SELECTIVE LEACHING OF MOLYBDENUM FROM MIXED COPPER-MOLYBDENUM SULFIDES

by

ARNALDO ANDRES ISMAY

Ing. Metalúrgico, Universidad Tecnológica Nacional, Córdoba, Argentina, 1973

A THESIS SUBMITTED IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE DEGREE OF MASTER IN APPLIED SCIENCE in THE FACULTY OF GRADUATE STUDIES (the Department of METALLURGY)

We accept this thesis as conforming to the required standard

THE UNIVERSITY OF BRITISH COLUMBIA

September 1976

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SEPTEMBER 1976

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Date Oct.4-1976
ABSTRACT

A study has been made of the oxidation of molybdenite in solutions of hypochlorite. The reaction was found to be first order in reagent concentration with a reaction rate constant of $1.90 \times 10^{-2} \text{ min}^{-1} \text{ cm}^{-2}$. at pH 9 and 45°C. The oxidation rate increases with increasing pH and later decreases if the pH is raised above 9.5. An activation energy of $6.3 \pm 0.8$ kcal/mole was observed for this reaction which was controlled by either chemical or mixed diffusion and chemical reactions. Other factors studied were the agitation, surface area, surface characteristics and effect of sulfates, chlorides, chlorites and chlorates.

It was observed that hypochlorite is capable of selectively leaching molybdenite from copper sulfides and positive results were obtained when applying this property to the extraction of molybdenite from copper rougher concentrates.

The formation of oxides during drying and/or leaching of copper sulfides was found to be detrimental to the process because they act as catalysts in the decomposition reaction of hypochlorite.

Rates of normal decomposition of the reagent were studied over the range 35 to 60°C and pH 7 to 10 and found to be negligible as compared to the rates of oxidation of molybdenite.

The leaching of rougher concentrates with hypochlorite was found not to affect considerably the subsequent flotation operation.
Data of on-site hypochlorite generator plants and factors that affect production and decomposition, have been presented with the purpose of proposing a process using the information obtained in this work for the extraction of molybdenite in the Copper Concentration Plants.
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Chapter 1

INTRODUCTION

1.1 General

Molybdenite (MoS$_2$) is often associated with copper sulfide minerals such as chalcopyrite (CuFeS$_2$) and chalcocite (Cu$_2$S) as a minor component of many gigantic, low grade disseminated copper deposits called "copper porphyries."

The most valuable components of these deposits are copper and molybdenum. The extraction of gold and silver is also significant. Rhenium is a byproduct of porphyry processing and although total world production is only of the order of 7400 lbs. [1,2], the molybdenite concentrate obtained from copper porphyries is the sole source of this metal at present.

A typical porphyry ore might contain:

- Cu = 0.8%  
- Au = 0.01-0.02 oz/ton  
- Re = 0.038% of MoS$_2$ concentrate 
- Mo = 0.015%  
- Ag = 0.05-0.1 oz/ton

Due to the large tonnage of porphyry material processed (540 x $10^6$ tons in 1973) the production figures for the molybdenum and rhenium
are very significant as shown in Table 1. Roughly 1-1.5 oz of Au and 3-10 oz of Ag can be recovered per ton of copper extracted.

Table 1
Comparison Between Production from Total Available Sources and Copper Porphyries
(based on 1973 statistics)

<table>
<thead>
<tr>
<th>Metal</th>
<th>Total World Production</th>
<th>Output from Copper Porphyries</th>
<th>% Produced from Copper Porphyries</th>
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<tr>
<td>Cu</td>
<td>8,100,000</td>
<td>3,500,000</td>
<td>43%</td>
</tr>
<tr>
<td>Mo</td>
<td>87,500</td>
<td>37,400</td>
<td>37%</td>
</tr>
<tr>
<td>Re</td>
<td>3.7</td>
<td>3.7</td>
<td>100%</td>
</tr>
</tbody>
</table>

From 1967 to 1972 the production of MoS$_2$ as a byproduct of copper porphyries in the U.S.A. rose over 42% [1]. It has been estimated [3] that these deposits account for some $5.5 \times 10^6$ tons of Mo, which represent 17% of the world's molybdenum reserves.

1.2 Production of Molybdenite Concentrates

Molybdenum consumed in its various end products is in the form of molybdic oxide (66%), ferromolybdenum (20%), ammonium and sodium molybdate (2%), and other materials (12%). To obtain these, a molybdenite concentrate is produced by flotation and then roasted to oxidize the MoS$_2$ to MoO$_3$, which is the starting compound for all subsequent products.
The task of producing specification MoS₂ concentrates (Table 2) from ores with an average of 150 ppm Mo in which copper and iron minerals outweigh MoS₂ by ratios of about 140 to 1 is quite formidable. The process is long and the recoveries are low.

Table 2
International Market Grade of Molybdenite Concentrates

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<tr>
<td>MoS₂</td>
<td>80% (min)</td>
</tr>
<tr>
<td>Cu</td>
<td>0.5% (max)</td>
</tr>
<tr>
<td>Pb</td>
<td>0.3% (max)</td>
</tr>
<tr>
<td>P, Sn, As</td>
<td>0.2% (max total)</td>
</tr>
</tbody>
</table>

A generalized description of the common practice of treating these ores is presented below with the intention of showing why MoS₂ recovery is so low. Although there are variations in the 30 plants for which there is available data it is felt that they do not affect this analysis. Figure 1 is a simplified flow sheet of the method described, indicating the efficiency of the successive stages and the cumulative drop in recovery.

MoS₂ is floated collectively with the Cu sulfides into a rougher copper concentrate which contains the bulk of Cu and Mo. This rougher concentrate has a high proportion of middlings and is therefore subjected to a careful size reduction in order to avoid the formation of slimes because of the ease with which MoS₂ grinds. It is then refloated in cleaner and recleaner circuits to produce a copper concentrate which contains 25-50% Cu and 0.2-1% MoS₂.
FIG. 1 - SIMPLIFIED GENERAL FLOWSHEET OF A COPPER BYPRODUCT MoS₂ CONCENTRATION PROCESS.
At this point MoS₂ is separated from the Cu minerals by selective flotation, either depressing the Cu and Fe minerals and floating MoS₂ or vice versa. The product of this operation is a "moly" rougher concentrate which is then subjected to regrinding and refloating in a closed-counter current cleaning circuit to produce a MoS₂ concentrate. If this product has in excess of 0.5% Cu it must be further processed by leaching to produce a marketable concentrate.

The cutoff point for operating a byproduct MoS₂ flotation circuit is considered economically to be 0.2% MoS₂ in the Cu concentrate. However in many cases plants will only operate if the assay is above 0.7% MoS₂. Any Mo and Re not recovered by flotation are unrecoverable in the subsequent pyrometallurgical treatment.

The factors that affect MoS₂ recovery [4] are:

1. The principal aim of the operation is maximum Cu recovery and this may result in less than optimum conditions for MoS₂ extraction as may be seen in the following examples:

   A. The addition of lime which is necessary to depress pyrite in order to insure good Cu flotation may hinder MoS₂ flotation by flocculating the gangue and trapping the fine MoS₂ particles.

   B. Hydrocarbon oils which raise the MoS₂ recovery are added only to the extent that there is no adverse effect on copper minerals.
2. The mineralization of the ore

Mineralization is of greater significance in MoS$_2$ flotation than in other flotation operations due to the very low grade of ore as shown in the next examples:

A. Due to the characteristics of copper porphyries in which MoS$_2$ has a very uneven distribution, while the Cu grade of the head may remain fairly constant the MoS$_2$ grade may be erratic and vary by several hundred percent in short periods of time.

B. MoS$_2$ can be present as well formed clean crystals, or as less well defined material with very altered surfaces, with or without a thin oxide coating. Also it may or may not be associated with other hydrophobic materials such as graphite, talc or carbonaceous products.

C. Molybdenite can also be coated with a colloidal chalcopyrite slime which prevents its flotation and causes a "drop out" in the cleaner circuit.

D. There is a so-called "crowding out phenomena" which can be explained as a counter effect on the differential flotation of two mineral species produced by an extraordinary difference in the number of particles of each species.
3. Cost of Reagents

The cost of reagents for depressing the other mineral species impedes the extraction of MoS$_2$ from Cu concentrates in which Mo content is very low.

Although considerable research has been directed towards solving many of these problems and increasing the efficiency of MoS$_2$ extraction from copper porphyries, present technology does not achieve much more than 50% recovery. This means that approximately 18,000 tons of Mo representing about 0.3% of the identified reserves of Mo in copper porphyries of the world, are lost annually in various parts of the process.

1.3 Production of Rhenium

To produce rhenium a MoS$_2$ concentrate is roasted at temperatures between 540°C and 650°C and about 90% of the Re it contains is volatilized. The gases are scrubbed using a combination of cyclones, electrostatic precipitators and a high energy Venturi type scrubber to remove Re along with some SO$_2$ and small amounts of Mo, Cu and Fe. By intensive recirculation the pregnant solution is concentrated to 0.2 to 0.5 g/l of Re. It is then conditioned by adding Cl$_2$ to oxidize Mo, Re and Fe values and subsequently Fe and Cu are precipitated as carbonates.

Re is then absorbed in ion-exchange columns or removed by solvent extraction. The elutriation product is treated with H$_2$S to precipitate Re as ReS$_2$ which is then treated with H$_2$O$_2$ and NH$_4$ OH to form a soluble perrhenate which is later crystallized.
Although the process is relatively simple it has several deficiencies which reduce the total Re production capacity. These are:

1. Reduced Re in feed due to low recoveries in the previous MoS₂ concentration process
2. Production of SO₂
3. Losses of Re in the scrubbing operations

The average recovery of rhenium from molybdenite concentrates is 60%. If present technology continues to be used in the future this would mean that from the estimated 4.2 million lbs. of Re reserves contained in copper porphyries only 1.5 million can be considered recoverable [5].

1.4 Alternative Hydrometallurgical Process

A list of principal commodities produced from copper porphyries and their respective prices is presented in Table 3.

Any new process which achieved greater recoveries of both molybdenum and rhenium could be of significant economic advantage specially in those copper porphyries in which the Cu grade is extremely low such as the ones in British Columbia.

If MoS₂ were preferentially leached from copper sulfide materials, the application of a hydrometallurgical process to an early stage of the copper concentration circuit might result in a favourable alternative to the present technology.

This process could have the following advantages:
Table 3
Copper, Molybdenum and Rhenium Products Prices (1975)

<table>
<thead>
<tr>
<th>Copper</th>
<th>Primary Cu</th>
<th></th>
<th>Refined Cu</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.61 $/lb</td>
<td></td>
<td>0.64 $/lb</td>
<td></td>
</tr>
</tbody>
</table>

Rhenium
all rhenium products in the range of 1000-1200 $/lb.

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>2.20-.255</td>
<td>2.60</td>
<td>2.65</td>
<td>2.30</td>
<td>2.90</td>
<td>3.10</td>
</tr>
</tbody>
</table>
1. Higher MoS$_2$ recoveries

2. Production of higher market value products, i.e. Mo salts, Mo metal powder

3. Higher Re recovery

4. Elimination of the roasting step and thus production of Mo and Re without SO$_2$ emission and without capital expenditure on roasting equipment.

Aqueous suspensions of MoS$_2$ must be oxidized to produce molybate ions to effect leaching; and, depending on the pH, these ions will either be HMoO$_4^-$ or MoO$_4^{3-}$ [6-9]. In similar aqueous oxidation, the sulfides of Cu and Fe form cations which under some conditions of pH, by hydrolysis, produce insoluble oxides or hydroxides. Therefore the selectivity of a leaching system might not only depend on the relative oxidation rates of molybdenite and the copper sulfides but on the solubility of the species formed, the nature of any solid products formed and their interaction with the reagent employed.

1.5 Literature Review

Studies on the oxidation of aqueous suspensions of molybdenite have been reported as early as 1952. E.S. Usataya et al. [11] investigated the effect of acids, bases, salts and oxidizing agents on MoS$_2$ concluding that the rate of decomposition increases with increasing pH and that solid protective layers are formed in the acid or weakly alkaline regions. The presence of strong oxidizing agents such as H$_2$O$_2$ in a strong alkaline solution was observed to prevent the formation of such a coating.

D.M. Yukhtanov and K.D. Leont'eva [12] (in 1953) were the first to use NaOCl at normal and high temperatures to oxidize MoS$_2$. 
W.H. Dresner et al. [7] in 1956 studied the kinetics of MoS$_2$ leaching in alkaline solutions in the temperature range of 100-175°C. They reported that MoS$_2$ could leach under moderate pressures of oxygen (100-200 p.s.i.). The overall reaction being:

$$\text{MoS}_2 + \frac{9}{2} \text{O}_2 + 6\text{OH}^- \rightarrow \text{MoO}_4^{2-} + 2\text{SO}_4^{2-} + 3\text{H}_2\text{O} \quad (1)$$

The end products after complete oxidation were MoO$_4^{2-}$ and SO$_4^{2-}$ ions. The presence of S$_2$O$_3^{2-}$ was detected only as an intermediate unstable species.


H. Cox and A.K. Schellinger [8] in 1958 studied the leaching of Mo from low grade ores, copper concentrates and high grade molybdenite concentrates using NaOCl. Although they obtained excellent extractions

- low grade molybdenum ore (0.015% MoS$_2$) Recovery = 93.3%
- copper concentrate (1.05% MoS$_2$) " = 90.6%
- High grade molybdenum concentrate (99.9% MoS$_2$) " = 99.9%

they did not perform a systematic study of the variables that affect the rate of oxidation. The best conditions they recommended for leaching were: 3% NaOCl solution, room temperature and 30 minutes leaching time. The equation suggested by these investigators was:

$$7\text{NaOCl} + \text{MoS}_2 + 4e^- \rightarrow \text{MoO}_4^{2-} + \text{S}_2\text{O}_3^{2-} + 7\text{NaCl} \quad (2)$$
K.V. Ioardanov and A.N. Zelikman [14] made an extensive study of the physico-chemical bases of the oxidation of MoS$_2$ in NaOCl solutions. They used pure MoS$_2$ pressed into compact samples and finely ground material. They assumed MoS$_2$ was oxidized according to the reaction:

$$\text{MoS}_2 + 9 \text{NaOCl} + 6 \text{NaOH} → \text{Na}_2\text{MoO}_4 + 2 \text{Na}_2\text{SO}_4 + 9 \text{NaCl} + 3 \text{H}_2\text{O}$$  \hspace{1cm} (3)

The conclusions reached in their study were:

a) The rate of oxidation increases with an increase in temperature and that the reaction is diffusion controlled.

b) The rate is directly proportional to the initial concentration of NaOCl.

They proposed a mechanism for the oxidation of MoS$_2$. The first stage is the adsorption of OCl$^-$ ions on the surface of the MoS$_2$,

$$\text{OCl}^-(\text{soln}) + \text{OCl}^-(\text{ads})$$  \hspace{1cm} (4)

the second stage is the interaction of the adsorbed OCl$^-$ and the solid to form an active complex

$$\text{MoS}_2(\text{solid}) + \text{OCl}^-(\text{ads}) → [\text{MoS}_2 + ⋯ + \text{OCl}^-]_{\text{active complex}}$$  \hspace{1cm} (5)

Then the formation of reaction products, oxygen replacing sulfur atoms and forming intermediate compounds and chloride ions.
The sulfur atoms are oxidized by OCl\(^-\), according to the reactions:

\[
2 \text{S} + 2 \text{OCl}^- \rightarrow \text{S}_2\text{O}_2\text{^-} + 2 \text{Cl}^- 
\]
\[
\begin{align*}
S_2O_3^{2-} + OC1^- & \rightarrow S_2O_3^{2-} + Cl^- \quad (12) \\
S_2O_3^{2-} + 3 OC1^- & \rightarrow 2 SO_4^{2-} + 3 Cl^- + H_2O \quad (13)
\end{align*}
\]

In an independent study R.B. Bhappu et al. [6] determined that the correct molar ratio between NaOCl and MoS₂, when the NaOCl is in excess, is 9:1. They showed that if sulfur was formed during the leaching process by

\[
6 OC1^- + MoS_2 + 4 OH^- \rightarrow MoO_4^{2-} + S^0 + SO_4^{2-} + 6 Cl^- + 2H_2O \quad (14)
\]

the excess of OC1⁻ present such as would be the case in leaching low grade materials would oxidize it to SO₄²⁻ as follows:

\[
3 OC1^- + S^0 + H_2O \rightarrow SO_4^{2-} + 3 Cl^- + 2H^+ \quad (15)
\]

therefore if OC1⁻ is in excess the only sulfur species present is SO₄²⁻. By combining reactions (14) and (15) they suggested the overall reaction identical to the one used by K.V. Ioardanov and A.N. Zelikman [14], which also agrees with the stoichiometry of the oxidation of MoS₂ in aqueous KOH-O₂ systems [7].

R.B. Bhappu et al. [6] also reported that:

a) There is practically no consumption of NaOCl by gangue materials (quartz and aplite in their experiments).

b) There is a decrease in the leaching rates both in concentrates and larger specimens of
MoS$_2$ which they attributed to dissolution of finer particles in the first case and to concentration phenomena in the second.

c) Due to economic considerations it was necessary to produce the NaOCl in situ either by combining purchased caustic soda and chlorine or by electrolysis of NaCl. For this second system they suggested the recycling of leach solution in order to reuse the NaCl produced in reaction (3).

K.A. Shapiro and B.B. Kulakeva [15] applied NaOCl digestion to lean intermediate products containing 2-6% Mo formed in the concentration of disseminated ore. No indication was given as to the other minerals in those intermediate products. They reported having to consume 400 and 500% the stoichiometric amount of NaOCl for complete extraction of Mo, no explanation was given of the cause of this excess consumption.

R.B. Bhappu et al. [16,17] studied the dissolution of MoS$_2$ using several oxidizing agents; NaOCl, ozone, oxygen-alkali; acid permanganate, persulfate, acid-ferric chloride, nitric acid, chlorine dioxide, acid-chlorate, manganese dioxide - sulfuric acid and bacterial leaching.

They reported that NaOCl in basic solutions presented the fastest rate of leaching and high selectivity towards MoS$_2$. The disadvantages indicated were its high production costs, its instability and its troublesome regeneration. Acid-NaClO$_3$ also leaches MoS$_2$ but not as fast as NaOCl. In comparison NaClO$_3$ is less expensive and easier to regenerate than NaOCl, but is not as selective.

B.J. Scheiner and R.E. Lindstrom [18] investigated the possibility of leaching MoS$_2$ from low grade ores by an electrooxidation technique that consists of generating NaOCl in situ by electrolysis of a brine-ore slurry.
This method had been previously used in treating carbonaceous gold ores [19,20] and for recovering mercury from cinnabar ores [21].

They claimed a 90-99% extraction of molybdenum, good selectivity of Mo over Cu and a power consumption of 16-24 kwh/lb of Mo extracted from a low grade MoS$_2$ ore.

However in a recent publication D.S. Barr et al. [22] indicated that the production of byproduct NaClO$_3$ during the electrooxidation, interferes with the recovery of molybdenum and consequently hinders the economics of the process. To minimize NaClO$_3$ production these authors suggested leaching at a low pH (4.0-5.0) and low temperature (<30°C).

The use of NaOCl as an oxidizing-leaching reagent has also been reported for stibnite [23], sphalerite [24] and chalcopyrite [25].

D. Stump and Y. Berube [26] claimed that the oxidation rates of chalcopyrite and molybdenite in an alkaline medium are similar and that it is unlikely that selective leaching of molybdenum from copper concentrates could be accomplished.
Chapter 2

SCOPE OF PRESENT INVESTIGATION

The research reported in this thesis is primarily aimed at studying the possibilities of extracting molybdenum from low grade-copper sulfide containing materials by a direct leaching operation using sodium hypochlorite as reagent.

The previous work on this subject suggested that a physico-chemical study was required in order to determine the factors that govern the oxidation and dissolution of $\text{MoS}_2$ in solutions of NaOCl. The variables selected for study were: agitation rate, temperature, pH, NaOCl concentration, surface area, neutral salts, $\text{ClO}_2^-$ and $\text{ClO}_3^-$ addition.

A comparative study was made for leaching rates and total leaching time between $\text{CuFeS}_2$ and $\text{MoS}_2$ under identical experimental conditions to determine if selective leaching using NaOCl was possible. This being satisfactory it was intended to design a simple flow sheet which would describe the practical application of this technique and at the same time provide a preliminary economic basis on which to judge the feasibility of the process.

As already outlined, previous workers had established the requirement of producing NaOCl in-situ to render the process economically
competent, therefore the selection of a direct NaOCl leach for our study, instead of a simultaneous electrooxidation procedure, meant that available data on NaOCl generating systems would have to be collected.

Another specific objective was to establish if solutions of NaOCl were stable under leaching conditions and if any of the materials used or products of reaction formed could catalyze the decomposition of this reagent.
Chapter 3

EXPERIMENTAL

The experimental work can be divided into four sections:

A. Determination of the kinetics of dissolution of molybdenite and chalcopyrite in NaOCl solutions.

B. Study of the leaching of molybdenite from rougher copper concentrates.

C. Determination of the flotation characteristics of leached rougher concentrates.

D. Establishment of the stability of NaOCl solutions and factors that cause its decomposition.

3.1 Materials

a. Molybdenite

With a few exceptions, molybdenite used in section A consisted of a cleaned molybdenite concentrate (Brenda Mines). The chemical analysis of the MoS$_2$ concentrate is given in Table 4. To prepare this material, the coarsest part of the MoS$_2$ concentrate was separated, washed in acetone to remove the organic reagents left from the flotation operation, dried at 80°C and wet screened to the size -70 + 140 mesh.
Table 4
Chemical Analysis of Molybdenite Concentrate

<table>
<thead>
<tr>
<th>Element</th>
<th>Weight %</th>
<th>Element</th>
<th>Weight %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total Molybdenum</td>
<td>52.57</td>
<td>Lead</td>
<td>0.02</td>
</tr>
<tr>
<td>Molybdenum (oxide) MoO₃</td>
<td>0.099</td>
<td>Iron</td>
<td>0.90</td>
</tr>
<tr>
<td>Sulfur</td>
<td>37.37</td>
<td>Calcium</td>
<td>0.19</td>
</tr>
<tr>
<td>Copper</td>
<td>0.59</td>
<td>Alumina</td>
<td>0.65</td>
</tr>
<tr>
<td></td>
<td></td>
<td>SiO₂</td>
<td>3.80</td>
</tr>
</tbody>
</table>

X-ray Diffraction Pattern of the Molybdenite Concentrate

<table>
<thead>
<tr>
<th>Line</th>
<th>dÅ</th>
<th>I/I₁ - Species Indentified</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>MoS₂</td>
</tr>
<tr>
<td>1</td>
<td>9.35</td>
<td>100</td>
</tr>
<tr>
<td>2</td>
<td>6.75</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>6.18</td>
<td>100</td>
</tr>
<tr>
<td>4</td>
<td>4.67</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>3.11</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>3.06</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>2.73</td>
<td>10</td>
</tr>
<tr>
<td>8</td>
<td>2.60</td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>2.72</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>2.05</td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>1.86</td>
<td></td>
</tr>
<tr>
<td>12</td>
<td>1.82</td>
<td></td>
</tr>
<tr>
<td>13</td>
<td>1.54</td>
<td></td>
</tr>
<tr>
<td>14</td>
<td>1.34</td>
<td></td>
</tr>
<tr>
<td>15</td>
<td>1.23</td>
<td></td>
</tr>
<tr>
<td>16</td>
<td>1.08</td>
<td></td>
</tr>
<tr>
<td>17</td>
<td>1.03</td>
<td></td>
</tr>
</tbody>
</table>

Large specimens of MoS₂ were purchased from David-New Minerals Providence, Utah and consisted of leafy fragments adhering to quartz rock from which they were easily separated and in some experiments ground to fine powder of composition 99.8% MoS₂.
b. Copper Rougher Concentrate

This material was supplied by Placer Development Inc. and was obtained from the normal output of the rougher flotation operation at Gibraltar (B.C.). Chemical and x-ray analysis are presented in Table 5.

Table 5(a)

Chemical Composition of Copper Rougher Concentrate

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Total Copper</td>
<td>12.40%</td>
</tr>
<tr>
<td>&quot; Molybdenum</td>
<td>9.3%</td>
</tr>
<tr>
<td>&quot; Sulfur</td>
<td>21.89%</td>
</tr>
<tr>
<td>&quot; Iron</td>
<td>32.29%</td>
</tr>
<tr>
<td>&quot; CaO</td>
<td>0.21%</td>
</tr>
</tbody>
</table>

Table 5(b)

X-ray Diffraction Pattern of the Rougher Concentrate

<table>
<thead>
<tr>
<th>Line</th>
<th>dA</th>
<th>I/I₁ - Species Identified</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>CuFeS₂</td>
</tr>
<tr>
<td>1</td>
<td>3.43</td>
<td>40</td>
</tr>
<tr>
<td>2</td>
<td>3.40</td>
<td>100</td>
</tr>
<tr>
<td>3</td>
<td>3.03</td>
<td>100</td>
</tr>
<tr>
<td>4</td>
<td>2.70</td>
<td>25</td>
</tr>
<tr>
<td>5</td>
<td>2.42</td>
<td>20</td>
</tr>
<tr>
<td>6</td>
<td>2.31</td>
<td>15</td>
</tr>
<tr>
<td>7</td>
<td>1.91</td>
<td>40</td>
</tr>
<tr>
<td>8</td>
<td>1.87</td>
<td>70</td>
</tr>
<tr>
<td>9</td>
<td>1.85</td>
<td>40</td>
</tr>
<tr>
<td>10</td>
<td>1.75</td>
<td>60</td>
</tr>
<tr>
<td>11</td>
<td>1.59</td>
<td>5</td>
</tr>
<tr>
<td>12</td>
<td>1.50</td>
<td></td>
</tr>
<tr>
<td>13</td>
<td>1.07</td>
<td></td>
</tr>
</tbody>
</table>
c. **Chalcopyrite**

The particulate material was a Phoenix concentrate consisting almost entirely of chalcopyrite. No preparation treatment was required. Some experiments involved using massive chalcopyrite for which samples were cut and mounted in Quik-mount and then polished.

d. **Sodium Hypochlorite**

The sodium hypochlorite used in all experiments was supplied by Chernetics International and was produced in an experimental membrane type hypochlorite generator. The various batches obtained varied over a wide range of concentrations of both NaOCl and NaCl. In all cases the pH was over 12.

3. **Other Materials**

All other chemicals used were reagent grade quality.

3.2 **Apparatus**

All dissolution experiments were done in a 1 l glass vessel equipped with four Teflon baffles fixed to the wall of the reactor at equal spacings. Agitation was provided by a four blade radial flow turbine. Both vessel and agitator dimensions were determined using geometrical relations that correspond to Standard Tank Configuration [27].

Stirring rate was controlled with a Fisher Dyna-Mix. The velocity of the turbine was measured using a Teclock hand tachometer.
Temperature uniformity was obtained by placing the reactor in a water bath heated electrically and controlled by a Thermistemp YSI Model 71 temperature controller. The temperature was maintained within ±0.5°C of the required value.

### 3.3 Procedure

Experiments in sections A and B were done in the following way:

A required volume of concentrated stock NaOCl was added to approximately 800 ml of H₂O and the pH lowered to the required value for the particular experiment. A weighed amount of buffer components (Na₂CO₃/NaHCO₃) was introduced and the solution made up to 1000 ml.

The NaOCl solution was transferred to the reactor and introduced in the water bath, slow agitation was induced until the reagent reached the experiment temperature. At this time agitation was increased, the first sample extracted for NaOCl analysis and blanks for molybdenum and copper analysis., the MoS₂ sample to be leached introduced and the chronometer started. Samples were withdrawn from the reactor with a pipette and filtered using a fritted glass tube or a filter paper.

The pH was measured using an Expandomatic pH-meter.

For the comparative leaching experiments with chalcopyrite and molybdenite, both minerals were wet screened to a size fraction -140 + 200 mesh and examined microscopically to determine their shape and surface conditions. Based on this information a shape factor was selected and using a nomogram for the Determination of Specific Surfaces [28] their surface area was determined.
Experiments in section C were done at Placer Development and consisted of standard flotation tests on samples of leached rougher concentrates to determine their flotability and reagent consumption.

3.4 Chemical Analysis

a. Molybdenum

Molybdenum was determined by a colorimetric method [29] using the brown-red $\text{H}_2\text{MoO}_4\text{(CNS)}_3$ complex. The optical density was measured using a Beckman Model B Spectrophotometer set at a wavelength of 460 nm. The concentration of Mo was read directly from a calibration curve prepared by using standard molybdenum solutions.

When copper bearing materials were leached simultaneously the analysis of molybdenum was done by atomic absorption spectrophotometry using a wavelength of 313.3 nm. To overcome any interference sample solutions were made up to be 10% in aluminum chloride and 5% in ammonium chloride.

b. Copper

Copper in leaching solutions was determined by atomic absorption spectrophotometry using the line of wavelength 324.7 nm. In analyzing solid materials the determination of copper was done electrogravimetrically in which case the interference of molybdenum was nullified by a redposition of copper.

The dissolution of molybdenite, chalcopyrite and copper rougher concentrates for the purpose of analysis, was found to be complete
following treatment with a mixture of concentrated nitric acid and potassium chlorate at low temperature.

c. Sodium Hypochlorite

Determination of sodium hypochlorite was done using the KI-Thiosulfate method according to ASTM-D-62-T [30]. Potassium iodide was added in excess to an acidified sample and the hypochlorite immediately titrated using a 0.1 N Na$_2$S$_2$O$_3$ solution until the disappearance of the starch blue colour as end-point.

This method does not differentiate between un-ionized NaOCl and ionized hypochlorite OCl$^-$, nor chlorine dioxide ClO$_2$. Therefore a potentiometric method was used for some experiments that required more precise data. This method [31] is based on different reducing rates of hypochlorite, and chlorite by arsenite. The reaction with chlorite is slow and may be deliberately accelerated by addition of OsO$_4$, which works as a catalyst. Chlorate is determined on the same sample by bromatometric titration and chloride may be titrated using AgNO$_3$. It was therefore possible to determine the concentration of OCl$^- +$ HClO by holding the sample of pH 12 and then dropping the pH to 8.5 to determine the concentration of ClO$_2^-$. 
Chapter 4

RESULTS AND OBSERVATIONS

4.1 Oxidation of Molybdenite by Sodium Hypochlorite

4.1.1 Reproducibility

The factors that could affect the reproducibility were:

a) Reactivity of reactor material to NaOCl solutions.

b) Analytical procedures for Mo and NaOCl.

To test if any of the reactor materials (baffles of Teflon and Ti stirrer covered with a film of Microstop) reacted with NaOCl a run was made of 40°C using a solution with an initial concentration of 5 g/l buffered at pH 9.3. Four samples were removed every 30 minutes and analyzed for NaOCl. The concentration of NaOCl remained constant during the entire run indicating that the materials used neither react nor catalytically decompose the reagent.

The consistency of sample extraction and analysis were tested by running two experiments under identical conditions. The molybdenite used in these experiments was the pure material obtained by grinding the massive specimens. The results of Mo dissolution and NaOCl consumption are shown in Figure 2 showing good agreement for both runs.
FIG. 2 - REPRODUCIBILITY OF THE RESULTS FOR THE LEACHING OF MOLYBDENITE PARTICLES.
4.1.2 Effect of Stirring Rate

It was established in preliminary experiments that the rate of reaction between MoS$_2$ and NaOCl solutions was dependent on the agitation. Finally a baffled vessel was made and experiments were carried out varying the rate of the turbine agitator while maintaining constant the other variables.

Runs were made adding 0.3 g of MoS$_2$ concentrate to 1000 ml of a solution containing 5.1 g/l of NaOCl buffered at pH 9.6 by a 0.1 N Na$_2$CO$_3$-0.1 N NaHCO$_3$ solution. The temperature of all experiments was 35°C ± 0.5°C.

Results of the extraction rates of molybdenum into solution are presented in Figure 3 for 5 agitation speeds. It was concluded from the above results that the reaction rate was independent of stirring above 750 rpm (Figure 4).

4.1.3 Effect of Temperature

The reaction was studied over the temperature range 9-70°C. The experimental conditions for these tests were: pH of buffered solution = 9; stirring rate = 780 r.p.m. Concentration of NaOCl = 8.35 g/l; amount of MoS$_2$ concentrate added = 0.3g. The extraction curves are presented in Figure 5.

An Arrhenius plot taken for a concentration of 15 mg/l Mo was constructed. The slope of this line (Figure 6) was found to be linear over the entire temperature range, and the experimental activation energy was calculated to be 6.3 ± 0.8 kcal/mole.
FIG. 3 - EFFECT OF AGITATION ON THE RATE OF OXIDATION.
FIG. 4- EFFECT OF AGITATION ON THE RATE OF
OXIDATION OF MOLYBDENITE.
FIG. 5 - EFFECT OF TEMPERATURE ON THE
OXIDATION OF MOLYBDENITE.
FIG. 6 - ARRHENIUS PLOT OF TEMPERATURE DATA.

SLOPE = -1.378
This value for the activation energy is in good agreement with the experiments done by Ioardanov and Zelikman [14] using compressed MoS$_2$ powder specimens in the temperature range 20-80°C giving a value of 5.25 kcal/mole.

4.1.4 Effect of Surface Area

Two experiments were done varying the amount of MoS$_2$ particles only and maintaining constant the other parameters. As shown in Figure 7 the rate of extraction of molybdenite was found to vary directly with the surface area. This indicates that the rate of leaching is controlled by a heterogeneous reaction on the surface of the MoS$_2$ or by diffusion of the hypochlorite or molybdate ions through the solution boundary layer on the surface of the MoS$_2$.

4.1.5 MoS$_2$ Crystalinity and Surface Characteristics

Leaching of MoS$_2$ particles would be expected to be anisotropic since they consist of a layered structure (Figure 8). In each layer Mo(IV) atoms are surrounded by six S atoms forming a triangular prism configuration sharing vertical edges with one another to form S-Mo-S planes normal to the c-axis. The repetition of these complete layers according to requirements of hexagonal close packing results in a MoS$_2$ crystal (Figure 9).

The bonding within each layer is about 80% covalent and the metallic luster it has, is attributed to some metallic bonding [32].
FIG. 7 - EFFECT OF SURFACE AREA ON THE RATE OF OXIDATION OF MOLYBDENITE.

NoOCl = 5 g/l
T = 30°C
pH = 8.5
FIG. 8 - LAYERED STRUCTURE OF MoS$_2$ PARTICLES.
FIG. 9 - MOLYBDENITE STRUCTURE
The layers are held together by Van der-Waal bonds yielding large S-S interlayer distances and permitting the distinctive cleavage along the (0001) plane.

Therefore MoS$_2$ particles have two types of surfaces each with different chemical activity. Those formed from rupture of Van der-Waal bonds are called "faces", they are hydrophobic and are considered inactive and the ones formed from breaking S-Mo covalent bonds, called edges, which are hydrophilic and chemically active. However examination of the "faces" of a recently cleaved MoS$_2$ particle with the S.E.M. reveals a surface which has multiple steplike hexagonal pits as shown in Figure 10, indicating that the "active" surface which can contribute to leaching is much greater than the surrounding "edge" surface of the particles.

4.1.6 Morphology of MoS$_2$ Leaching

Coarse molybdenite concentrate (-70 + 140 mesh) was leached at room temperature (26°C) in a solution of 5 g/l NaOCl and solids were removed after 5, 10, 15, 20 and 30 minutes. A comparison between the surface of the particles leached for different periods is presented in Figure 11.

The unleached particles are smooth and do not present the pits of a normal MoS$_2$ particle such as shown in Figure 10, this is likely to be due to the grinding action during size reduction. However, immediately after leaching begins the appearance of such active sites is observed and they contribute largely to the reaction as can be observed at a higher magnification in Figure 12. It can also be observed that after
FIG. 10- VIEW OF THE "FACE" SURFACE MoS$_2$.
FIG. II - $\text{MoS}_2$ PARTICLES OXIDIZED OVER INCREASING PERIODS.
FIG. 12 - MoS$_2$ PARTICLES AFTER 10 MIN. OF REACTION IN NaOCl.
30 minutes of leaching under moderate conditions of concentration and temperature, MoS\textsubscript{2} particles have dissolved almost completely.

The reaction of hypochlorite on MoS\textsubscript{2} occurs therefore not only on the "edges" of the particles but also on the steps of hexagonal pits formed on the "faces" of the particles and is aided by a free flow of reagent deep into the MoS\textsubscript{2} particles through interlayer spacing such as can be observed in Figure 12c.

Molybdenite may have up to approximately 5\% MoO\textsubscript{3} on its surface due to dry oxidation. Under alkaline conditions only, MoO\textsubscript{3} and other non-stoichiometric oxides are soluble. It has been reported [33] that some MoO\textsubscript{2} may also be present on the MoS\textsubscript{2} surface in very small amounts and is not soluble under alkaline conditions.

4.1.7 Effect of NaOCl Concentration on the Rates of Mo Extraction

Samples of molybdenite were leached at 45°C in solutions of NaOCl buffered with Na\textsubscript{2}CO\textsubscript{3}-NaHCO\textsubscript{3} at pH 9 of different initial concentrations. The extraction curves are plotted in Figure 13 and indicate that the reaction rates increase with higher initial NaOCl concentrations.

A plot of reaction rates at 15 mg/\textit{l}:Mo against initial NaOCl concentration (Figure 14) gives a straight line of slope \(\cong 1\) indicating that the reaction between MoS\textsubscript{2} and NaOCl is first order with respect to sodium hypochlorite. This is in agreement with previous work reported by Ioardanov and Zelikman [14] and Bhappu et al. [6].
**FIG 13 - EFFECT OF NaOCl CONCENTRATION ON THE OXIDATION OF MOLYBDENITE**
FIG. 14 - PLOT OF REACTION RATES VS. INITIAL HYPOCHLORITE CONCENTRATION.
4.1.8 Effect of pH on the Rate of Reaction

The effect of $[H^+]$ on the rate of the reaction between MoS$_2$ and NaOCl was studied over the pH range of 6.7 to 12. This range was selected on the basis that NaOCl solutions are stored at a pH of 12 to prevent any decomposition and that they are stable only in alkaline solutions.

In these experiments the pH was maintained either by preparing a buffer solution (higher pH's) or by adding Na$_2$CO$_3$ to the solutions at intervals in order to keep the solutions within a narrow pH region.

It was observed that MoS$_2$ dissolves faster with increasing pH up to approximately pH 8.5 and that the rates decrease for pH's above 10 (Figure 15). A plot of reaction rates against pH of the solution (Figure 16) indicates a peak between pH 8.3 and 9.8 in which the reaction rate is a maximum.

This observation has not been reported by previous workers although the same region of pH was selected for working probably due to the stability of the NaOCl at this pH. Ioardanov and Zelikman [14] reported finding no effect on the rate of oxidation when the concentration of NaOH was above the theoretically required amount.

4.1.9 Effect of Sulfate Concentration on the Reaction Rate

When there is sufficient hypochlorite all the sulfur in the MoS$_2$ will be oxidized to SO$_4^{2-}$. Therefore the effect of sulfate on the reaction rate was investigated.
FIG. 15 - EFFECT OF pH ON THE RATE OF OXIDATION OF MOLYBDENITE.
FIG. 16 - PLOT OF REACTION RATES VS. pH.
Experiments were set up maintaining identical reaction conditions by adding an excess amount of Na$_2$SO$_4$ to the solution before introducing the MoS$_2$. Two runs with one and ten times the stoichiometric amount of SO$_4^{2-}$ to be produced are compared in Figure 17 with an extraction curve not containing any initial SO$_4^{2-}$.

The slight variation of reaction rates are within experimental error and the increase in [SO$_4^{2-}$] can be regarded as having no effect on the reaction. Since the [SO$_4^{2-}$] examined is much larger than what would be produced in a MoS$_2$ leach, it may be concluded that the Na$_2$SO$_4$ formed in the course of the reaction is also without effect.

4.1.10 Effect of NaCl on the Reaction Rate

Sodium chloride is always present in solutions of NaOCl in greater or smaller concentrations according to the method used to generate it, and the salt utilization if it is produced by NaCl electrolysis. It is also formed as a product of the reaction between NaOCl and MoS$_2$ and it was therefore considered important to establish its effect if any upon the reaction rate.

To this end an experiment was conducted adding 50 g of NaCl to a solution of 7.9 g/l NaOCl already containing 70 g/l of NaCl. MoS$_2$ concentrate was leached in this solution and compared to a run under identical conditions with no NaCl added.

No effect whatsoever was detected on the reaction rate.
FIG. 17 - EFFECT OF SULFATES ON THE OXIDATION OF MOLYBDENITE.

NaOCl = 8.1 g/l
T = 30°C
pH = 9
4.1.11 **Effect of ClO$_2^-$ and ClO$_3^-$ on the Rate of Reaction**

Solutions of sodium hypochlorite are unstable to a certain degree even in the alkaline region and decompose into sodium chlorate and sodium chloride. Most of the mechanisms proposed to explain its decomposition show the formation of ClO$_2^-$ ions as an intermediate step.

Experiments were done to establish if these species have any effect on the rate of oxidation of MoS$_2$ by NaOCl. Solutions of NaOCl of 8.0 g/l were prepared and buffered at pH 9 and different amounts of NaClO$_2$ and Na$_2$ClO$_3$ were added and the rates of extraction compared. The information obtained was plotted in Figure 18.

It can be observed that ClO$_2^-$ ions have no effect on the rates of extraction of Mo. The presence of ClO$_3^-$ however lowers the rate of Mo extraction. In both cases the amounts added were far in excess of what would be expected from the normal decomposition of NaOCl under the conditions of our leaching studies and therefore the effects observed would not hinder the leaching reaction. The presence of chlorate would be hazardous only in the case in which solutions of NaOCl had been stocked for long periods of time under unfavourable conditions.

4.1.12 **Effect of Molybdate Ions on the Rates of Reaction**

Two experiments are reported in this section. In the first one the effect of [MoO$_4^{2-}$] on the rate of reaction was determined at a fixed pH value. In the second, the effect of MoS$_2$ particles on the [MoO$_4^{2-}$] was established for different OH$^-$ concentrations.
FIG. 18 - EFFECT OF CHLORITE AND CHLORATE ON THE OXIDATION OF MOLYBDENITE.
As mentioned in 1.5, it has been reported that in the presence of excess oxidizing agent in alkaline solutions the Mo(IV) in MoS$_2$ is entirely oxidized to (VI) in the MoO$_4^{2-}$ ions. It was therefore decided to investigate if the presence of larger concentrations of MoO$_4^{2-}$ affected the reaction.

A run was made using a buffered solution (pH 9.5) of 7.5 g/l NaOCl at 35°C, leaching 0.3 g MoS$_2$ coarse particles in the presence of an initial [MoO$_4^{2-}$] five times the amount that would be produced by the total reaction of the MoS$_2$ employed. The dissolution curves were then compared to an identical run with no initial MoO$_4^{2-}$ present. In this experiment MoO$_4^{2-}$ ions evidently had no effect on the leaching reaction.

From the stoichiometry of reaction (3) it could be expected that the rate of the reaction should depend on the concentration of hydroxide; however experiments reported in 4.1.8 indicate an increase in rates of extraction up to pH 8.5 but a decrease in the reaction rates when the pH exceeds 10.5.

Consequently it was decided to examine if there was any reaction between MoO$_4^{2-}$ ions and MoS$_2$ particles which would decrease the molybdate concentration at higher pH's.

Three runs were made with solutions of 10 g/l Na$_2$MoO$_4$ at 26°C with the pH controlled at 8.5, 10.5 and 11.5. In all cases 50 g of MoS$_2$ fine concentrate were added.

In Figure 19 it can be observed that while the [MoO$_4^{2-}$] remains constant after 60 min. at the lower pH, the runs at pH 10.5 and 11.5 indicate a decrease in the [MoO$_4^{2-}$] in the first 20 min. and then the concentration remains constant. The occurrence of a reaction was also
FIG. 19 - EFFECT OF MOLYBDATES - MoS₂ INTERACTION.
observable when an additional run was made with an initial pH of 10.5 and the solution was not buffered. There was a decrease in the pH in the first 30 min. of reaction.

No difference in the surface of the MoS$_2$ particles were observed after the reaction; the observations in this section however, indicate that there is some interaction between the MoO$_4^{2-}$ in solution and the MoS$_2$ particles at higher OH$^-$ concentrations which results in a decrease of the $[\text{MoO}_4^{2-}]$.

4.2 Oxidation of Chalcopyrite by Sodium Hypochlorite

Since chalcopyrite was the major copper mineral in the rougher concentrate and because apparently it was an important contributor to the excess consumption of hypochlorite as determined from preliminary leaching experiments of the rougher concentrate, it was decided to investigate the extent of its reaction with solutions of sodium hypochlorite.

4.2.1 Leaching of Chalcopyrite Concentrate

Samples of a Phoenix chalcopyrite ground to -200 mesh were leached in solutions of sodium hypochlorite under similar conditions as those for the best extraction from molybdenite concentrates. In each run the concentration of copper ions and sodium hypochlorite was determined. In all cases it was observed that the reaction was accompanied by a decrease in the $[\text{H}^+]$. Some runs were then repeated maintaining the pH constant by buffering the solutions.
The results of one run are presented in Figure 20. It can be observed that the concentration of Cu increased rapidly and then remained constant through the entire experiment. In contrast the concentration of NaOCl decreased continuously almost reaching zero after 24 hours. In this run the pH had decreased in the last 12 hours and the decrease in hypochlorite concentration may have been influenced by the higher H\(^+\) concentration.

As was observed in all other leaching experiments using chalcopyrite, its surface was slightly darkened by the reaction. This apparent coating was easily removed by dilute sulfuric acid.

4.2.2 Leaching of Massive Specimens

To investigate if the consumption of NaOCl was due to any topotactic reaction within the chalcopyrite particles, large CuFeS\(_2\) specimens were leached and their cross-sections later examined using the electron microprobe.

In preparation for these tests the CuFeS\(_2\) specimens were previously polished and areas free of foreign impurities specially FeS\(_2\) were detected and marked. They were then immersed in solutions of NaOCl for different periods and experimental conditions and finally sectioned through the marked areas.

A similar tarnishing of the surface was observed as in the case of the fine particles. The CuFeS\(_2\) areas after leaching were brown and transparent while the FeS\(_2\) areas formed a black-opaque coating.
FIG. 20 - EXTRACTION OF COPPER AND CONSUMPTION OF HYPOCHLORITE DURING LEACHING OF CHALCOPYRITE.

- Theor. NaOCl consumption.
- Experim. " "

T - 26°C
CuFeS - 10g
pH - 9.2
Using the x-ray energy analyzer of the SEM on the leached CuFeS$_2$ areas it was possible to determine a decrease in the sulfur-copper ratio when compared to untreated CuFeS$_2$. An example of these observations is presented in Table 6. It was also observed that the S/Cu ratio did not change significantly with the duration of leaching the specimens.

Table 6
Comparison of S/Cu Ratios for Leached and Nonleached Chalcopyrite

Leaching Conditions
NaOCl = 15g/l
Temp = 31°C
pH = 9.6 (controlled)
Time = 4 hours

S/Cu ratio untreated CuFeS$_2$ = .79
" " leached " = .37

This reduction in the S/Cu ratio could be interpreted as an oxidation of the CuFeS$_2$ surface. However as there was sulfur remaining after the reaction, although there was an excess of oxidizing reagent in solution, this procedure could not discriminate between an incomplete oxidation of the CuFeS$_2$ surface and the interference of lower CuFeS$_2$ layers excited by the x-ray beam penetration.

The microprobe analysis of leached cross-sections indicated that a limited topotactic reaction had occurred. The surface of the CuFeS$_2$ was altered only to a maximum depth of 20 microns and it was not possible to determine the extent of the reaction between the NaOCl and the CuFeS$_2$ within this depth because of the erratic signals for Cu and S originating from the emission of diffracted beams from the uneven edge of the specimen.
These last observations demonstrate that the reaction between NaOCl and CuFeS₂ occurred only at the surface forming a protective layer consisting at least in part by some form of oxide or hydroxide of copper II. It was reasonable to speculate therefore, that the further decrease in [NaOCl] was due to some decomposition reaction which is catalyzed by the altered CuFeS₂ surface.

4.2.3 Comparative Oxidation and Dissolution of MoS₂ and CuFeS₂ in Solutions of NaOCl

In a rougher concentrate the weight ratio between CuFeS₂ and MoS₂ is approximately 80. It is therefore convenient to determine how each of them behave when exposing equal surface areas in solutions of NaOCl under the conditions of previous experiments. This could then establish if selective leaching is possible.

MoS₂ and CuFeS₂ of the same screened size (-140 + 200 mesh) were examined using the SEM to determine the surface roughness. Examples of each are presented in Figure 21. It was observed that the presence of multiple steps and edges on the molybdenite particles increased its surface area. The specific area was determined using a nomogram [28] on the basis of particle diameter, shape factor and the materials density.

This method of surface area determination is not as accurate as any of the adsorption methods but it was considered to be adequate for comparative purposes in the leaching experiment.
FIG. 21 - SURFACE ROUGHNESS OF MoS$_2$ AND CuFeS$_2$. 
Table 7

Values for Determination of Surface Area for Molybdenite and Chalcopyrite

<table>
<thead>
<tr>
<th>Material</th>
<th>Average Particle Diameter (μm)</th>
<th>Shape Factor</th>
<th>Density</th>
<th>Specific Surface Area (\text{m}^2/\text{g})</th>
</tr>
</thead>
<tbody>
<tr>
<td>MoS(_2)</td>
<td>100</td>
<td>5</td>
<td>4.8</td>
<td>0.06 (\text{m}^2/\text{g})</td>
</tr>
<tr>
<td>CuFeS(_2)</td>
<td>&quot;</td>
<td>4</td>
<td>5.1</td>
<td>0.02 (\text{m}^2/\text{g})</td>
</tr>
</tbody>
</table>

Samples of molybdenite and chalcopyrite particles corresponding to equal surface areas were leached together in a solution of NaOCl. The extraction curves for molybdenum and copper are shown in Figure 22.

It was possible to observe that the relative dissolution between these minerals favors molybdenite by at least a ratio 100:1 and that the reaction of MoS\(_2\) was complete. Therefore the selective leaching of MoS\(_2\) from CuFeS\(_2\) should be possible.

4.2.4 Effect of Chalcopyrite on the Rates of NaOCl Consumption and MoS\(_2\) Dissolution

Runs in this section were made by adding progressively greater amounts of CuFeS\(_2\) to leaching experiments in which the initial molybdenite and concentration of sodium hypochlorite were identical.

Results for molybdenite dissolution are presented in Figure 23. It was observed that greater amounts of chalcopyrite (several times the weight and surface area of molybdenite) did not have a significant effect on the dissolution rates since times for total extraction remained unchanged.
[NaOCl] = 7.2 g/l
pH = 9
T = 30°C

Mo extracted = 100%
Cu extracted = 0.6%

FIG. 22 - EXTRACTION OF Cu AND Mo DURING LEACHING OF MoS₂ AND CuFeS₂ OF EQUAL INITIAL SURFACE AREAS.
FIG. 23 - EFFECT OF CHALCOPYRITITE ON THE RATE OF MOLYBDENITE DISSOLUTION.
4.3 Leaching of Molybdenite from Copper Rougher Concentrates

Using the optimum leaching conditions established with pure MoS$_2$, experiments were performed to extract molybdenum from copper mill products. Some initial experiments using a copper ore showed erratic results which were attributed to the extremely low grade (<.01% Mo) of the ore sample.

It was then decided to use a copper rougher concentrate, which was dried in an oven at 110-120°C, with the purpose of eliminating most of the attached flotation reagents.

The results of preliminary experiments using a concentration of sodium hypochlorite up to 10 times that theoretically required to oxidise all the molybdenite present to MoO$_4^{2-}$ and SO$_4^{2-}$ showed as was expected, that the extracted Mo/Cu ratio was very high. However some Cu was present in the solution and the consumption of NaOCl was far in excess of the theoretically calculated amount.

The result of one such experiment is reported in Figure 24. The % extracted Mo and Cu refer to the total of each in the initial sample. It can be observed that the rates of molybdenum extraction are very high in the initial part (50% reacted in 8 minutes) but decrease rapidly to zero after 40 minutes. At this time the concentration of NaOCl had decreased to zero and the total extraction of Mo was only 83%.

The dissolution of copper was observed to go through a maximum and later remain constant after the NaOCl concentration reached zero. In this run the maximum Cu detected in solution was 1.2%. In no case did the Cu extraction exceed 3%.

It is assumed that in the presence of an excess [NaOCl]- the reaction between chalcopyrite and sodium hypochlorite will have the following stoichiometry:
FIG. 24 - EXTRACTION OF Mo AND Cu FROM A COPPER ROUGHER CONCENTRATE.
\[
2 \text{CuFeS}_2 + 17 \text{NaOCl} + 8 \text{NaOH} + \text{H}_2\text{O} \rightarrow \\
2 \text{Cu(OH)}_2 + 2 \text{Fe(OH)}_3 + 4 \text{Na}_2\text{SO}_4 + 17 \text{NaCl}
\]

In the leaching of the rougher concentrate, the analysis of [NaOCl] measured even in the first samples indicated that the consumption of reagent was much greater than theoretically required to completely oxidize all the Mo and the Cu dissolved at those stages.

As in the case of leaching CuFeS\(_2\), clear filtered solutions from the rougher concentrate leach were observed to form a black fine precipitate. It was not possible to collect sufficient of this material for NaOCl decomposition studies.

4.3.1 Influence of Particle Size on the Extraction of Molybdenum

The influence of particle size was investigated by separating two size fractions of the rougher concentrate and subjecting them to identical leaching experiments.

The results are presented in Figure 25. It was observed that the sample with greater surface area presented a higher extraction rate but the total molybdenite leached was lower. The reason for this was believed to be a faster decrease in NaOCl strength.

This was confirmed in the following experiments in which a finely ground rougher concentrate sample was leached.

A comparison of the extraction rates and NaOCl consumption is presented in Figure 26, between the leaching of the "as received" rougher concentrate and the ground sample. Although the concentration of NaOCl
FIG. 25 - EFFECT OF PARTICLE SIZE ON THE RATES OF Mo EXTRACTION FROM Cu ROUGHER CONCENTRATES.
FIG. 26 - Mo EXTRACTION AND NaOCl CONSUMPTION IN THE LEACHING OF GROUND AND NORMAL ROUGHER CONCENTRATES.
was over three times the theoretically required to leach all the molybdenite present it decreased to zero in less than 10 minutes at which time only 46% of Mo had been extracted from the ground sample. Equal conditions extracted 84% of the coarser concentrate.

4.3.2 Quantity of NaOCl Required for Total Molybdenum Extraction

Several runs were performed increasing the concentration of sodium hypochlorite with the purpose of determining the minimum quantity that would extract almost all the molybdenum. The experimental conditions were set at: initial pH 9.5, temperature 30°C.

It was determined that for the complete extraction of MoS$_2$ from the rougher concentrate used, the quantity of NaOCl required was equivalent to 4.2 times the theoretically needed to completely oxidize the molybdenum and sulfur in the sample.

4.3.3 Effect of Pretreating the Rougher Concentrate with Sulfuric Acid

With the intention of eliminating any oxides present with the copper sulfide minerals in the rougher concentrate which could be increasing the NaOCl consumption, a portion of the concentrate was leached in a dilute solution of sulfuric acid (0.5%) and later leached with sodium hypochlorite under similar conditions as the untreated rougher concentrate.

It was observed that this pretreatment had a remarkable effect on the sodium hypochlorite consumption. Consequently several runs were performed as in section 4.3.2 and it was determined that total molybdenite
extraction was obtained using a solution of NaOCl with an initial concentration equivalent to 1.5 to 1.8 times the theoretically required to dissolve the MoS\(_2\) present.

4.3.4 **Extraction of Molybdenite from "In-Pulp" Rougher Concentrate**

The experiments in section 4.3.3 were performed simultaneously with the Flotation studies reported below. The results of both indicated that the rougher concentrate used could have an excess of copper oxide as compared to the unprepared "in-pulp" rougher concentrate obtained in the primary flotation circuit. This was confirmed by chemical analysis as indicated in Table 8.

<table>
<thead>
<tr>
<th></th>
<th>Oxide Copper Content for Dried and In-Pulp Rougher Concentrates</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gibraltar R.C. washed and dried for Leaching Experiments</td>
<td>Oxide Copper = 1.26%</td>
</tr>
<tr>
<td>Gibraltar R.C. untreated</td>
<td>&quot; = 0.52%</td>
</tr>
</tbody>
</table>

The cause of the excess copper oxide was attributed to high temperatures of the drying process used in preparing the samples for leaching experiments and storing the dried rougher concentrate in contact with air for long periods of time.

Consequently a new batch of rougher concentrate was obtained from Gibraltar Mines and maintained as a dense pulp. The addition of rougher concentrate to the leaching experiments reported in this section was by measured volumes after stirring the pulp one-half hour.
Several runs were performed with the untreated rougher concentrate using similar conditions as in section 4.3 and 4.3.2 with the purpose of determining the effect of the excess copper oxide on the extraction rates of molybdenite and the consumption of reagent.

The results of one run are presented in Figure 27. Also plotted is the extraction curves of the leaching of a treated rougher concentrate. It is not possible to compare the approximate reaction rates from these two curves because of the difference in the initial concentration of the reagent. Furthermore the determination of reaction rates in this reaction would have required a more sophisticated sampling technique which was not judged convenient for the purpose of this study. For the purpose of a practical application it is possible to say that there was no significant change either in the reaction rates nor in the total leaching times between these two concentrates.

However the NaOCl consumption was noticeably different. By using the procedure of leaching with increasing initial NaOCl concentration and following the Mo extraction until total NaOCl consumption it was possible to determine that 98% of the MoS$_2$ in the untreated rougher concentrate was extracted with a NaOCl solution with an initial concentration 1.6 times the theoretically required to oxidize all MoS$_2$ to MoO$_4$ and SO$_4$.$^2$.

4.3.5 Flotation of Leached Rougher Concentrates

To compare the effect of leaching on the flotability of rougher concentrates, tests were performed using three materials:
FIG. 27 - MOLYBDENITE DISSOLUTION AND HYPOCHLORITE CONSUMPTION IN THE LEACHING OF TREATED AND IN PULP ROUGHER CONCENTRATES.
A. Treated Rougher Concentrate directly leached in a solution of NaOCl (complete extraction of molybdenite).

B. Treated Rougher Concentrate previously leached in a 1% H₂SO₄ at 25°C for one hour and later leached in a solution of NaOCl (complete extraction of MoS₂).

C. Treated Rougher Concentrate not leached to serve as comparison.

In all cases the standard technique for the preferential flotation of chalcopyrite was used, carefully controlling the pH at which the several flotation and cleaning stages were performed. Z200 was used as the collector having the property of selectivity of chalcopyrite over pyrite.

The recovery grade relationship has been plotted in Figure 28. It was observed that the flotability of the leached rougher concentrate was inferior to the unleached material. In contrast the rougher concentrate which received the same NaOCl leach but had been previously treated with a dilute H₂SO₄ had a slightly better flotability.

In all cases the consumption of collector was far in excess of the normal quantities employed for the secondary flotation of the rougher concentrates in the normal copper concentration process and it was suspected that the surface of the minerals could have been altered during the drying process in preparation for leaching, and that this condition was responsible to a larger degree for the poor flotability than any changes produced on the mineral surface during leaching with NaOCl.
FIG. 28 - RECOVERY - GRADE CURVES FOR THE SECONDARY FLOTATION OF LEACHED ROUGHER CONCENT.
4.3.6 Flotation of "In-Pulp" Rougher Concentrates

Flotation studies reported in this section were performed on the Gibraltar copper rougher concentrate kept as "in-pulp." Samples of this material were leached without any pretreatment in solutions of NaOCl and then floated as in 4.3.5. A sample of unleached material was floated for comparison.

Although a solids/liquid separation was used after leaching, care was taken to prevent the residue from drying or excessive contact with air. The same filtering procedure was applied to the unleached material and times between S/l separation and flotation were approximately the same for both materials.

The recovery-grade relationship was plotted in Figure 29. It is possible to observe that this relationship is similar for both rougher concentrates.

On the basis of reagent consumption it was determined that the flotability of the leached rougher concentrate is lower than the untreated material, i.e. the flotation recovery is lower although the concentrate grade is higher for identical reagent consumption.

It is likely that the recovery of the leached rougher concentrate could be increased by adjusting the reagents either by increasing the dosage of the one used in our experiments or using a different type.

The determination of the appropriate flotation procedure would have required many more experiments and was not in the scope of this project. However the information gathered is sufficient to indicate that the leaching of a copper rougher concentrate with sodium hypochlorite does not decrease
FIG. 29 - RECOVERY- GRADE CURVES FOR THE SECONDARY FLOTATION OF LEACHED ROUGHER CONCENTRATES.
to a great extent the flotability of the material and that the additional costs of flotation reagents if a leaching circuit were introduced to a conventional concentration process might not be significant.

4.3.7 Stability of Sodium Hypochlorite Solutions

Several experiments were performed to determine the stability of NaOCl under the conditions used in the leaching studies. The region of pH influence studied was between 12 at which NaOCl is generally stored for minimum decomposition and 7 at which the reaction to HOCl is rapidly favored. Two temperatures were selected for comparison over the same range as investigated in the molybdenite dissolution, and the initial concentration of NaOCl was similar in all runs. \([\text{NaOCl}]\) as used in this section is a measure of the total active chlorine species, that is \(\text{OCl}^-, \text{HOCl}^+\) and \(\text{ClO}_2^-\).

Results for some runs have been plotted in Figure 30 and 31. The detrimental effect of both higher temperatures and lower pH are observed. At lower temperatures there is no measurable decrease in the concentration of NaOCl at a hydrogen ion concentration in which the fastest rates of molybdenite dissolution were observed.

In two runs, samples were analyzed using the potentiometric technique with the purpose of distinguishing \(\text{ClO}_2^-\) from \(\text{OCl}^-\) and \(\text{HC}10\). No \(\text{ClO}_2^-\) was observed at high pH and the concentration was very small and erratic at pH 7 obstructing any quantitative analysis.
FIG. 30 - EFFECT OF pH ON THE DECOMPOSITION OF HYPOCHLORITE AT 60° C.
FIG. 31- EFFECT OF pH ON THE DECOMPOSITION OF HYPOCHLORITE AT 35°C.
Chapter 5

DISCUSSION

5.1 Oxidation of Molybdenite

The results of the dissolution experiments indicate that the reaction between molybdenite and aqueous solutions of sodium hypochlorite goes to completion very rapidly under the conditions used in this study. This was found to be true both with a high grade molybdenite concentrate and copper rougher concentrates in which the MoS$_2$ content is very small. Total dissolution of MoS$_2$ from dilute pulps was obtained in all cases within 45 minutes leaching time.

The overall stoichiometry of the reaction as determined by [6,14] is:

$$\text{MoS}_2 + 9 \text{NaOCl} + 6 \text{NaOH} \rightarrow \text{Na}_2\text{MoO}_4 + 2 \text{Na}_2\text{SO}_4 + 9 \text{NaCl} + 3 \text{H}_2\text{O} \quad (3)$$

which is valid in the cases in which NaOCl is in excess and therefore both Mo and S can be assumed to be oxidized to their highest state. This reaction was found to accurately represent all the experiments using the MoS$_2$ concentrate and at least the initial stages in the dissolution of MoS$_2$ from the rougher concentrates. No attempts have been reported of
establishing the stoichiometry of the reaction when MoS\(_2\) is in excess, as would be the case in the final stages of the rougher concentrate dissolution when the [NaOCl] is very low, and was not attempted in this study because of the complexities of parallel reactions and catalyzed decomposition of the reagent.

The \(\Delta G^0\) of reaction (3) was calculated as -670 kcal, which predicts the highly favorable thermodynamic tendency of dissolution of MoS\(_2\).

A linear dependence was observed between the rates of dissolution of MoS\(_2\) and the surface area indicating a heterogeneous reaction.

The apparent activation energy of the reaction (6.3 kcal/mole) is on the border of the region characteristic of diffusion controlled reactions. Therefore the rate determining step could be either under exclusive chemical or possibly mixed chemical and diffusion control.

It is considered that the activation energy of 6.3 kcal/mole obtained in this work is in close agreement with the value of 5.25 kcal/mole obtained by [14] using compressed specimens of high grade MoS\(_2\).

It has been observed in this study, that the reaction between CuFeS\(_2\) and NaOCl produces a protective coating which prevents further dissolution. The reaction of NaOCl with ZnS has also been studied [24] and the observation of a zinc hydroxide and zinc ferrite layer on the surface of sphalerite was considered to be the cause of the decrease in the reaction rate. The apparent activation energies have been measured in both cases; 5 kcal for the reaction with CuFeS\(_2\) and 4.6 kcal for the reaction with ZnS.
The similar values of activation energy for reactions in which the reaction products are entirely different in nature would support the concept that the rate controlling step is the diffusion of NaOCl through the boundary layer.

Since NaOCl has a high solubility it can be expected that most of it is ionized in alkaline solutions even at low temperatures. The quantity of OCl⁻ ions however will be determined by the pH of the solution since there exists an equilibrium between OCl⁻ and molecular HOCl which is influenced directly by the [H⁺] as represented by reaction (17)

\[
Ka \quad \text{OCl}^- + H^+ \rightleftharpoons HOCl
\]  

(17)

The proportion of each species has been plotted against pH in Figure 32.

Fig. 32. Hypochlorite and hypochlorous acid concentrations as a function of pH.
Although it has been reported that the oxidizing power of the ionized and molecular species of hypochlorite are similar [34] it was observed in this work that the rates of oxidiation of MoS$_2$ increase with increasing pH until a maximum is obtained in the region pH 8.5-9.5 in which all hypochlorite exists as OCl$^-$ ions suggesting that it is the OCl$^-$ ion which plays the major role in the oxidation reaction.

The influence of [H$^+$] on the rates of oxidation is complex as shown in Figure 10. It would be expected from reaction (3) that any increase in the [OH$^-$] would favor the formation of MoO$_4^{2-}$. This was observed in leaching experiments varying the pH from 7 to 9.5. But any increase over this region resulted in a decrease of the reaction rates. These results differ from the work of Ioardanov [14] who reported that the rate of oxidation is not increased by an increase in free sodium base above the theoretically required. Although most of the other investigations on this reaction [6,8] have worked in the high alkaline region it is felt that this was selected only on the basis of reagent stability.

To explain the decrease in the rates of oxidation above pH 10 it was considered that there could exist competition between OCl$^-$ adsorption and some other species which decreased the concentration of oxidant on the surface of the MoS$_2$.

The zeta potential of molybdenite in the absence of any collectors is shown in Figure 33 indicating an increase in the negative value of $\xi$ for both higher acid and higher alkaline solutions.

S. Chander and D.W. Fuerstenau [33] in studying the natural flotability of molybdenite were able to observe that on addition of MoO$_4^{2-}$
ions in alkaline solutions the zeta potential was even more negative and suggested that MoO$_4^{2-}$ ions are strongly specifically absorbed on molybdenite.

It seems likely then that in alkaline solutions an increase in the pH results in some preferential adsorption of MoO$_4^{2-}$ and possibly OH$^-$ instead of OCl$^-$. In the leaching experiments performed at higher pH's it was observed that lower rates of dissolution of MoS$_2$ were obtained when MoO$_4^{2-}$ ions were intentionally added to the hypochlorite solutions. Under these conditions the lower rates of molybdenite dissolution can be explained if it assumed that some MoS$_2$ sites adsorb MoO$_4^{2-}$ ions and react forming an insoluble porous oxide through which the OCl$^-$ must penetrate in order to react with the MoS$_2$ and that the diffusion through it retards the velocity of dissolution.

Fig. 33. $\xi$ potential of molybdenite as a function of pH.
The possible reactions are:

\[ 7 \text{MoO}_4^{2-} + \text{MoS}_2 + 4 \text{OH}^- + 2 \text{Mo}_4\text{O}_{11} + 2 \text{SO}_4^{2-} + 2 \text{H}_2\text{O} \]  
\[ \text{(18)} \]

\[ \text{MoO}_4^{2-} + \text{MoS}_2 \rightarrow 2 \text{MoO}_2 + 2 \text{S} \]  
\[ \text{(19)} \]

There appears to be great discrepancy between the results obtained in this study and those obtained with electrooxidation leaching of molybdenite. In their first report B.J. Scheiner and R.E. Lindstron [18] determined the pH for optimum extraction as being in the range of 6-8. Later work on the control of chlorate formation during electrooxidation lead D.S. Barr, R.E. Lindstron and J.T. Hendrix [22] to suggest that maximum molybdenite dissolution is obtained at a pH between 4.5 and 5. In their study they observed a decrease in the rate of molybdenite dissolution when increasing the pH from 5.5 to 8.

It is impossible to compare both processes directly as there is no mention of any specific rates. However it is possible to observe in [22] that for equal concentrations of hypochlorite, the electrooxidation process produces at least 50 times more chlorate than a normal hypochlorite containing solution regardless of the pH. Contrary to the belief that because $\text{ClO}_3^-$ is stable it does not affect the molybdenite dissolution, it was observed in this work (Figure 12) that the presence of $\text{ClO}_3^-$ decreases the reaction rates.

In this study the lowest pH at which dissolution of MoS$_2$ was performed was 7 and in these solutions, as can be observed from Figure 33,
HC10 acid predominates over OCl\(^-\). The reasons for not studying the effects below this region are two: first as already pointed out, there is evidence that it is the OCl\(^-\) ions which participate mostly in the dissolution of MoS\(_2\) and second regardless of the type of mechanism adopted to explain hypochlorite decomposition to chlorate (which will be dealt with below), it is generally accepted that it is strongly dependent on HC10 acid and therefore from theoretical considerations it would be expected that the losses of hypochlorite due to decomposition would prohibit its application.

The slope of the straight line in the plot reaction rates for oxidation of MoS\(_2\) against initial hypochlorite concentration is approximately one indicating a first order dependence on the reagent. This is in agreement with the work of Ioardanov and Zelikman [14] and on extrapolation of Bhappu et al. [6] data.

If it is assumed that in the pH region 7-8.5 the concentration of OH\(^-\) ions does not affect the rate of reaction directly but through the availability of OCl\(^-\) as described in reaction (17) and that in the pH region 8.5-9.5 the rates are independent of [OH\(^-\)] then the reaction between MoS\(_2\) and NaOCl can be described as a second order reaction, therefore,

\[
\text{Rate of Oxidation of MoS}_2 = \frac{d \text{MoO}_4}{dt} = k_1[\text{MoS}_2][\text{NaOCl}] \quad (20)
\]

The experimental rate constant \(k_1\) was determined using the data in Figure 7 obtained from leaching experiments in which the initial surface area of molybdenite was identical, by plotting a double logarithmic
curve of the rates of MoO$_4^{2-}$ appearance against concentration of NaOCl, Figure 34. Actually the variation with respect to [NaOCl] is only considered, in the form of

$$\frac{d \text{MoO}_4^{2-}}{dt} = k_2[\text{NaOCl}]$$ \hspace{1cm} (21)

but as the surface area was identical at the start of every experiment and rates were obtained only in the initial stage it is possible to include the variation with respect to MoS$_2$ in the empirical constant $k_2$. The value of $k_2$ was determined as 2.29 min$^{-1}$. As the surface area was calculated as 120 cm$^2$ the specific rate constant $k_2' = 1.90 \times 10^{-2}$ min$^{-1}$ cm$^{-2}$.

There exists no data on reaction rate constants for this system with which to compare this result.

The upper limit of a reaction rate in a diffusion controlled reaction is reached when it is assumed that the chemical reaction is instantaneous, in which case the concentration at the interface is zero. Therefore

$$\frac{d[\text{NaOCl}]}{dt} = \frac{\text{D.A.C.}}{\delta}$$ \hspace{1cm} (22)

in which:

- $D =$ Diffusion coefficient of hypochlorite in aqueous media $= 1.84 \times 10^{-5}$ cm$^2$/sec [35]
- $A =$ Surface area of molybdenite $= 120$ cm$^2$
- $C =$ Concentration in g/l of hypochlorite $= 16$ g/l
- $\delta =$ diffusion layer thickness for an intensely agitated system $= 10^{-3}$ cm [36]
FIG. 34 - LOG-LOG CURVE OF THE RATES OF OXIDATION VS. [NaOCl].

Slope = 0.97

Log $k_2 = 0.36$
and the maximum rate of hypochlorite consumption for these conditions is:

\[
\frac{d(NaOCl)}{dt} = 2.12 \text{ g/min}
\]

Since the stoichiometry of the reaction dictates a consumption of 9 moles of NaOCl per mole of molybdenite, the maximum rate of molybdate appearance was calculated as:

\[
\frac{d(MoO_4^{2-})}{dt} = 505 \text{ mg/min}
\]

The experimental rate for these conditions was measured, and:

\[
\frac{d(MoO_4^{2-})_{exp}}{dt} = 54 \text{ mg/min}
\]

The calculated diffusion rate being ten times faster than the observed rate would suggest chemical control of the leaching. However, the low activation energy and the marked dependency of the leach rate on agitation could favor the concept of mixed diffusion and chemical control of the leaching rate being operative.

5.2 Oxidation of Chalcopyrite

Both chalcopyrite and pyrite were observed to react with sodium hypochlorite but the extent of the reactions are very small in comparison with molybdenite.

Although the fast elimination of the coating formed on CuFeS₂ using dilute H₂SO₄ suggested that it was an oxide, observations of the
precipitation of copper out of solution when the concentration of NaOCl decreased indicated that the nature of the products formed on the surface of CuFeS\textsubscript{2} was complex.

It is reported in the literature [37] that Cu precipitates from alkaline solutions as compounds which are probably solid solutions of CuO and Cu(OH)\textsubscript{2}, the appearance being similar to the precipitates obtained from the leaching of CuFeS\textsubscript{2} and rougher concentrates. Both species are thermodynamically stable in this pH region.

This coating formed on CuFeS\textsubscript{2} effectively inhibits any further reaction and the results from microprobe analysis on cross sections of leached particles demonstrates that the distribution of elements in the next to surface layers is unaltered. The continued consumption of reagent is therefore exclusively of a decomposition nature.

The rate of formation of the oxide coating is difficult to calculate from the data obtained since no redissolution experiments were performed. The observations of the leaching time effect on the S/Cu ratio change on the CuFeS\textsubscript{2} surface indicates that the formation of the oxide layer is faster than the dissolution of copper in the leach solution.

Therefore it is probable that the oxidation rate of CuFeS\textsubscript{2} is similar to the oxidation rates of MoS\textsubscript{2} when equal surface areas are exposed. This similarity of the oxidation rates of these two minerals was also suggested by B.-Stump and Y. Berube [26] working with a dissolved oxygen-caustic system. However their conclusion that because of the similar oxidation rates, preferential leaching cannot be achieved is not supported by this work.
The principal difference between the oxidation of CuFeS$_2$ and MoS$_2$ is that while the first forms a very effective protective layer, the later forms a readily soluble ionic species immediately exposing fresh surface.

This was confirmed by leaching equal surface areas of CuFeS$_2$ and MoS$_2$ in a solution with a great excess of NaOCl, Figure 22. The favorable dissolution of molybdenite in this experiment demonstrates that if a material which consists mainly of these two minerals is ground to its liberation size and agitated vigorously in a solution of NaOCl the preferential extraction of molybdenum should be possible.

Furthermore the results plotted in Figure 23 indicate that although the presence of CuFeS$_2$ lowers the MoS$_2$ dissolution rates slightly, there is not a great variation in the total leaching times. This fact will be important in the design of the capacity of leaching equipment as there are continued variations in the MoS$_2$ content of rougher concentrates.

5.3 Leaching of Molybdenite from Copper Rougher Concentrates

The results of the excessive consumption of hypochlorite when leaching rougher concentrates was attributed in later experiments to be due principally to the high content of copper oxide produced in its preparation for experiments. The process of drying the rougher concentrate in order to eliminate flotation reagents and to conveniently add mass samples to the experiments, was undertaken without much consideration of the change it would produce in its reactivity. Neither was it known
at this stage, that the oxides of some heavy metals acted catalytically on the decomposition of hypochlorites.

Therefore the data obtained from leaching experiments of the pretreated rougher concentrate is of little significance to the general aim of this thesis, and the most useful information derived from it, is that special precautions would have to be taken in a practical process in order to maintain a low content of oxidized copper minerals in the feed.

In these experiments with a content averaging 1.6% CuO it was observed that complete extraction of MoS$_2$ could only be obtained with a consumption of at least 400% the theoretically required. Similar hypochlorite consumption was reported by K.A. Shapiro et al. [9] for the leaching of a low molybdenum intermediate concentrate. No explanation was given of this excessive consumption, however the concentrate received a drying process similar to the one used in this work.

The explanation of this great NaOCl consumption is that the copper oxide formed on the surface of CuFeS$_2$ during drying acts as a catalyst in the decomposition of the reagent, accelerating the rate of decomposition to a value similar to the rate of MoS$_2$ oxidation.

The result of maintaining the rougher concentrate in a pulp to minimize contact with the air, reduced the hypochlorite consumption considerably. In the experiments with a copper oxide content of 0.52% total recovery was obtained with only 150% of the theoretically required hypochlorite.

If a leaching process is incorporated immediately after the primary flotation, it should be possible to control the oxide content below 0.5% securing the low reagent consumptions obtained in these batch experiments.
5.4 Flotation of Leached Rougher Concentrates

As the surfaces of the component minerals (noticeably CuFeS$_2$ and FeS$_2$) in the copper rougher concentrate are oxidized during the hypochlorite leaching of molybdenite, it was necessary to determine if the rougher concentrate could be refloated economically in the secondary flotation in order to obtain the final concentrate.

The results shown in Figure 29 indicate that the leached rougher concentrate still has a similar recovery-grade correspondence as the non-leached material, the difference is in the consumption of collector. In these experiments in which the same collector was used for both materials, the net addition for the secondary flotation would be 2 kgms/ton of concentrate. The cost of the extra collector dosage is very small compared to the molybdenum recovered [38]. It is also necessary to indicate that experimentation with other reagents more specific to oxidized sulfide surfaces could decrease this cost even more.

The information gathered is sufficient to indicate that the leaching of copper rougher concentrates with NaOCl does not decrease to a great extent the flotability and that the additional costs of flotation reagents if a leaching circuit were introduced to a conventional concentration process might not be significant.

5.5 Production of Sodium Hypochlorite

A process designed to extract molybdenum from copper rougher concentrate using NaOCl would require that the reagent be produced in-situ. Purchasing, transporting and storing either sodium hypochlorite or the
reagents required for its direct production, chlorine and caustic most likely would render the process uneconomical.

Not considering any side reactions nor decomposition of sodium hypochlorite, the consumption of this reagent as indicated by stoichiometry of the reaction between MoS$_2$ and NaOCl is 7 kg per kg of Mo extracted. The price of purchased NaOCl is between 20 and 32 cents per kg which would allow a narrow margin under the price of contained Mo which is approximately 3 $/kg.

Sodium hypochlorite is produced by reacting chlorine and sodium hydroxide, both these reagents are generated simultaneously by electrolyzing a sodium chloride brine.

There are two alternatives in the selection of electrochemical cells for on-site generation of sodium hypochlorite based on the separation of the anodic and cathodic compartments. They are the diaphragm and the membrane cells. Diaphragm cell technology has been employed for many years in the production of chlorine while the membrane technology has been commercially proven only in small scale.

There are no significant differences in current efficiency between these two processes [48]. The advantages of the membrane cell are a higher concentration of NaOCl and better salt utilization.

In both cases the chlorine formed at the anode is separated from the depleted brine and hydrogen is removed from the caustic formed in the cathode compartment. Chlorine and caustic immediately combine in the reactor to form sodium hypochlorite following the reaction

\[
2 \text{NaOH} + \text{Cl}_2 \rightarrow \text{NaOCl} + \text{NaCl} + \text{H}_2\text{O}
\]  

(23)
The possibility of forming NaOCl directly in the cells by carefully controlling conditions to maintain some secondary reactions that produce NaOCl is not economically practical because solutions produced this way have a low concentration of NaOCl and the electrical efficiency is low.

The operating costs of a hypochlorite generator depend principally on the salt utilization and the power consumption.

The theoretical consumption of NaCl is 1.6 Kg per kg of NaOCl produced. In membrane cells salt utilization can reach 80% of the total NaCl fed to the process.

The minimum values for current and voltage are 755 amp hr per kg of chlorine and 2.15 volts per cell.

Data from operating on-site generators of hypochlorite for the treatment of water [39] indicates a consumption of 3.52 Kwh and 2.1 kg of NaCl per kg of NaOCl produced.

Projected costs for a plant producing NaOCl at a rate of over 500 kg/day with the assumptions stated in Table 9 is about 12¢/kg which is between 1/2 and 1/3 of the purchased price.

### Table 9

<table>
<thead>
<tr>
<th>Economic Assumptions for the Estimation of Costs in the Operation of a Hypochlorite Generator [39]</th>
</tr>
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<tbody>
<tr>
<td>1) power charge including demand charge = 2.8¢/Kwh</td>
</tr>
<tr>
<td>2) salt (standard grade) bulk delivery = 15$/Ton</td>
</tr>
<tr>
<td>3) process water - negligible</td>
</tr>
<tr>
<td>4) labor = 5.71 $/hr</td>
</tr>
<tr>
<td>5) length of amortization = 20 years</td>
</tr>
<tr>
<td>6) interest = 5%</td>
</tr>
</tbody>
</table>
It is possible to compare the power consumption between this process and the extraction of molybdenite by electrooxidation, although the data for the later was obtained from leaching a low grade molybdenite ore in which the content of Cu was only 0.01% and therefore the consumption of hypochlorite due to catalytic decomposition should be expected to be negligible.

To arrive at the power consumption of this process it has been estimated that total recovery from a copper rougher concentrate can be achieved with 160% of the theoretical amount or 11.2 kg NaOCl/kg of Mo and that the power ratio is 3.52 kwh/kg of NaOCl. Therefore:

Power consumption estimated for this process = 40 kwh/kg molybdenum
Power consumption obtained in electrooxidation process = 53 kwh/kg molybdenum

5.6 Kinetics of Sodium Hypochlorite Decomposition

The process by which sodium hypochlorite solutions decompose has been studied extensively. It is known that the reaction can be spontaneous and catalyzed even in slightly alkaline solutions. The products of reaction are chlorides, chlorate and oxygen. However the mechanisms remain controversial principally due to analytical difficulties.

The reactions that most generally describe the decomposition of NaOCl solutions are:

\[ \text{HClO} + 2 \text{OCI}^- \rightarrow \text{ClO}_3^- + 2 \text{Cl}^- + \text{H}^+ \] (24)
Reactions (24) and (25) represent the same process, when the solution is alkaline OCl⁻ predominates and it will follow (24), when the solution is acidified it follows (25).

As there was no agreement with respect to the order of the reaction nor with regard to rate constants, it was not possible to determine theoretically the rate of decomposition for variations in such variables as pH and temperature. Therefore a few experiments on decomposition were performed to establish the region in which the reagent could be used safely.

The NaOCl used was the same as that used in some leaching experiments, it had been generated in the same experimental cell as all the NaOCl solutions used in this work and could differ from other batches in the concentration of chloride. No purification was performed before the decomposition reactions.

The rates obtained from Figure 32 were plotted on a double logarithmic plot, log rate of decomposition in mg/l/min vs. log concentration of NaOCl in g/l. The results were a good fitting straight line with a slope of 2.5. This order is similar to the third order reported by several other workers.

As it is not the intention of this work to study the mechanism of NaOCl decomposition a brief summary of some of the most common papers in this subject is presented to indicate the wide variations in results and interpretations.
1. N.V.S. Knibbs and H. Palfreeman [40] suggested that the rate

\[ \frac{d \text{NaOCl}}{dt} = K [\text{HC}10]^2 [\text{OCl}^-] \] (27)

and that chlorate formed by the reaction

\[ \text{OCl}^- + 2 \text{HOC}1 \rightarrow \text{ClO}_3^- + 2 \text{H}^+ + 2 \text{Cl}^- \] (25)

with a fast reformation of HOC1 by

\[ 2 \text{OCl}^- + 2 \text{H}^+ + 2 \text{Cl}^- \rightarrow 2 \text{HOC}1 + 2 \text{Cl}^- \] (28)

2. M.W. Lister [41] and B.P. Nikolskii et al. [42]. Both agree that it is a second order reaction and corroborate earlier work by F. Foerster [50] that the reaction goes through the intermediate formation of chlorite, therefore ClO\(_3\)\(^-\) is formed in alkaline solutions by the reactions

\[ \text{HC10} + \text{ClO}^- \rightarrow \text{ClO}_2^- + \text{Cl}^- + \text{H}^+ \]

\[ \text{ClO}_2^- + \text{ClO}^- \rightarrow \text{ClO}_3^- + \text{Cl}^- \]

\[ \text{HC10} + 2 \text{ClO}^- \rightarrow \text{ClO}_3^- + 2\text{Cl}^- + \text{H}^+ \] (29)

3. J. D'ans and H.E. Freund [43] describe the formation of chlorate via the formation of a complex of two moles of HC10 and one mole of OC1\(^-\) followed by the rearrangement of the complex according to
a first order rate controlling reaction to form chlorate. No chlorite was found in their work which shows that it is a third order reaction.

4. H. Imagama et al. [44] also indicates a third order reaction, however the mechanism proposed is that HClO reacts with ClO₂⁻ liberating chlorine dioxide in the first step followed by a reaction between ClO₂ and OCl⁻ to form chlorate.

In such a complex system it is difficult to explain the 2.5 order obtained in this work, but as the experiments were performed with the reagent in the same conditions as was used in the leaching experiments, the rate constants obtained here are useful for comparing with rate constants for the leaching of MoS₂.

From the intercept of the lines on Figure 35 at log NaOCl = 0 it is possible to obtain the decompositions reactions rate constants k₃ for the different pH's at 50°C.

From this data it is possible to determine the effect of pH on the decomposition rates. At pH 8 the rate is 13 times the velocity at pH9, and at pH 7 the rate is 60 times faster than at pH 9.

An Arrhenius curve was plotted using the rates from the decomposition at pH 7 at the two temperatures experimented (60° and 35°C). The results show an activation energy of approximately 20 kcal.

With the information of the activation energy and the rate constants for the decomposition reaction it is possible to calculate the losses of hypochlorite due to decomposition for a wide range of operating variables.
FIG. 35 - LOG-LOG CURVES OF RATE OF DECOMPOSITION OF NaOCl VS. [NaOCl].

<table>
<thead>
<tr>
<th>pH</th>
<th>log k</th>
</tr>
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<tbody>
<tr>
<td>7</td>
<td>.18</td>
</tr>
<tr>
<td>8</td>
<td>-.48</td>
</tr>
<tr>
<td>9</td>
<td>-1.60</td>
</tr>
</tbody>
</table>
The decomposition rate constant was calculated for the operating conditions at which the rougher concentrate was leached, that is pH = 9 and T = 30°C. The value of $k_3 = 4.89 \times 10^{-3} \text{ (min}^{-1})$. Higher temperatures of leaching could be experimented in the future as it was observed that the maximum rates of decomposition of the reagent at these high pH's are slow in comparison to the rates of consumption of NaOCl in the reaction with MoS$_2$.

One example is presented in which the following conditions have been set:

- Initial Concentration of NaOCl = 50 g/l
- Weight of MoS$_2$ leacheable with this amount of NaOCl = 3.6 g
- If composed of particles -70 + 140 mesh the surface area = 1432 cm$^2$
- Operating pH = 9
- Operating Temperature = 50°C
- Volume of Reagent = 1000 cm$^3$

To calculate the decomposition rate:

$$\frac{d(\text{NaOCl})}{dt} = k_3 [\text{NaOCl}]^{2.5}$$

at pH 9 and 50°C \hspace{1cm} k_3 = 0.0251 \frac{1}{\text{min}}

$$\frac{d(\text{NaOCl})}{dt} = 0.0251 (15)^{2.5} = 218.7 \text{ mg/l/min}$$

The reaction rate is calculated as:
\[
\frac{d(\text{NaOCl})}{dt}_{\text{(Max)}} = \frac{D \times A \times C_{\text{NaOCl}}}{\delta \times v}
\]

\[
\frac{d(\text{NaOCl})}{dt} = \frac{2 \times 10^{-5} \times 1432 \times 15 \times 60}{10^{-3} \times 10^3} = 25.78 \text{ g/l/min}
\]

From this, it is possible to observe that the rate of consumption of NaOCl will be approximately 100x faster in the reaction step than in the decomposition one even at this high temperature. However, these results must be taken with care as they do not represent the influence of the catalysis of the copper oxide present in real situations.

5.6.1 Effect of Excess Chloride on the Decomposition Rates

The increase in the rate of decomposition of NaOCl with increases of the Cl\(^-\) concentration is now considered to be due to the increase in ionic strength of the solutions and not any direct participation of the chloride ion in the reaction [41,42,43].

Although [Cl\(^-\)] was not measured in the NaOCl solutions used, the influence of this variable is small compared to the ones already considered and as already mentioned the same solutions were used for leaching experiments and decomposition experiments.

5.6.2 Effect of Cations on Decomposition Rates

The decomposition rate depends considerably on the cation of the alkaline solution. The order of stability of hypochlorite solutions of different base has been found to be [46].
5.6.3 Catalytic Agents in Hypochlorite Decomposition

When a NaOCl solution has been purified from catalytic agents, reactions (24) or (25) contribute much more than reaction (26) in the decomposition of the solution.

The platinum group metals have been reported to catalyze both reactions and the mechanism of decomposition in the presence of metallic catalysts has been claimed to be identical to the spontaneous reaction [45].

Oxides of heavy metals (Co, Cu and Ni) are also known to catalyze NaOCl decomposition. It has been shown that copper oxide does not affect the reactions leading to \( \text{ClO}_3^- \) formation, instead copper and nickel oxides strongly catalyze reaction (26) accelerating the formation of oxygen [41].

Normally the formation of oxygen and chlorate take place in parallel [46, 47] and it was found that the amount of \( \text{ClO}_3^- \) formed increases with the amount of oxygen evolved. The maximum evolution was observed in an acid medium [47]. Again this point is contradictory and M.W. Lister [41] and I.E. Flis et al. [47] found that substances that produce great increases in \( O_2 \) production do not increase \( \text{ClO}_3^- \) formation.

In this area the work performed was limited to the observation that in the process of leaching with hypochlorite solutions, copper minerals form a coating which consists of copper oxide and that this compound was responsible for excessive losses due to its catalytic action. No attempt was made of establishing a quantitative influence.
5.7 Hypochlorite Leaching Process for the Extraction of Molybdenite From Copper Rougher Concentrates

The experimental work has established that molybdenite can be selectively leached from copper rougher concentrates without significant changes in the flotation properties of the copper sulfide minerals.

On this basis, a process is proposed for the application of this technique to the extraction of molybdenum. The flow-sheet in Figure 36 shows the position of the leaching process in the copper concentration plant.

The molybdenum extraction should be included immediately after the primary flotation operation. This will ensure that no more than 15% of the total Mo in the ore will be lost and prevent oxidation of the copper minerals.

The leached rougher concentrate is washed and returns to the copper flotation circuit before the regrinding stage in preparation for the secondary cleaning flotation.

A schematic flow-sheet for the molybdenum extraction process is presented in Figure 37. The fundamental unit operations are:

1) Hypochlorite generator
2) Leaching
3) S/L Separation
4) Molybdenum recovery

Sodium hypochlorite should be of high concentration (20-30 g/l) when emerging from the hypochlorinator since it will be diluted when contacted with the concentrate slurry. Due to the high velocity of the
Cu-Mo Ore

Size Reduction

Primary Flotation

Cu Rougher Concentrate

Hyochlorite Leaching Process

Regrinding

Molybdenum & Rhenium

Secondary Flotation

Copper Concentrate

Fig. 36 - Position of Proposed Leaching Process in the General Cu Concentration Flowsheet.
FIG. 37 - FLOWSHEET OF THE PROPOSED METHOD FOR EXTRACTING MoS₂ FROM COPPER ROUGHER CONCENTRATES.
leaching reaction, the reagent will be added directly to the leaching reactors. The addition of caustic for pH control will also be added to the reactors.

Residence time in the leach section for a 40% slurry was determined experimentally as 7-10 minutes, and the amount of alkali needed for maintaining the pH in the narrow region 9.5 to 8.5 was between 3.0 and 3.5 g/l when the rougher concentrate has 0.3% Mo.

A recycle circuit is included in order to build up the concentration of molybdenum. The amount of cycles will be determined by the maximum tolerance of $\text{SO}_4^{2-}$ in the electrolytic cells.

Calcium, magnesium and sulfate ions are detrimental in the brine electrolytic cell as they precipitate on the diaphragm or membrane [48]. It will be necessary to include a $\text{SO}_4^{2-}$ removal operation in any recycle circuit.

The solution containing NaCl free of $\text{MoO}_4^{2-}$ and $\text{SO}_4^{2-}$ must be concentrated in order to be recycled as an anolyte. This would require an evaporation stage. The economics of recycling the leaching solution to minimize salt consumption requires further study. For cost estimates of the process, total salt has been considered without any recycling.

A major problem of this process is the molybdenum recovery from solution. The concentration of $\text{MoO}_4^{2-}$ would be low due to the recycling problems already outlined. Instead chlorides and sulfates will be high. This subject will have to be studied in future investigations.

The ideal process would require that molybdenum be removed from alkaline solutions. A literature search has shown that almost all molybdenum recovery processes using either solvent extraction or ion
exchange are worked on acid solutions. This would be undesirable in the proposed flowsheet because of the acid consumed in the pH adjustment for extraction and alkali addition for recycle.

It has been reported that Aliquat 336, a quaternary amine is capable of extracting MoO$_4^{2-}$ ions from alkaline solutions although with a decreased loading capacity [49]. However this reagent would not be appropriate to the process because its loading capacity is decreased by the presence of Cl$^-$ ions in alkaline solutions.

A few attempts were made (in our work) of reducing MoO$_4^{2-}$ ions in alkaline solutions without success. The reducing agents experimented were sodium dithionate, sodium formaldehyde sulfoxylate and hydrazine.

From the present information it appears that Mo would have to be recovered from acid solutions. This alternative can be accomplished either by ion exchange, solvent extraction or hydrogen reduction.

On the basis of simplicity of operation and availability of hydrogen from the electrolytic cell the later option has been selected and included in the flowsheet with the consideration that further studies are required. The disadvantage that hydrogen reduction has over the other two options is the difficulty in separating rhenium, which because of its chemical similarity will likely follow molybdenum in the extraction.

The consumption of acid was measured by adding sulfuric acid to solutions of sodium hypochlorite at an initial pH of 9.5 and lowering the pH to 4 and 3. It was observed that there was a difference of consumption in relation to the concentration of molybdate ions. Therefore two concentrations were used at 1 and 4 g/l of Mo. The information is presented in Table 10.
Table 10
Consumption of Acid in the Reduction of pH of Molybdenum Containing Hypochlorite Solutions

<table>
<thead>
<tr>
<th>Consumption of Acid (as concentrated H₂SO₄)</th>
<th>Reduced to pH 4</th>
<th>Reduced to pH 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 g/l Mo-pH 9</td>
<td>.41 ml/1000 ml</td>
<td>.50 ml/1000 ml</td>
</tr>
<tr>
<td>4 g/l Mo-pH 9</td>
<td>1.54 ml/1000 ml</td>
<td>1.81 ml/1000 ml</td>
</tr>
</tbody>
</table>
Chapter 6

CONCLUSIONS

1. The reaction between MoS$_2$ and NaOCl is first order in hypochlorite.

2. The apparent activation energy is 6.3 kcal/mole.

3. This reaction was probably controlled in these experiments by either chemical or mixed diffusion and chemical reactions.

4. The reaction rate constant was estimated as $1.90 \times 10^{-2}$ min$^{-1}$ cm$^{-2}$ at pH9 and 45°.

5. Sodium hypochlorite is capable of selectively leaching molybdenite from chalcopyrite.

6. Minerals accompanying molybdenite in the copper rougher concentrates form protective coatings which prevent any significant dissolution. In the case of CuFeS$_2$, this layer was described as a solid solution of CuO - Cu(OH)$_2$.

7. The presence of CuO is undesirable in the feed to the hypochlorite leaching system because it is a catalyst in the decomposition reaction of this reagent.
9. The rates of decomposition of NaOCl are negligible when compared with the rate of reaction with molybdenite when the solution is at pH 9 and ambient temperatures.

10. The consumption of NaOCl from copper rougher concentrates can be kept as low as 1.6 times the stoichiometric consumption of the molybdenite present if the concentrate is not allowed to oxidize before leaching.

11. With the information gathered a flowsheet has been proposed for the application of this method. The general concept is that leaching of molybdenite be accomplished immediately after the primary flotation in the copper concentration plant, using NaOCl as the reagent which has been produced by an on-site generator and that molybdenum be recovered by a hydrogen reduction procedure.
Chapter 7

SUGGESTIONS FOR FUTURE WORK

This study has opened up several areas of work that could be usefully pursued:

1) Hydrogen reduction of molybdenum from solutions with high concentrations of chlorides and sulfates such as would be obtained from the hypochlorite leaching operation.

2) Recirculation of loaded solution through the electrolytic cell to obtain better salt utilization. This study would also determine the allowable concentration of detrimental ions and what type of pre-treatment is required.

3) Flotation of copper concentrates from rougher concentrates which have been slightly oxidized by hypochlorite.
REFERENCES


