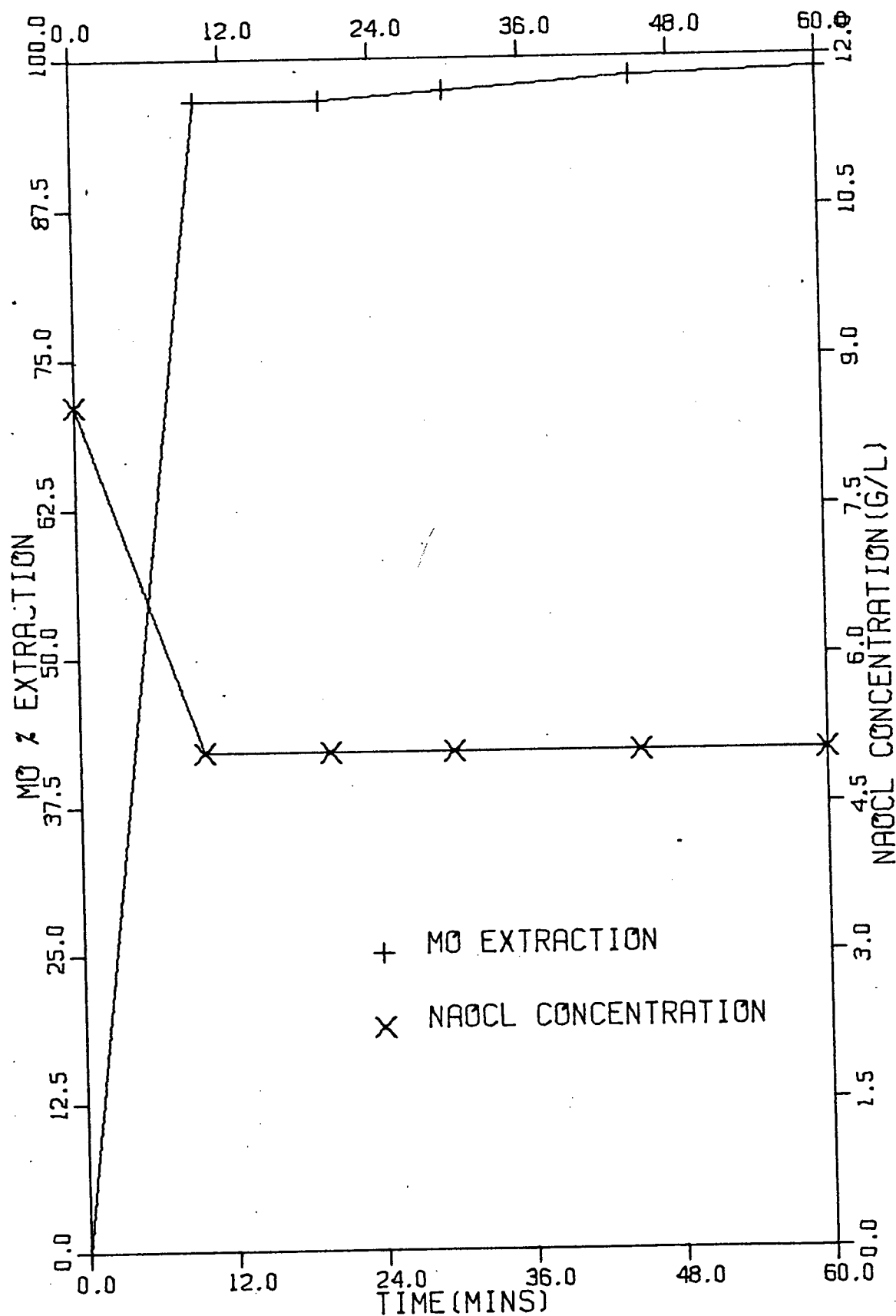
Figure 49: NaOCl oxidation of molybdenite and chalcopyrite in the presence of Na_2SiO_3.

Additive (g/l)	[Ca] in soln. (ppm)	Additive (Moles)	[Ca] ppt (Moles)	Ratio
--	94.12	--	2.35×10^{-2}	
$[CO_3^{2-}]$:				$CO_3^{2-}:Ca^{2+}$
0.25	90.31	4.166×10^{-3}	9.50×10^{-4}	4.39:1
0.50	53.17	8.33×10^{-3}	1.02×10^{-3}	8.17:1
1.00	18.8	1.66×10^{-2}	1.88×10^{-3}	8.83:1
$[SiO_3^{2-}]$:				
0.25	20.03	3.28×10^{-3}	1.85×10^{-3}	1.77:1
1.00	3.45	1.31×10^{-2}	2.26×10^{-3}	5.04:1
$[PO_4^{3-}]$:				
0.25	53.17	3.16×10^{-3}	1.02×10^{-3}	3.09:1
1.00	25.20	1.27×10^{-2}	1.70×10^{-3}	7.47:1

Table 9: Effect of SiO_3^{2-}, CO_3^{2-} and PO_4^{3-} (sodium salts) on Calcium Precipitation at pH 9.0, in Hypochlorite Solutions.

CHAPTER 4

Discussion

4.1.1 Sodium Hypochlorite Leaching of
       Copper Sulphide Minerals in the
       Presence of Carbonate

Initial tests to investigate the leaching behaviour of covellite,

chalcocite and chalcopyrite in sodium hypochlorite solutions at pH 9.0

reaffirmed Ismay's observation made during leaching experiments with

copper rougher concentrates, that a certain amount of copper was rapidly

extracted by the hypochlorite and held in solution.

The thermodynamic solubility of copper hydroxide which is the

stable species at pH 9.0, as given by Pourbaix[73] is 8.0 x 10^{-9} which is

several orders of magnitude less than the observed experimental value

of 10^{-3} M. It thus seemed likely that complexing of some kind was

occurring. Copper, in common with other elements of the first transition

series, is capable of forming aqueous complexes with a large number of

anions, but these are more limited on the alkaline side of neutrality

than in acid solutions. The most common at higher pH levels are ammonia

and cyanide, but the only components present in the system under study

were chloride (as Cl^- and as OCl^-) and carbonate, as well as sulphide con-

tained in the copper ores which would be expected to oxidize to sulphate,

SO_4^{2-}, in hypochlorite solution. To determine if one or more of these

species could complex copper under the prescribed conditions, relevant

literature was reviewed and it was found:

     i) Certain cupric chloride complexes are known to exist, but

are found predominantly in acid solution.[39,40]

ii) Copper hypochlorite can exist in aqueous solution but the only known method of preparation is with acidic hypochlorite, and the species is relatively unstable.[79] Various references to $Cu - OCl^-$ complexes were found but none contained definite proof that such a complex could be made.

iii) Bivalent copper can combine with various intermediate sulphur oxidation species to form a number of salts, such as $CuS_2O_6 \cdot 4H_2O$, CuS_4O_6, some of which are soluble in aqueous solution.[79]

iv) Cupric carbonate complexes exist, and are relatively stable in alkaline solution.[27-40]

Thus carbonate seemed to be the most likely complexing agent at a pH value of 9.0, and the fact that the leaching solutions showed such strong blue colouration for the amounts of copper they contained was in line with observations made by Deville, Pickering and Appleby[27,30,31] that the alkaline 'cupricarbonates' have a characteristic deep blue colour.

Although slight variations in the amount of copper dissolved occurred between the three minerals, they were all of the same magnitude (0.12 - 0.13 g/l equivalent to 2.0×10^{-3} M copper).

The fact that the same amount of sample was used in each case, implying that different amounts of copper were initially present, suggests that this value represented the maximum amount of copper which is soluble under the given conditions of pH, temperature and carbonate concentration.

For a total carbonate content of 10^{-1} M, De Zoubov et al. show the solubility of copper^{II} to be 4.0×10^{-5} M at pH 9.0, where it exists as

the cupricarbonate ion $Cu(CO_3)_2^{2-}$ [36] (Figure 51). This is slightly lower than the value obtained in this study and suggests that carbonate may not be the only complexing agent for copper. Assuming that $Cu(CO_3)_2^{2-}$ forms the major complex species, however, and that all the sulphide associated with extracted copper is oxidized to sulphate, the reaction can be described by the equation:

$$CuS + 4NaOCl + 2NaOH + 2HCO_3^- \longrightarrow$$
$$Cu(CO_3)_2^{2-} + 4NaCl + Na_2SO_4 + 2H_2O \qquad (55)$$
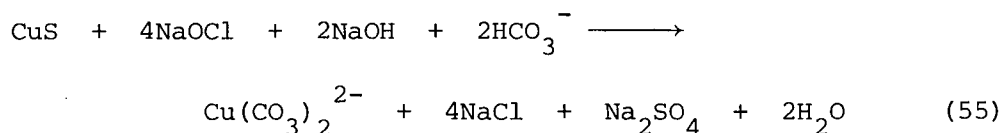
The reasons why such apparently random variations in the copper content occurred throughout a leaching run, or why a black precipitate was deposited from filtered solutions on standing overnight, were not immediately apparent.

4.1.2   Removal of Carbonate from the System

Experiment confirmed that the carbonate buffer components were primarily responsible for holding copper in solution: negligible amounts were dissolved when the $NaHCO_3/Na_2CO_3$ mixture was replaced by sodium hydroxide solution.

This would seem to be an important factor when considering a leaching process which requires the selective extraction of molybdenum from porphyry copper ores. The solubility of copper in carbonate solutions has been overlooked by a number of other workers including Shapiro and Kulenkeva[14] who claimed that in a carbonate system, any metal sulphides other than molybdenum would be precipitated as insoluble carbonates;

and Bhappu[17] and Scheiner et al.[20,21,22] both of whom suggested hypo-chlorite leaching in the presence of carbonate would give a selective molybdenum leach.

However, the potential advantage of removing the carbonate, and hence any soluble copper, from the system is offset by the observed effects on the hypochlorite. The small amounts of copper dissolved in the carbonate buffered case consumed very little hypochlorite and no further loss of strength was observed for up to four hours leaching. On the other hand, leaching with no carbonate caused rapid decomposition of the hypochlorite, accompanied by a drop in the pH of the solution, necessitating the addition of sodium hydroxide as an external buffer component.

Sodium hypochlorite is a strong oxidant and it is likely that the surfaces of the copper minerals are rapidly oxidized on contact with it. At pH 9.0 and with no complexing agent present, the copper precipitates as a hydroxide on the mineral surface, thereby preventing any copper dissolution:

$$CuS + 4NaOCl + 2NaOH \longrightarrow Cu(OH)_2 + NaSO_4 + 4NaCl \qquad (56)$$
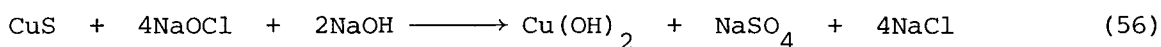
The fact that molybdenite and chalcopyrite have approximately equal oxidation rates suggested to Stumpf and Berube[25] that a selective molybdenum leach was not possible, but these authors seem to have over-looked the relative solubilities of the two species in alkaline solution.

The formation of a surface hydroxide is presumably the cause of the observed hypochlorite decomposition: oxides and hydroxides of various transition metals, including copper, are known to be active catalysts

for the heterogeneous decomposition of hypochlorite solutions.[43-51]

Decomposition can occur either to oxygen and chloride or to chloride
and chlorate. The former reaction is generally thought to be the more
common in alkaline solutions. It was reported by Prokopchik, however,[51]
that some chlorate is produced at high pH values, and that in the presence
of copper hydroxide catalysts this reaction becomes more predominant as
the pH is lowered. Thus at pH 9.0 a ratio of $ClO_3:O_2$ of about 3:1
was obtained. Sodium chlorate is undesirable in a hypochlorite system
utilizing complete salt recycle for regeneration of the lixiviant. The
production of $NaClO_3$ in large amounts would therefore necessitate solu-
tion treatment to remove it; for example, using SO_2 reduction, as
reported in the U.S. Bureau of Mines process.[20] Chlorate has also been
shown to interfere with the subsequent recovery of molybdenum from leach-
ing solutions.[23,24]

4.1.4 Decomposition Products During the Leaching of Copper Sulphide Minerals

The production of $NaClO_3$ as a result of NaOCl decomposition in the
present study was found to vary from mineral to mineral. The fact that
chlorative decomposition increased with respect to time during chalcocite
leaching, but decreased in the cases of covellite and chalcopyrite may be
associated with their relative catalytic rates, considering that chalco-
cite produced a much slower rate of decomposition than the other two.
In no case was a $ClO:O_2$ ratio of anything approaching the 3:1 reported
by Prokopchik at pH 9.0 found to exist.

The most obvious reason for the observed differences in catalytic

decomposition rate between chalcocite, chalcopyrite and covellite would be a difference in the active surface area, since the reaction is heterogeneous. Calculations for the overall surface area of -200 mesh samples of covellite and chalcocite, give values of 33,300 cm^2 and 27,000 cm^2 respectively (Appendix B). The difference is therefore insufficient to account for the 6:1 ratio observed between the rates of decomposition given by CuS and Cu_2S. Furthermore, the use of synthetic copper sulphides indicated a constant rate of NaOCl decomposition for both cupric and cuprous salts. This could be the actual rate of catalysis of copper hydroxide, with that observed during covellite and chalcopyrite leaching being caused by some sort of "promoted catalysis." Both these minerals were found to contain traces of nickel and cobalt as impurities. Nickel salts have been shown by several workers to be more active catalysts than the corresponding copper salts, and it is known that negligible amounts of both nickel and cobalt can cause significant hypochlorite decomposition.[45,49,51] Chirnoaga also reported that the action of 'mixed' catalysts produced a more rapid reaction than either one alone. This was confirmed by Lewis who proposed a mechanism for this type of reaction.[45,46] It is therefore suggested that the enhanced rates of decomposition observed in the present study are caused by the combined action of copper and nickel hydroxide catalysts, giving a faster rate than would be produced by copper alone.

The presence of carbonate in the system obviously deactivates the mineral surface: complexing a small amount of oxidized copper as the cupri-carbonate ion, $Cu(CO_2)_3^{2-}$, prevents formation of a hydroxide catalyst, and the soluble copper species does not in itself act as a

catalyst, so that no hypochlorite decomposition occurs.

4.1.5 Sodium Hypochlorite Leaching of Massive Samples of Copper Sulphide Minerals

Experiments using massive samples were carried out to obtain more information, both qualitatively and quantitatively, about the nature of surface reactions occurring during leaching. Covellite was found to have a more rapid reaction with the hypochlorite than chalcocite, whether or not carbonate was present in the system. Cu_2S has been shown to leach in a two stage process in acid solution, with the second stage resembling the leaching of CuS or similar mineral.[80,81] It is possible that even in the limited reaction which occurs on exposure to hypochlorite solutions, there is a difference between the oxidation behaviour of chalcocite and covellite. This would represent a more fundamental cause for the differences in the rates of NaOCl decomposition noted above.

The patchy white areas present on the covellite surface after immersion into hypochlorite containing carbonate solutions for short periods probably indicate sulphate formation although why elemental sulphur should be present in certain areas as well is a little puzzling. Choppin and Faulkenberry[16] reported that elemental sulphur could be produced during the oxidation of aqueous sulphide solutions by hypochlorite whenever the ratio of $S:OCl^-$ was less than 1:4. In all other cases sulphate, SO_4^{2-}, was the only end product. It is thus possible that hypochlorite depletion occurred in localized areas of the mineral surface, enabling small amounts of sulphur to be formed.

Green deposits produced on both covellite and chalcocite surfaces after longer periods of exposure to hypochlorite solutions are almost certainly malachite, $Cu_2(OH)_2CO_3$. This substance forms the stable phase in the $Cu-CO_2-H_2O$ system at pH 9.0 (Figure 2). Further oxidation of the mineral surface after the saturation point for the cupri-carbonate species in solution has been reached will result in precipitation of a basic copper carbonate.

In the absence of carbonate, copper hydroxide forms on the mineral surface as a light green, powdery deposit. Micro-probe analysis confirmed that both deposits had a significantly increased Cu:S surface ratio, due to a large increase in the copper content at the surface.

The appearance of a black deposit on top of both green substances coating the original covellite surface, accompanied by a loss of blue colouration from the carbonate containing solutions was taken to be analogous to the deposition of a black precipitate from filtered solutions obtained during the leaching of CuS and Cu_2S powders. Subsequent leaching of ground material with variable amounts of carbonate in the system, consideration of the findings of Prokopchik[51] and others on the mechanism of hypochlorite decomposition in the presence of copper hydroxide catalysts, together with extensive analysis of the compounds made by the action of NaOCl on copper salts at pH 9.0 (Section 3.2.1) led to the conclusion that these black substances are tri-valent copper compounds.

4.1.6 Variation of the Total Carbonate Content During Leaching

A lower amount of carbonate in the leaching system caused less

copper to be dissolved, and it was held in solution for only a finite period of time. This time period, and the copper concentration in solution were found to be proportional to the contained carbonate. The rapid drop in copper concentration which subsequently occurred, accompanied by simultaneous hypochlorite decomposition can be explained by assuming sodium hypochlorite is capable of oxidizing copper to the tri-valent state, and that it is held in solution in this oxidation state by the complexing action of carbonate until such time as a solid copper^{III} compound is able to nucleate and precipitate on the mineral surface. This then becomes an active catalyst for hypochlorite decomposition. In the absence of any carbonate, the hydroxide formed on the mineral surface is therefore a copper^{III} compound rather than normal cupric hydroxide, $Cu(OH)_2$, and hypochlorite decomposition presumably occurs by the mechanism outlined by Prokopchik (applicable to pH values below 12.0):

$$ClO^- + 2Cu(OH)_2 + H_2O \longrightarrow Cl^- + 2Cu(OH)_3 \tag{57}$$

$$4Cu(OH)_3 \longrightarrow 4Cu(OH)_2 + O_2 + H_2O \tag{58}$$

$$(4Cu(OH)_3 + ClO^- \longrightarrow 4Cu(OH)_2 + ClO_3^- + 2H_2O) \tag{59}$$
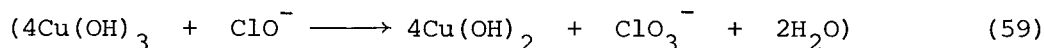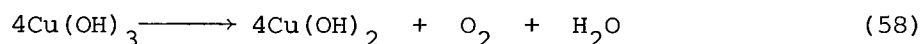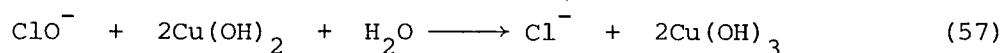
The observation that exposure of a small surface area of copper to a hypochlorite solution with minimal agitation, results in formation of copper^{II} hydroxide before deposition of the black copper^{III} hydroxide illustrates step (i) of this mechanism and subsequent hypochlorite decomposition would presumably follow a +2/+3 oxidation-reduction cycle.

The loss of copper from solution containing 10 g/l carbonate accompanying hypochlorite decomposition amounted to about 0.06 g/l Cu.

If the total surface area of mineral present is taken to be 33,000 cm^2

for covellite and 27,000 cm^2 for chalcocite, then it can be shown that

this 60 ppm copper is sufficient to form a mono-molecular layer covering

the entire surface (Appendix B). Analysis showed that the compound made

in the presence of carbonate was actually a tri-valent copper^{III} carbonate,

rather than the tri-valent oxide/hydroxide made with no carbonate present.

The black precipitate observed to be deposited from filtered leach solu-

tions is therefore a copper^{III} carbonate and is presumably the same

substance which coats the mineral surface when precipitated from solutions

still in contact with mineral samples. The fact that this compound and

the tri-valent hydroxide apparently catalyze the decomposition of hypo-

chlorite at the same rate is not too surprising; but the reason why

chalcocite, covellite and synthetic copper sulphide still produce differ-

ent rates of decomposition after loss of copper from a carbonate system,

when it is assumed that the entire surface is covered by a Cu^{III} carbon-

ate layer in each case, is less obvious. It could well be that catalysis

is enhanced at certain active sites on the mineral surface and although

the entire surface is covered by Cu^{III}, only certain areas produce cataly-

sis. Any area in which adsorption can occur more readily than in other

surrounding areas will act as a preferential site for catalysis.

The redox potential of a sodium hypochlorite solution at pH 9.0

has a value of 1.2 V (Appendix B). This is within the region shown by

Delhez and coworkers to contain tri-valent copper as a stable compound,

described as hydrated Cu_2O_3.[74] Various other studies have shown that

copper^{II} salts can be oxidized to the +3 oxidation state in the presence

of hypochlorite solutions, although most of this work was carried out at

pH levels greater than 9.0.[62,66,72] In fact Prokopchik specifically states that tri-valent copper compounds cannot be made at pH less than 11.5, and the black product so obtained is merely dehydrated copper[II] hydroxide. The present study would seem to dispute this view.

In their paper acknowledging the existence of cupri-carbonate ions and the role they play in the solubility of malachite, De Zoubov et al.[36] do not consider the possibility that at sufficiently high redox potentials a tri-valent copper - carbonate complex species could exist, rather than the Cu_2O_3 solid substance shown in the relevant Eh-pH diagrams (Figure 3). It is unlikely that these workers used sufficiently strong oxidizing solutions to produce such a species, but it seems perfectly reasonable to assume that a complexing agent for copper[II] is equally capable of holding copper[III] in solution, given that the aqueous medium has a sufficiently high potential which the hypochlorite solution does. Equation 55 could then be modified:

$$CuS \ + \ 4NaOCl \ + \ 3NaOH \ + \ 3HCO_3^- \longrightarrow$$
$$Cu(CO_3)_3^{3-} \ + \ Na_2SO_4 \ + \ 4NaCl \ + \ 3H_2O \quad (60)$$
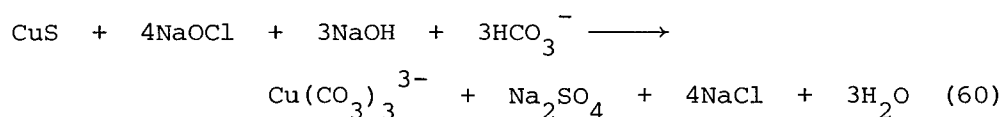
The Cu^{3+} ion is not generally thought of as being stable in solution: its half life has been suggested by Magee and Wood[63] to be of the order of 25 seconds. However, Lister,[66] Malatesta,[64] Malaprode,[65] Berka et al.[68] and others, have all shown that complexing agents such as tellurates and periodates will stabilize copper[III] in solution. Tri-valent cuprates are also known to be soluble and relatively stable[61,62] but these substances occur only at higher pH values.

Due to its relevance to the present study, it is interesting to note Lister's observation that any copper present in solution in an

uncomplexed state, as $Cu(OH)_4^-$ for example, showed catalytic activity towards sodium hypochlorite; but addition of complexing ions to the system prevented any such decomposition. This is in line with the observation noted above that copper existing in solution as a Cu^{III} - carbonate complex did not produce any hypochlorite decomposition, but as soon as any solid material precipitated the decomposition reaction was catalyzed heterogeneously.

4.1.7 Effect of Varying the Hypochlorite Concentration

The fact that more copper could exist in leaching solutions containing 7 - 8 g/l hypochlorite in the presence of carbonate, than that thermodynamically calculated by De Zoubov et al. for an equivalent amount of carbonate and no oxidant, suggests that more copper can exist as a Cu^{III} complex than for the corresponding Cu^{II} complex. This was also illustrated in experiments done in the absence of hypochlorite (see below). The increase in soluble copper caused by an increase in the hypochlorite concentration is thus a related phenomenon: the presence of chloride is known to increase the solubility of certain metal salts and in the present study this was found to apply to calcium in relation to another part of the work (Section 4.3.4.2). It seems likely therefore that copper is an analogous case, and that while carbonate is the principal complexing agent, chloride increases both the solubility and stability of the complex, giving a longer nucleation time to Cu^{III} precipitation.

4.1.8 Effect of Hypochlorite Removal

Removal of hypochlorite from a copper sulphide carbonate leach-
ing system showed quite clearly that less copper existed as the $Cu(CO_3)_2^{2-}$
species than as $Cu(CO_3)_3^{3-}$. It was a little surprising that any copper
at all was dissolved by agitating covellite in a solution of sodium
carbonate/bicarbonate, but this is probably attributable to air-oxidation
of the copper during agitation.

It is significant that the dissolved copper content of these
solutions containing no hypochlorite, was identical to that contained by
the leaching solutions after decomposition of the hypochlorite. It
was ascertained that at the higher values of total carbonate (5.0 g/l;
7.5 g/l and 10.0 g/l) a second 'plateau' level corresponding to the
Cu^{II} carbonate complex existed before this also decomposed, leaving no
copper in solution. At lower values of contained carbonate the amounts
of copper and time periods involved are too low to observe a distinct
"3-stage" curve. The reason why a small drop in the copper content of
the solution was so consistently observed in all experiments carried
out in the presence of carbonate within the first five minutes of leach-
ing is still not known precisely. It could be a result of super-
saturation by the very rapid oxidative action of hypochlorite on the
mineral surface, necessitating precipitation of a small amount of
copper to retain equilibrium solubility.

While it is clear that the black precipitate put down from hypo-
chlorite containing solutions is an oxidized form of the malachite precip-
itated from copper^{II} carbonate solutions, the appearance of either substance,
and the related precipitation of copper during leaching is most peculiar.

Ismay's hypothesis that the substance could be a partially oxidized sulphur species was dismissed by showing that the same amount of copper was dissolved in the presence of carbonate and hypochlorite whether the starting material was a copper sulphide or copper sulphate. It is now clear, however, that copper^{III} was also produced in this study during the leaching of chalcopyrite with an unspecified, but presumably small, amount of carbonate buffer at pH 9.0, because the curves obtained were very similar to those shown in Figures 11 and 13 for covellite and chalcocite leaching. Observations made during copper sulphate agitation in carbonate solutions bare a strong resemblance to those in similar experiments carried out by Pickering[28] and Appleby and Lane.[31] These workers found that mixing $Na_2CO_3/NaHCO_3$ solutions with copper sulphate or copper acetate produced a deep blue solution which subsequently precipitated either a greeen powder, $Cu(OH)_2CO_3$, or well defined blue crystals assumed to be a sodio-cupric double salt, $Na_2Cu(CO_3)_2$. The green powder observed in the present work is almost certainly malachite. Appleby noted that precipitation of the double salt could not be accelerated by "seeding," but in this case it was found that addition of previously precipitated powder, either as copper^{III} to hypochlorite solutions, or as malachite to copper^{II} carbonate, gave loss of copper and further precipitation within a very short time.

This would seem to confirm that the observed precipitation can only occur after nucleation of a small amount of solid has taken place, and that this is the slow step of the process. Filtered solutions take longer to put down a precipitate than the corresponding leaching solutions in contact with a mineral because the mineral surface can provide

favourable sites on which nuclei can form. Nucleation generally occurs when the super-saturation of the separating phase has reached a certain value such that the activation barrier has been surmounted. The free energy of formation of a nucleus consists of two terms:

$$\Delta G_j = \frac{-4\pi r^3}{3V} kT \ln \frac{a}{a_o} + 4\pi r^2 \delta$$

where a/a_o is the concentration ratio or degree
of supersaturation

V = molecular volume

δ = interfacial energy

r = radius

The second term represents the work necessary to create a new surface, i.e. for the formation of a new phase, while the first takes account of the energy involved in making new bonds. This assumes the nuclei to be spherical.

As the degree of supersaturation increases, then ΔG_j will decrease, and this usually results in smaller nuclei forming by a decrease in radius, r.

The term describing the rate of formation of crystal nuclei, J, can be expressed:

$$J = A_{exp} - \frac{\Delta G_a}{kT}$$

where A represents the efficiency of ionic or molecular collisions.

Homogeneous nucleation is a very slow process which rarely occurs in practice; various foreign particles can act as 'catalysts' for nucleation

by reducing the energy barrier presented by ΔG, thus inducing heterogen-
eous nucleation.

The induction period for nucleation may be defined by the expression

$$k = t c^{(n-1)}$$

where n = number of ions required
to form a cluster of critical
size

c = concentration of solution

k = constant

n is effectively reduced during heterogeneous nucleation by the incorpor-
ation of foreign particles into a nucleation site.

The induction period involved in the precipitation of copper^{III}
from leaching solutions in the presence of varying amounts of carbonate
under otherwise identical conditions, follows an almost linear relation-
ship with carbonate concentration.

After nucleation and precipitation of copper^{III} has occurred
leaving a solution containing a copper^{II} - carbonate complex, the same
cycle is repeated with precipitation of malachite after another induction
period for the nucleation of copper^{II} crystals. Appleby's suggestion
that delayed precipitation occurs due to a very slow rate of crystalliza-
tion,[31] thus appears to be reasonable. His observation that seeding did
not enhance precipitation of the double salt, $Na_2Cu(CO_3)_2$, may be an
indication that solutions decomposing to give malachite, $Cu(OH)_2(CO_3)_2$,
are more super-saturated.

The reason for the observed variations in copper concentration of

some leaching solutions (Section 3.1.1), is probably precipitation of some copper^{III} prior to analysis. Pickering[28] noted that excess water could induce precipitation of the solid compound. It was found in this study that filtered solutions sometimes turned black on dilution with water. Subsequent analysis would therefore indicate a lower copper content than was actually present on initial removal of the sample.

4.2.1 Analysis of Copper^{III}

Because insufficient of the precipitated material could be collected to carry out any meaningful analysis, similar material was manufactured in much larger quantities by the action of sodium hypochlorite on copper^{II} salts at pH 9.0. The black compound so formed was assumed to be the same as that produced by Lister[66] under almost identical conditions, which he subsequently complexed with periodate or tellurate to give a tri-valent copper salt. He presumed the initial material was a copper^{III} hydroxide. Similarly in the present study the gas evolved on acidification of the black precipitate was taken to be oxygen, produced as a result of the reduction of $Cu^{III} \longrightarrow Cu^{II}$:

$$2Cu(OH)_3 + 4HCl \longrightarrow 2CuCl_2 + 5H_2O + \tfrac{1}{2}O_2$$

$$Cu^{3+} + e^- \longrightarrow Cu^{2+} \tag{61}$$
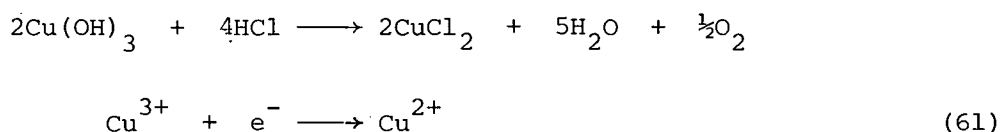
The presence of oxygen was proven by iodometric titration and gas chromatography, and its volume measured by the use of a mercury column. Compounds made in the absence of carbonate did not contain carbon dioxide.

The results consistently showed, however, that insufficient oxygen was present for the black powder to be 100% copper^{III}, and the various analytical methods indicated that 25 - 30% available oxygen existed. While the percentage of copper^{III} did increase slightly with pH, there was no significant change in appearance of the compound when prepared in more strongly alkaline solutions. A number of other workers have stated that the sesquioxide, Cu_2O_3, occurs as a red compound, and that its formation is catalyzed by the presence of barium and calcium ions. In the present study, addition of these ions to solutions containing 0.1 M hypochlorite made little difference to the final product, and no red material was ever detected.

It is therefore proposed that the black compound produced is a mixed copper oxide or hydroxide, consisting partially of copper in the +3 state, and partially in the +2 state, with the latter actually representing the majority. The fact that it is black would support this view: this is a characteristic of mixed oxides. Delhez[72] also reported obtaining a mixture of copper^{III} and copper^{II}, with the tri-valent state again amounting to no more than 30% of the total, but his compound was exclusively red. It should be noted however that he was using solutions significantly more concentrated in hypochlorite than 0.1 M, at a higher pH level and with a greater ionic strength than in this case. It is quite likely that he obtained a mixture of the two different oxides: 30% Cu_2O_3 + 70% CuO which appeared red, while the black compound described here is actually a mixed valence state compound consisting of Cu_2O_3 and CuO together. Assuming a mixture of 75% copper^{II} and 25% copper^{III} the ratio $Cu^{2+}:Cu^{3+}$ would be 3:1.

$$Cu_2O_3 + 3CuO \longrightarrow Cu_5O_6 \qquad . \qquad (62)$$
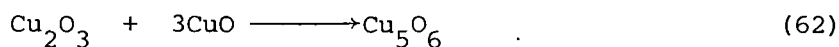
This gives a compound having an oxidation state of 2.4. By further analogy with Delhez's work, and from the results obtained by infra-red spectrophotometry, it appears that the compound fluctuates between an oxide and a hydroxide. Thus it could consist of $Cu(OH)_3$ and $Cu(OH)_2$ giving a compound such as $Cu_2(OH)_5$ with an oxidation state of 2.5. This would have a copper content of about 60% which fits the experimental analysis more closely.

Magnetic susceptibility tests further confirmed that the compound is only partially Cu^{III}, while X-ray diffraction suggested it to be cupric oxide. No reported X-ray diffraction data for copper^{III} compounds was found. It is possible that Cu_2O_3 is amorphous, in which case no diffraction peaks would be detected.

4.2.2 Precipitation of copper^{III} in the presence of carbonate

X-ray tests carried out on compounds made in hypochlorite containing carbonate solutions showed peaks corresponding to both malachite and cupric oxide, confirming it to be a mixture of a carbonate and an oxide. There were also some unidentified peaks which could represent the difference between Cu^{II} carbonate and the Cu^{III} salt.

Infra-red studies and limewater tests suggested further that this compound was at least partially a carbonate. The nucleation times involved in its preparation are not linear with respect to carbonate concentrations. The conditions of temperature, agitaiton etc. were not

maintained perfectly constant during preparation of each sample however, as they were in the leaching experiments. It was again shown that 'seeding' would induce precipitation of the compound.

Both oxide/hydroxide and carbonate samples were found to catalyze the hypochlorite decomposition reaction at approximately the same rate, when added in equal amounts to a 0.1 M solution. This is to be expected, because both compounds contain approximately the same amount of copper^{III}, and it has been shown by Lister,[66] Prokopchik[64] and Delhez[72] that Cu^{III} is the active catalyst for decomposition. When none is present initially oxidation of Cu^{II} must take place before the reaction occurs, thereby setting up a Cu^{2+}/Cu^{3+} oxidation-reduction cycle. This is presumably why cupric oxide showed a slower rate of decomposition under identical conditions.

4.3 Sodium Hypochlorite Leaching of Molybdenite, MoS$_2$

Leaching molybdenite mineral in sodium hypochlorite solutions at pH 9.0 did not initially yield 100% molybdenum as MoO_4^{2-} in solution. Examination of leach residues revealed the presence of iron, copper, zinc and silica, as well as lead molybdate which is insoluble. Thus the assumption of 100% MoS$_2$ was a false one, and spectroscopic analysis of unleached samples revealed at least a 3% impurity content. Subsequent leaching with "98% +" molybdenum disulphide produced extractions in excess of 97%, confirming Ismay's findings that molybdenite leaches rapidly and completely at pH 9.0, 35°C and in solutions containing about 0.1 M OCl^-. Hypochlorite consumption was found to correspond to the

previously reported stoichiometry:

$$MoS_2 + 9NaOCl + 6NaOH \longrightarrow$$

$$Na_2MoO_4 + 9NaCl + 2Na_2SO_4 + 3H_2O \qquad (63)$$
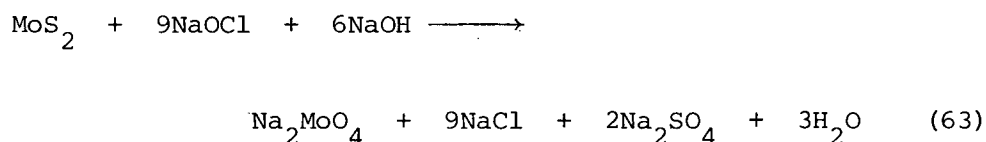
4.3.1 Sodium hypochlorite leaching of molybdenite and copper sulphide minerals at pH 9.0

It has already been reported in conjunction with the leaching

behaviour of copper sulphide minerals, that carbonate plays a significant

role in this system besides that of a buffering reagent. In addition

to acting as a complexing agent for copper and hence a stabilizer of the

hypochlorite however, it was also found to affect molybdenum extraction.

When excluded from the system, the level of molybdenum extraction dropped

from 98% to only 76 - 84%. The actual depression was a function of the

particular mineral being leached.

It was postulated that copper molybdate compounds were interfering

with molybdenum extraction, but it was rather surprising that the case in

which no copper was present in solution showed the greatest molybdenum

loss. Oxidation of molybdenite in the presence of $CuSO_4$ solution suggest-

ed further that precipitation of copper molybdate was occurring. This

did not explain why molybdenum was also precipitated from a covellite/

sodium molybdate leach, in which no copper had been dissolved.

4.3.2 Leaching of molybdenite and copper sulphides at pH 5.5

Experiments were carried out in acidic solutions to see if an
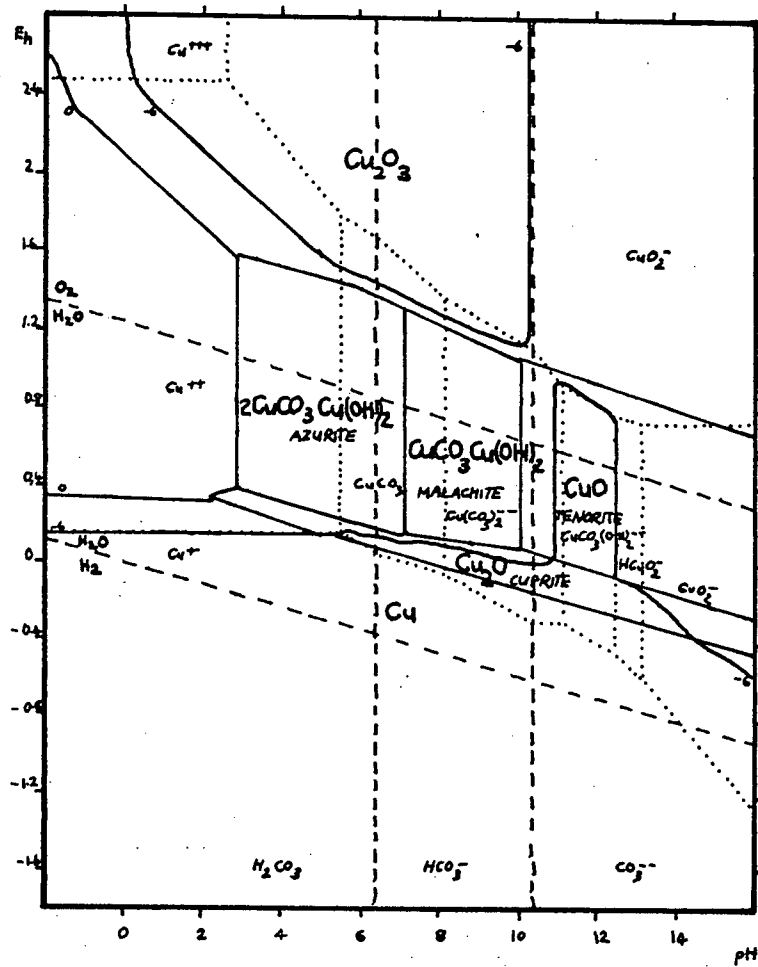
Figure 51: Potential - pH diagram for the system Cu-CO$_2$-H$_2$O with 10^{-1}M [CO$_3^=$]T.

improved molybdenum yield could be obtained, even if this incurred

production of more sodium chlorate than at pH 9.0.

Copper exists in solution to a maximum concentration of 10^{-2} M

as the Cu^{2+} ion at pH 5.5. This fact proved very detrimental to molyb-

denum extraction. Cu^{2+} ions can combine with the molybdate species

MoO_4^{2-} giving insoluble $CuMoO_4$. The rapid loss of 90% of the molybdenum

in slution on introduction of a copper sulphide mineral can be interpreted

as precipitation of this molybdate salt.

The presence or otherwise of carbonates in the system did not have

the effect of preventing molybdenum losses that had been observed in

alkaline solutions. The only detectable difference between a carbonate

and non-carbonate leach in the experiments at pH 5.5 was a slightly

higher copper content in the former case. The fact that such a small

increase in pH, a value of 6.0, resulted in the carbonate being able

to suppress formation of copper molybdate, can be explained by careful

consideration of the Eh-pH diagrams given by De Zoubov et al.[36] showing

the existence of the stable copper carbonate compounds and complex ions

for the $Cu-H_2O-CO_2$ system (Figure 3). The $Cu(CO_3)$ aq. molecule exists

as a soluble species at pH levels between 5.0 and 7.0 dependent on the

total carbonate content of the solution. At the level used here (10 g/1

$HCO_3^- \equiv 1.6 \times 10^{-1}$ M $[CO_3]_T$) it is stable at pH values above 5.4; below

this the copper exists exclusively as the Cu^{2+} ion (Figure 51). Thus

leaching at pH 5.5 puts copper at the stability boundary between Cu^{2+}/

$Cu(CO_3)$ aq. The experimental results indicated that copper is only com-

plexed by carbonate to a very small degree, shown by the small increase

in dissolved copper, and that this association is insufficient to prevent

copper molybdate formation. An increase in pH to 6.0 puts copper into the region where $Cu(CO_3)$ aq. is stable in solution, thereby preventing a reaction with the molybdate. Leaching in the absence of carbonate, however, enables Cu^{2+} and MoO_4^{2-} to combine as before. The observed rapid decomposition of the hypochlorite was presumed to be caused by copper molybdate catalysis, suggesting again that this cannot form in carbonate solutions above pH 5.5 - 6.0 where no excess hypochlorite decomposition was observed.

As the pH of the leaching system is further increased, the solubility of the Cu^{2+} ion decreases to 1.6 x 10^{-5} M. This is still sufficient to give a 60% loss of the molybdenum, coupled with an even greater loss of hypochlorite i) due to $CuMoO_4$ catalysis and ii) because this is the region in which hypochlorite most readily decomposes to chlorate.

These findings would seem to question the feasibility of the U.S. Bureau of Mines electrooxidation process at the suggested pH levels of 5.0 - 7.0.[20,21,23] The statement made in conjunction with this investigation that a minimum of copper solubility occurs at pH 7.0 is in itself a little dubious since this is shown to occur for CuO and $Cu(OH)_2$ at a value of 9.0,[73] and is not greatly modified by the presence of chlorides. Secondly, no mention in the literature of the soluble compounds $Cu(OH)_2CO_3$ or $CuCl_2CO_3$ which Scheiner et al. claim as being responsible for copper solubility in alkaline solutions, has been found; and the cupri-carbonate ion, $Cu(CO_3)_2^{2-}$ appears to be the only species which can impart significant solubility to copper at pH values above 9.0. Scheiner mentions the compound copper molybdate as being detrimental to molybdenum extraction

and reports detecting it in leaching tails, but does not appear to have studied the conditions for its formation. In this electrooxidation process the pH is allowed to rise during leaching by the addition of sodium carbonate on a semi-continuous basis. In the light of present findings any copper molybdate which did form, would be in the initial stages of a run when the pH is still below 6.0. The most surprising conclusion of the U.S. Bureau of Mines study, however, is the fact that chalcopyrite is unaffected by hypochlorite, but that chalcocite is oxidized to a certain extent giving soluble copper compounds which are capable of combining with the molybdate ions to form insoluble copper molybdate. In the present study no difference in the leaching behaviour of the different copper sulphide minerals exposed to hypochlorite solutions has been detected, except in the catalyzed rate of hypochlorite decomposition. Furthermore, and in contrast to Scheiner's statement, it is in the presence of the soluble copper compound $Cu(CO_3)_2$ aq. that copper molybdate formation is suppressed. Only when copper exists in solution as the cupric ion Cu^{2+}, in the absence of carbonate or at pH <6.0 can a reaction with molybdate ions occur. This should hold true for any copper mineral introduced into the system.

This implies that leaching copper - molybdenum concentrates on the acid side of neutrality is only feasible in the presence of carbonate, and in a limited pH region of $\simeq 6.0 - 7.5$. This would not give any improvement in molybdenum selectivity over that at pH 9.0 in the presence of carbonate, and would have the added disadvantage of producing large amounts of sodium chlorate. Barr and coworkers have shown that this represents a source of power loss in the electrooxidation process and that

it also interferes with subsequent molybdenum recovery.[25,26] Their

suggestion of leaching at pH values of 4.0 - 5.0 to overcome the chlorate

problem, is hardly practical on account of the stability of copper molyb-

date in this region.

4.3.3 Copper molybdate

The simple molybdate, $CuMoO_4$, is not well documented in the

literature. It is known to be insoluble, in common with most other

transition metal molybdate salts. Zelikman[82] quotes this solubility

as 0.017 M which is slightly higher than that found in the present work

of 0.00783 M.

X-ray data for a number of copper molybdate species has been pub-

lished. The one corresponding closely to diffraction patterns obtained in

this study (Table 8), is the hydrated species $Cu_3(MoO_4)_2(OH)_2$ which occurs

in nature as the mineral Lindgrenite. Data for other copper molybdates

are shown in Table 10:

Species	d$\overset{\circ}{A}$ (1)	d$\overset{\circ}{A}$ (2)	d$\overset{\circ}{A}$ (3)
$CuMoO_4$	3.72	3.36	2.71
$CuMoO_4$	3.05	3.30	3.53
Cu_2MoO_5	3.54	3.45	3.32
$Cu_3Mo_2O_9$	3.44	2.63	3.39
$Cu_{4-x}Mo_3O_{12}$	3.42	3.31	2.65
$Cu_{4-x}Mo_3O_{12}$	3.42	2.64	2.76
$Cu_6Mo_4O_{15}$	3.38	2.89	2.63
(This study	3.52	4.20	2.53)
($Cu_3(MoO_4)_2(OH)_2$	3.50	4.15	2.67)

Table 10: Strongest X-ray Peaks for Various Copper Molybdate Species

The catalytic effects on hypochlorite decomposition observed during leaching in acid solutions were confirmed by agitating copper molybdate in sodium hypochlorite solutions. This is a further reason for preventing 'in-situ' formation of the compound even in small amounts during molybdenite leaching.

An Eh-pH diagram for the $Cu-H_2O-MoO_4$ system was constructed to confirm the thermodynamic stability of copper molybdate in acid hypochlorite solutions. In Figure 52 the solid species considered are Cu, Cu_2O, CuO, $CuMoO_4$ and Cu_2O_3, and in Figure 53, Cu, Cu_2O, $Cu(OH)_2$, $CuMoO_4$ and Cu_2O_3. In both diagrams the dissolved species have been taken as Cu^+, Cu^{2+}, Cu^{3+}, CuO_2H^-, CuO_2^{2-} and MoO_4^{2-}, $HMoO_4^-$. The diagrams show the equilibria between stable substances when the activities of copper containing ions in solution are 10^{-6} M, and of molybdenum species are 10^{-1} M.

Considering the solid species to be oxides, Figure 52 shows that copper molybdate has a region of stability from pH -0.3 to 8.65, with an oxidation potential varying from ≈0.03 to 2.4 V. Thus at pH 9.0 there should be no interference with molybdenum extraction from $CuMoO_4$ formation. An increase in copper concentration would decrease the pH limit for $CuMoO_4$ stability, while decreasing molybdenum activity would increase it (and vice versa).

In Figure 53, in which the hydroxides are shown as the stable phase, the zone of copper molybdate stability is extended slightly to a pH value of 9.18. As the hydroxide is the meta-stable phase and would form prior to the oxide, it is apparent from this diagram that $CuMoO_4$ formation could pose a problem to a leach at pH 9.0. It also shows clearly why a molybdenite - copper sulphide leach would not be feasible
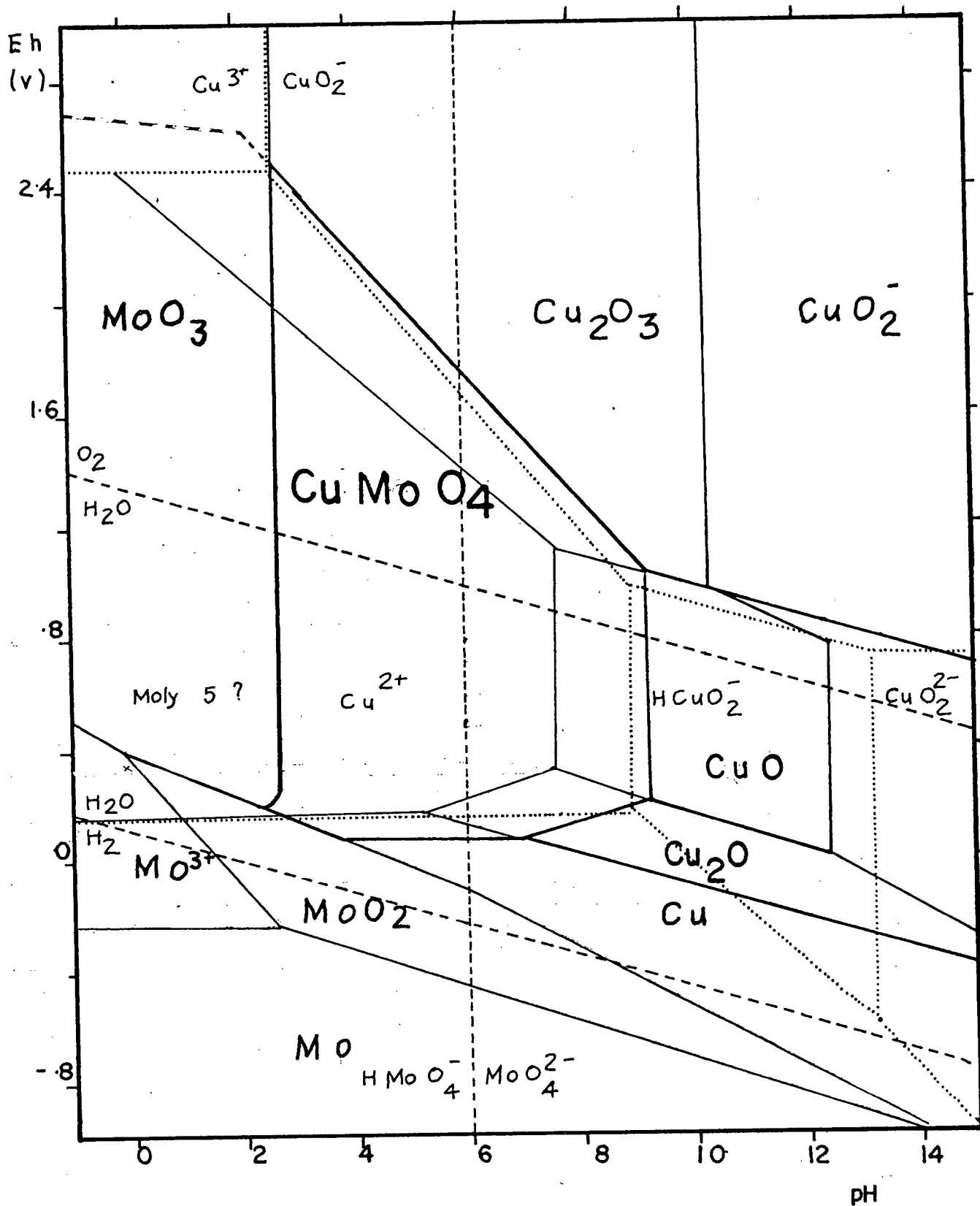
Figure 52: Eh-pH diagram for the system $Cu-H_2O - M_oO_4$ (oxide species). (Activities of copper ions $10^{-6}M$ and activities of molybdenum ions $10^{-1}M$).
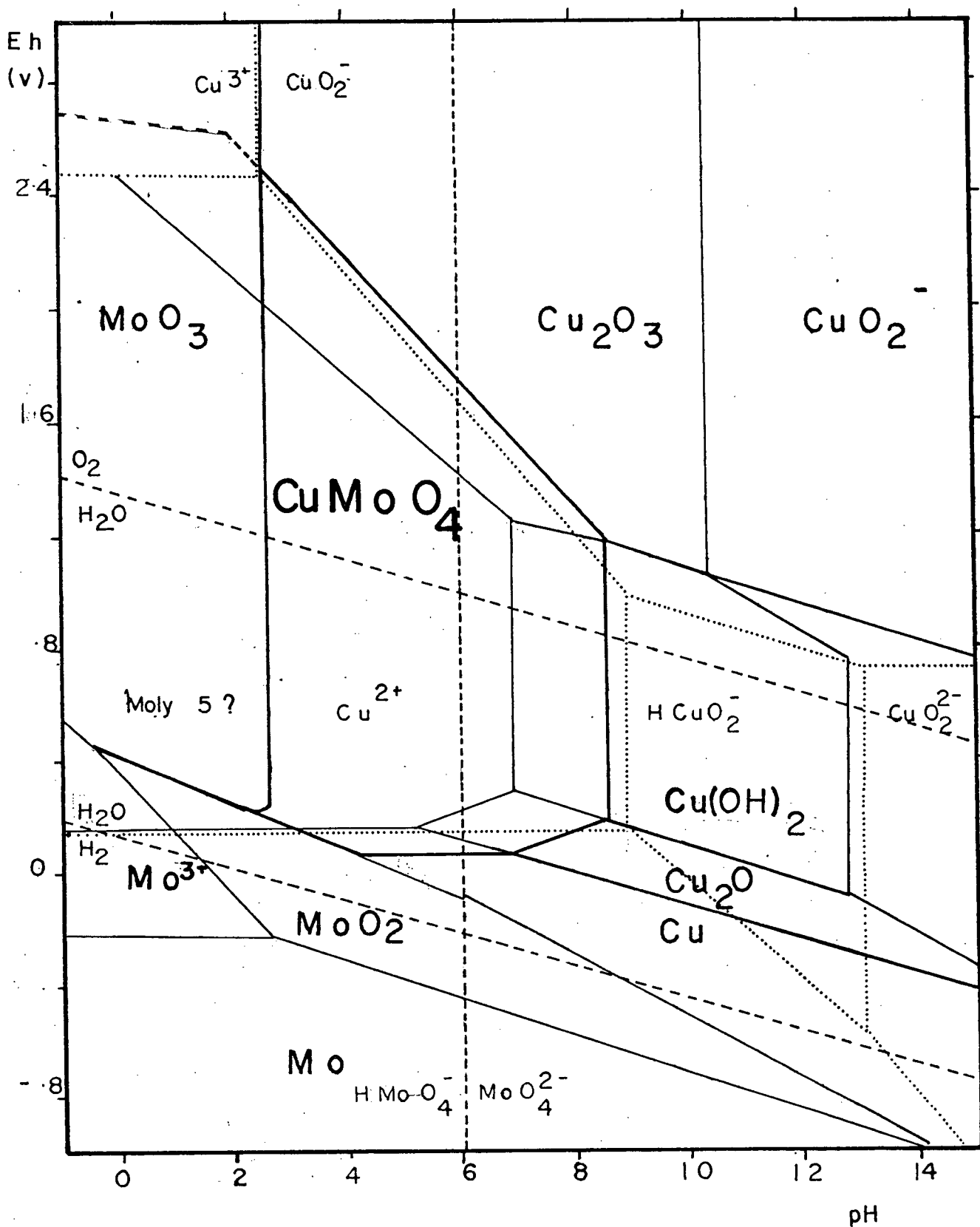
Figure 53: Eh-pH diagram for the system $Cu-H_2O - M_oO_4$ (hydroxide system). (Activities of copper ions $10^{-6}M$ and activities of molybdenum ions $10^{-1}M$).

in the pH region from 5.0 - 7.0, and illustrates that copper[III] formation would not be encountered in acid solutions due to the higher redox potential of the +3 state.

Although copper molybdate could therefore exist at pH 9.0 from a thermodynamic point of view, the fact that no copper was dissolved in the absence of carbonate, together with results obtained from leaching with synthetic copper sulphides and at pH 10.0 (Section 3.3.4), confirmed that copper itself was not the principal cause of poor molybdenum recovery at this pH value.

In addition to this, aging of copper containing molybdate solutions showed that at pH 5.5 $CuMoO_4$ readily formed as a stoichiometric compound while at pH 9.5 a co-precipitation phenomenon occurred. Any copper added to a solution at this pH will precipitate as $Cu(OH)_2$, and the fact that some molybdenum dropped out of solution initially but reappeared on standing or heating, is strongly indicative of the molybdenum co-precipitating with the copper.

A similar effect would explain why molybdenum was lost from a leaching solution to which copper sulphate was added at pH 9.0, i.e. due to co-precipitation with the copper as $Cu(OH)_2$.

4.3.4 Solubility of calcium in hypochlorite solutions

A combination of these various factors brought to light the fact that other elements, contained in the copper sulphide minerals under study as impurities, could be capable of forming insoluble molybdates and thus be detrimental to good molybdenum recovery. In order to

elucidate which one or more elements were responsible in the present case, as well as to determine if any other likely gangue elements could cause similar problems with other ore samples, the following factors were taken into consideration:

i)   whether an element can combine with the molybdate ion and form an insoluble species which is thermodynamically stable at pH 9.0.

ii)   whether hypochlorite oxidation leads to the element existing as a stable cation in solutions at pH 9.0.

iii)   whether the element is likely to be found as an impurity in copper - molybdenum porphyries, and associated minerals.

To determine the regions of stability of the simple molybdates of elements known to be contained in the copper sulphide minerals under study, Eh-pH diagrams were constructed for the following systems:

$$Ca-H_2O-MoO_4$$
$$Fe-H_2O-MoO_4$$
$$Pb-H_2O-MoO_4$$
$$Cd-H_2O-MoO_4$$
$$Zn-H_2O-MoO_4$$
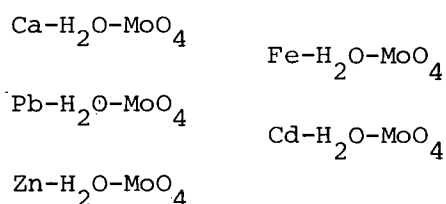
shown as Figures 54-58 respectively. The activity of the molybdate ion has been taken as 10^{-1} M in all cases, and that of the metal containing species is $\{10^{-6}\}$ except for lead, where $\{10^{-4}\}$ was found to more appropriate.

Figure 54: calcium molybdate: The diagram drawn up for calcium species and their interaction with molybdate, shows that the Ca^{2+} ion has a much larger zone of stability than the corresponding region for Cu^{2+} resulting in a calcium molybdate compound with a wide range of stability.
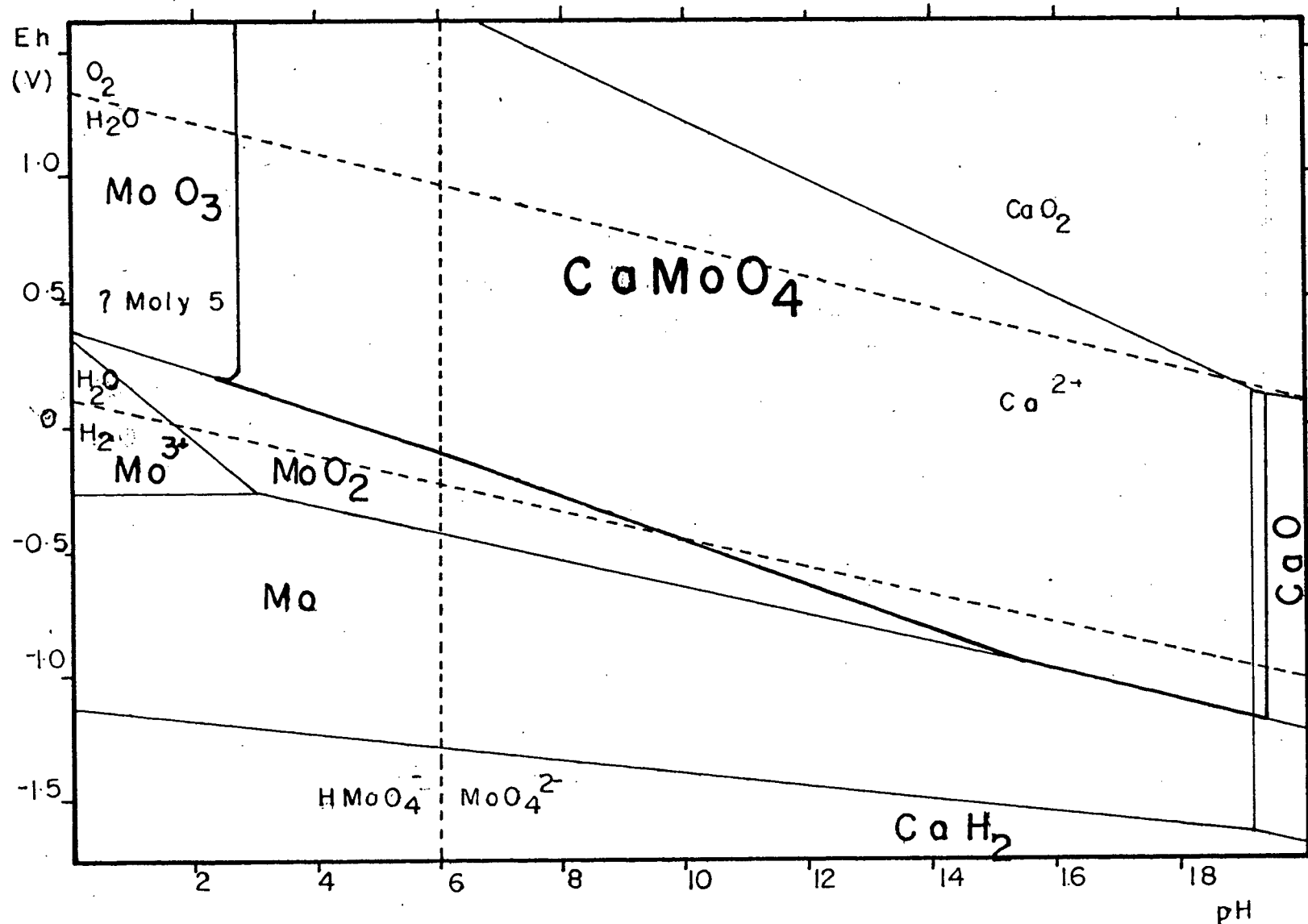
Figure 54: Eh-pH diagram for the system $Ca-H_2O-MoO_4$ (Activities of calcium ions $10^{-6}M$, activities of molybdenum ions $10^{-1}M$).

When considering the solid species CaO, calcium molybdate is stable up to a pH of 19.14, while for the hydroxide system the molybdate would extend to a pH of 14.0.

Figure 55: lead molybdate: $PbMoO_4$ is stable up to a pH value of 14.2 before dissolution into plumbite ions, $HPbO_2^{2-}$, occurs. The redox potential varies between 0.3 V at this pH, to 2.0 V at pH 0. Thus at a value of 9.0, the potential at which $PbMoO_4$ decomposes to give PbO_2 is 0.92 V and this molybdate should not be stable in hypochlorite solutions with a predicted value of 1.2 V below pH values of 13.5.

Figure 56: zinc molybdate: It is seen that zinc molybdate has a large zone of stability which exists at all potentials more positive than 0.4 V and up to a pH value of 18.6. The white, amorphous zinc hydroxide was considered as the stable oxide phase in setting up the diagram, and it is apparent that the molybdate is more stable thermo-dynamically than Zn^{2+}, $Zn(OH)_2$, $HZnO_2^-$ and ZnO_2^{2-} until dissolution of this final species occurs at pH 18.0.

Figure 57: iron molybdate: Iron is of major interest with respect to its interaction with molybdate, being present in large amounts in chalcopyrite, $CuFeS_2$ and bornite, Cu_5FeS_4, as well as a common impurity in chalcocite and covellite. It is unlikely however that ferrous iron could exist in hypochlorite solutions, thus $FeMoO_4$ should not pose a problem. This is confirmed in the Eh-pH diagram; $FeMoO_4$ is stable up to a pH of 10.8, but the maximum potential it can withstand is 1.2 V, at pH 2.4, and at pH 9.0 decomposition to $Fe(OH)_3$ would occur at less than 0.5 V.

Zelikman[92] mentions the existence of a ferric molybdate compound,
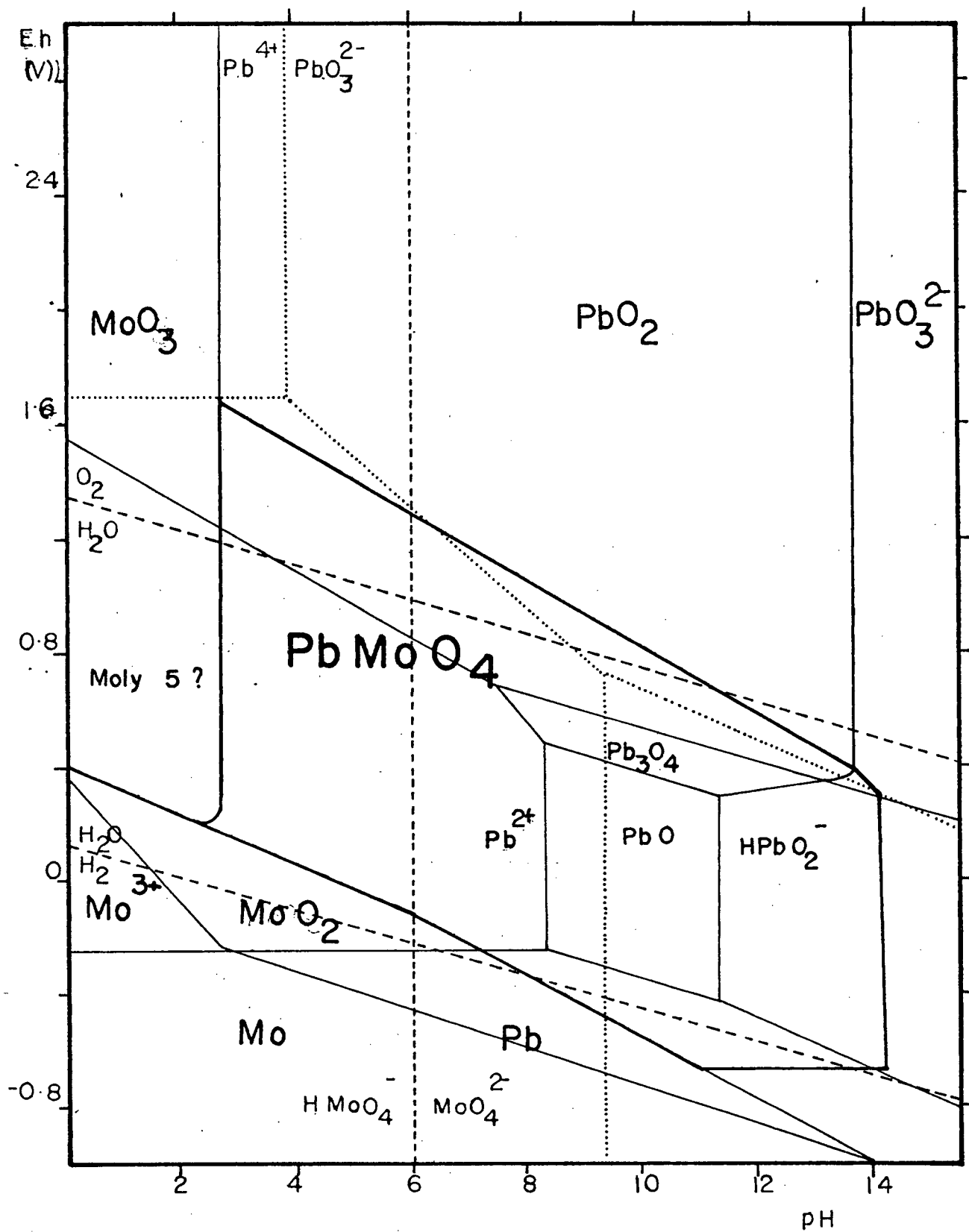
Figure 55: Eh-pH diagram for the system $Pb-H_2O-MoO_4$ (Activities of lead ions $10^{-4}M$, activities of molybdenum ions $10^{-1}M$).

Figure 56: Eh-pH diagram for the system $Zn-H_2O-MoO_4$. (Activities of zinc ions 10^{-6}M, and activities of molybdenum ions 10^{-1}M).
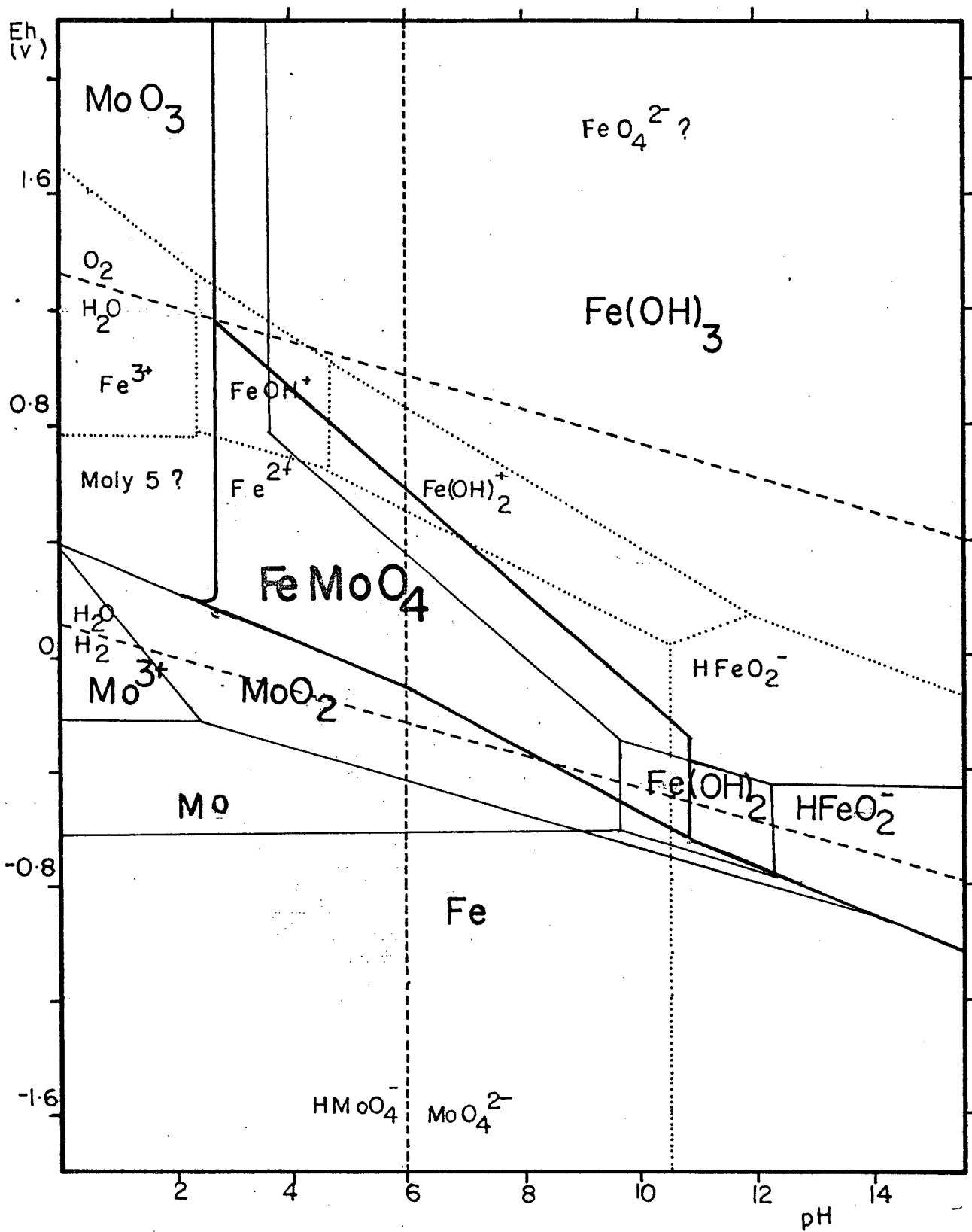
Figure 57: Eh-pH diagram for the system Fe-H_2O MoO_4 (Activities of ferric and ferrous ions 10^{-6}M, and activities of molybdenum ions 10^{-1}M).

$Fe_2(MoO_4)_3$ and notes that it will precipitate from aqueous solution under certain conditions. The mineral ferrimolybdite, $Fe_2(MoO_4)_3 \cdot 8H_2O$, is quite commonly found in nature but is not a source of molybdenum metal. No thermodynamic data for such an iron[III] molybdate compound could be found and it has not been included in the Eh-pH diagram shown.

Figure 58: cadmium molybdate: Cadmium and zinc have several chemical similarities and are found in close association in many ore bodies. The present study also shows that their respective molybdates form under similar conditions: $CdMoO_4$ is stable up to pH 12.5 and above a potential of 0.4 V (pH 0.0)- -0.9 V (pH 14.0). The presence of Cd^{2+} ions in solution is thus undesirable during molybdenite leaching.

The stability boundary between the simple molybdate ion MoO_4^{2-} and polymolybdate species, described as $HMoO_4^-$, occurs at pH 6.0. Above this value, combination with metal cations will result in precipitation of a simple molybdate salt such as $CuMoO_4$. In more acidic solutions it is possible that a complex molybdate species will form the stable species. On the other hand, with a sufficiently large concentration of MoO_4^{2-} in equilibrium with $HMoO_4^-$, a simple molybdate may still precipitate. Experimental results for molybdenite - copper sulphide leaching carried out at pH 5.5 suggests a stoichiometric Cu:Mo ratio of 1:1, indicating formation of the simple molybdate $CuMoO_4$. The exact nature of molybdenum species at low pH values is not known. MoO_3 is the stable species at higher potentials below pH 3.0. MoO_2 precipitates at a potential of 0.4 V (pH 0.0), decreasing to -0.1 V at pH 6.0 and -0.55 at pH 10.0. Between these two species molybdenum probably exists in the +5 oxidation state.[9]
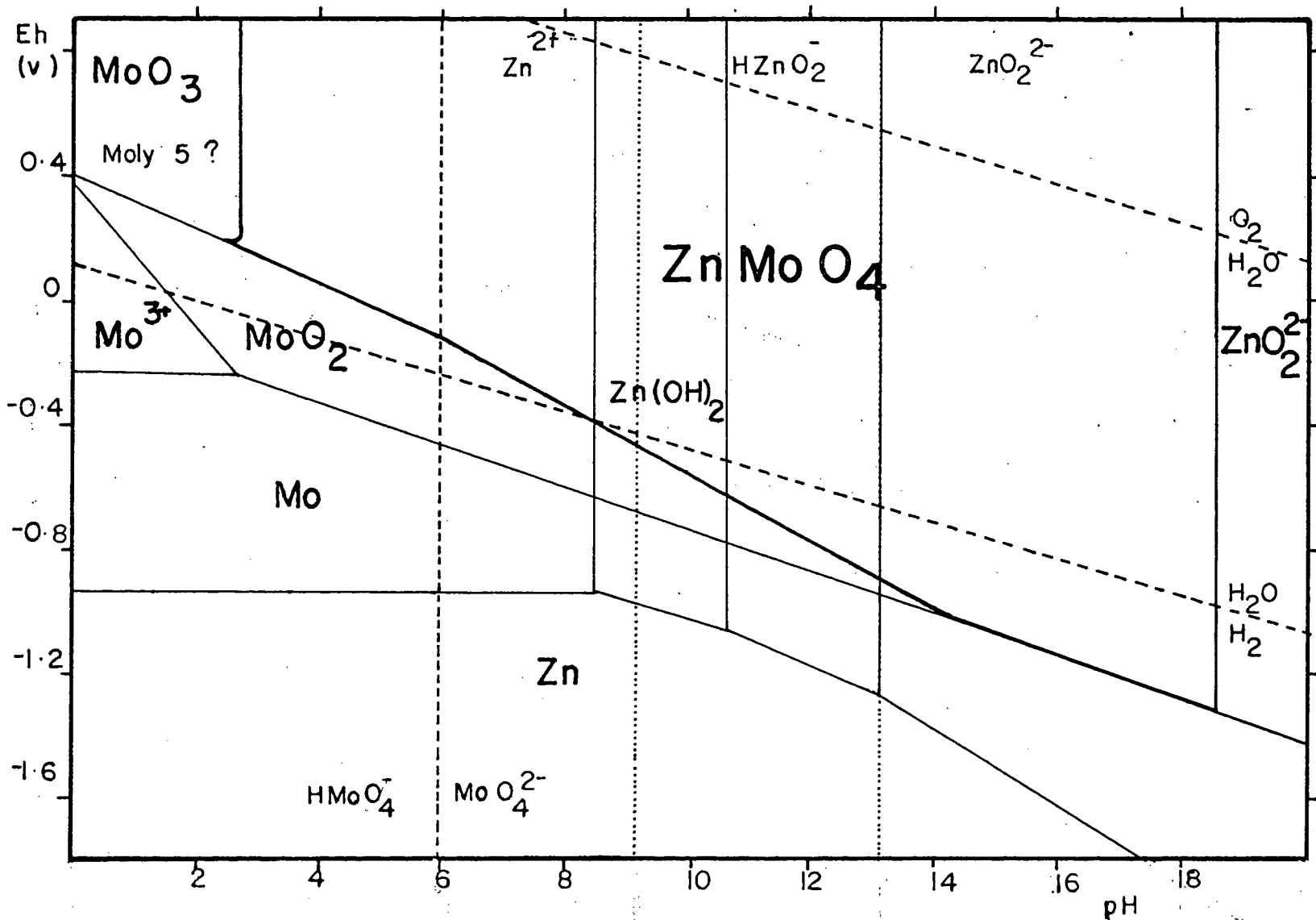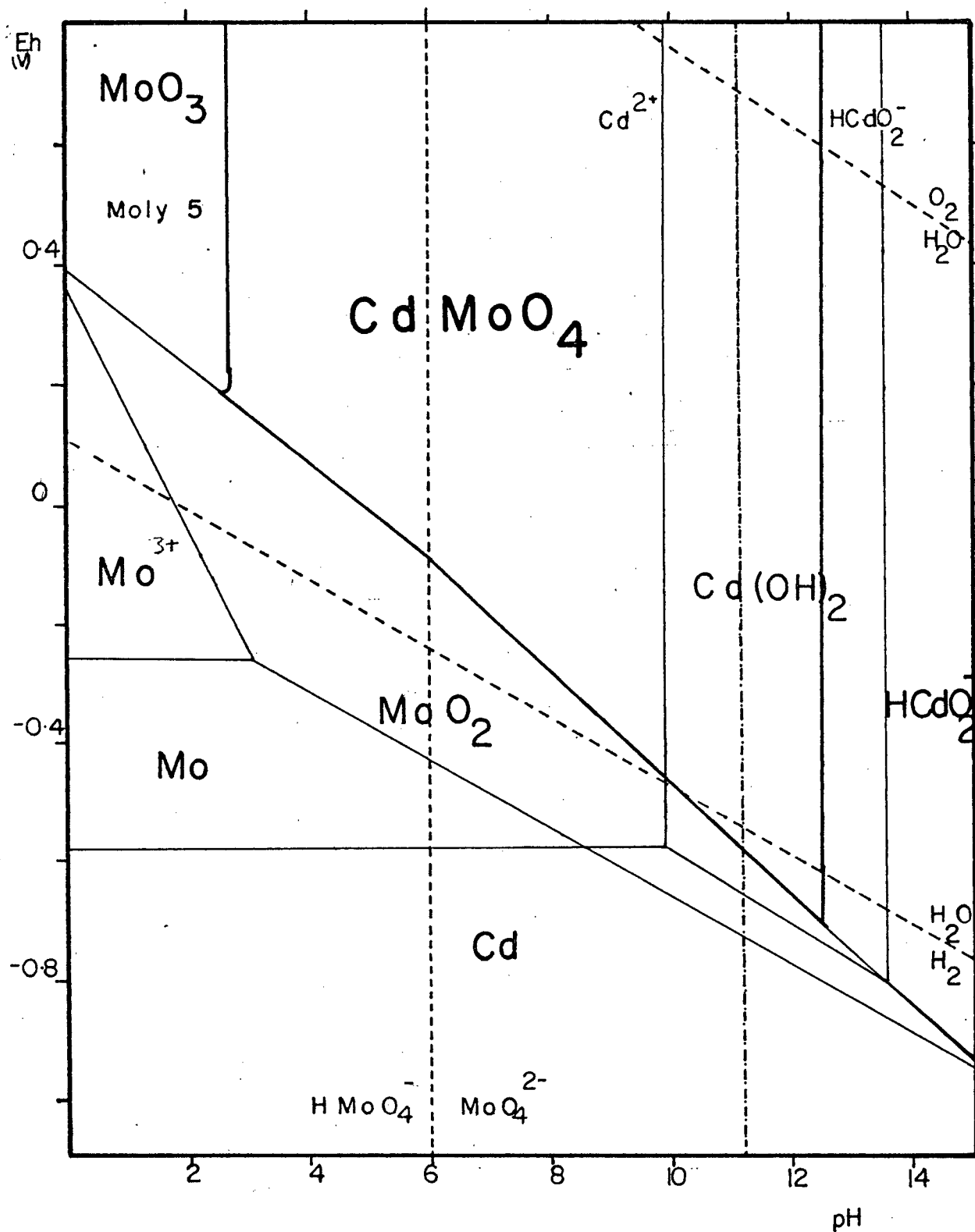
Figure 58: Eh-pH diagram for the system $Cd-H_2O-MoO_4$. (Activities of cadmium ions $10^{-6}M$ and activities of molybdenum ions $10^{-1}M$)

In conjunction with these thermodynamic considerations for the stability of various molybdates, the following data was accumulated for the solubility of a number of molybdate compounds:

Compound	Solubility (g MoO_4/l)	Source
$PbMoO_4$	1.2×10^{-6}	83
$SrMoO_4$	3.0×10^{-4}	83
$CaMoO_4$	a) 5.0×10^{-4}; b) 1.3×10^{-3}	a) 83; b) 82
$BaMoO_4$	5.5×10^{-4}	83
$CdMoO_4$	6.7×10^{-4}	83
$FeMoO_4$	7.6×10^{-4}	82
$CuMoO_4$	3.8×10^{-3}	82
Ag_2MoO_4	3.86×10^{-3}	83
$ZnMoO_4$	a) 3.70×10 ; b) 5.0×10^{-2}	a) 82; b) 83

Of the above elements barium, strontium and silver were not considered because it was not felt they would be present in sufficiently large quantities to cause molybdenum losses.

From the remainder it appears from the Eh-pH diagrams that lead and iron are both insoluble in hypochlorite solutions as discussed above. This was borne out experimentally: samples of galena, PbS and pyrite, FeS_2 were leached under identical conditions to those used for copper/molybdenum minerals and no lead or iron whatsoever was detected in solution.

Copper molybdate can be described as a borderline case with respect

to leaching at pH 9.0 since the thermodynamic boundary occurs at pH

8.65 for the oxide and 9.2 for the hydroxide; but the fact that both

these salts are insoluble should prevent any molybdate formation.

As noted previously, the presence of carbonate imparts a certain degree

of solubility to copper in alkaline solution, and experimental results

suggested that a copper - carbonate association occurred in preference to

$CuMoO_4$ formation.   The relevant equilibria are:

$$Cu^{2+} + 2CO_3^{2-} \rightleftharpoons Cu(CO_3)_2^{2-} \qquad \log k = 9.83$$

$$Cu^{2+} + MoO_4^{2-} \rightleftharpoons CuMoO_4 \qquad \log k = -2.027$$
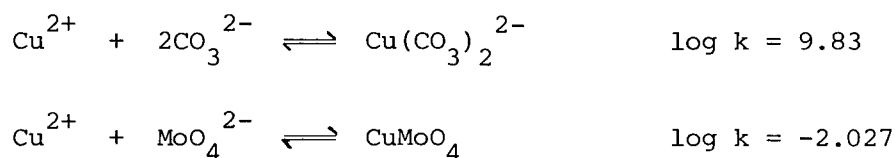
It was observed, however, that leaching in the presence of small

amounts of carbonate did result in some copper molybdate formation

(Section 3.3.4.3), suggesting that less carbonate produced a weaker

$Cu-CO_3$ bond.

Zinc, cadmium and calcium are all undesirable elements in this

system on account of their ability to exist as soluble species at pH

9.0 and hence to combine with MoO_4^{2-} and precipitate.   It has been shown

that sodium hypochlorite is a feasible lixiviant for the extraction of

zinc from sphalerite ores.[84]   However, it is not likely that either zinc

or cadmium would be present in more than trace amounts in most copper -

molybdenum ore bodies, and analysis certainly showed that insufficient

amounts were present to account for the large losses of molybdenum

observed during leaching experiments.

By a process of elimination in consideration of all the above

factors it was concluded that calcium was the element primarily respons-

ible for the observed poor molybdenum recoveries.   This would readily

explain the loss of molybdenum from combined copper sulphide molybdenite experiments in the absence of carbonate. Calcium was present as an impurity in all three mineral samples used; it can exist as a soluble species at pH 9.0, and has a very insoluble molybdate salt. In the presence of carbonate, however, the calcium will precipitate preferentially as $CaCO_3$ so that negligible interference with molybdate occurs. The fact that copper is also dissolved in the latter case is coincidental.

$$Ca^{2+} + MoO_4^{2-} \rightleftharpoons \qquad \log k_s = -7.38$$

$$Ca^{2+} + CO_3^{2-} \rightleftharpoons \qquad \log k_s = -8.55$$

Stoichiometric amounts of calcium and molybdenum to give a 1:1 ratio for $CaMoO_4$ were precipitated from a solution containing molybdenite and calcium chloride, except in the presence of carbonate buffers when all the calcium was precipitated with no effect on the molybdenum.

The fact that extraction in the presence of carbonate and copper sulphide minerals was slightly below the levels obtained for leaching molybdenite alone, could be attributed to one or more of the following factors:

     i)   formation of small amounts of copper molybdate, even in the presence of soluble $Cu(CO_3)_2^{2-}$,

     ii)   co-precipitation of the molybdenum with calcium carbonate,

     iii)   slight solubility of $CaCO_3$ due to the presence of chloride, enabling $CaMoO_4$ to form in small amounts.

The implications of calcium molybdate precipitation are unfavourable for an alkaline leaching process in which the potential feed material is a copper - rougher concentrate, which would unavoidably contain a certain amount of gangue material as well as the copper - molybdenum

metal values. The problems of such gangue materials being soluble in hypo-
chlorite solution and capable of forming insoluble molybdates would pose
an even greater threat to an 'in-situ' leaching process where good selec-
tivity of metal values is a necessity. It is interesting to note Bhappu's[17]
comments in this respect: he states that either a basic carbonate -
hypochlorite or an acid chlorate leach would be capable of dissolving
molybdenum from mixed sulphide - oxide ores, but that an alkali leach
would be preferable on account of the tendency of ferric iron, calcium
and aluminum to precipitate as insoluble molybdates in acid solution.
Presumably he was also relying on the presence of carbonate to suppress
molybdate formation in alkali solution.

The major calcium minerals likely to be associated with copper -
molybdenum porphyry ores were considered to be calcite and gypsum, and
a brief review of the geology of porphyry type deposits confirmed this:

Chalcopyrite, molybdenite and pyrite are the most commonly occurring
minerals in such ore bodies. Other sulphides found in association with
these three include bornite, chalcocite, galena, sphalerite, covellite,
pyrrhotite, bismuthinite and enargite. The most abundant gangue material
is quartz but magnetite, tourmaline, hematite and fluorite are also
common. Calcite, $CaCO_3$, and gypsum, $CaSO_4 \cdot 2H_2O$, are found in association
with either quartz or tourmaline distributions. In most ore deposits
they occur in the youngest rocks present, and represent late stage veining
which is therefore usually post-ore. Calcite, together with zeolite can
intergrow with the sulphide minerals and is also found, with gypsum in
veins and fracture fillings in the quartz. Fibrous gypsum can also be
present as vugs in the main late stage quartz - sulphide veins.

The distribution of the copper and molybdenum mineralization can

vary considerably between different ore bodies. In some cases both metals are contained within the central core of a deposit, while in others the copper especially is found in the outer zones, and therefore in association with quartz, sericite, pyrite etc. The molybdenite is often unsystematically distributed throughout the ore body and can cross cut the areas in which calcite and gypsum are found.

Of the molybdenum-bearing porphyry copper ores mined in British Columbia, deposits at Bethlehem Copper, Lornex, Valley Copper, Ox Lake, Brenda and the 'J.A.' ore body are all known to contain calcite and/or gypsum in close proximity to the metal sulphides. In the so-called molybdenum porphyries, calcium containing minerals are less common, but in the Boss Mountain deposit and at Endako, significant amounts of calcite are found in association with quartz and clay minerals contained in the ore bodies.[4]

4.3.4.1 Sodium hypochlorite leaching of calcium minerals

Having established that calcite and gypsum are likely gangue materials in low grade copper-molybdenum ores, experiments were carried out in which samples of these minerals were leached in hypochlorite solutions under identical conditions to those used for molybdenite.

It was confirmed that both minerals yield Ca^{2+} in solution in the presence of hypochlorite, and that the amounts extracted were sufficient to account for the observed molybdenum losses during copper sulphide - molybdenite leaching.

4.3.4.2 Effect of chloride concentration on calcium solubility

Samples of calcite and gypsum leached in the presence of varying

amounts of total chloride showed that calcium solubility increases as a function of $[Cl^-]$ and that the results were in good agreement with literature values (Table 11). Stronger hypochlorite solutions can thus be expected to extract more calcium. Identical results were obtained whether OCl^- or an equivalent amount of NaCl alone were used. This did not support the suggestion made in conjunction with the experimental observation that calcium sulphate is soluble in hypochlorite solutions, namely that this was due to calcium complexing agents contained in a commercial bleach. Furthermore, an assurance was obtained from the manufacturers of JAVEX that the product, when sold, consists exclusively of sodium hypochlorite and water.[89]

The reason for the increased solubility of calcium in chloride solutions is a change in activity coefficient due to an increased ionic strength. The thermodynamic solubility product for calcium sulphate is derived from the equation:

$$CaSO_4 \cdot xH_2O \rightleftharpoons Ca^{2+} + SO_4^{2-} + xH_2O \ .$$
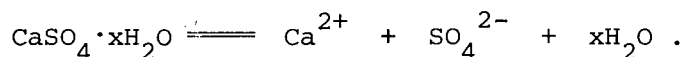
i) Calcium sulphate

Chloride Content (Moles Cl⁻)	[Ca] Dissolved (Experiment) g/l	[Ca] Dissolved (Reported) g/l	Source
0.0	0.712	0.666	85
		0.825	86
0.2	1.326	1.068	85
		1.224	87
0.5	1.528	1.532	87
		1.442	88
0.7	1.688	1.496	88
1.0	1.860	1.833	88
		1.800	87
1.5	2.012	1.959	88
2.0	2.024	2.116	88
		2.180	87

ii) Calcium carbonate

Chloride Content (Moles Cl⁻)	[Ca] Dissolved (Experiment) g/l	[Ca] Dissolved (Reported) g/l	Source
0.0	0.016	0.022	85
		0.014	86
0.25	0.016	0.048	85
0.60	0.049	0.056	85
0.70	0.060	0.056	85
1.37	0.055	0.055	85

Table 11: Comparison of Experimental and Literature Values for Solubility of i) CaSO$_4$ and ii) CaCO$_3$ in Chloride Solutions of Varying Strengths

for which

$$k^{\circ}_{sp} = [m_{Ca^{2+}}] \, [m_{SO_4^{2-}}] \, [\delta_{Ca^{2+}}] \, [\delta_{SO_4^{2-}}] \, [a_{H_2O}]^x$$

where m_{Ca}, m_{SO_4} are molal concentrations

δ_{Ca}, δ_{SO_4} are activity coefficients

x = number of moles of water

a = water activity in the solution.

Substituting for activity coefficients of Ca^{2+} and SO_4^{2-} from the Debye Huckel expression:

$$\log \delta_i = \frac{-A \, z_i^2 \, \sqrt{I}}{1 + B\sqrt{I}}$$

where ionic strength $I = 4 \, m \, CaSO_4 = m \, NaCl$

z = charge on ion i

A,B are constants

then $\log k_{sp} = \log k^{\circ}_{sp} + 2 \dfrac{A \cdot 4\sqrt{I}}{1 + B\sqrt{I}} - x \log a_{H_2O}$.

Assuming that $m_{Ca^{2+}} = m_{SO_4^{2-}}$,

then, $\log S = \log S^{\circ} + 4A \dfrac{I^{\frac{1}{2}}}{1 + BI^{\frac{1}{2}}} - \dfrac{x}{2} \log a_{H_2O}$

where S = molal solubility fo $CaSO_4$ at any ionic strength, I

and S° is the theoretical solubility when I = 0.

It is apparent therefore that S increases with an increase in m_{NaCl}, and hence of ionic strength, I.

4.3.4.3 Removal of calcium from
leaching solutions

The minimum carbonate:calcium ratio for effective precipitation

of CaCo$_3$ and prevention of calcium molybdate formation was found to be

3.19 M [CO$_3^{2-}$]: 1 M [Ca^{2+}]. For the amount of calcium contained in the

covellite mineral under study, 0.058 g/l, this gave a minimum carbonate

requirement of 0.55 g/l. However, leaching with this value of total

[CO$_3^{2-}$] at pH 9.0 gave almost instantaneous precipitation of copper^{III}

and rapid decomposition of the sodium hypochlorite, as noted earlier.

Increasing the carbonate above the stoichiometric requirement lengthened

the induction period to precipitation of copper^{III}, but gave more copper

in solution initially. The fact that the presence of molybdenite seeming-

ly decreased this induction period is probably due to the lower hypo-

chlorite content of solution as a result of the oxidation of MoS$_2$ to

Na$_2$MoO$_4$, rather than any effect of the molybdenum itself. The small

degree of copper molybdate formation which occurred at lower carbonate

levels has been pointed out previously to be detrimental to molybdenum

recovery and an undesirable catalyst for hypochlorite decomposition.

There would seem to be two alternatives therefore for the extraction

of molybdenum from molybdenite - copper sulphide concentrates:

i) to leach in the presence of large amounts of carbonate buffer

reagents and hence to precipitate calcium, as well as other soluble im-

purities such as zinc and cadmium, as insoluble carbonate salts and to

prevent any copper molybdate precipitation. At the same time a small

percentage of the copper would be dissolved. This would enable all the

molybdenum to be extracted before nucleation of copper^{III} and decomposition

of the hypochlorite lixiviant could occur, but would probably necessitate a copper - molybdenum separation step prior to molybdenum recovery from the solution.

ii) to leach with no carbonate in the system, and thereby to obtain complete selectivity of molybdenum over copper, but to decompose all the hypochlorite reagent as a result of heterogeneous copper catalysis. This would necessitate constant regeneration of the leaching solution.

In case (ii) an alternative suppressant for calcium would have to be found, and experiment suggested either phosphates or silicates may be feasible. Leaching chalcopyrite and molybdenite together in the presence of silicate in fact showed that very good molybdenum recoveries were obtained, coupled with no copper dissolution and an apparent stabilization of the hypochlorite. Copper meta-silicate, $CuSiO_3$, is known to exist, and such a compound could form at the mineral surface in preference to $Cu(OH)_2$ and/or $Cu(OH)_3$ and thus prevent rapid catalytic decomposition of the hypochlorite.

While the use of silicate appears to be a very viable alternative for leaching at pH 9.0, it should be noted:

i) Silicates and polymolybdates can combine in acid solutions and problems could be incurred during subsequent molybdenum recovery if silicate was present in the leaching solutions.

ii) Silicate reagents are likely to be more expensive than carbonates.

The most favourable process thus seems to be one incorporating leaching in the presence of sodium carbonate/bicarbonate at pH 9.0, provided a suitable method for copper - molybdenum separation after leaching can be found.

CHAPTER 5

5.1 Conclusions

1) The selective extraction of molybdenum from copper sulphide -
molybdenite concentrates can be rapidly and completely obtained by leach-
ing with sodium hypochlorite solutions at pH 9.0 and a temperature of
35°C, in the absence of carbonate buffer reagents.

2) Under these conditions the surfaces of the copper minerals
act as catalysts for the heterogeneous decomposition of sodium hypochlor-
ite due to the formation of an oxide or hydroxide salt of tri-valent
copper on the mineral surface.

3) Alkaline carbonate solutions are capable of dissolving small
amounts of copper as copper - carbonate complexes which are considerably
more soluble than the Cu^{2+} ion alone at pH values above 7.0. It is
suggested that the presence of hypochlorite in such solutions enables
the copper to exist as a tri-valent cupri-carbonate species, and that
precipitation of a solid carbonate compound containing up to 30% of the
copper in the +3 oxidation state occurs after a suitable nucleation
period has passed. This time period and the original copper content of
the solution are a function of the total carbonate concentration in the
system.

4) Soluble impurity elements which have insoluble molybdate
salts are detrimental to good molybdenum extraction. Calcium is suggested
as being the principal source of potential molybdenum losses in the

proposed copper sulphide - molybdenite leaching process. The presence of carbonate in the system would prevent calcium molybdate formation by the alternative precipitation of calcium carbonate, and a similar mechanism would apply to zinc and cadmium impurities. The use of silicates would provide an alternative means of calcium precipitation without the coincidental side effects of copper complexing, but may prove detrimental to subsequent molybdenum recovery.

6) Lead and iron do not exist as soluble species in hypochlorite solutions at pH 9.0 and will not interfere with molybdenum extraction. Copper molybdate is of minor importance at pH 9.0 due to the low solubility of the Cu^{2+} ion in alkaline solution, but in acid solution precipitation of 90% of the dissolved molybdenum can be attributed to copper molybdate formation. This compound is a catalyst for hypochlorite decomposition and has a solubility of about 1.25 g/l as $CuMoO_4$.

7) Leaching in acid solutions would be feasible only in the presence of carbonate and above a pH value of 6.0, because this is the region in which the cupric ion, Cu^{2+}, is complexed by carbonate anions, and copper molybdate formation is therefore prevented. The pH region 6.0 - 7.0 has previously been shown to be the most favourable for sodium chlorate formation.

8) Leaching in alkaline hypochlorite solutions in the presence of sufficiently large amounts of carbonate (25 g/l $[CO_3^{2-}]_T$ for example) would give good molybdenum extraction with approximate stoichiometric consumption of the lixiviant; but would entail simultaneous dissolution of a certain amount of copper. This copper would probably require separation

from the molybdenum before the recovery stage. To minimize sodium hypochlorite decomposition such a separation step should be made before copper^{III} precipitation can occur.

5.2 Suggestions for Future Work

Further work could be usefully done in the following areas relating to the present study:

i) A more detailed study of the surface reactions occurring between hypochlorite and different copper sulphide minerals would determine more precisely why such variations were observed in the rates of catalyzed decomposition.

ii) Further analysis of the carbonate containing hypochlorite solutions, to provide a more conclusive indication of the soluble copper species present. Polarographic techniques would probably give different half wave potentials for copper carbonate complexes in the +2 and +3 oxidation states.

iii) Analysis of solid compounds thought to contain tri-valent copper proved to be somewhat difficult due to a lack of published data for standard compounds. If pure samples of Cu_2O_3 or $Cu_2(CO_3)_3$ could be manufactured, X-ray diffraction patterns, gram magnetic susceptibilities, solubility data etc. could be usefully obtained.

iv) Leaching was found to be most successful in alkaline solutions. It would therefore be logical to research into ways of recovering molybdenum from leach solutions without lowering pH. The ideal method would

be one of solvent extraction or ion exchange operating at pH 9.0. This would give copper - molybdenum separation and molybdenum recovery in a single stage and would prevent unnecessary chlorate formation by maintaining an alkaline system throughout the process.

v) Use of typical copper rougher concentrates as feed material would illustrate the feasibility of this type of process more clearly; and show whether or not the suggested conditions are optimum for good molybdenum recovery. Flotation studies on the leaching tails could also be usefully pursued.

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APPENDIX A

Tables of Experimental Results

Table I: NaOCl leaching of covellite in the presence of carbonate buffers (Figures 6,8)

Temp. 35°C, pH 9.0, Agitation 748 rpm, [NaOCl] 7.68 g/l,
CuS 10 g, NaHCO$_3$ 14.15 g, Na$_2$CO$_3$ 1.01 g.

Time (mins)	[Cu] ppm	[NaOCl] g/l
5	133	5.64
10	133	
15	125	
20	127	5.60
30	127	
45	127	
60	121	5.62
90	126	
120	128	
150	130	5.64

Table II: <u>NaOCl leaching of chalcocite in the presence</u>
<u>of carbonate buffers (Figures 6,8)</u>

Temp 35°C, Agitation 720 rpm, [NaOCl] 7.8 g/l, pH 9.0, Cu_2S 10 g,
$NaHCO_3$ 14.15 g, Na_2CO_3 1.01 g

Time (mins)	[Cu] ppm	[NaOCl] g/l
5	122.5	7.08
10	122	
15	115	6.07
30	116	
45	118	6.10
60	118	
90	113	6.05
120	118	
150	115	6.07

Table III: NaOCl leaching of chalcopyrite in the presence of
carbonate buffers (Figures 6,8)

Temp 35°C, Agitation 803 rpm,   [NaOCl] 8.13 g/l, pH 9.0, $CuFeS_2$ 10 g,
$NaHCO_3$ 14.15 g, Na_2CO_3 1.01 g.

Time (mins)	[Cu] ppm	[NaOCl] g/l
2	105	
5	104	7.56
10	96	7.44
20	99	7.36
30	96	7.29
50	101	7.24
60	106	7.24
80	106	
100	99	7.22
120	95	
150	101	
180	104	7.20
210	106	

Table IV: <u>Effect of separating leaching solution from mineral</u>
<u>slurry during agitation of CuFeS$_2$ in NaOCl (Figure 7)</u>

Temp 35°C, Agitation 760 rpm, [NaOCl] 8.0 g/l, pH 9.0, CuFeS$_2$ 10 g,
NaHCO$_3$ 14.15 g, Na$_2$CO$_3$ 1.01 g.

Time (mins)	[Cu] slurry ppm	[Cu] filtered soln ppm
5	118	129
10	111	129
15	108	129
20	105	130
30	103	128
45	109	130
65	105	129
100	104	130
140	110	130
180	117	131

Table V: Effect of separating leaching solution from mineral slurry
during agitation of Cu_2S in NaOCl (Figure 7).

Temp 35°C, Agitation 782 rpm, NaOCl 7.45 g/l, pH 9.0, Cu_2S 10 g,
$NaHCO_3$ 14.15 g, Na_2CO_3 1.01 g.

Time (mins)	[Cu] slurry ppm	[Cu] filtered soln ppm
5	112	123
10	115	123
15	106	123
20	110	122
30	108	122
45	113	123
70	109	123
90	110	123
145	106	123

Table VI: NaOCl leaching of covellite in the absence of carbonate
buffers (Figures 9,11)

Temp 35°C,   Agitation 784 rpm,   pH 9.0,   [NaOCl] 7.61 g/1,   CuS 10 g.

Time (mins)	[Cu] ppm	[NaOCl] g/1	[NaClO$_3$] g/1	NaClO$_3$ %
0	0.05	7.61	0.179	
5	0.29	5.93	0.304	13.70
10	0.22	2.70	0.429	
20	0.40	0.39	0.490	9.40
30	0.30	0.08	0.537	9.57
45	0.20	--	0.540	

Table VII: <u>NaOCl leaching of chalcocite in the absence of carbonate buffers (Figures 9,11)</u>

Temp 35°C, Agitation 780 rpm, pH 9.0, [NaOCl] 7.69 g/l, Cu_2S 10 g.

Time (mins)	[Cu] ppm	[NaOCl] g/l	[$NaClO_3$] g/l	$NaClO_3$ %
0	0.13	7.69	0.304	
5	0.19	6.98	0.340	8.73
10		6.60	0.358	9.21
20	0.20	6.30	0.429	17.70
30		5.63	0.501	21.22
45	0.25	5.03	0.633	22.81
60		4.53	0.716	20.20
80	0.21	3.91		
100		3.30	0.859	23.42
120	0.19	2.78	0.913	23.03
150		2.18	0.922	23.31
180	0.23	1.56		

Table VIII: NaOCl leaching of chalcopyrite in the absence of
carbonate buffers (Figures 9.11)

Temp 35°C, Agitation 785 rpm, pH 9.0, [NaOCl] 7.73 g/l, CuFeS$_2$ 10 g.

Time (mins)	[Cu] ppm	[NaOCl] g/l	[NaClO$_3$] g/l	NaClO$_3$ %
0	0.03	7.73	0.358	
5	0.09	5.70	0.751	35.0
10	0.08	4.54	0.805	25.9
20	0.11	2.78	0.966	22.8
30	0.10	1.73	1.048	21.4
45	0.09	0.64	1.199	20.7
60	0.05	0.23	1.180	
80	0.11	0.11	1.191	20.2
100	0.10	--		

Table IX: Microprobe examination of massive chalcocite before and after leaching in NaOCl.

Temp 35°C, Agitation 729 rpm, pH 9.0, [NaOCl] 7.06 g/l
Polished Cu_2S surface 3.2 cm^2

Area	S Count Before	Cu Count Before	Cu/S Ratio	S Count After	Cu Count After	Cu/S Ratio
	7287	81631	11.18	4873	71025	14.58
	7963	74964	9.41	4429	70794	15.98
	5699	71766	12.59	4463	70688	15.84
1	4698	73564	15.66	4555	71092	15.61
	5136	75063	14.19	4517	71194	15.76
	5449	75061	13.33	4496	71196	15.84
	5528	75144	13.59	4508	70874	15.72
	7283	82548	11.33	7867	79133	10.06
	7094	82268	11.60	8000	77862	9.73
2	7232	82722	11.44	8072	78918	9.78
	7243	82370	11.37	8030	79544	9.91
	7220	82314	10.95	8459	76290	8.88

Table X: Microprobe examination of massive covellite, before and
after leaching in NaOCl

Temp 34.9°C, Agitation 730 rpm, pH 9.0, [NaOCl] 8.1 g/l, Polished
CuS surface 4.5 cm^2.

Area	S Count Before	Cu Count Before	Cu/S Ratio	S Count After	Cu Count After	Cu/S Ratio
	14161	67660	4.78	10338	67705	6.55
	14132	67131	4.75	10434	67189	6.44
1	14408	66725	5.63	10264	66974	6.53
	14356	66850	4.66	9733	66380	6.82
	14516	66570	4.59	9593	66683	6.95
	14191	66695	4.70	29880	32991	1.10
	14020	66912	4.77	28731	33094	1.15
2	13932	66553	4.78	28605	52541	1.84
	14111	66321	4.69	29641	50942	1.72
				13400	64360	4.80
	After CuCl$_4$ Wash			13352	64230	4.81
				12751	64821	4.71
				13748	64491	4.69
3 (Green	13704	66909	4.88	00541	79590	147.11
Deposit)	13826	66894	4.84	00670	83579	124.74

Table XI: NaOCl leaching of cupric sulphide, CuS in the absence
of carbonate (Figure 10)

Temp 35°C, Agitation 821 rpm, pH 9.0, [NaOCl] 7.67 g/l CuS 10.0 g.

Time (mins)	[Cu] ppm	[NaOCl] g/l
3	0.15	7.52
10	0.17	7.48
20	0.19	6.17
35	0.20	5.04
80	0.20	3.01
100	0.20	1.65

Table XII: <u>NaOCl leaching of cuprous sulphide, Cu$_2$S, in the absence</u>
            <u>of carbonate (Figure 10)</u>

Temp 35°C,   Agitation 806 rpm,   pH 9.0,   [NaOCl] 7.14 g/l,   Cu$_2$S 10.0 g.

Time (mins)	[Cu] ppm	[NaOCl] g/l
0	0.02	7.14
5	0.10	6.84
25	0.10	5.49
45	0.10	4.04
55	0.08	2.73
85	0.10	1.63
100	0.10	0.45

Time (mins)	0.55 g/l [CO₃]		1.0 g/l [CO₃]		2.0 g/l [CO₃]		5.0 g/l [CO₃]		7.5 g/l [CO₃]		10.7 g/l [CO₃]	
	[Cu] ppm	NaOCl g/l	[Cu] ppm	NaOCl g/l	[Cu] ppm	NaOCl g/l	[Cu] ppm	NaOCl g/l	[Cu] ppm	NaOCl g/l	[Cu] ppm	NaOCl g/l
0		7.82	0.19	7.67		7.66	0.2	7.44		7.45	0.9	7.85
5	5.6	6.94	14.5	6.84	21.5	7.05	46.4	6.43	84.0	6.69	119.2	7.07
10	5.0	5.48	3.0	6.24	12.0	6.69	44.1		76.8		119.3	6.31
20	1.3	3.38	3.9	4.29	12.0	6.59	40.3	6.43	77.4	6.64	114.3	
30	3.8	1.13	3.3	1.32	13.0	6.39	38.0		77.8		105.8	
45	2.5	--	3.5	0.38	7.5	4.96	37.6	6.47	80.0		113.7	
60	2.5	--	3.4	--	4.5	0.52	29.0	5.53	77.2	6.62	117.2	6.32
90					1.5	0.09	20.2	0.25	75.0	6.69	116.5	
120							17.3	--	67.2	6.65	116.2	6.31
140									41.8	4.71	107.3	
180									42.1	--	110.1	
200											110.8	
240											116.1	6.30
255											91.0	5.00
280											64.0	2.00
320											64.0	--

Table XIII: NaOCl leaching of covellite with variable $[CO_3^{2-}]_T$ at pH 9.0, 35°C (Figures 12,13)

Time (mins)	1.0 g/l $[CO_3^{2-}]$		2.0 g/l $[CO_3^{2-}]$		5.0 g/l $[CO_3^{2-}]$	
	[Cu] ppm	[NaOCl] g/l	[Cu] ppm	[NaOCl] g/l	[Cu] ppm	[NaOCl] g/l
0		8.12		7.89		8.06
5	2.93	7.67	8.5	7.52		
10	1.00	7.52	8.0	7.52	40.8	7.59
20	1.55	7.14	8.0			
30	0.85	6.92	6.3	7.52		7.52
45	0.33	6.39			38.3	
60		6.00	6.3	6.47	35.2	7.52
90	0.33	5.45	4.8	5.65	23.5	7.00
120	0.28	4.49	2.8	4.86	22.5	5.94
160	0.25	3.81			22.5	4.90
190	0.30	3.08	2.3	3.30	22.0	4.35
240			2.2	0.45		
300			3.0	--		

Table XIV: NaOCl leaching of chalcocite with variable $[CO_3^{2-}]_T$ at pH 9.0, 35°C (Figures 14,15)

Table XV: NaOCl leaching of synthetic copper sulphides with 5 g/l
            $[CO_3^{2-}]$ (Figures 16,17)

pH 9.0,   Temp 35°C,   Agitation 821 rpm

Time (mins)	CuS		Cu_2S	
	[Cu] ppm	[NaOCl] g/l	[Cu] ppm	[NaOCl] g/l
0		7.67		7.14
5	46.6	7.52	44.8	
15	44.8		43.8	7.07
30	44.0	7.52	43.8	
45	40.0	7.48	43.7	6.84
60	27.5	6.17	30.0	5.49
80	27.5	5.04	23.8	4.04
100	24.6	3.01	10.0	2.73
120	11.0	1.65	7.1	1.63
140	6.7		5.4	0.45

Table XVI: <u>NaOCl leach of covellite in the presence of 5 g/l $[CO_3^{2-}]$ and 20 g/l [NaOCl] (Figure 18)</u>

Temp 35°C, pH 9.0, Agitation 800 rpm, CuS 10 g, $NaHCO_3$ 6.5165 g, Na_2CO_3 0.4720 g.

Time (mins)	[Cu] ppm	[NaOCl] g/l
0		19.17
2	106	18.04
10	117	
25	109	
40	103	16.54
60	97	
155	94	13.53
195	49	5.86
205	28	3.35
225	22	0.75
265	22	--

Table XVII: <u>Agitation of covellite in the presence of $NaHCO_3$/Na_2CO_3 $\pm$</u>
<u>NaCl (Figure 19)</u>

Temp 35°C, Agitation 817 rpm, pH 9.0, CuS 10g,

$NaHCO_3$ 14.15 g, Na_2CO_3 1.01 g.

Time (mins)	Carbonate only [Cu] ppm	Carbonate and 14.0 g/l NaCl [Cu] ppm
10	62.5	64.5
20	62.3	64.5
35	60.0	64.0
60	28.5	53.0
75	11.9	41.5
90	9.5	25.0
120		16.0

Table XVIII: NaOCl leaching of covellite in the presence of 10 g/l $[CO_3^{2-}]$, and Na_2MoO_4 (Figure 20)

Temp 35°C, [NaOCl] 7.82 g/l, Agitation 803 rpm, pH 9.0, $NaHCO_3$ 14.15 g, Na_2CO_3 1.01 g, CuS 10 g, Na_2MoO_4 1.538 g ≡ 0.6 g/l Mo.

Time (mins)	[Cu] ppm	[NaOCl] g/l	[Mo] g/l	Mo %
0		7.82	0.66	100
5	136	6.76	0.63	95.5
20	133			
60	133	6.54	0.63	95.5
120	131	6.54		
180	133	6.52	0.65	98.5
255	132	6.50		
270	118	4.96	0.65	98.5
290	85	1.65		
305	66	0.60	0.61	92.0
360	64	--		
410	20	--	0.65	98.5
440	9	--		

Table XIX: Sodium hypochlorite decomposition in the presence
             of tri-valent copper salts (Figure 21)

Temp 35°C,   Agitation 700 - 760 rpm,   pH 9.0,

copper samples: 2 g.

Time (mins)	copper[III] oxide [NaOCl] g/l	copper[III] carbonate [NaOCl] g/l	cupric oxide, CuO [NaOCl] g/l
0	7.74	7.67	7.82
5	5.94	6.75	7.80
10	3.99	5.40	7.37
20	1.80	3.50	7.22
30	0.38	2.05	6.58
45	--	0.20	6.35
60		--	6.00
90			5.45

Table XX: NaOCl oxidation of molybdenite (Figure 22)

Temp 35°C, pH 9.0, Agitation 780 rpm, [NaOCl] 7.7 g/l,
MoS_2 0.3 g.

Time (mins)	[Mo] ppm	Mo extracted %	[NaOCl] g/l
0	--	--	7.70
5	168	93.3	6.83
10	168	93.3	
15	169	93.8	
20	170	94.4	6.82
30	170	94.4	
45	170	94.4	
60	169	93.8	6.82

Table XXI: NaOCl oxidation of 'reagent grade' molybdenum
disulphide (Figures 23,24)

Temp 35°C, Agitation 803 rpm, pH 9.0, MoS_2 1.0 g

Time (mins)	Reagent grade MoS_2			98% + MoS_2		
	[Mo] g/l	Mo extrn. %	[NaOCl] g/l	[Mo] g/l	Mo extrn. %	[NaOCl] g/l
0	--	--	8.54	--		8.72
5	0.535	89.3	5.62	0.375	62.5	6.91
10	0.535	89.3		0.531	88.5	6.05
20	0.535	89.3	5.60	0.587	97.9	5.68
30	0.536	89.3		0.587	97.9	
45	0.536	89.3	5.59	0.584	97.9	5.00
60	0.536	89.3	5.59	0.587	97.9	4.65

Table XXII: <u>NaOCl oxidation of molybdenite and covellite, with</u>
<u>and without carbonate buffers (Figure 25)</u>

Temp 35°C, Agitation 800 rpm, pH 9.0, MoS_2 0.3 g
CuS 10.0 g (10 g/l total carbonate)

Time (mins)	MoS_2, CuS + $NaHCO_3/Na_2CO_3$				MoS_2, CuS + NaOH			
	[Mo] ppm	Mo extr. %	[Cu] ppm	[NaOCl] g/l	[Mo] ppm	Mo extr. %	[Cu] ppm	[NaOCl] g/l
0	--	--	--	7.37	--	--	--	7.43
5	160	88.9	110		132	73.3	0.25	4.44
10	160	88.9	108	4.89	132	73.3	0.30	3.01
20	160	88.9	106		133	73.8	0.27	1.13
30	160	88.9	104	4.66	133	73.8	0.23	0.38
45	160	88.9	107		133	73.8	0.32	--
60	160	88.9	103	4.04	133	73.8	0.27	--

Table XXIII: <u>NaOCl oxidation of molybdenite and chalcocite, with and without carbonate buffers (Figure 26)</u>

Temp 35°C, Agitation 785 rpm, pH 9.0, MoS_2 0.3 g, Cu_2S 10.0 g (10 g/l total carbonate).

Time (mins)	MoS_2, Cu_2S + $NaHCO_3$/Na_2CO_3				MoS_2, Cu_2S + NaOH			
	[Mo] ppm	Mo extr. %	[Cu] ppm	[NaOCl] g/l	[Mo] ppm	Mo extr. %	[Cu] ppm	[NaOCl] g/l
0	--	--	--	7.89	--	--	--	7.35
5	159	88.5	96.0		139	77.2	0.13	6.50
10	169	89.2	93.0	4.61	139	77.2	0.13	6.35
20	160	89.0	94.0		139	77.2	0.25	6.02
30	162	89.9	93.0	4.53	139	77.2	0.25	5.57
45	162	89.9	90.0		139	77.2	0.25	4.95
60	162	90.0	89.0	4.44	139	77.2	0.23	3.60

Table XXIV: <u>NaOCl oxidation of molybdenite and chalcopyrite with and without carbonate buffers (Figure 27)</u>

Temp 34.9°C, Agitation 792 rpm, pH 9.0, MoS_2 0.3 g,
$CuFeS_2$ 10.0 g (10 g/l total carbonate).

Time (mins)	MoS_2, $CuFeS_2$ + $NaHCO_3$/Na_2CO_3				MoS_2 $CuFeS_2$ + NaOH			
	[Mo] ppm	Mo extr. %	[Cu] ppm	[NaOCl] g/l	[Mo] ppm	Mo extr. %	[Cu] ppm	[NaOCl] g/l
0		--	--	7.50	--	--	--	7.13
5	154	86.1	106	5.32	143	79.4	0.53	4.51
10	156	86.6	100		144	80.0	0.41	4.17
20	156	86.6	98	5.30	142	78.8	0.32	2.82
30	158	87.8	98		144	80.0	0.32	1.97
45	158	87.8	94	5.25	144	80.0	0.27	0.94
60	158	87.8	99	5.20	144	80.0	0.11	--

Table XXV: <u>NaOCl oxidation of molybdenum disulphide and chalcopyrite</u>
<u>with and without carbonate buffers</u>

Temp 35°C, Agitation 780 rpm, pH 9.0, CuFeS$_2$ 10 g,

MoS$_2$ 5 g (reagent grade)

Time (mins)	MoS$_2$ only			MoS$_2$, CuFeS$_2$ + NaOH			MoS$_2$, CuFeS$_2$ + [CO$_3^{2-}$]		
	[Mo] g/l	Mo extr. %	[NaOCl] g/l	[Mo] g/l	Mo extr. %	[NaOCl] g/l	[Mo] g/l	Mo extr. %	[NaOCl] g/l
0	--	--	24.55	--	--	20.32	--	--	20.21
5	2.67	89.0	11.32	2.54	84.7	8.32	2.64	87.5	7.37
10	2.66	88.7		2.54	84.7	4.62	2.64	87.5	
20	2.68	89.3	11.30	2.54	84.7	2.83	2.62	87.5	7.28
30	2.67	89.0		2.54	84.7	1.56	2.62	87.3	
45	2.67	89.0	11.27	2.54	84.7	0.34	2.62	87.3	7.26
60	2.67	89.0	11.25	2.54	84.7	--	2.64	87.5	

Table XXVI: <u>NaOCl oxidation of molybdenite in the presence of</u>
<u>copper sulphate solution</u>

Temp 35.1°C,   NaOCl 7.5 g/l,   Agitation 792 rpm, pH 9.0,

MoS_2 0.3 g, $CuSO_4$ 0.4 g/l ≡ 0.1 g/l Cu

Time (mins)	Cu added ppm	[Cu] in soln ppm	[Mo] ppm	Mo extrd. %
0	--	--	--	--
5	--	--	168	93.3
10	12.8	0.05	142	79.1
20	25.6	0.10	136	75.3
30	38.4	0.08	135	75.2
45	67.5	0.08	134	74.8
60	100	0.11	132	73.5

Table XXVII: NaOCl oxidation of covellite in the presence of sodium
molybdate solution

Temp 35.1°C,   Agitation 821 rpm,   pH 9.1,   CuS 10.0 g,

Na_2MoO_4 2.15g ≡ 0.1 g Mo,   [NaOCl] 7.63 g/l

Time (mins)	Mo added ppm	[Mo] in soln ppm	Mo in soln %	[Cu] ppm
10	11.04	9.79	89.0	0.23
20	25.55	22.48	88.0	0.31
30	39.23	33.38	85.1	0.31
45	51.80	44.55	86.0	0.32
60	75.45	62.62	83.0	0.33
90	100.00	81.00	81.0	0.33

Table XXVIII: <u>NaOCl oxidation of molybdenite at pH 5.5 (Figure 28)</u>

Temp 35°C, Agitation 880 rpm, pH 5.4,

[NaOCl] 6.92 g/l, Mo S$_2$ 1.0 g

Time (mins)	[Mo] g/l	Mo extracted %	[NaOCl] g/l
0	--	--	6.92
5	0.550	91.6	
10	0.563	93.8	2.71
20	0.548	91.3	
30	0.563	93.8	2.53
45	0.564	94.0	
60	0.563	93.8	2.21

Table XXIX: <u>NaOCl oxidation of molybdenite and chalcopyrite at pH 5.5</u>
<u>(Figure 29)</u>

Temp 35°C, Agitation 803 rpm, pH 5.55, [NaOCl] 6.54 g/l

$CuFeS_2$ 10 g, MoS_2 0.3 g.

Time	MoS_2, $CuFeS_2$ + NaOH			MoS_2, $CuFeS_2$ + 10 g $NaHCO_3$		
	[Mo] ppm	Mo extr. %	[Cu] ppm	[Mo] ppm	Mo extr. %	[Cu] ppm
5	142	78.8	--	146	82.2	--
($CuFeS_2$ added)						
10	4.1	2.27	12.9	0.2	0.10	37.5
20	4.5	2.50	8.7	0.3	0.16	33.7
30	4.6	2.56	8.1	1.7	0.94	27.2
45	4.5	2.50	8.1	1.6	0.88	25.0
60	4.6	2.56	8.4	1.2	0.66	25.0

Table XXX: <u>NaOCl oxidation of molybdenite and covellite at pH 5.5</u>
<u>(no carbonate)(Figure 30 a)</u>

Temp 35°C, Agitation 802 rpm, pH 5.45, [NaOCl] 6.17 g/l
CuS 10.0 g, MoS_2 0.3 g.

Time (mins)	[Mo] ppm	Mo extracted %	[Cu] ppm	[NaOCl] g/l
5	141	78.3	--	5.55
(CuS added)				
10	5.8	3.2	18.0	1.54
20	6.2	3.4	15.2	0.03
30	6.6	3.6	13.5	--
45	6.6	3.6	12.9	--
60	6.7	3.7	12.8	--
90	6.2	3.4	12.4	--

Table XXXI: NaOCl oxidation of molybdenite and covellite at pH 5.5, with sodium bicarbonate (Figure 30 b)

Temp 34.9°C, Agitation 800 rpm, pH 5.50, [NaOCl] 6.92 g/l
CuS 10 g, Mo S$_2$ 0.3 g, NaHCO$_3$ 10.0 g.

Time (mins)	[Mo] ppm	Mo extracted %	[Cu] ppm	[NaOCl] g/l
5	153	85.0	--	6.92
(CuS added)				
10	2.4	1.33	36.0	0.15
20	2.4	1.33	35.0	--
30	2.5	1.38	32.0	--
45	3.0	1.66	30.0	--
60	2.4	1.33	30.0	--

Table XXXII: NaOCl leaching of chalcopyrite at pH 5.5 with
and without bicarbonate in the system

Temp 35°C, Agitation 805 rpm, pH 5.40,

[NaOCl] 7.2 g/l, CuFeS$_2$ 10 g, NaHCO$_3$ 9.28 g.

Time (mins)	CuFeS$_2$ only		CuFeS$_2$ + HCO$_3^-$	
	[Cu] ppm	[NaOCl] g/l	[Cu] ppm	[NaOCl] g/l
5	36.5	5.7	48.8	5.64
10	34.2	4.6	46.2	4.52
20	30.6	3.4	45.3	3.30
30	28.5	1.7	44.8	3.30
45	25.0	0.5	43.6	3.28
60	24.1	--	42.5	3.25
90	24.3	--		

Table XXXIII: <u>NaOCl leaching of molybdenite and chalcocite at pH 6.5,</u>
<u>with bicarbonate in the system (Figure 31 a)</u>

Temp 35°C, Agitation 880 rpm, pH 6.5, [NaOCl] 6.92 g/l
Cu_2S 10 g, MoS_2 1.0 g, $NaHCO_3$ 10 g.

Time (mins)	[Mo] g/l	Mo extracted %	[Cu] ppm	[NaOCl] g/l
0	--	--		6.92
10	0.531	88.3	34.7	2.71
20	0.531	88.3	29.5	2.11
30	0.529	88.1	25.0	2.11
45	0.529	88.1	25.0	2.10
60	0.529	88.1	25.0	2.06

Table XXXIV: <u>NaOCl leaching of molybdenite and chalcocite at</u>
<u>pH 6.5, with no carbonate present (Figure 31 b)</u>

Temp 35°C, Agitation 880 rpm, pH 6.5,

[NaOCl] 7.52 g/l, Mo S$_2$ 1.0g, Cu$_2$S 10 g

Time (mins)	[Mo] g/l	Mo extracted %	[Cu] ppm	[NaOCl] g/l
10	0.515	85.8	32.6	2.65
20	0.472	78.6	30.0	2.34
30	0.465	77.5	29.5	1.97
45	0.387	64.5	24.3	1.03
60	0.280	46.6	18.7	0.20
90	0.253	42.2	16.2	--

Table XXXV: <u>NaOCl leaching of molybdenite and cupric sulphide at</u>
<u>pH 6.0 in the presence of carbonate (Figure 32)</u>

Temp 35°C, Agitation 803 rpm, pH 6.5,

[NaOCl] 7.04 g/l, CuS 10.0 g, MoS_2 1.0 g, $NaHCO_3$ 10.0 g

Time (mins)	[Mo] g/l	Mo extracted %	[Cu] ppm	[NaOCl] g/l
10	0.539	89.8	39.5	5.04
20	0.531	88.5	24.5	2.86
30	0.549	91.5	25.5	
45	0.560	93.3	25.5	2.63
60	0.560	93.3	24.9	
100	0.560	93.3	25.0	2.56

Table XXXVI: <u>NaOCl leaching of molybdenite and cupric sulphide at</u>
<u>pH 6.0, with no carbonate present</u>

Temp 35°C, Agitation 857 rpm, pH 6.5, [NaOCl]
6.39 g/l, CuS 10.0 g, MoS_2 1.0 g.

Time (mins)	[Mo] g/l	Mo extracted %	[Cu] ppm	[NaOCl] g/l
10	0.473	78.8	32.7	3.39
20	0.455	75.8	37.2	2.63
30	0.441	73.5	17.2	2.18
45	0.288	48.0	11.8	2.03
60	0.093	15.5	4.5	1.28
90	0.061	10.2	0.3	0.38

Table XXXVII: <u>NaOCl leaching of molybdenite and chalcopyrite at</u>
<u>pH 7.0 with bicarbonate present (Figure 33 a)</u>

Temp 35°C, Agitation 785 rpm, pH 7.0, [NaOCl]
6.5 g/l, $CuFeS_2$ 10 g, MoS_2 1.1 g, $NaHCO_3$ 10 g

Time (mins)	[Mo] g/l	Mo extracted %	[Cu] ppm	[NaOCl] g/l
5	0.62	93.9	56.6	2.63
10	0.64	96.9	58.2	0.23
20	0.65	98.5	52.5	--
30	0.64	96.9	48.5	--
50	0.65	98.5	42.5	--
70	0.65	98.5	41.3	--

Table XXXVIII: NaOCl leaching of molybdenite and chalcopyrite at pH
7.0, no carbonate (Figure 33 b)

Temp 35°C, Agitation 785 rpm, pH 7.0, [NaOCl]
6.54 g/l, CuFeS$_2$ 10 g, MoS$_2$ 1.0 g.

Time (mins)	[Mo] g/l	Mo extracted %	[Cu] ppm	[NaOCl] g/l
5	0.173	28.75	12.5	
10	0.180	30.00	8.2	3.01
20	0.185	30.83	3.0	2.11
30	0.190	31.66	1.9	
60	0.195	32.50	1.3	1.96
120	0.195	32.50	0.7	
205	0.203	33.75	0.5	1.94

Table IXL: NaOCl decomposition in the presence of copper molybdate at pH 5.5 (Figure 35)

Temp 35°C, Agitation 792 rpm, pH 5.40, [NaOCl] 6.84 g/l, Cu MoO$_4$ 2 g.

Time (mins)	[NaOCl] g/l	[NaClO$_3$] g/l
0	6.84	--
10	6.39	0.109
20	5.30	0.785
30	4.14	1.430
45	2.31	1.480

Table XL: <u>Determination of the solubility of copper molybdate at</u>
<u>pH 5.0 (Figure 34)</u>

pH 5.0 $Na_2MoO_4 \cdot 2H_2O$ 4.13 g $\equiv$ 0.096 g/l Mo

$CuSO_4 \cdot 5H_2O$ 6.22 g $\equiv$ 0.064 g/l Cu

Mo added (Moles)x10^2	Mo in soln (Moles)x10^2	Cu in soln (Moles)x10^2	Mo pptd (Moles)x10^3	Cu pptd (Moles)x10^3
0.2	0.188	0.889	0.12	0.24
0.4	0.350	0.884	0.50	0.29
0.6	0.604	0.883	--	0.30
0.8	0.792	0.860	0.08	0.53
1.0	0.881	0.795	1.20	1.18
1.2	0.880	0.595	3.20	3.18
1.4	0.881	0.385	5.20	5.28

Table XLI: Sodium hypochlorite leaching of molybdenite and covellite
pH 10.0, with carbonate (Figure 37 a)

Temp 35.1°C, Agitation 789 rpm, pH 10.0, [NaOCl]
7.54 g/l, MoS$_2$ 0.3 g, CuS 10.0 g, Na$_2$CO$_3$ 5.37 g,
NaHCO$_3$ 7.24 g.

Time (mins)	[Mo] ppm	Mo extrn. %	[NaOCl] g/l
5	148	82.2	6.63
10	150	83.3	
20	154	85.5	6.43
30	158	87.8	
45	160	88.9	6.25
60	164	91.1	6.23

Table XLII: Sodium hypochlorite leaching of molybdenite
             and covellite at pH 10.0 with no carbonate (Figure 37 b)

Temp 35°C, Agitation 790 rpm, pH 10.0, [NaOCl]
7.61 g/l, CuS 10 g, MoS_2 0.3 g.

Time (mins)	[Mo] ppm	Mo extrn. %	[Cu] ppm	[NaOCl] g/l
5	142	78.9	0.5	6.01
10	142	78.9	0.7	3.10
20	142	78.9	0.5	0.60
30	141	78.3	0.5	0.05
45	143	79.4	0.4	--
60	143	79.4	0.3	--

Table XLIII: NaOCl leaching of molybdenum disulphide and cuprous
              sulphide at pH 9.0, with no carbonate (Figure 36)

Temp 35°C,   Agitation 808 rpm,   pH 9.0,   [NaOCl]
33.32 g/l, MoS_2 5 g, Cu_2S 10 g.

Time (mins)	[Mo] g/l	Mo extrn. %	[NaOCl] g/l
5	2.66	88.67	
10	2.65	88.30	19.36
20	2.66	88.67	
30	2.66	89.0	10.53
45	2.68	89.0	
70	2.68	89.0	4.14

Table XLIV: <u>NaOCl leaching of molybdenum disulphide and cuprous</u>
<u>sulphide at pH 9.0, with 10 g/l carbonate (Figure 36)</u>

Temp 35°C, Agitation 803 rpm, pH 9.0, [NaOCl]
33.08 g/l, MoS_2 5 g, Cu_2S 10 g.

Time (mins)	[Mo] g/l	Mo extrn. %	[NaOCl] g/l
5	2.68	89.01	20.14
10	2.68	89.01	
20	2.70	90.00	19.36
30	2.72	90.67	
45	2.72	90.67	16.16
60	2.72	90.67	13.90

Table XLV: <u>NaOCl leaching of chalcopyrite, chalcocite and covellite</u>
<u>at pH 9.0 with no carbonate (Figure 38)</u>

Temp 35°C, Agitation 799 rpm, pH 9.0, [NaOCl]
7.74 g/l, Cu samples 10 g.

Time (mins)	CuFeS$_2$		Cu$_2$S		CuS	
	[Ca] ppm	[Cu] ppm	[Ca] ppm	[Cu] ppm	[Ca] ppm	[Cu] ppm
5	65.0	0.68	3.48	0.07	8.0	0.13
10	65.3	0.75	3.55	0.12	9.2	0.15
20	66.2	0.52	5.35	0.15	9.5	0.09
30	66.8	0.33	4.03	0.08	8.1	0.05
40	66.8	0.32	4.10	0.04	8.5	0.12
50	66.6	0.30	4.18	0.07	8.8	0.17
60	66.8	0.52	4.20	0.13	9.8	0.13

Table XLVI: <u>NaOCl leaching of MoS_2 and Cu_2S in the presence of 0.1 g/l</u>
<u>calcium as $CaCl_2$ solution</u>

Temp 35°C, Agitation 821 rpm, pH 9.0, [NaOCl]
8.0 g/l, MoS_2 1 g (reagent grade), Cu_2S 10 g,
$CaCl_2$ 0.3703 g ≡ 0.1 g Ca.

Time (mins)	[Ca] ppm	[Mo] g/l	Mo extr. %	Mo pptd. (x 10^4M)	Ca pptd. (x 10^4M)
0	97.25	--	--	--	--
10	92.50	0.522	87.2	1.56	1.24
20	91.25	0.522	87.2	1.56	1.50
30	92.50	0.525	87.5	1.25	1.24
45	92.50	0.525	87.5	1.25	1.24
60	92.50	0.525	87.5	1.25	1.24

Table XLVII: NaOCl leaching of molybdenite and chalcocite in the presence of $CaCl_2$ and $Na_2CO_3/NaHCO_3$

Temp 34.9°C, Agitation 820 rpm, pH 9.0, [NaOCl] 7.89 g/l, MoS_2 1.0 g, Cu_2S 10 g, $CaCl_2$ 0.3703 g, $NaHCO_3$ 14.15 g, Na_2CO_3 1.01 g.

Time (mins)	[Mo] g/l	Mo extr. %	[Ca] ppm
5	0.487	81.5	2.15
10	0.538	89.2	1.90
30	0.537	89.0	1.90
60	0.538	89.2	1.90
100	0.540	89.9	1.90
135	0.542	90.0	1.90

Table XLVIII: NaOCl leaching of molybdenite and calcite with no carbonate (Figure 40)

Temp 34.9°C, Agitation 805 rpm, pH 9.0, [NaOCl] 9.5 g/l, MoS_2 1 g, $CaCO_3$ 10 g.

Time (mins)	[Mo] g/l	Mo extrn. %	[Ca] ppm
10	0.495	82.5	9.00
20	0.495	82.5	10.12
30	0.495	82.5	10.13
60	0.500	83.3	10.25
120	0.505	83.4	10.36

Table IL: <u>NaOCl leaching of powdered calcite, CaCO$_3$, at pH 9.0</u>
<u>(Figure 39)</u>

Temp 35°C, Agitation 780 rpm, pH 9.0, [NaOCl] 6.69 g/l
CaCO$_3$ 10 g ≡ 4 g Ca

Time (mins)	[Ca] ppm	Ca extr. %
0	0.25	--
5	13.35	0.33
10	13.40	0.34
20	14.50	0.36
30	15.25	0.38
50	15.50	0.39
70	16.00	0.40

Table L: NaOCl leaching of plaster of paris, $CaSO_4 \cdot \frac{1}{2}H_2O$ at pH 9.0
(Figure 39)

Time (mins)	[Ca] g/l	Ca extrn. %	[NaOCl]
5	1.81	60.2	7.89
10	1.87	62.1	
20	1.89	63.0	7.89
30	1.89	63.0	
50	1.90	64.5	7.94
70	1.90	64.5	

Temp 35°C, Agitation 805 rpm, pH 9.0, [NaOCl] 8.01 g/l,
$CaSO_4 \cdot \frac{1}{2}H_2O$ 10 g

LI: i) $CaSO_4 \cdot \frac{1}{2}H_2O$

Time (mins)	0 g/l NaCl [Ca] g/l	12 g/l NaCl [Ca] g/l	28 g/l NaCl [Ca] g/l	40 g/l NaCl [Ca] g/l	58.5 g/l NaCl [Ca] g/l	86.8 g/l NaCl [Ca] g/l	117 g/l NaCl [Ca] g/l
10	0.435	0.960	1.394		1.860		2.06
20			1.548	1.684	1.864	2.012	2.08
30	0.659	1.314					
40				1.688		2.012	2.10
50			1.528		1.868		
60	0.712	1.326		1.686			2.10
90	0.712	1.326	1.528	1.690	1.860	2.012	

LII: ii) $CaCO_3$

Time (mins)	0 g/l NaCl [Ca] ppm	13 g/l NaCl [Ca] ppm	20 g/l NaCl [Ca] ppm	35 g/l NaCl [Ca] ppm	40 g/l NaCl [Ca] ppm	80 g/l NaCl [Ca] ppm
10	6.5	12.25	16.80	21.50	43.20	35.75
20		14.50	18.30	33.50		55.05
30	15.5	15.25	34.75	48.75	56.80	
45	16.0	15.50		49.00	58.60	
60	16.5	16.00	35.0	49.00	60.30	55.00

Tables LI, LII: Effect of increasing chloride concentration on calcium dissolution from i) calcium sulphate ii) calcium carbonate (Figure 41-44)

pH 9.0,   Temp 35°C,   Agitation 780 - 860 rpm

Table LIII: Effect of carbonate on calcium content in hypochlorite
             solutions (Figure 45)

pH 9.0, Temp 35°C, NaOCl 8.0 g/l

$[CO_3^{2-}]_T$ added g/l	$[CO_3^{2-}]_T$ (moles)	[Ca] ppm	[Ca] (moles)	[Ca] pptd. (moles)
0	--	1.750	0.0438	--
2.838	0.047	0.330	0.0082	0.0356
5.00	0.083	0.110	0.0027	0.0411
10.00	0.167	0.020	3.8×10^{-4}	0.0434
25.00	0.417	0.005	9.3×10^{-5}	0.0437

Table LIV: NaOCl leaching of covellite and molybdenite with 5 g/l
carbonate (Figure 46)

Temp 35°C, Agitation 821 rpm, pH 9.0, [NaOCl]
8.77 g/l, CuS 10 g, MoS_2 1 g, $[CO_3^{2-}]_T$ 5 g/l

Time (mins)	[NaOCl] g/l	[Cu] ppm	[Mo] g/l	Mo extrn. %
10	2.71	14.3	0.510	85.0
30	2.71	14.0	0.510	85.0
45	2.11	10.0	0.516	86.0
65	0.75	6.5	0.510	85.0
85	0.23	4.0	0.546	91.0
120	--	5.0	0.540	90.0

Table LV: <u>NaOCl leaching of molybdenite and covellite in the presence of 10 g/l carbonate (Figure 46)</u>

Temp 35°C, Agitation 803 rpm, pH 9.0, [NaOCl] 7.5 g/l
MoS_2 1.0 g, CuS 10 g, $[CO_3^{2-}]_T$ 10.7 g/l.

Time (mins)	[Cu] ppm	[Mo] g/l	Mo extrn. %	[NaOCl] g/l
5	109	0.485	80.8	2.33
10	89	0.490	81.7	2.20
40	99	0.535	89.1	2.18
60	98	0.542	90.3	2.18
120	98	0.542	90.3	2.02
150	79	0.543	90.5	0.25
180	63	0.542	90.5	--

Table LVI: <u>NaOCl leaching of covellite and sodium molybdate with</u>
<u>5 g/l carbonate (Figure 48)</u>

Temp 35°C, Agitation 785 rpm, pH 9.0, CuS 10 g,
Na_2MoO_4 0.5 g ≡ 0.35 g [Mo], $NaHCO_3$ 0.46 g, Na_2CO_3
6.52 g, [NaOCl] 7.5 g/l.

Time (mins)	[Cu] ppm	[Mo] g/l	Mo in soln %	[NaOCl] g/l
10	39.0	0.341	97.4	6.32
30	37.0	0.323	92.3	5.68
60	27.5	0.315	90.0	1.95
70	19.5	0.305	87.1	1.65
85	8.4	0.295	84.3	0.60

Table LVII: <u>NaOCl leach of molybdenum disulphide and chalcocite with</u>
<u>10 g/l carbonate (Figure 47)</u>

Temp 35°C, Agitation 803 rpm, pH 9.0, MoS_2 1.0 g,
Cu_2S 10 g, $[CO_3^{2-}]_T$ 10.68 g/l.

Time (mins)	[Cu] ppm	[Mo] g/l	Mo extrn. %	[NaOCl] g/l
0	--	--	--	7.06
10	96.0	0.403	67.16	3.61
30	93.0	0.555	92.50	2.71
60	90.0	0.570	95.00	2.48
120	89.0	0.570	95.00	2.36
150	66.0	0.570	95.00	1.55
180	64.0	0.570	95.00	0.60
240	16.0	0.570	95.00	--

Table LVIII: <u>NaOCl oxidation of molybdenum disulphide and chalcopyrite</u>
<u>with 1 g/l SiO$_3$$^{2-}$ added to the system, pH 9.0 (Figure 49)</u>

Temp 35°C,   Agitation 803 rpm,   [NaOCl] 8.4 g/l,

MoS$_2$ 1 g,   CuFeS$_2$ 10 g,   Na$_2$SiO$_3$ 3.29 g, pH 9.0.

Time (mins)	[Cu] ppm	[Mo] g/l	Mo extrn. %	[NaOCl] g/l
10	0.25	0.579	96.5	5.04
20	0.13	0.579	96.5	
30	0.17	0.583	97.2	5.04
60	0.22	0.590	98.4	
90	0.15	0.593	98.9	5.04

APPENDIX B

B.1 Calculation of surface areas for ground mineral samples

The specific surface (surface per unit weight) of a screened material is given by the expression:

$$\Omega = \frac{S_{x_1}^{x_2}}{\Delta V_{x_1}^{x_2}} = \frac{6hk}{\Delta(k-1)} \cdot \frac{x_2^{k-1} - x_1^{k-1}}{x_2^{k} - x_1^{k}}$$

where x_1 = unit crystal size

x_2 = size of -mesh particle

h = shape factor

k = constant

Δ = specific gravity

For copper sulphide minerals ground to pass a -200 mesh screen:

$x_1 = 5 \times 10^{-8}$ cm

$x_2 = 0.0074$ cm

$h = 1.75$ (i.e. assume irregularly shaped particles have 1.75 x the surface area of a cube for same screen size)

$k = 1.02$

$\Delta = 5.6 - 5.8$ (Cu_2S)

$= 4.5 - 4.6$ (CuS)

$$\Omega_{Cu_2S} = \frac{6 \times 1.75 \times 1.02}{5.65 \times 0.02} \cdot \frac{0.0074^{(0.02)} - (5 \times 10^{-8})^{0.02}}{0.0074^{(1.02)} - (5 \times 10^{-8})^{1.02}} \ cm^2 g^{-1}$$

$$= 94.779 \times 28.632 \ cm^2 g^{-1}$$

$$= 2713.71 \ cm^2 g^{-1}$$

$$\Omega_{CuS} = \frac{6 \times 1.75 \times 1.02}{4.60 \times 0.02} \cdot \frac{0.0074^{(0.02)} - (5 \times 10^{-8})^{0.02}}{0.0074^{(1.02)} - (5 \times 10^{-8})^{1.02}} \, cm^2 g^{-1}$$

$$= 116.41 \times 28.632 \, cm^2 g^{-1}$$

$$= 3333.05 \, cm^2 g^{-1}$$

10 g of chalcocite will have a total surface area of 27,137 cm^2 and 10 g of covellite will have a total surface area of 33,330 cm^2.

(Error of calculation can be 30 - 50%)[90]

B.2 Calculation of available copper for precipitation on mineral surface after copper[III] formation

Radius of copper molecule $\simeq 1\mathring{A} = 10^{-8}$ cm

    copper precipitated $\simeq$ 60 ppm = 0.06 g/l

      Avagadro's number = 6×10^{23}

Number of Cu molecules $= \dfrac{0.06}{63.5} \times 6 \times 10^{23}$

$$= 5.660 \times 10^{21}$$

Total area of Cu $= 5.669 \times 10^{21} \times 10^{-8} = 5.669 \times 10^{15} \, cm^2.$

This compares with a surface area of $2.71 \times 10^4 \, cm^2$ for a 10 g sample of chalcocite, and $3.33 \times 10^4 \, cm^2$ for a 10 g sample of covellite. The small amount of copper precipitated as Cu^{III} is thus sufficient to form a mono-molecular layer on the mineral surface.

B.3 Hypochlorite redox equilibria at pH 9.0

1) $HClO + H^+ + e^- = \frac{1}{2}Cl_2(aq) + H_2O$

$$E = 1.59 + 0.0591 \{log (HClO) - \tfrac{1}{2}log (Cl_2) - pH\}$$

2) $\frac{1}{2}Cl_2(aq) + e^- = Cl^-$

$$E = 1.40 + 0.0591 \{\frac{1}{2}\log (Cl_2) - \log (Cl^-)\}$$

(1) + (2):

3) $HClO + H^+ + 2e^- = Cl^- + H_2O$

$$E = 1.49 + \frac{0.0591}{2} \{\log (HClO) - \log (Cl^-) - pH\}$$

4) $HClO = HClO = H^+ + ClO^-$

$$E° = 1.49$$

(2) - (4) + (1):

5) $ClO^- + 2H^+ + 2e^- = Cl^- + H_2O$

$$E = 1.738 + \frac{0.0591}{2} \{\log (ClO^-) - \log (Cl^-) - 2pH\}$$

at pH 9.0

$$E = 1.738 + \frac{(0.0591)}{2} \cdot (-18)$$

$$= 1.738 - 0.532$$

$$E = 1.206 \text{ V}$$

APPENDIX C

Reactions and equilibria pertaining to potential-pH diagrams for various metal molybdate systems shown in Figures 52-58

C.1 $\underline{Cu-H_2O-MoO_4 \text{ system}}$

C.1.1 Substances considered.

Oxidation Number	Species	$\Delta G°$ (kcal)	Source of Data
0	$Cu°$	--	
+1	Cu_2O	-34.98	73
+1	Cu^+	+12.00	73
+2	CuO	-30.40	73
+2	$Cu(OH)_2$	-85.30	73
+2	$CuMoO_4$	-202.70	91
+2	Cu^{2+}	+15.53	73
+2	CuO_2^{2-}	-43.50	73
+2	CuO_2H^-	-61.42	73
+3	Cu_2O_3	-41.50	74
+3	CuO_2^-	-26.87	74
+3	Cu^{3+}	+72.50	74
(+4	MoO_3	-120.00)	73
(+6	$HMoO_4^-$	-161.95)	73
(+6	MoO_4^{2-}	-213.60)	73
+6	$CuMoO_4$	-205.42	35

Activity of copper containing species in solutions has been taken as 10^{-6} M, and that of molybdenum containing species as 10^{-1} M.

C.1.2 Two dissolved substances

1) $Cu^+ \longrightarrow Cu^{2+} + e^-$

$$E = 0.153 + 0.0591 \log \frac{(Cu^{2+})}{(Cu^+)}$$

$$E = 0.153$$

2) $Cu^+ + 2H_2O \longrightarrow HCuO_2^- + 3H^+ + e^-$

$$E = 1.733 - 0.1773 \, pH + 0.0591 \log \frac{(HCuO_2^-)}{(Cu^+)}$$

$$E = 1.733 - 0.1773 \, pH$$

3) $Cu^+ + 2H_2O \longrightarrow CuO_2^{2-} + 4H^+ + e^-$

$$E = 2.510 - 0.2364 \, pH + 0.0591 \log \frac{(CuO_2^{2-})}{(Cu^+)}$$

$$E = 2.510 - 0.2364 \, pH$$

4) $Cu^{2+} + 2H_2O \longrightarrow HCuO_2^- + 3H^+$

$$\log \frac{(HCuO_2^-)}{(Cu^{2+})} = -2.72 + 3pH; \quad pH = 8.91$$

5) $HCuO_2^- \longrightarrow CuO_2^{2-} + H^+$

$$\log \frac{(CuO_2^{2-})}{(HCuO_2^-)} = -39.88 + 4 \, pH; \quad pH = 13.15$$

6) $Cu^{2+} \longrightarrow Cu^{3+} + e^-$

$$E = 2.475 + 0.0591 \log \frac{(Cu^{3+})}{(Cu^{2+})}; \quad E = 2.475$$

7) $CuO_2^{2-} \longrightarrow CuO_2^- + e^-$

$$E = 0.721 + 0.0591 \log \frac{(CuO_2^-)}{(CuO_2^{2-})}; \quad E = 0.721$$

8) $HCuO_2^- \longrightarrow CuO_2^- + e^-$

$$E = 1.498 - 0.0591 \ pH + 0.0591 \log \frac{(CuO_2^-)}{(HCuO_2^-)}$$

$$E = 1.498 - 0.0591 \ pH$$

9) $Cu^{2+} + 2H_2O \longrightarrow CuO_2^- + 4H^+ + e^-$

$$E = 3.078 - 0.2364 \ pH + 0.0591 \log \frac{(CuO_2^-)}{(Cu^{2+})}$$

$$E = 3.078 - 0.2364 \ pH$$

10) $Cu^{3+} + 2H_2O \longrightarrow CuO_2^- + 4H^+$

$$\log \frac{(CuO_2^-)}{(Cu^{3+})} = -10.28 + 4 \ pH; \ pH = 2.57$$

C.1.3 One solid substance and one dissolved substance

11) $Cu_2O + 2H^+ \longrightarrow 2Cu^{2+} + H_2O + 2e^-$

$$E = 0.203 + 0.0591 \ pH + 0.0591 \log (Cu^{2+})$$

$$E = -0.152 + 0.0591 \ pH$$

12) $Cu_2O + 3H_2O + 4H^+ + 2e^- \longrightarrow 2HCuO_2^- + 4H^+ + 2e^-$

$$E = 1.783 - 0.1182 \ pH + 0.0591 \log (HCuO_2^-)$$

$$E = 1.428 - 0.118 \ pH$$

13) $Cu \longrightarrow Cu^{2+} + 2e^-$

$$E = 0.337 + 0.0295 \log (Cu^{2+}); \ E = 0.337$$

14) a) $Cu^{2+} + H_2O \longrightarrow CuO + 2H^+$

$\log (Cu^{2+}) = 7.89 - 2 \, pH; \quad pH = 6.93$

b) $Cu^{2+} + 2H_2O \longrightarrow Cu(OH)_2 + 2H^+$

$\log (Cu^{2+}) = 9.071 - 2 \, pH; \quad pH = 7.54$

15) a) $CuO + H_2O \longrightarrow HCuO_2^- + H^+$

$\log (HCuO_2^-) = -18.83 + pH; \quad pH = 12.83$

b) $Cu(OH)_2 \longrightarrow CuO_2^- + 2H^+$

$\log (CuO_2^-) = -30.80 + 2 \, pH; \quad pH = 12.4$

16) $CuO + H_2O \longrightarrow CuO_2^{2-} + 2H^+$

$\log (CuO_2^{2-}) = -31.98 + pH; \quad pH = 12.99$

17) $Cu^{2+} + 3H_2O \longrightarrow Cu_2O_3 + 6H^+ + 2e^-$

$E = 1.783 - 0.1182 \, pH + 0.0591 \log (HCuO_2^-)$

$E = 1.428 - 0.118 \, pH$

18) a) $CuO + H_2O \longrightarrow CuO_2^- + 2H^+ + 2e^-$

$E = 2.609 - 0.1182 \, pH + 0.0591 \log (CuO_2^-)$

$E = 2.254 - 0.118 \, pH$

b) $Cu(OH)_2 \longrightarrow CuO_2^- + 2H^+ + 2e^-$

$E = 1.267 - 0.118 \, pH - \dfrac{0.0591}{2} \log (CuO_2^-)$

$E = 1.149 - 0.118 \, pH$

19) $Cu^{3+} + 3H_2O \longrightarrow Cu_2O_3 + 6H^+$

$$\log (Cu^{3+}) = -6.09 + 3 \text{ pH}; \text{ pH} = -0.3$$

20) $Cu_2O_3 + H_2O \longrightarrow 2CuO_2^- + 2H^+$

$$\log (CuO_2^-) = -16.31 + \text{pH}; \text{ pH} = 10.31$$

21) $CuO_2^{2-} + MoO_4^{2-} + 4H^+ \longrightarrow CuMoO_4 + 2H_2O$

$$4 \text{ pH} = 67.18 - 0.0591 \log ((CuO_2^{2-}) \cdot (MoO_4^{2-})); \text{ pH} = 10.815$$

22) $CuO_2H^- + MoO_4^{2-} + 3H^+ \longrightarrow CuMoO_4 + 2H_2O$

$$3 \text{ pH} = 49.06 - 0.0591 \log ((CuO_2H^-) \cdot (MoO_4^{2-})); \text{ pH} = 9.99$$

23) $CuMoO_4 \longrightarrow Cu^{3+} + MoO_4^{2-} + e^-$

$$E = 3.026 + 0.0591 \log ((Cu^{3+}) \cdot (MoO_4^{2-}))$$

$$E = 2.671$$

24) $CuMoO_4 + 2H_2O \longrightarrow CuO_2^- + MoO_4^{2-} + 4H^+ + e^-$

$$E = 3.626 - 0.236 \text{ pH} + 0.0591 \log ((CuO_2^-) \cdot (MoO_4^{2-}))$$

$$E = 3.271 - 0.236 \text{ pH}$$

C.1.4 Two solid substances

25) $2Cu + H_2O \longrightarrow Cu_2O + 2H^+ + 2e^-$

$$E = 0.471 - 0.0591 \text{ pH}$$

26) a) $Cu + H_2O \longrightarrow CuO + 2H^+ + 2e^-$

$$E = 0.570 - 0.0591 \text{ pH}$$

b) $Cu + 2H_2O \longrightarrow Cu(OH)_2 + 2H^+ + 2e^-$

$E = 0.609 - 0.0591 \, pH$

27) a) $Cu_2O + H_2O \longrightarrow 2CuO + 2H^+ + 2e^-$

$E = 0.669 - 0.0591 \, pH$

b) $Cu_2O + 3H_2O \longrightarrow 2Cu(OH)_2 + 2H^+ + 2e^-$

$E = 0.741 - 0.0591 \, pH$

28) $Cu_2O + 2MoO_4^{2-} + 2H^+ \longrightarrow 2CuMoO_4 + H_2O + 2e^-$

$E = 0.35 + 0.0591 \, pH - 0.029 \, \log (MoO_4^{2-})$

$E = 0.379 + 0.0591 \, pH$

29) a) $CuO + MoO_4^{2-} + 2H^+ \longrightarrow CuMoO_4 + H_2O$

$2 \, pH = 17.23 - 0.0591 \, \log (MoO_4^{2-})$

$pH = 8.62$

b) $Cu(OH)_2 + MoO_4^{2-} + 2H^+ \longrightarrow CuMoO_4 + 2H_2O$

$2 \, pH = 18.46 - 0.0591 \, \log (MoO_4^{2-})$

$pH = 9.25$

30) a) $CuO + H_2O \longrightarrow Cu_2O_3 + 2H^+ + 2e^-$

$E = 1.648 - 0.0591 \, pH$

b) $2Cu(OH)_2 \longrightarrow Cu_2O_3 + H_2O + 2H^+ + 2e^-$

$E = 1.572 - 0.0591 \, pH$

31) $2CuMoO_4 + 3H_2O \longrightarrow Cu_2O_3 + 2MoO_4^{2-} + 6H^+ + 2e^-$

$$E = 2.658 - 0.0197 \text{ pH} - 0.0197 \log (MoO_4^{2-})$$

$$E = 2.677 - 0.0197 \text{ pH}$$

32) $Cu + MoO_4^{2-} \longrightarrow CuMoO_4 + 2e^-$

$$E = 0.0589 - 0.0591 \log (MoO_4^{2-})$$

$$E = 0.118$$

C.2   Ca-H₂O-MoO₄ system

C.2.1   Substances considered

Oxidation Number	Species	ΔG° (kcal)	Source of Data
-2	CaH_2	-35.80	73
0	Ca	--	
+2	CaO	-144.40	73
+2	$Ca(OH)_2$	-157.64	73
+2	$CaMoO_4$	-345.80	91
+2	Ca^{2+}	-132.18	73
+4	CaO_2	-143.00	73
(+4	MoO_2	-120.00)	73
(+6	MoO_3	-161.95)	73
(+6	$HMoO_4^-$	-213.60)	73
+6	MoO_4^{2-}	-205.42	35

Activity of calcium containing species in solution has been taken as 10^{-6} M and the activity of molybdenum containing species as 10^{-1} M.

C.2.2 <u>One solid substance and one</u>
        <u>dissolved substance</u>

1) a) $Ca^{2+} + H_2O \longrightarrow CaO + 2H^+$

   $\log (Ca^{2+}) = 32.63 - 2pH;\ pH = 19.315$

   b) $Ca^{2+} + H_2O \longrightarrow Ca(OH)_2 + 2H^+$

   $\log (Ca^{2+}) = 22.91 - 2\ pH;\ pH = 14.45$

2) $CaH_2 \longrightarrow Ca^{2+} + 2H^+ + 4e^-$

   $E = -1.045 - 0.0295\ pH - 0.0148\ \log (Ca^{2+})$

   $E = -1.134 - 0.0295\ pH$

3) $Ca \longrightarrow Ca^{2+} + 2e^-$

   $E = -2.866 - 0.0295\ \log (Ca^{2+});\ E = -3.043$

C.2.3 <u>Two solid substances</u>

4) $CaH_2 \longrightarrow Ca + 2H^+ + 2e^-$

   $E = 0.776 - 0.0591\ pH$

5) a) $CaH_2 + H_2O \longrightarrow CaO + 4H^+ + 4e^-$

   $E = -0.563 - 0.0591\ pH$

   b) $CaH_2 + 2H_2O \longrightarrow Ca(OH)_2 + 4H^+ + 4e^-$

   $E = -0.706 - 0.0591\ pH$

6) a) $Ca + H_2O \longrightarrow CaO + 2H^+ + 2e^-$

   $E = -1.902 - 0.0591\ pH$

b) $Ca + 2H_2O \longrightarrow Ca(OH)_2 + 2H^+ + 2e^-$

$$E = -2.189 - 0.0591 \, pH$$

7) $Ca + MoO_4^{2-} \longrightarrow CaMoO_4 + 2e^-$

$$E = -3.044 - \frac{0.0591}{2} \log (MoO_4^{2-}); \quad E = -3.0.14$$

8) a) $CaO + MoO_4^{2-} + 2H^+ \longrightarrow CaMoO_4 + H_2O$

$$2 \, pH = 38.36 + \log (MoO_4^{2-})$$

$$pH = 19.15$$

b) $Ca(OH)_2 + MoO_4^{2-} + 2H^+ \longrightarrow CaMoO_4 + 2H_2O$

$$2 \, pH = 28.99 + \log (MoO_4^{2-})$$

$$pH = 14.00$$

9) $CaH_2 + MoO_4^{2-} \longrightarrow CaMoO_4 + 2H^+ + 4e^-$

$$E = -1.134 - 0.0295 \, pH - 0.0148 \log (MoO_4^{2-})$$

$$E = -1.192 - 0.0295 \, pH$$

10) $CaMoO_4 + 2H_2O \longrightarrow CaO_2 + MoO_4^{2-} + 4H^+$

$$4 \, pH = 81.09 - \log (MoO_4^{2-})$$

$$pH = 20.52$$

11) a) $CaO + H_2O \longrightarrow CaO_2 + 2H^+ + 2e^-$

$$E = 1.260 - 0.0591 \, pH$$

b) $Ca(OH)_2 + H_2O \longrightarrow CaO_2 + 2H^+ + 2e^-$

$$E = 1.547 - 0.0591 \, pH$$

C.3 Pb-H$_2$O-MoO$_4$ system

C.3.1 Substances considered

Oxidation Number	Species	$\Delta G°$ (kcal)	Source of Data
0	Pb	--	73
+2	PbO	-45.25	91
+2	PbMoO$_4$	-205.42	73
+2	Pb^{2+}	-5.81	73
+2	HPbO$_2^-$	-81.00	73
+2.67	Pb$_3$O$_4$	-147.6	73
+3	Pb$_2$O$_3$	-98.42	73
+4	PbO$_2$	-52.34	73
+4	Pb^{4+}	+72.30	73
+4	PbO$_3^{2-}$	-66.34	73
+4	PbO$_4^{2-}$	-67.42	73
(+4	MoO$_2$	-120.00)	73
(+6	MoO$_3$	-161.95)	73
(+6	HMoO$_4^-$	-213.60)	73
+6	MoO$_4^{2-}$	-205.42	35

Activity of lead containing species in solution taken as 10^{-4} M, and of molybdenum containing species as 10^{-1} M.
Stable bi-valent oxide considered to be anhydrous plumbous oxide, PbO.

C.3.2 <u>Two dissolved substances</u>

1) $Pb^{2+} + 2H_2O \longrightarrow HPbO_2^- + 3H^+$

$$\log \frac{(HPbO_2^-)}{(Pb^{2+})} = -28.02 + 3\ pH; \quad pH = 9.34$$

2) $Pb^{4+} + 3H_2O \longrightarrow PbO_3^{2-} + 6H^+$

$$\log \frac{(PbO_3^{2-})}{(Pb^{4+})} = -23.06 + 6\ pH; \quad pH = 3.84$$

3) $PbO_3^{2-} + H_2O \longrightarrow PbO_4^{4-} + 2H^+$

$$\log \frac{(PbO_4^{4-})}{(PbO_3^{2-})} = -40.87 + 2\ pH; \quad pH = 20.44$$

4) $Pb^{2+} \longrightarrow Pb^{4+} + 2e^-$

$$E = 1.694 + 0.0295 \log \frac{(Pb^{4+})}{(Pb^{2+})}$$

$$E° = 1.694$$

5) $Pb^{2+} + 3H_2O \longrightarrow PbO_3^{2-} + 6H^+ + 2e^-$

$$E = 2.375 - 0.177\ pH = 0.0295 \log \frac{(PbO_3^{2-})}{(Pb^{2+})}$$

6) $HPbO_2^- + H_2O \longrightarrow PbO_3^{2-} + 3H^+ + 2e^-$

$$E = 1.547 - 0.0886\ pH + 0.0295 \log \frac{(PbO_3^{2-})}{(HPbO_2^-)}$$

$$E = 1.547 - 0.0886\ pH$$

C.3.3 Two solid substances

7) $Pb + H_2O \longrightarrow PbO + 2H^+ + 2e^-$

$$E = 0.248 - 0.0591 \; pH$$

8) $3PbO + H_2O \longrightarrow Pb_3O_4 + 2H^+ + 2e^-$

$$E = 0.972 - 0.0591 \; pH$$

9) $2Pb_3O_4 + H_2O \longrightarrow 3Pb_2O_3 + 2H^+ + 2e^-$

$$E = 1.228 - 0.0591 \; pH$$

10) $Pb_3O_4 + 2H_2O \longrightarrow 3PbO_2 + 2H^+ + 2e^-$

$$E = 1.127 - 0.0591 \; pH$$

11) $Pb_2O_3 + H_2O \longrightarrow 2PbO_2 + 2H^+ + 2e^-$

$$E = 1.093 - 0.0591 \; pH$$

12) $Pb + MoO_4^{2-} \longrightarrow PbMoO_4 + 2e^-$

$$E = -0.672 + \log (MoO_4^{2-})$$

$$E = -0.613$$

13) $PbMoO_4 + 2H_2O \longrightarrow PbO_2 + MoO_4^{2-} + 4H^+ + 2e^-$

$$E = 1.99 - 0.1182 \; pH + 0.0591 \log (MoO_4^{2-})$$

$$E = 1.931 - 0.1182 \; pH$$

14) $3PbMoO_4 + 4H_2O \longrightarrow Pb_3O_4 + 3MoO_4^{2-} + 8H^+ + 2e^-$

$$E = 3.724 - 0.236 \; pH + 3(0.0591) \log (MoO_4^{2-})$$

$$E = 3.547 - 0.236 \; pH$$

C.3.4 One solid substance and one dissolved substance

15) $Pb^{2+} + H_2O \longrightarrow PbO + 2H^+$

$$\log (Pb^{2+}) = 12.65 - 2\ pH; \quad pH = 8.325$$

16) $PbO + H_2O \longrightarrow HPbO_2^- + H^+$

$$\log (HPbO_2^-) = -15.36 + pH; \quad pH = 11.36$$

17) $Pb^{4+} + 2H_2O \longrightarrow PbO_2 + 4H^+$

$$\log (Pb^{4+}) = -8.26 - 4\ pH; \quad pH = -1.065$$

18) $PbO_2 + H_2O \longrightarrow PbO_3^{2-} + 2H^+$

$$\log (PbO_3^{2-}) = -31.22 + 2\ pH; \quad pH = 13.66$$

19) $Pb \longrightarrow Pb^{2+} + 2e^-$

$$E = -0.126 + 0.0295 \log (Pb^{2+})$$

$$E = -0.244$$

20) $Pb + 2H_2O \longrightarrow HPbO_2^- + 3H^+ + 2e^-$

$$E = 0.702 - 0.0886\ pH + 0.0295 \log (HPbO_2^-)$$

$$E = 0.584 - 0.0886\ pH$$

21) $3Pb^{2+} + 4H_2O \longrightarrow Pb_3O_4 + 8H^+ + 2e^-$

$$E = 2.094 - 0.2364\ pH - 0.0886 \log (Pb^{2+})$$

$$E = 2.448 - 0.2364\ pH$$

22) $3HPbO_2^- + H^+ \longrightarrow Pb_3O_4 + 2H_2O + 2e^-$

$$E = -0.390 + 0.295\ pH - 0.0886 \log (HPbO_2^-)$$

$$E = -0.0356 + 0.0295 \text{ pH}$$

23) $Pb^{2+} + 2H_2O \longrightarrow PbO_2 + 4H^+ + 2e^-$

$$E = 1.449 - 0.1182 \text{ pH} - 0.0295 \log (Pb^{2+})$$

$$E = 1.567 - 0.1182 \text{ pH}$$

24) $HPbO_2^- + MoO_4^{2-} + 3H^+ \longrightarrow PbMoO_4 + 2H_2O$

$$\log (HPbO_2^-) = -46.33 + 3\text{pH}; \quad \text{pH} = 14.11$$

25) $PbMoO_4 \longrightarrow Pb^{4+} + 4e^-$

$$E = 3.347 - 0.0147 \log (Pb^{4+})$$

$$E = 3.288$$

26) $PbMoO_4 + 3H_2O \longrightarrow PbO_3^{2-} + MoO_4^{2-} + 6H^+ + 2e^-$

$$E = 2.915 - 0.177 \text{ pH} + 0.0295 \log (PbO_3^{2-})$$

$$E = 2.797 - 0.177 \text{ pH}$$

C.4 Zn-H$_2$O-MoO$_4$ system

C.4.1 Substances considered

Oxidation Number	Species	$\Delta G°$ (kcal)	Source of Data
0	Zn	--	73
+2	Zn(OH)$_2$	-76.94	91
+2	ZnMoO$_4$	-294.40	73
+2	Zn^{2+}	-35.18	73
+2	HZnO$_2^-$	-110.90	73
+2	ZnO$_2^{2-}$	-93.03	73
+2	ZnOH$^+$	-78.70	73
(+4	MoO$_2$	-120.00)	73
(+6	MoO$_3$	-161.95)	73
(+6	HMoO$_4^-$	-213.60)	73
+6	MoO$_4^{2-}$	-205.42	35

Activity of zinc containing species taken to be 10^{-6} M, and of molybdenum containing species as 10^{-1} M.

Stable oxide considered to be zinc hydroxide Zn(OH)$_2$ (orthorhombic).

C.4.2 Two dissolved substances

1) $Zn^{2+} + H_2O \longrightarrow ZnOH^+ + H^+$

$$\log \frac{(ZnOH^+)}{(Zn^{2+})} = -9.67 + pH; \quad pH = 9.67$$

2) $ZnOH^+ + H_2O \longrightarrow HZnO_2^- + 2H^+$

$$\log \frac{(HZnO_2^-)}{(ZnOH^+)} = -17.97 + 2\,pH; \quad pH = 8.98$$

3) $Zn^{2+} + 2H_2O \longrightarrow HZnO_2^- + 3H^+$

$$\log \frac{(HZnO_2^-)}{(Zn^{2+})} = -27.63 + 3\,pH; \quad pH = 9.21$$

4) $HZnO_2^- \longrightarrow ZnO_2^{2-} + H^+$

$$\log \frac{(ZnO_2^{2-})}{(HZnO_2^-)} = -13.11 + pH; \quad pH = 13.11$$

C.4.3 Two solid species

5) $Zn + 2H_2O \longrightarrow Zn(OH)_2 + 2H^+ + 2e^-$

$$E = -0.439 - 0.0591\,pH$$

6) $Zn(OH)_2 + MoO_4^{2-} + 2H^+ \longrightarrow ZnMoO_4 + 2H_2O$

$$2\,pH = 91.84 + \log (MoO_4^{2-})$$

$$pH = 45.42$$

7) $Zn + MoO_4^{2-} + 2e^- \longrightarrow ZnMoO_4$

$$E = -1.929 - 0.0295 \log (MoO_4^{2-})$$

$$E = -1.899$$

C.4.4 One solid substance and one dissolved substance

8) $Zn(OH)_2 + H_2O \longrightarrow HZnO_2^- + H^+$

$$\log (HZnO_2^-) = -16.68 + pH; \quad pH = 10.68$$

9) $HZnO_2^- + MoO_4^{2-} + 3H^+ \longrightarrow ZnMoO_4 + 2H_2O$

$$3\ pH = 66.94 - \log((HZnO_2^-) \cdot (MoO_4^{2-}))$$

$$pH = 20.31$$

10) $ZnO_2^{2-} + MoO_4^{2-} + 4H^+ \longrightarrow ZnMoO_4 + 2H_2O$

$$4\ pH = 80.04 - \log((ZnO_2^-) \cdot (MoO_4^{2-}))$$

$$pH = 18.51$$

11) $Zn \longrightarrow Zn^{2+} + 2e^-$

$$E = -0.763 + 0.0295 \log(Zn^{2+}); \quad E = -0.94$$

12) $Zn + H_2O \longrightarrow ZnO_2^{2-} + 4H^+ + 2e^-$

$$E = 0.441 - 0.1182\ pH + 0.0295 \log(ZnO_2^{2-})$$

$$E = 0.264 - 0.1182\ pH$$

13) $Zn^{2+} + 2H_2O \longrightarrow Zn(OH)_2 + 2H^+$

$$\log(Zn^{2+}) = 10.96 - 2\ pH; \quad pH = 8.48$$

14) $Zn + 2H_2O \longrightarrow HZnO_2^- + 3H^+ + 2e^-$

$$E = 0.054 - 0.0886\ pH + 0.0295 \log(HZnO_2^-)$$

$$E = -0.123 - 0.0886\ pH$$

C.5 Fe-H$_2$O-MoO$_4$ system

C.5.1 Substances considered

Oxidation Number	Species	$\Delta G°$ (kcal)	Source of Data
0	Fe	---	
+2	Fe(OH)$_2$	-58.88	73
+2	Fe^{2+}	-20.30	73
+2	HFeO$_2^-$	-90.63	73
+2	FeMoO$_4$	-235.30	91
+3	Fe(OH)$_3$	-161.93	73
+3	Fe^{3+}	-2.53	73
+3	Fe(OH)$_2^+$	-106.20	73
+3	FeOH^{2+}	-55.91	73
(+4	MoO$_2$	-120.00)	.73
(+6	MoO$_3$	-161.95)	73
(+6	HMoO$_4$	-213.60)	73
+6	MoO$_4^{2-}$	-205.42	35
+6	FeO$_4^{2-}$	-111.69	73

Activity of iron containing species in solution taken as 10^{-6} M, and of molybdenum species as 10^{-1} M. Ferrous and ferric hydroxides, Fe(OH)$_2$ and Fe(OH)$_3$ have been used as the stable oxides.

C.5.2 Two dissolved species

1) Fe^{2+} + 2H$_2$O $\longrightarrow$ HFeO$_2^-$ + 3H$^+$

$$\log \frac{(HFeO_2^-)}{(Fe^{2+})} = -31.58 + 3\,pH; \quad pH = 10.53$$

2) $Fe^{3+} + H_2O \longrightarrow FeOH^{2+} + H^+$

$$\log \frac{(FeOH^{2+})}{(Fe^{3+})} = -2.43 + pH; \quad pH = 2.43$$

3) $FeOH^{2+} + H_2O \longrightarrow Fe(OH)_2^+ + H^+$

$$\log \frac{(Fe(OH)_2^+)}{(Fe(OH)^{2+})} = -4.69 + pH; \quad pH = 4.69$$

4) $Fe^{2+} \longrightarrow Fe^{3+} + e^-$

$$E = 0.771 + 0.0591 \log \frac{(Fe^{3+})}{(Fe^{2+})}$$

$$E = 0.771$$

5) $Fe^{2+} + H_2O \longrightarrow Fe(OH)^{2+} + H^+ + e^-$

$$E = 0.914 - 0.0591 \, pH + 0.0591 \log \frac{(Fe(OH)^{2+})}{(Fe^{2+})}$$

$$E = 0.914 - 0.059 \, pH$$

6) $Fe^{2+} + 2H_2O \longrightarrow Fe(OH)_2^+ + 2H^+ + e^-$

$$E = 1.91 - 0.1182 \, pH + 0.0591 \log \frac{(Fe(OH)_2^+)}{(Fe^{2+})}$$

$$E = 1.91 - 0.1182 \, pH$$

7) $HFeO_2^- + H^+ \longrightarrow Fe(OH)_2^+ + e^-$

$$E = -0.675 + 0.0591 \, pH + 0.0591 \log \frac{(Fe(OH)_2^+)}{(FeO_2H^-)}$$

$$E = -0.675 + 0.0591 \, pH$$

8) $HFeO_2^- + 2H_2O \longrightarrow FeO_4^{2-} + 5H^+ + e^-$

$$E = 1.001 - 0.0738 \, pH + 0.0148 \log \frac{(FeO_4^{2-})}{(HFeO_2^-)}$$

$$E = 1.001 - 0.0738 \, pH$$

9) $Fe^{3+} + 4H_2O \longrightarrow FeO_4^{2-} + 8H^+ + 3e^-$

$$E = 1.700 - 0.1580 \, pH + 0.0197 \, \log \frac{(FeO_4^{2-})}{(Fe^{3+})}$$

$$E = 1.700 - 0.1580 \, pH$$

10) $Fe(OH)^{2+} + 3H_2O \longrightarrow FeO_4^{2-} + 7H^+ + 3e^-$

$$E = 1.652 - 0.1379 \, pH + 0.0197 \, \log \frac{(FeO_4^{2-})}{(Fe(OH)^{2+})}$$

$$E = 1.652 - 0.1379 \, pH$$

11) $Fe(OH)_2^+ + 2H_2O \longrightarrow FeO_4^{2-} + 6H^+ + 3e^-$

$$E = 1.559 - 0.1182 \, pH + 0.0197 \, \log \frac{(FeO_4^{2-})}{(Fe(OH)_2^+)}$$

$$E = 1.559 - 0.1182 \, pH$$

C.5.3 Two solid substances

12) $Fe + 2H_2O \longrightarrow Fe(OH)_2 + 2H^+ + 2e^-$

$$E = -0.047 - 0.0591 \, pH$$

13) $Fe + 3H_2O \longrightarrow Fe(OH)_3 + 2H^+ + 2e^-$

$$E = 0.059 - 0.0591 \, pH$$

14) $Fe(OH)_2 + H_2O \longrightarrow Fe(OH)_3 + 2H^+ + 2e^-$

$$E = 0.271 - 0.0591 \, pH$$

15) $Fe + MoO_4^{2-} + 2e^- \longrightarrow FeMoO_4$

$$E = -0.648 - 0.0295 \, \log (MoO_4^{2-})$$

$$E = -0.6185$$

16) $Fe(OH)_2 + MoO_4^{2-} + 2H^+ \longrightarrow FeMoO_4 + 2H_2O$

$$2 \ pH = 61.804 + \log (MoO_4^{2-})$$

$$pH = 30.402$$

17) $\quad FeMoO_4 + 3H_2O \longrightarrow Fe(OH)_3 + 3H^+ + MoO_4^{2-} + e^-$

$$E = 1.637 - 0.1773 \ pH + 0.0591 \log (MoO_4^{2-})$$

$$E = 1.578 - 0.1773 \ pH$$

C.5.4 One solid substance and one dissolved substance

18) $\quad Fe^{2+} + 2H_2O \longrightarrow Fe(OH)_2 + 2H^+$

$$\log (Fe^{2+}) = 13.29 - 2pH$$

$$pH = 9.645$$

19) $\quad Fe(OH)_2 \longrightarrow HFeO_2^- + H^+$

$$\log (HFeO_2^-) = -18.30 + pH$$

$$pH = 12.30$$

20) $\quad Fe^{3+} + 3H_2O \longrightarrow Fe(OH)_3 + 3H^+$

$$\log (Fe^{3+}) = 4.84 - 3 \ pH$$

$$pH = 3.613$$

21) $\quad Fe(OH)^{2+} + 2H_2O \longrightarrow Fe(OH)_3 + 2H^+$

$$\log (Fe(OH)^{2+}) = 2.41 - 2 \ pH$$

$$pH = 4.205$$

22) $\quad Fe(OH)_2^+ + H_2O \longrightarrow Fe(OH)_3 + H^+$

$$\log (Fe(OH)_2^+) = -2.28 - pH$$

$$pH = 4.28$$

23) $Fe \longrightarrow Fe^{2+} + 2e^-$

$$E = -0.440 + 0.0295 \log (Fe^{2+})$$

$$E = -0.617$$

24) $Fe + 2H_2O \longrightarrow HFeO_2^- + 3H^+ + 2e^-$

$$E = 0.493 - 0.0886\,pH + 0.0295 \log (Fe^{2+})$$

$$E = 0.316 - 0.0886\ pH$$

25) $Fe \longrightarrow Fe^{3+} + 3e^-$

$$E = -0.037 + 0.0197 \log (Fe^{3+}); \quad E = -0.1552$$

26) $Fe^{2+} + 3H_2O \longrightarrow Fe(OH)_3 + 3H^+ + e^-$

$$E = 1.057 - 0.1773\ pH - 0.0591 \log (Fe^{2+})$$

$$E = 1.4116 - 0.1773\ pH$$

27) $HFeO_2^- + H_2O \longrightarrow 2Fe(OH)_3 + e^-$

$$E = -0.810 - 0.0591 \log (HFeO_2^-); \quad E = -0.4356$$

28) $FeMoO_4 + 2H_2O \longrightarrow HFeO_2^- + MoO_4^{2-} + 3H^+$

$$3\ pH = 38.46 + \log ((HFeO_2^-) \cdot (MoO_4^{2-}))$$

$$pH = 10.82$$

29) $FeMoO_4 \longrightarrow Fe^{3+} + MoO_4^{2-} + e^-$

$$E = 1.186 + 0.0591 \log (MoO_4^{2-}); \quad E = 1.127$$

30) $FeMoO_4 + H_2O \longrightarrow Fe(OH)^{2+} + MoO_4^{2-} + H^+ + e^-$

$$E = 1.326 - 0.0591 \text{ pH} + 0.0591 \log ((FeOH^{2+}) \cdot (MoO_4^{2-}))$$

$$E = 0.971 - 0.0591 \text{ pH}$$

31) $FeMoO_4 + 2H_2O \longrightarrow Fe(OH)_2^+ + 2H^+ + e^- + MoO_4^{2-}$

$$E = 1.599 - 0.1182 \text{ pH} + 0.0591 \log ((FeOH^+) \cdot (MoO_4^{2-}))$$

$$E = 1.244 - 0.1182 \text{ pH}$$

C.6 Cd-H$_2$O-MoO$_4$ system

C.6.1 Substances considered

Oxidation Number	Species	ΔG° (kcal)	Source of Data
0	Cd	--	73
2	$Cd(OH)_2$	-56.44	73
2	$CdMoO_4$	-283.30	91
2	Cd^{2+}	-18.58	73
2	$HCdO_2^-$	-86.50	73
6	MoO_4^{2-}	-205.42	35

Activity of cadmium containing species in solution taken as 10^{-6} M, and that of molybdenum species as 10^{-1} M. 'Inactive' cadmium hydroxide, $Cd(OH)_2$, has been used as the oxide species.

C.6.2 Two dissolved species

1) $Cd^{2+} + 2H_2O \longrightarrow HCdO_2^- + 3H^+$

$$\log \frac{(HCdO_2^-)}{(Cd^{2+})} = -33.34 - 3\ pH; \quad pH = 11.11$$

C.6.3 Two solid species

2) $Cd + H_2O \longrightarrow Cd(OH)_2 + 2H^+ + 2e^-$

$$E = 0.05 - 0.0591\ pH$$

3) $Cd(OH)_2 + MoO_4^{2-} + 2H^+ \longrightarrow CdMoO_4 + 2H_2O$

$$2\ pH = 65.73 + \log (MoO_4^{2-})$$

$$pH = 32.365$$

4) $Cd + MoO_4^{2-} + 2e^- \longrightarrow CdMoO_4$

$$E = -0.713 - 0.0295 \log (MoO_4^{2-}); \quad E = -0.684$$

C.6.4 One solid substance and one dissolved substance

5) $Cd^{2+} + 2H_2O \longrightarrow Cd(OH)_2 + 2H^+$

$$\log (Cd^{2+}) = 13.81 - 2\ pH; \quad pH = 9.905$$

6) $Cd(OH)_2 \longrightarrow HCdO_2^- + H^+$

$$\log (HCdO_2^-) = -19.54 + pH; \quad pH = 13.54$$

7) $Cd \longrightarrow Cd^{2+} + 2e^-$

$$E = -0.403 + 0.0295 \log (Cd^{2+}); \quad E = -0.508$$

8) $Cd + 2H_2O \longrightarrow HCdO_2^- + 3H^+ + 2e^-$

$$E = 0.583 - 0.0886 \, pH + 0.0295 \log (HCdO_2^-)$$

$$E = 0.406 - 0.0886 \, pH$$

9) $CdMoO_4 + 2H_2O \longrightarrow HCdO_2^- + MoO_4^{2-} + 3H^+$
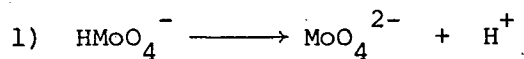
$$\log (HCdO_2^-) - 3 \, pH = -43.69$$

$$pH = 12.564$$

C.8 Molybdenum species (all systems)

C.8.1 Substances considered

Oxidation Number	Species	$\Delta G°$ (kcal)	Source of Data
0	Mo	--	
+3	Mo^{3+}	-13.80	73
+4	MoO_2	-120.00	73
+6	MoO_3	-161.95	73
+6	MoO_4^{2-}	-205.42	73
+6	$HMoO_4^-$	-213.60	73

Activity of dissolved species taken as 10^{-1} M. Hexa-valent oxide considered to be molybdic trioxide, MoO_3.

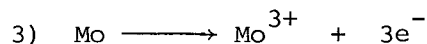### C.8.2 Two dissolved substances

1) $HMoO_4^- \longrightarrow MoO_4^{2-} + H^+$

$$\log \frac{(MoO_4^{2-})}{(HMoO_4^-)} = -6.00 + pH; \quad pH = 6.0$$

C.8.3 One solid substance and one dissolved substance

2) $MoO_3 + H_2O \longrightarrow HMoO_4^- + H^+$

$$\log (HMoO_4^-) = -3.70 + pH; \quad pH = 2.70$$

3) $Mo \longrightarrow Mo^{3+} + 3e^-$

$$E = -0.200 + 0.0197 \log (Mo^{3+}); \quad E = -0.2197$$

4) $Mo + 4H_2O \longrightarrow MoO_4^{2-} + 8H^+ + 6e^-$

$$E = 0.154 - 0.0788 \, pH + 0.0098 \log (MoO_4^{2-})$$

$$E = 0.144 - 0.0788 \, pH$$

5) $Mo^{3+} + 2H_2O \longrightarrow MoO_2 + 4H^+ + e^-$

$$E = 0.311 - 0.2364 \, pH - 0.0591 \log (Mo^{3+})$$

$$E = 0.370 - 0.2364 \, pH$$

6) $Mo^{3+} + 3H_2O \longrightarrow MoO_3 + 6H^+ + 3e^-$

$$E = 0.317 - 0.1182 \, pH - 0.0197 \log (Mo^{3+})$$

$$E = 0.337 - 0.1182 \, pH$$

7) $MoO_2 + 2H_2O \longrightarrow HMoO_4^- + 3H^+ + 2e^-$

$$E = 0.429 - 0.0886 \, pH + 0.0295 \log (HMoO_4^-)$$

$$E = 0.399 - 0.0886 \, pH$$

8) $MoO_2 + 2H_2O \longrightarrow MoO_4^{2-} + 4H^+ + 2e^-$

$$E = 0.606 - 0.1182 \, pH + 0.0295 \log (MoO_4^{2-})$$

$$E = 0.577 - 0.1182 \, pH$$

C.8.4 <u>Two solid substances</u>

9) $Mo + 2H_2O \longrightarrow MoO_2 + 4H^+ + 4e^-$

$$E = -0.072 - 0.0591 \ pH$$

10) $MoO_2 + H_2O \longrightarrow MoO_3 + 2H^+ + 2e^-$

$$E = 0.320 - 0.0591 \ pH$$