

DEVELOPMENT OF A MATHEMATICAL MODEL OF
A MOLYBDENITE LEACHING PROCESS

by

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to the required standard

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ABSTRACT

A mathematical model has been developed for the more critical section of a proposed molybdenite/nitric acid leaching process. The model accounts for the unit operations of leaching, grinding and flotation, with the leaching simulation involving the most rigorous formulation. The accuracy of the model could not be evaluated at this stage owing to the lack of an operating pilot- or commercial-scale plant.

Simulation of leaching is based on mass balancing with determination of reaction rates from the individual components of the rate equations. The rate of leaching of molybdenite is accounted for as a function of solution reactivity, active surface area per reference weight, pulp density and temperature. The leaching of contained pyrite and chalcopyrite are similarly accounted for but in a more simplified manner. The grinding model is based on a combination of theory and empiricism while the flotation model is derived from the simple first-order rate equation.

The simulation is still subject to some uncertainty since verification is not possible at this stage of process development. However, the model effectively accounts for the complex system

involving a solids recycle stream. The effects of new solids flow and analysis, leachant flow and strength, leaching temperature, partial flotation bypass, leaching vessel size and number, grinding mill size, number and size of flotation cells are all considered.

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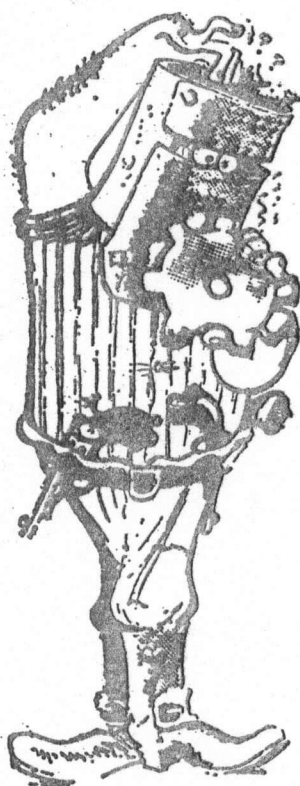
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"So You want to be a Metallurgist!"

CHAPTER 1

INTRODUCTION

1.1 General

The complete quantitative description of an industrial process is often quite complex. However, the expansion in computer facilities has enabled the formulation of numerous types of mathematical models which can contain much of this complexity and provide a reasonably realistic analysis. Computerized mathematical models provide an economical means for design or for simulation of processes and may be used either in a predictive capacity, or interactively with the process to attain efficient control. Once the model is sufficiently well developed to establish reliability it may be used with confidence to determine the consequences of changes in operating variables without risking the expense of pilot- or plant-scale experiments.

Mathematical models are developed to varying degrees of sophistication depending on the state of knowledge of the process and the initial aims for the formulation. The development may be restricted by the accuracy with which the influencing variables

can be measured thus resulting in a range of models from relatively simple simulations with numerous broad assumptions to more complex descriptions which account for many process variables.

The process of model building generally follows a stepwise development as outlined by Himmelblau [1]. A highly idealized, and hence simplified, mathematical description is initially formulated. This may result in an unrealistic model but provides a basis for analysis of deficiencies and for construction of more realistic models.

The purpose of this study was to establish a metallurgical simulation model for a proposed molybdenite/nitric acid leaching process. The approach to formulation was dictated by the fact that no industrial-scale or pilot-scale plant was in existence. Hence the model was based on available theory, laboratory experimentation, analogies to other systems and plausible assumptions where information was lacking.

The section of the process modelled in the study involved a number of unit operations. Varying degrees of emphasis were placed on the modelling of these different units with the ultimate aim of formulating a satisfactory computer simulation within reasonable limits.

1.2 Model Classification

Mathematical models may be classified into two types on a time basis:

1. Steady state - where the process properties are time invariant at any particular location and accumulation terms are equal to zero. This applies to uniform operations after the effects of parameter variations or fluctuations have come to consistent levels.
2. Dynamic - where the model describes the changing state of the system. That is, process properties at any particular location may vary as a function of time.

The dynamic simulation may be more versatile but it is more difficult and hence more costly to develop. Its formulation therefore requires greater justification than for a steady-state simulation. Often the development of a steady-state model precedes the development of the dynamic model in accordance with the stepwise construction of more realistic simulations.

At this stage of development of the molybdenite/nitric acid leach only a steady state model is required for the prediction of plant behaviour under steady operating conditions. Dynamic modelling

may be considered when a commercial plant is in operation.

Mathematical models may also be broadly classified into two extremes on the basis of the method of formulation:

1. Fundamental or mechanistic models - which are based on known or assumed mechanisms for the process. This enables a relatively complete characterization but may require considerable time and effort to develop. Since there is a reasonable understanding of the mechanisms involved these models may be applicable over wide ranges of operations, provided that there are no changes in mechanism. Although based on fundamentals, numerous industrial models of this type require empirical or semi-empirical corrections to achieve satisfactory agreement between predicted and practical results.
2. Empirical or statistical models - which rely on analysis of experimental or operating data. Completely empirical models rely on the determination (or fitting) of operating relationships in terms of measurable variables for the actual plant units. Although the fitting of relationships is based on statistical analysis the form of the equations may be influenced by some fundamental or practical knowledge of the process. This form of simulation may be a simpler and less expensive approach particularly where the governing theories have not been developed to a sufficient degree. As a consequence of the method of formulation empirical models are generally applicable only over the

the ranges of operating variables within which the model was determined. The resulting relationships are usually valid only for the process units on which they were determined. Even units superficially of the same size and configuration may vary in their operational behaviour due to subtle differences in construction and operation.

Himmelblau [1,2] considers a third category termed population-balance models which include residence-time distributions and other age distributions.

In the case of the molybdenite leaching process the lack of an operating plant prevents the construction of a purely empirical model with equation coefficients determined from the results of plant experimentation. For leaching, the lack of established theory and the nature of this heterogeneous process prevents the formulation of a purely fundamental model. A similar argument applies to the other unit operations in the leach cycle. As a consequence, this process was simulated by a combination of empirical relationships determined experimentally or by analogy and by some fundamentals such as chemical reaction theory.

1.3 The Process

The proposed hydrometallurgical process for the production

of high grade molybdc oxide from molybdenite concentrates was based on a twelve month period of research during 1974-75 at U.B.C. by E. Peters and A. Vizsolyi. The experimental program and results were presented in a series of monthly reports with the tentative design for a 10 ton per day plant outlined in report No. 12 [3,4]. The possibility for such a process had been demonstrated in earlier unpublished work at U.B.C. by Peters and Vizsolyi [5].

The process flowsheet was modified slightly for the modelling study, as shown in Figure 1. It must still be considered that this flowsheet design is not necessarily the optimum that could be used for the process. However, it is this flowsheet which is modelled with the objective of determining the potential of the nitric acid leaching process with a recycle solids stream. The flowsheet is based on the required operations so that there is some flexibility on the choice of actual units to perform these functions.

The complete process can be described as follows:

(i) Leach Section

Both the new and refloated concentrates are treated for the removal of the flotation oils to prevent potential frothing and increased nitric acid consumption within the leaching vessels. The

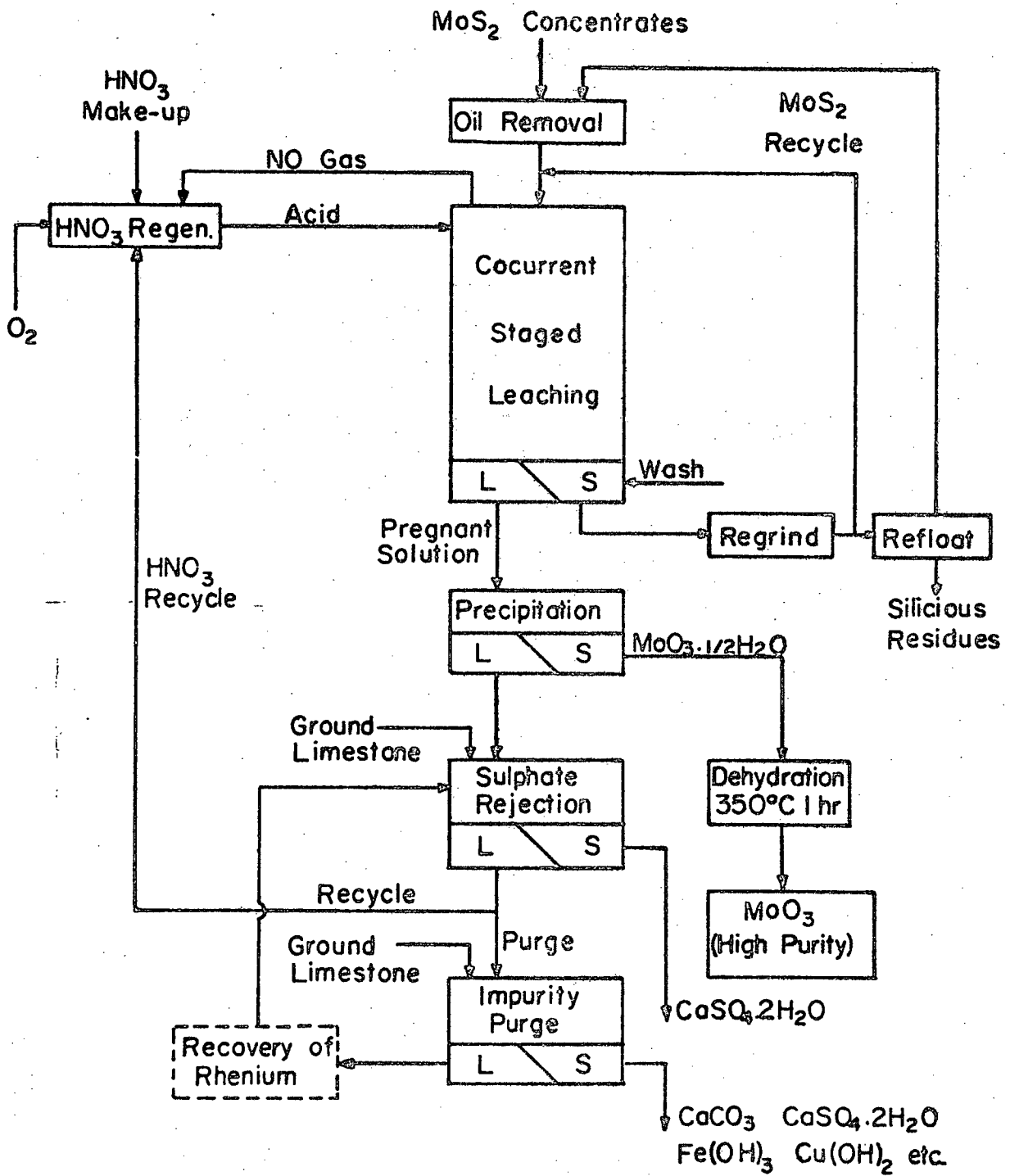


Figure 1. Process flowsheet used for modelling study.

combined solids are then subjected to cocurrent multistaged leaching with nitric acid at temperatures not exceeding about 40°C. Although counter-current leaching would maintain a maximum driving force for molybdenum dissolution cocurrent leaching has been considered for the model to eliminate repeated phase separations required by the former method. Also, the recycling of unleached solids avoids the criterion of attaining high degrees of extraction on a single pass through a leaching train. The slurry is well mixed in any leach stage either by mechanical means in agitator vessels or by NO lifting gas in pachuca vessels.

The slurry exiting the final leaching stage is filtered and washed, with the filtrate passing on to the precipitation section. The filtered solids are repulped and fed to a continuous grinding mill to reactivate the partially leached solids by creating new active surface area. The reactivated solids are then split with a portion passing directly back to the leach train after filtering and the remainder passing on to the flotation section. In reality some form of classifying stream splitter may be more advantageous, possibly in a closed loop configuration in the flowsheet. However, the aim in this section was to determine the level of insoluble elimination in order to maintain satisfactory insoluble levels within the leach.

The reflation section is designed to reject a considerable

portion of the insoluble content into a low molybdenum tailing. The refloated concentrate is then passed back to the leach after filtration and deoiling.

(ii) Precipitation Section

The pregnant solution is heated to about 80°C to precipitate molybdenum as $\text{MoO}_3 \cdot \frac{1}{2}\text{H}_2\text{O}$. The precipitate is in a fibrous form and is thus quite readily filtered. Scanning electron microscope photographs of typical molybdenite concentrate and the molybdic oxide hemihydrate product are shown in Figures 2 and 3. MoO_3 is produced by relatively low temperature calcination of the hemihydrate.

(iii) Solution Purification

Before recycling, the solution must be purified by partial elimination of impurities built up in the leach. The major aqueous by-product of the leach is the sulphate ion. This can be reduced to low levels by the addition of calcium ions in some form to precipitate gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$). The soluble impurities, particularly iron and copper, are not removed by the purification step. To eliminate these a portion of the low sulphate solution is purged and treated separately. The purged and purified solution is then recycled to the sulphate rejection step. Rhenium may also be recovered

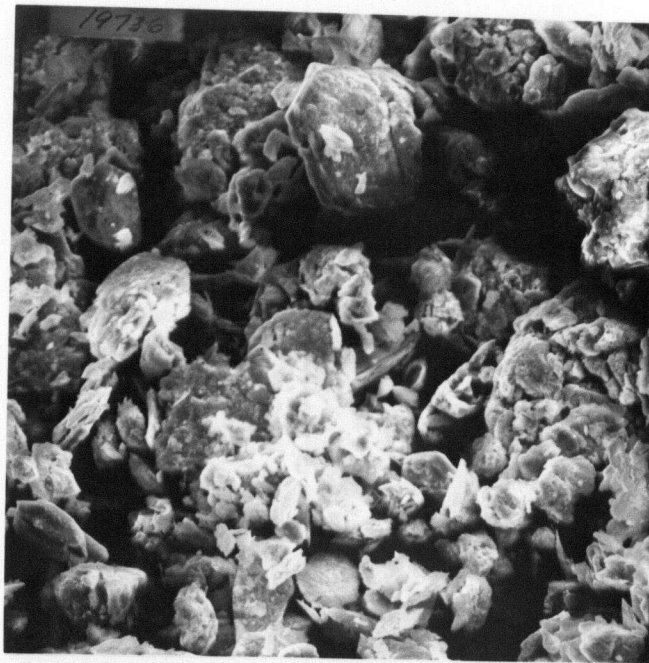


Figure 2. Endako molybdenite concentrate (600x)

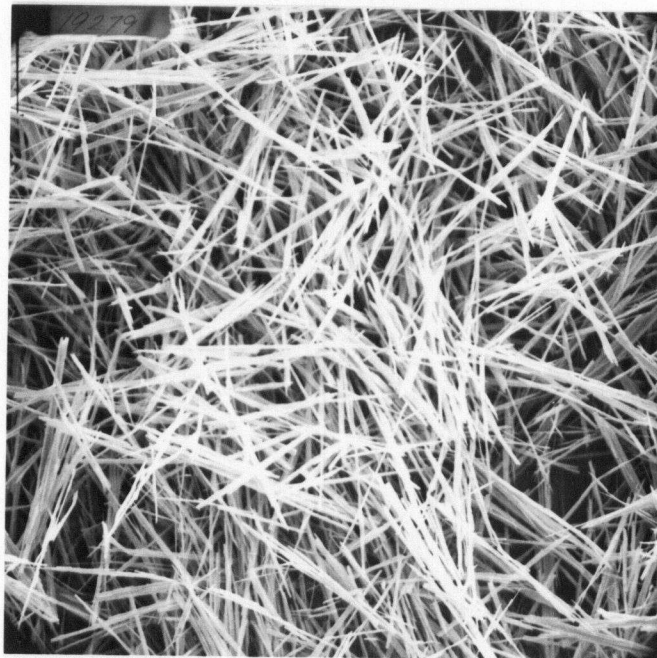


Figure 3. Precipitated molybdic oxide hemihydrate ($\text{MoO}_3 \cdot 1/2\text{H}_2\text{O}$) (400x)

from the purge recycle solution.

(iv) Acid Regeneration

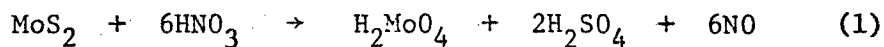
Nitric acid is regenerated by conventional methods using nitric oxide from the leaching reactions together with oxygen and recycle solution.

1.4 Process Chemistry

1.4.1 Leach Chemistry

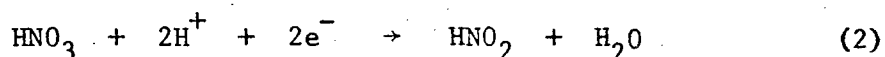
Nitric acid can dissolve molybdenum from molybdenite at slow to moderate rates at temperatures not exceeding about 40°C. At temperatures greater than 40°C the rate of leaching is considerably enhanced but the simultaneous precipitation of $\text{MoO}_3 \cdot \frac{1}{2}\text{H}_2\text{O}$ becomes appreciable. Precipitation of molybdenum in the leach must be avoided as it is not recovered from the leach residue.

The overall reaction can be represented by the following balance:



Equation (1) represents an overall balance only and does not necessarily describe the correct form of all the species present. Although the initial unused nitric acid may contain nitrogen essentially in the form of nitrate ion the recycle solution or solution after reaction has proceeded may contain other nitrogen species such as the nitrite ion. The mechanism of reaction may therefore be quite complex. It is possible that other nitrogen species may be more reactive to the mineral than the nitrates. Figure 4 shows the Eh - pH relationship for the nitric and nitrous species under acid conditions. The slightly higher oxidizing potential of the nitrites over the nitrates result from the diagram being drawn for "standard states", ie. soluble component concentrations of one mole/litre and gas component pressures of one atmosphere. It would not be thermodynamically possible for the concentration of nitrous acid to build up to one mole/litre; in fact, its concentration would be limited to that at which its oxidation potential just equals that of the residual nitric acid.

A possible sequence of leaching involving nitrous acid as the main reactive component for molybdenum dissolution can be outlined [6]. Nitrous acid may be formed as an initial reduction product in nitric acid solutions by reaction (2).



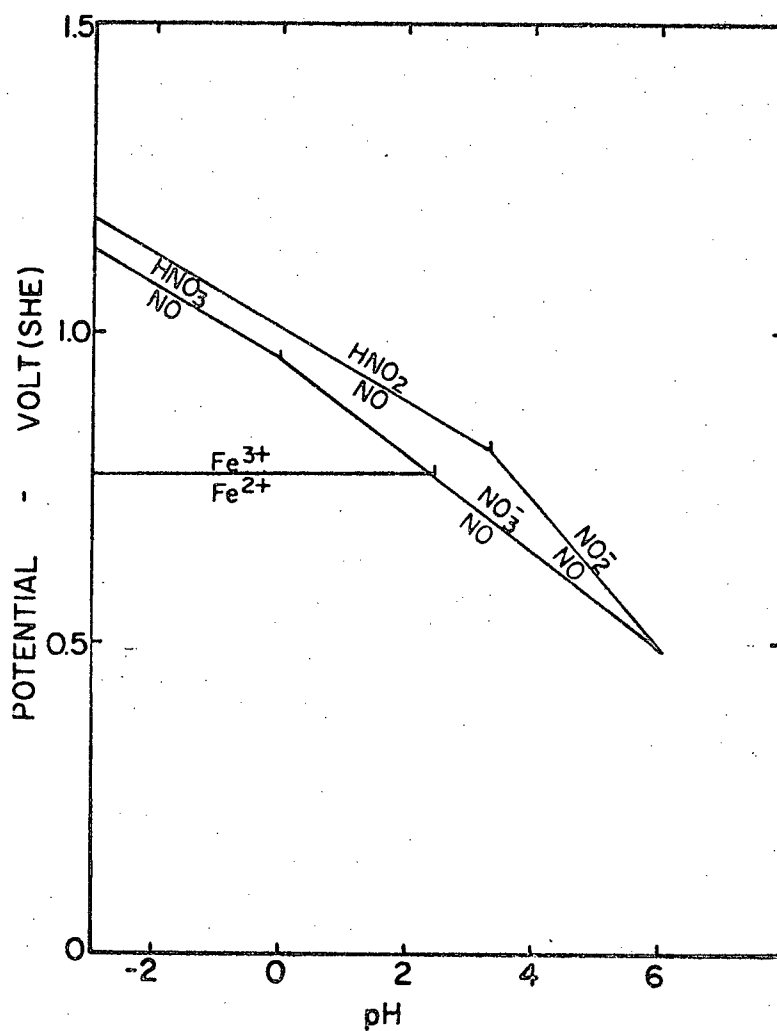
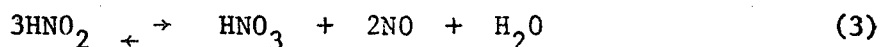
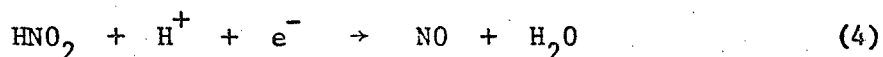


Figure 4. Eh-pH relationship for nitric and nitrous species in acid solutions. Basis- one mole/litre in solution and one atmosphere pressure.

The electrons in Equation (2) are supplied by oxidation of the mineral. The nitrous acid will tend to equilibrate with nitric acid and nitric oxide gas by the reversible reaction of Equation (3)

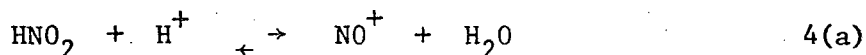


The nitrous acid could react by Equation (4) with the electrons again supplied by oxidation of the mineral.



The nitric oxide produced by Equation (4) would enhance the stability of nitrous acid by pushing reaction (3) to the left although this would ultimately be determined by the total pressure in the system, assuming that nitric oxide is the only gas component other than water vapour.

The nitrosyl ion ($\text{NO}^+_{(\text{aq})}$) has been suggested as a highly reactive sulphide oxidant [7]. It is however, only an ionization product of HNO_2 due to the presence of a strong acid (ie. HNO_3 and H_2SO_4 in this case), as shown in Equation 4(a)



Thus, any special reactivity of the NO^+ ion would show up at strong acidities and high HNO_2 concentrations, as when nitrogen dioxide is sparged directly into the system.

The overall balance of Equation (1) represents the dissolved molybdenum as molybdic acid (H_2MoO_4) but its exact form in solution is uncertain. The precise ionic form is also a function of pH. Above a pH of about 6 (ie. outside the range of this process) the molybdenum is present in solution as the molybdate anion (MoO_4^{2-}). With increasing acid strength the molybdenum is predominantly present in other anionic forms such as bimolybdate (HMoO_4^-) and paramolybdate ($\text{Mo}_7\text{O}_{24}^{6-}$). At acidities exceeding the isoelectric point at a pH of 0.9 the molybdenum is in the form of cations with the most likely specie being the molybdenyl cation (MoO_2^{2+}) or its polymers [8]. The complex ion $[(\text{MoO}_2)(\text{MoO}_3)_{x-1}]^{2+}$ has also been suggested as the ionic form in strongly acid solutions [9]. The high solubilities of molybdenum attained under certain conditions are an indication that polymerization does occur. Table I shows the solubilities of molybdenum in various acid solutions as a function of time and temperature. The effects of acidity and temperature are clearly demonstrated. The results indicate that although precipitation can occur from saturated solutions at room temperature the kinetics of this process are extremely slow. Under the conditions of leaching it is likely that the molybdenum would

dissolve in a cationic form and remain in this form throughout the leach despite the consumption of nitric acid. Acid conditions are maintained to an extent by the production of sulphuric acid as

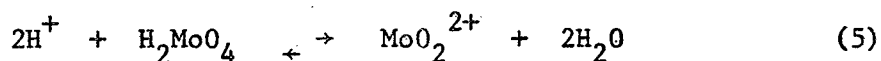
Table I
CONCENTRATIONS OF Mo^{VI} REMAINING IN
VARIOUS SOLUTIONS* g/l Mo^{VI}

Concentration	HNO ₃				HNO ₃ /H ₂ SO ₄		
	1N	2N	3N	4N	½N/½N	1½N/½N	1N/1N
24 hrs/24°C	1.1	52.1	95.5	121.0	1.4	78.7	79.0
48 hrs/24°C	-	-	90.0	-	-	-	-
96 hrs/24°C	-	-	75.7	-	-	-	-
2 hrs/55°C	-	-	9.9	-	-	-	-
4 hrs/55°C	-	-	8.1	-	-	-	-
24 hrs/55°C	0.5	1.6	3.4	4.9	0.7	5.3	7.7
2 hrs/80°C	-	-	3.8	-	-	-	-
4 hrs/80°C	-	-	2.7	-	-	-	-
24 hrs/80°C	0.5	1.4	2.0	2.6	0.5	2.7	7.2
24 hrs/boiling	0.5	1.2	1.8	2.3	0.5	1.7	6.5

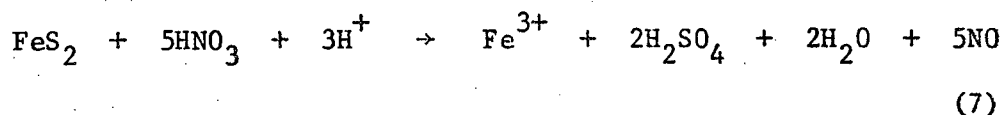
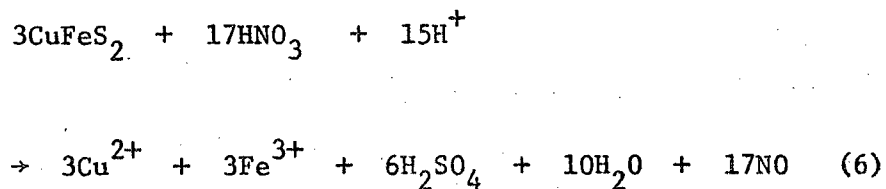
* After saturating with reagent grade H₂MoO₄

indicated in reaction (1). The acidity relationship becomes more

complicated when considering the degree of dissociation of the acid radicals and the form of molybdenum produced on dissolution. The latter point is demonstrated by hydrogen ion requirement in the formation of the molybdenyl cation. (Equation 5)



Other base-metal sulphides are leached by nitric acid but only chalcopyrite and pyrite are considered in this study as these were the major sulphide impurities in the concentrates studied. They are considered to leach by the overall stoichiometry of the following equations.



Initially all the sulphur may not be oxidized to sulphate as shown by Equations (6) and (7). The non-sulphate sulphur is present as elemental sulphur; the yield of which depends on the mineral, nitric acid

strength, temperature and time of contact. Of the two minerals considered only chalcopyrite can have an appreciable initial yield of elemental sulphur. Sulphur may dissolve directly by Equation (8)



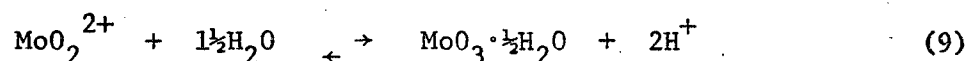
Molybdenite, particularly as a by-product from copper porphyries can contain significant quantities of rhenium. Since rhenium is in solid solution in the molybdenite crystals it dissolves quantitatively with molybdenum during the leach.

-1.4.2- Precipitation Chemistry

The pregnant solution from the leach is supersaturated with molybdenum since the kinetics of $\text{MoO}_3 \cdot \frac{1}{2}\text{H}_2\text{O}$ precipitation are immeasurably slow at operating temperature. At temperatures in excess of about 40°C the rate of precipitation becomes appreciable with close to complete possible precipitation occurring within 2 hours at 80°C (see Table I).

Complete precipitation of the contained molybdenum is not possible since there is a finite solubility in the acid solutions. This solubility will be at a minimum at the isoelectric point and will

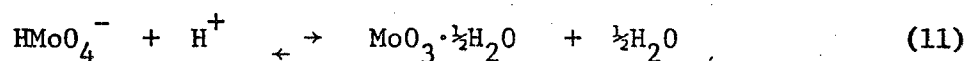
increase with changes in pH. The rate at which the solubility changes with pH will be dependent on the particular cations or anions in solution. The following equations and Figure 5 illustrate this point when considering only MoO_2^{2+} and HMoO_4^- as the ionic species. For precipitation from MoO_2^{2+} in solution the reaction is:



Given an equilibrium constant K_1 for this reaction the equilibrium solubility is expressed by Equation (10)

$$\log[\text{MoO}_2^{2+}] = -\log K_1 - 2\text{pH} \quad (10)$$

For precipitation from HMoO_4^- in solution the reaction is:



The corresponding solubility relationship for an equilibrium constant K_2 is then:

$$\log[\text{HMoO}_4^-] = -\log K_2 + \text{pH} \quad (12)$$

The solubility will always decrease with increasing pH for

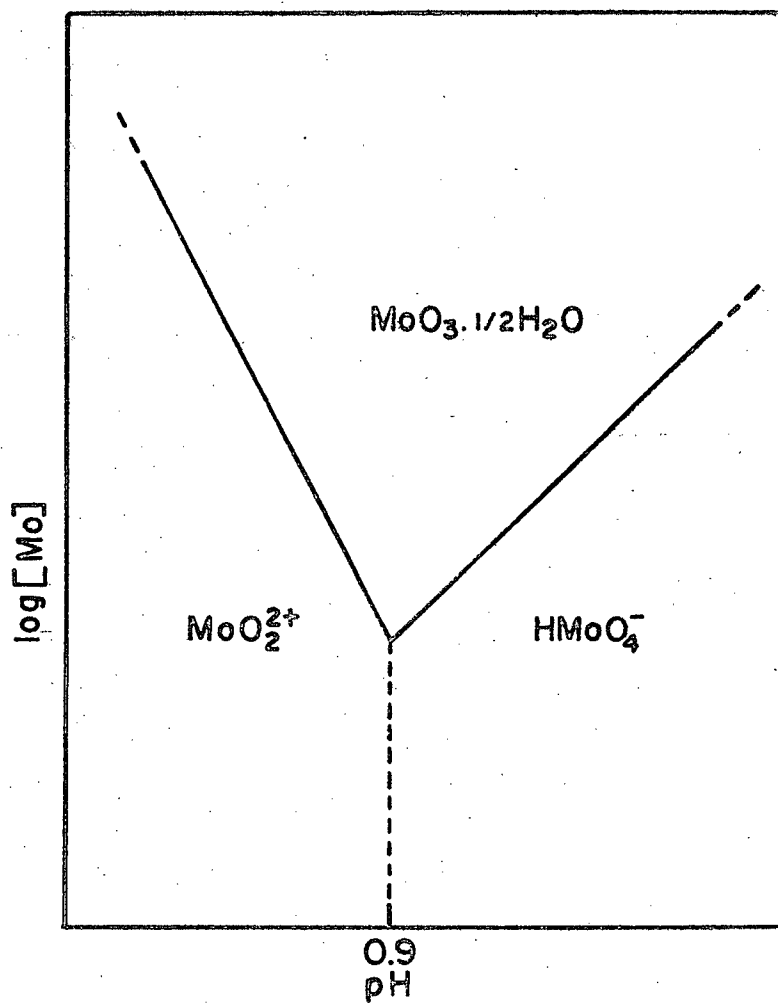


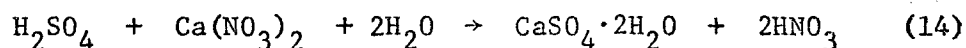
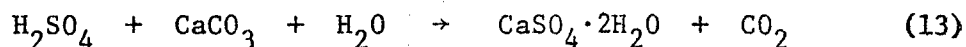
Figure 5. Solubility of molybdenum vs. pH in acid solutions.

cationic molybdenum and increase with increasing pH for anionic forms.

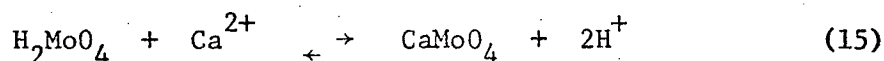
From the point of view of maximum precipitation the solution pH should be near that for the minimum solubility. This would lead to a minimum recirculating load of dissolved molybdenum but may not result in optimum leaching conditions.

1.4.3 Solution Purification Chemistry

Sulphate rejection to low levels is achieved by the addition of calcium ions to precipitate gypsum. Two equations are shown for adding calcium as limestone or externally produced calcium nitrate:



Elimination of sulphate is not taken to completion since the high levels of calcium ion in solution would lead to molybdenum losses to the precipitate by the following overall reaction:



To prevent the continual build up of impurities such as iron and copper in the recycle acid a minor portion of the solution exiting the sulphate rejection step is purged for further treatment. The purge treatment involves overliming to the extent that the soluble metallic impurities are precipitated as hydroxides along with the gypsum formed from the residual sulphate. The remaining solution is separated from the solids and recycled to the sulphate rejection stage to utilise the high calcium content.

The rhenium present in the leach liquor is unaffected by the precipitation or purification steps and is hence continuously recycled. This would allow a build up of a suitable rhenium concentration to allow possible recovery by solvent extraction or ion exchange [10,11].

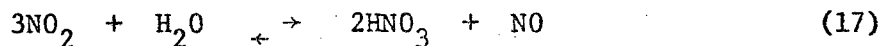
1.4.4 Acid Regeneration Chemistry

The nitric acid content of the recycled, purified solution must be regenerated for further leaching. Acid regeneration is achieved by oxidizing the nitric oxide evolved from the leach to form nitrogen dioxide which is then absorbed into the recycle solution as nitric acid. The following equations describe the overall reactions taking place.

Oxidation of nitric oxide:



Absorption of nitrogen dioxide:



The complete absorption chemistry is more complicated than Equation (17) suggests, consisting of a number of steps involving intermediate species. However, the detailed process need not be considered here.

1.5 Scope of Model

From the prior studies of the process [4] it was evident that leaching of molybdenite in nitric acid is relatively slow compared to other similar systems. A typical batch extraction curve for a molybdenite concentrate at an initial total pulp density of 126 g/litre of solution and 4 molar nitric acid concentration, shown in Figure 6, illustrates this aspect. High degrees of extraction cannot be obtained within reasonable time periods since the rate of dissolution becomes prohibitively slow after relatively low levels of extraction. An economic design requires sufficiently high rates of extraction while maintaining high recoveries of valuable product. This leads to the following design strategies:

1. Maximize reaction rates by operating at high pulp densities while accepting low degrees of extraction for a single

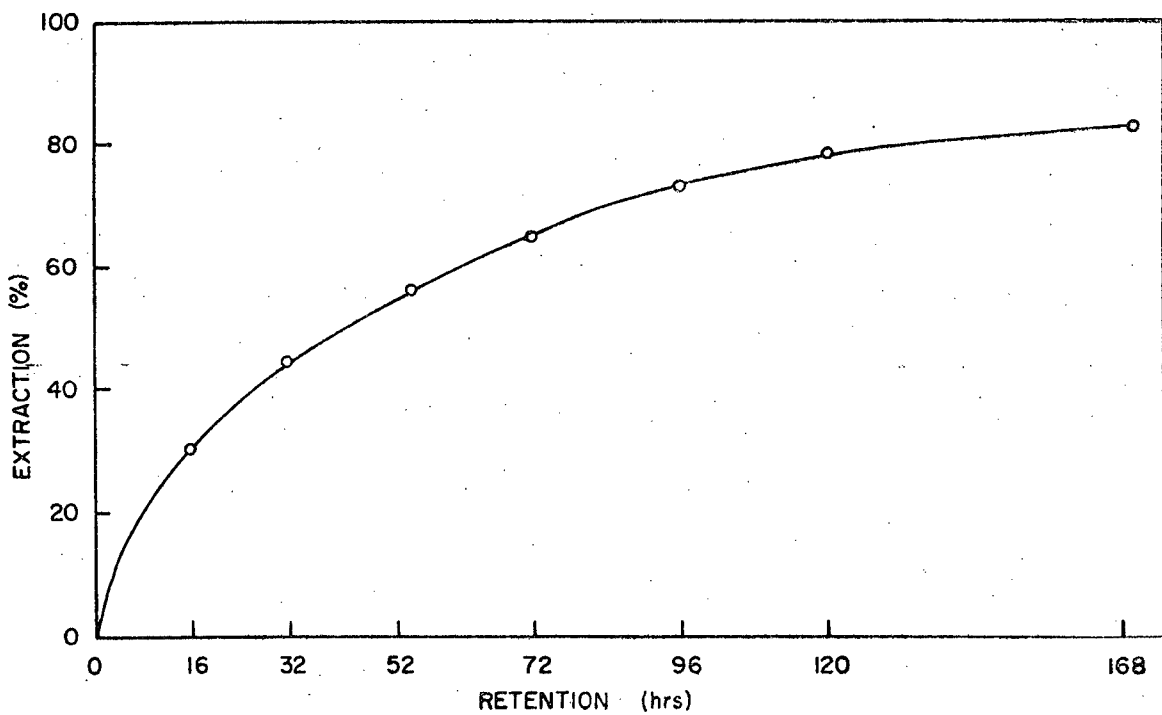


Figure 6. Batch extraction curve for Gibraltar molybdenite concentrate. 49.9%Mo, initial pulp density 126 grams/litre solution, initial 4M HNO_3 , ambient temperature, atmospheric exposure. [4]

pass through the leach.

2. Reactivate the leach residue by regrinding and partially eliminate the insoluble gangue by refloatation before recycling to the leach.

Examination of the overall flowsheet shows that the leaching section is the rate limiting step in the overall process. The kinetics of the other unit operations are considerably faster than those of importance in the leach. Hence any modelling effort should be concentrated on simulating the leaching section with the aim of maximizing the mass transfer of molybdenum from the solids to the solution, consistent with operations of the other sections of the process.

Since the leaching section involves a recycle solids stream the unit operations associated with that stream were also modelled. Greater emphasis was placed on the leach simulation with more simplified models being used for the regrind and refloatation units. Less critical units in the cycle such as filtration, washing and stream splitting were considered to operate ideally so that 100% efficiencies and negligible kinetic effects are assumed.

The limitations in available data for such a process that has not yet been developed on a pilot or commercial scale hinders

accurate simulation. Although considerable laboratory data was generated during the previous work [4], the experiments were not conducted with the intention of formulating a kinetic model of the process. This work demonstrated the feasibility of the process and allowed an overall approximation to possible plant behaviour for a particular flowsheet configuration. The use of the previous data in this kinetic simulation was also restricted by the fact that most of the previous experiments were conducted with atmospheric exposure. This allowed partial in-situ nitric acid regeneration which made accurate mass balancing of the nitric acid impossible. This phenomenon was shown by a high pulp density test in which more molybdenum was dissolved than could be accounted for by the stoichiometry of Equation (1).

1.6 Source and Supply of Molybdenum

Molybdenite is by far the most abundant molybdenum mineral and the only one presently of commercial importance. A small number of other molybdenum minerals do exist, some of which have contributed minor amounts to production figures in the past. Table II lists the chemical composition of a few of the molybdenum minerals. On an atomic scale molybdenite has a three-layered structure of a S-Mo-S form with strong covalent bonds between the sulphur and molybdenum

Table II

IMPORTANT MOLYBDENUM MINERALS AND COMPOSITION

Molybdenite	MoS_2
Molybdite (or Ferrimolybdite)	$\text{Fe}_2\text{O}_3 \cdot 3\text{MoO}_3 \cdot 8\text{H}_2\text{O}$
Powellite	CaMoO_4 (up to 10% W)
Wulfenite	PbMoO_4

The mineralogical properties of the dominant mineral, molybdenite are given in Table III [12].

Table III

MOLYBDENITE: MINERALOGICAL DATA

Crystal System	:	Hexagonal
Common Form	:	Massive, scales, granules
Cleavage	:	Perfect basal-flexible laminae
Colour	:	Lead-grey
Streak	:	Greenish lead-grey
Lustre	:	Metallic, opaque
Tenacity	:	Sectile
Hardness	:	1 - 1.5
Specific Gravity	:	4.7 - 4.8

atoms. The cleavage properties of molybdenite arise from the weak bonding between these S-Mo-S groups. The exposure of sulphur atoms on the plate surface give the mineral its hydrophobic properties and hence its natural floatability. This is not as dominant at the plate edges since at these locations both sulphur and molybdenum atoms are exposed to the environment and result in greater reactivity in aqueous solutions.

The sources and recovery of molybdenum have been outlined in a number of publications by Sutulov [13,14,15]. These references cover many aspects of the molybdenum-bearing deposits, their milling behaviour and conversion technology as well as the sources and recovery of rhenium.

Molybdenite may be found in a number of geological environments as follows [16]:

1. Porphyries including stockwork and breccia pipes
2. Contact metamorphic zones
3. Quartz veins
4. Pegmatites
5. Sedimentary deposits

Nearly all the known resources of molybdenum fall into one of the first three categories with porphyries being the most important.

Of the current recoverable world reserves of 4.5×10^9 kg roughly one half is found in primary molybdenum porphyries where molybdenite is the only economic mineral. The remainder is found mostly as a secondary mineral in copper porphyries and is mined as a by-product [17]. Although this source represents a major supply of molybdenum it is tied to the production of the major component and hence is subject to conditions of the copper market. Only in a very few cases is the molybdenum mined as a co-product where the value of molybdenum recovered is similar to the value of the copper. Small quantities of molybdenum have also been recovered from tungsten and uranium ores. Typical analysis ranges of the major ore types currently mined are outlined in Table IV.

Table IV

METAL CONTENT RANGES OF MOLYBDENUM ORES

Primary molybdenum porphyries	:	0.05 - 0.5% MoS ₂
Copper porphyries	:	0.01 - 0.05 MoS ₂
	:	0.4 - 1.8% Cu

Despite the uniformity of mineral type the metallurgical behaviour of molybdenum deposits varies quite widely. Recoveries

depend on the physical form of the molybdenite, the associated mineralisation and degree of oxidation. The mill recoveries from primary deposits can be quite high, in the order of 80 to 90 percent whereas recoveries from copper porphyries can range from as high as 75 percent to less than 25 percent.

Molybdenum morphology can vary from well crystallized with a large plate surface to edge surface ratio and hence good floatability to poorly crystallized forms with poor flotation properties. Although molybdenite is relatively stable to oxidation some surface alteration can occur in the more oxidized upper zones of ore bodies. The formation of molybdate minerals on the surface of molybdenite results in poorer milling recoveries.

The lower recoveries of molybdenite from copper porphyries results from the complicated mineralogy and the more extensive milling requirements. The usual associated sulphides are pyrite and chalcopyrite although some deposits contain high contents of secondary copper minerals such as chalcocite. Molybdenum is not only lost to the tailings stream but to the copper concentrate stream as well. With emphasis placed on the recovery of the dominant component, copper, the recovery of molybdenum in the bulk flotation concentrate may suffer. This compounds the losses involved in the selective flotation where generally molybdenite is floated while the copper mineralization is depressed.

Usually many cleaner flotation stages are required to produce an acceptable concentrate. However, further chemical treatment is often required to reduce impurity contents to satisfactory levels. This aspect is discussed in Section 1.8. The Russian philosophy differs from that of the West. The larger Russian plants produce a low grade concentrate, with associated higher recovery, and hydrometallurgically purify the roasted oxide.

Although molybdenite represents the only source of rhenium it is only recoverable from molybdenite extracted from porphyry coppers. The rhenium contents from by-product molybdenite usually range from 200 to 2000 ppm of MoS_2 while primary sources usually contain less than 80 ppm of MoS_2 . At current prices this can be an attractive economic by-product but overall recoveries are very low, in the order of 30%.

Geographically molybdenite production is concentrated in very few countries with the United States by far the most dominant. The 1976 production for the three leading non-communist producers is listed in Table V.

Table V

1976 MOLYBDENUM PRODUCTION OF LEADING COUNTRIES

(10⁶ KG CONTAINED Mo)

United States	50
Canada	14
Chile	9.5

These three countries are estimated to contain 75% of known world reserves. Small but significant production is accounted for by U.S.S.R. and the People's Republic of China. In the early 1970's very minor production was also reported from Peru, Japan, Bulgaria, Norway, Australia, South Korea and Mexico.

1.7 Economic Situation of Molybdenum

Over the last twenty years the price of molybdenum (as MoO₃) has been relatively consistent in terms of constant dollars [19]. The price in current dollars has risen considerably since 1973 so that the present price is favourable in terms of the increased production costs and the effects of inflation. The pricing stability arises in part from the localization of supply with the domination of a few large suppliers, particularly Amax, Inc. of the U.S. Despite

the current recession in many metal markets the molybdenum demand is expected to grow at a rate of 6 to 7 percent per annum due to its specialized application, mainly in alloy steels.

The future supply and conditions of supply will partly be dependent upon the supply/demand situation. At present world production is increasing and has further potential for increasing. However, in periods of short supply some speculation does occur with premium prices being paid for alternative sources. In such times the purity requirements of the molybdenite concentrate become less critical with final product purity maintained within the limits by some form of leaching or by blending with high grade material.

At the current North American price of \$US 4.01 per pound of contained molybdenum in sulphide concentrate (fob mine) there is considerable incentive for improved recoveries from ores. This is particularly so for by-product molybdenite where present recoveries may be quite low. With the roasted oxide selling price at \$US 4.31 per pound (\$US 9.49/kg) of contained molybdenum [20] it is imperative the treatment losses be kept to very low levels because of the small added value in relation to the material value.

1.8 Current Methods for Processing Molybdenite Concentrates

Most molybdenite concentrate undergoes roasting to molybdic oxide (MoO_3) although the overall process from molybdenite concentrate to final product may vary according to impurity contents and ultimate use. Penalties are usually charged to concentrate producers for impurity contents above specified minimum levels. In most cases standard penalties are applied to copper contents in excess of 0.1% in concentrate. Table VI lists the penalty scale for copper current in February, 1978.

Table VI

COPPER PENALTIES IN MOLYBDENITE CONCENTRATE

% Cu	Penalty ¢/lb Mo
0.1 - 0.6	5
0.61 - 0.80	6
0.81 - 1.00	7
1.01 - 1.20	10
1.21 - 1.40	13
1.41 - 1.50	15

Penalties exist for other impurities such as lead and bismuth but

these occur more rarely and are usually determined on an individual basis. The usual limit for these impurities is a maximum content of 0.05 percent. Gangue impurities have a greater influence on the molybdenum grade since they are usually present in greater proportions. These can be controlled to a large degree by the flotation practice by ensuring that the molybdenite content exceeds the minimum 85 percent MoS_2 . The iron content of concentrates is usually not of great importance since this element is not detrimental to the major use for the products.

Pretreatment of the concentrate before roasting may be required depending on the intended use of the final product. (see Appendix A). High limestone contents lead to high residual sulphur in the roaster calcine by formation of stable calcium compounds. The sulphur content of oxide is required to be less than 0.1% for use in steels. In one operation this is reduced by leaching the molybdenite concentrate in hydrochloric acid for 6 to 8 hours [21]. By maintaining a slurry pH of 2.5 the CaO content is reduced from 0.5 to 0.05 percent.

In some cases copper may be leached by sodium cyanide. However, this reagent is only effective in leaching secondary copper minerals such as chalcocite and covellite and is ineffective with chalcopyrite. Examples of this procedure in literature quote a

lowering of copper content from 2 percent to less than 0.5 percent at one U.S. operation and attainment of less than 0.2 percent copper in two Chilean operations [15]. This leachant has also been used on the roasted product. The copper content, as chalcopyrite, can be significantly reduced by a hot chloride leach [22,23,24]. This is also effective in lowering the lead (as galena) and calcium contents. Current practice involves approximately a 30 minute leach at 110°C with additions of ferrous chloride, sodium chloride and chlorine. The process can lower the copper content from an average 0.34 percent to less than 0.07 percent while lead when present (up to 2.0 percent) is reduced to less than 0.05 percent. Another process designed to remove lead [25] involves a 16 hour leach at 85°C in 5% HCl.

Most molybdenite roasting is accomplished by multiple hearth roasting although other means such as rotary reverberatory furnaces or fluid-bed roasters have been used. The process is semi-autogenous in that the reaction is exothermic although additional heat is often required for initiation of the reaction and to ensure completion of desulphurization. With multiple-hearth roasting the solids are fed in at the top while air is admitted in a controlled manner on most hearths. Air flow manipulation is important to temperature control in roasting, a necessary aspect considering the

volatility of molybdenic oxide and the 'stickiness' problems that can occur in the furnace. Increasing the air flow from low levels results in higher hearth temperatures due to greater rates of reaction. This increases to a maximum where-after higher air flows result in lower temperatures from the diluting effect of excess air. Cooling with excess air can be detrimental to SO_2 scrubbing since this practice dilutes the flue gas. Adequate temperature control may be achieved by shaft cooling and use of water sprays in the hearth space [26].

The roasting sequence involves the volatilization and combustion of flotation oils followed by partial oxidation to molybdenum dioxide (MoO_2) which on further roasting is converted to MoO_3 . During roasting rhenium is volatilized as heptoxide (Re_2O_7) which enables recovery by gas scrubbing (at $< 80^\circ\text{C}$) if sufficient quantities are present.

As with all sulphide pyrometallurgical processes dust laden sulphur-bearing gases are produced. The dust must be collected by some means such as multiclones and electrostatic precipitators to avoid excessive losses and to protect the environment. Dust burdens in the gas may be in the order of 10-15% of the charge and may even fluctuate to higher levels [27]. The cost of the dust-collection

equipment can represent up to 20 to 30 percent of the overall plant investment [28]. In many cases environmental considerations require that the emission of sulphur in the off gases be reduced to acceptably low levels. This is achieved by wet scrubbing and neutralization with lime [21,29] or by manufacture of sulphuric acid.

The technical molybdic oxide produced by roasting can be used directly as additions to alloy steelmaking or may be briquetted with a pitch binder for the same purpose. The technical oxide is also the usual starting material for production of other molybdenum products. The principal process routes and final products are shown in Figure 7 [16]. As can be seen the oxide may be processed by chemical means or by sublimation to obtain high purity chemical forms and electric furnace reduction or hydrogen reduction to produce metallic molybdenum.

A number of hydrometallurgical processes for treatment of molybdenite concentrate have been proposed including leaching in hypochlorite solutions, under oxygen pressure in alkaline solutions and with nitric acid. To date most have not been developed past the pilot stage. Apparently one commercial operation in the U.S.S.R. uses a nitric acid process to decompose molybdenite but details were not available [30].

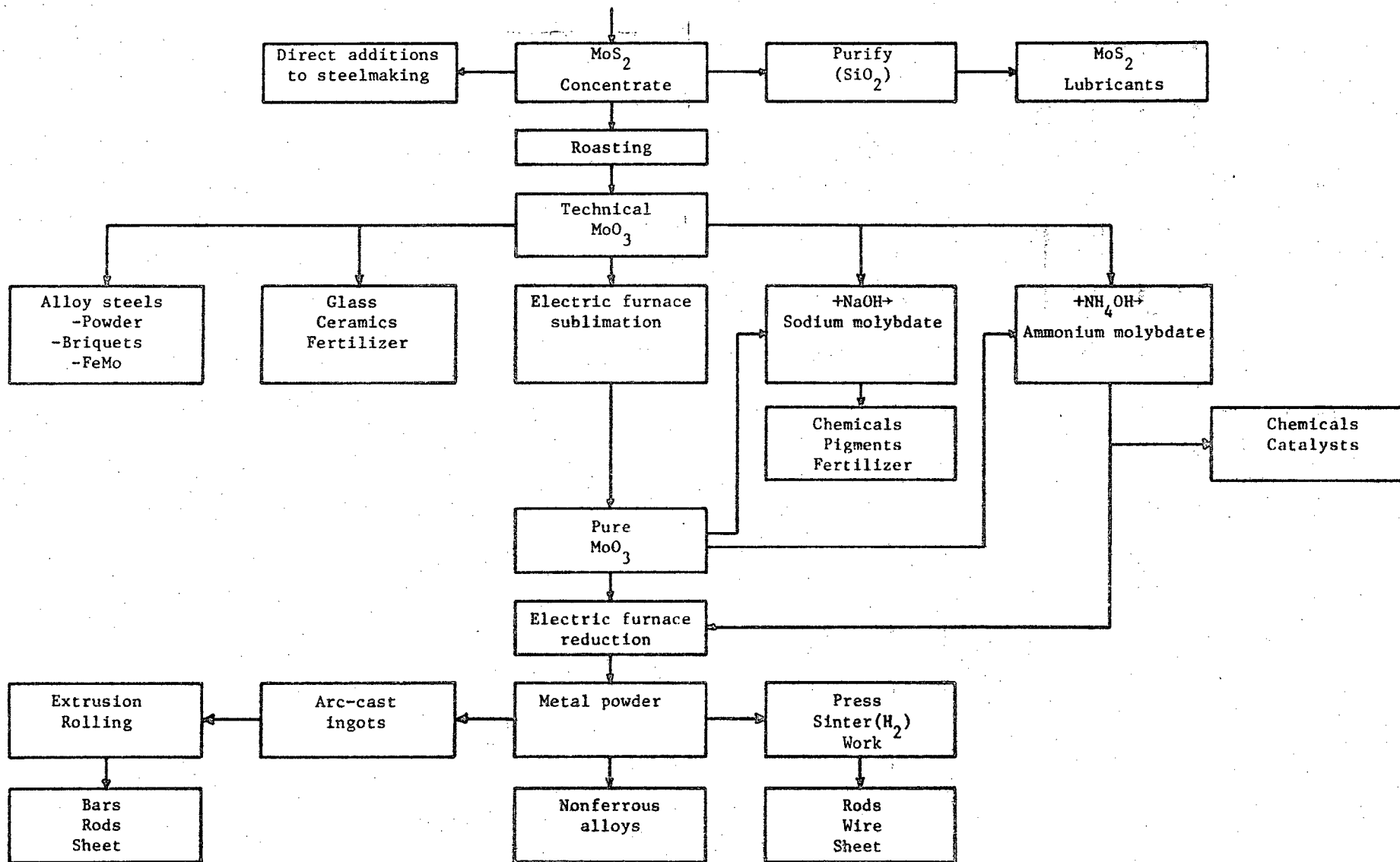


Figure 7. Molybdenum production flowsheet.
(condensed from reference [16])

1.9 Advantages of the Nitric Acid Leach Process

Conventional roasting represents a relatively simple single major step process for production of technical grade molybdc oxide.

However, it may suffer from a number of limitations:

- (i) Purity of oxide is subject to purity of concentrate feed.
- (ii) High grade products require additional treatment by sublimation or hydrometallurgy.
- (iii) Roasting produces dusty, sulphur-bearing off-gases which must be cleaned for reasons of economy and environmental protection.
- (iv) Rhenium recovery may be low.

The proposed low temperature nitric acid leach offers a number of advantages as follows:

- (i) Production of high grade material directly by leaching and precipitation (99.9% purity) as shown by laboratory experimentation.
- (ii) Potential to treat off-grade concentrates and obtain a satisfactory product. The limits of this aspect have yet to be experimentally established but on a commercial scale may be dependent on plant operating conditions.

This enables the possibility of producing lower grade flotation concentrates with associated higher recoveries which would then lead to higher overall molybdenum recoveries.

- (iii) Elimination of smelter gas handling problems by rejection of sulphur as gypsum.
- (iv) Higher possible recovery of rhenium.

The nitric-acid leach process must also consider environmental aspects particularly with respect to emissions of toxic oxides of nitrogen. In-plant environmental safety can be enhanced by operating the leach vessels under a slight negative pressure to avoid accidental leakage. Although the nitrogen in the system moves essentially in a closed cycle a small bleed stream may be necessary to eliminate other nitrogen oxides. Catalytic conversion of nitrogen oxides to harmless forms would be required before emission to the atmosphere but this technology is currently available.

The potential for the process ultimately depends on economics. It is not the object of this study to undertake an economic evaluation but rather a metallurgical evaluation. However, the viability of the process may be influenced by the prices of the feed and product. ie. -if impurity penalties are significant and if a premium price is

received for high purity oxide.

1.10 Nitric-Acid Leaching of Sulphides

Nitric acid has been considered as an oxidant for sulphide ores and concentrates since early in the 20th century but commercial application has been virtually non-existent. The studies to date have concentrated predominantly on sulphides of copper although those of nickel and molybdenum have received some attention. The oxidizing power of nitric acid also provides incentive for its use in place of other aqueous oxidants. Nitric acid may also be used in a "catalyst" capacity with small additions made to other leaching agents. However, significant oxygen pressure may be required to at least partially regenerate the nitric acid in-situ.

A general study of the reaction of nitric acid on a number of sulphides was reported by Björling and Kolta in 1964 [31]. They examined the behaviour of pyrite, pyrrhotite, chalcopyrite, sphalerite, galena and molybdenite with nitric acid under various conditions. The examination of molybdenite was not extremely detailed although some of the potential for such a system was recognized.

A somewhat general process utilizing nitric acid has been

proposed by Posel et al for the leaching of transition metals from iron bearing sulphide ores [32,33]. The leach system is based on an elevated temperature, pressurized reactor with recovery of copper nickel, zinc and silver as well as other precious metals and sulphur by various means including solvent extraction and electrowinning. The dissolved iron is removed by precipitation, under pressure and elevated temperatures if necessary.

1.10.1 Molybdenum Sulphide

The behaviour of molybdenite in nitric acid has been studied by Zelikman et al [30,34]. They demonstrated the leach/precipitation behaviour within the same vessel as a function of time, temperature and acid concentration. Oxidation curves at 20 and 80°C and a solution curve at 80°C show the expected behaviour. The utilization of nitric acid is increased by the injection of oxygen to regenerate nitric and nitrous acids. A stagewise decomposition flowsheet is proposed by Zelikman which involves additional intermediate leaching with ammonium hydroxide.

Smirnov et al [35] performed laboratory-scale studies on the oxidation of molybdenite in nitric acid at 80°C in the presence of relatively large quantities of particular impurities or additives.

The rate of leaching was increased by direct injection of nitrogen dioxide. The apparent activation energy is quoted as 20-26 Kcal/mole indicating that the reaction is chemically controlled unless precipitation hinders reagent access to the mineral surface.

Nitric acid oxidation studies were also conducted by Fedulov et al [36]. The oxidation rate was shown to increase rapidly over 40-70°C but was slowed by diffusion once precipitation commenced.

A high-temperature, high-pressure process for the nitric acid oxidation of molybdenite has been developed by Noranda Mines Ltd. [37]. The basis of the process is the oxidative leaching and precipitation in the one vessel. The conditions applied ensure reasonable reaction rates with elimination of soluble impurities. However insoluble impurities such as silica, alumina and any precipitated gypsum would remain with the molybdenum product. With sufficiently high temperatures and pressures a dehydrated molybdenum oxide is produced in the leach rather than the hydrated form. A bleed stream is also required for sulphate removal following recovery of residual nitrate, molybdenum and rhenium.

Nitric acid is also used to purify roasted calcines containing residual sulphur [38]. As well as lowering the sulphur content the level of metallic impurities is also decreased.

1.10.2 Copper Sulphides

A number of studies on the nitric acid leaching of copper sulphides have been conducted in recent years although the strategies of the possible processes differ in some aspects. Prater et al [39,40] developed a flowsheet for nitric acid leaching of copper concentrate which involved residue recycle with upgrading by flotation and regrinding (with new feed). Test work showed the elemental sulphur yield to be dependent on acid conditions, temperature and the mineralogy. When nitric acid is present in excess any increase in acidity or temperature results in lower elemental sulphur yields. Elemental sulphur is considered as a more desirable form for subsequent disposal. Dissolved sulphur is precipitated by lime in a separate step. Under suitable conditions the iron is precipitated as a jarosite rather than a less easily filtered hydroxide. The dissolved copper is recovered by solvent extraction and electrowinning.

Habashi [47] investigated the recoveries of copper and elemental sulphur under varying conditions of acid concentration, temperature, pressure and time of contact. These laboratory tests showed the increasing copper extraction rates with increasing nitric acid concentration, temperature and time of contact. The elemental sulphur yields were more complex, showing a maximum in most cases,

which did not exceed 50 percent. The elemental sulphur yield could be increased slightly by prior heat treatment of the chalcopyrite. Under conditions of high temperature and pressure the iron remains in the leach residue as an oxide.

More recently Björling et al have proposed a nitric acid process for treatment of chalcopyrite [42]. The concentrate is leached in a sulphuric acid nitric acid mixture at elevated temperatures with recovery of copper and iron sulphates by crystallization. To separate the iron and copper the crystals are dissolved in water and oxidized in an autoclave at elevated temperatures. The iron is precipitated as goethite leaving a solution of sufficient purity for copper electro-winning. This process also enables the recovery of zinc by solvent extraction from the leach liquor as well as recovering an iron compound of sufficient purity for recovery. The paper also presents a brief economic analysis.

A rather detailed study based on a continuous, integrated semi-pilot plant operation has been presented by Brennecke et al [43] with process improvements detailed by Davies et al [7]. The process is based on a high-temperature, countercurrent leach with eventual copper recovery by electrowinning after removal of residual nitrogen, iron as jarosite and selenium. Molybdenum, if present, is dissolved

and may be recovered by liquid ion exchange but this applies to relatively low concentrations, below the saturation limit. An economic evaluation shows the process to be more viable for relatively small operations where pyrometallurgical costs per unit of production would be extremely high.

The suggested improvements to the process involve the use of a two-stage leach with direct injection of NO_2 gas regenerated from the nitric oxide evolved. Besides increased leach reactor performance the reduced equipment requirements enhance the economic position of the process.

Acidified nitrate solutions have also been suggested as a possible reagent for in-situ leaching of copper ores [44]. The presence of nitrates would enhance the conventional in-situ acid leaching rates.

1.10.3 Nickel Sulphides

Habashi also presented a study on the extraction of nickel, copper and elemental sulphur from a low-grade, pyrrhotite-pentlandite concentrate [45]. Under suitable conditions of acid concentration, and temperature high batch recoveries of nickel and copper could be

attained in relatively short times.

The effects of the sulphuric-nitric system on a pentlandite concentrate was investigated on a laboratory scale by Ouellet et al [46]. They studied the influences of time, temperature, sulphuric and nitric acid concentrations and pulp density on the extractions of nickel, cobalt and copper. This system was determined to be diffusion controlled by the formation of a film of elemental sulphur and basic ferric sulphate on the mineral surface. The plot of Fig. 8 demonstrates the slight effect of sulphuric acid concentration over the range 0 - 1.0 moles/litre on extraction for a nitric acid concentration of 1.97 moles/litre.

Bjorling and Mulak investigated the dissolution of synthetic millerite (NiS) in nitric acid [47], and determined the process to be chemically controlled. Nickel extractions increased with temperature and nitric acid concentration and almost complete sulphur dissolution was achieved with nitric acid concentrations in excess of 2 molar.

A pilot-scale study of a nitric acid process for treatment of high-grade nickel matte or a nickel-cobalt sulphide precipitate has been described [48]. The feed is leached in nitric acid at atmospheric pressure and 90°C . Several flowsheets are presented but

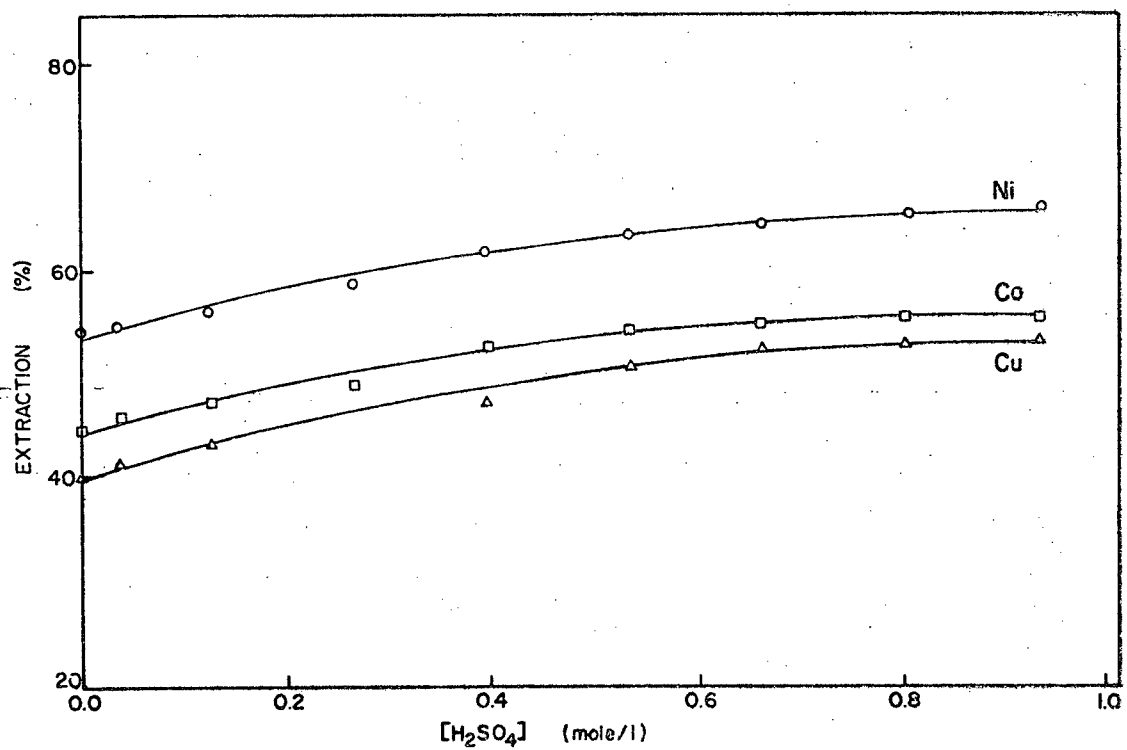


Figure 8. Extraction of nickel, cobalt and copper from pentlandite by nitric acid as a function of initial sulphuric acid concentration. [46]

the basis of the subsequent processing is purification and denitrification prior to electrolysis. Purification is achieved by hydrolysis for iron, H_2S precipitation for copper and zinc and nickel hydroxide or sodium hypo-chlorite additions for cobalt removal. Nitrate elimination is accomplished by crystallization of nickel sulphate or by precipitation of basic nickel carbonate.

1.11 Modelling in Hydrometallurgy

With the increasing emphasis on hydrometallurgy in recent years there has been greater interest in the modelling of such processes. Often, due to the proprietary nature of the work, the details of the modelling are not published but may be referred to as existing. However, the approaches of a number of hydrometallurgical modelling studies have been published.

Owing to the scope of this work, hydrometallurgical modelling will be discussed only with respect to leaching. Simulation of leaching involves the analysis of the kinetics of the system generally involving irreversible reactions under steady state or unsteady state conditions. Equilibrium modelling, where the transient period is relatively small and only the final distributions are important is generally of minor significance in leaching.

1.11.1 Leaching

The metallurgical description of leaching process can be considered on two scales:

(1) Micro-scale which involves a characterization of the chemical processes or boundary-layer mass-transfer kinetics occurring in these heterogeneous reactions.

(2) Macro-scale which describes the physical distribution of the system and which influences the rates of the chemical reactions.

Usually the rate of reaction is controlled by the chemical processes which occur on the particle surfaces or by mass transfer of species to the reacting surfaces. In rare cases the dispersion of oxidant, such as dissolved oxygen, may be the rate limiting step. At the usual temperatures of operation in hydrometallurgy the chemical surface reaction is rate controlling unless reagent access is hindered by unleached solid or precipitated material. This latter phenomenon can lead to mixed control with the chemical reaction as the rate controlling step for low degrees of extraction while mass transfer becomes the rate-limiting factor when diffusion cannot maintain an adequate reagent supply [49].

Two extremes of leaching practice can be considered. The first applies to leaching of high grade materials such as concentrates

where a high proportion of the input solids mass is leached. The second case applies to low grade material where only a small fraction of the mass of solids is leached from an essentially inert matrix. A popular approach to the modelling of the leaching of particles containing disseminated leachable mineral in an inert matrix is the shrinking core assumption. The reaction front is considered to be quite narrow and gradually proceeds toward the centre of the particle. The particles may be considered spherical or allowances made for non-sphericity, pore structure and nonuniform mineralization or exposure [50]. A similar approach is often used for leaching of particles which leach completely or almost completely to soluble products. The particles are assumed spherical with or without appropriate correction factors and simply shrink as the reaction proceeds. Although the particles are almost certainly non-spherical before leaching, the progression of the leaching front may smooth out the "roughness", particularly if the process is isotropic. Bjorling [42] utilized a grain-age term based on the diminution of a characteristic dimension of the particle to account for the change in surface area.

It can be seen then, that the description of leaching kinetics can be quite complicated, with variation in reaction control, ranges in particle size and mineral distribution. One simplified approach is to group the rate-limiting effects into a variable activation energy term [51]. As the reactive mineral becomes more inaccessible or more refractory

the activation energy is increased to account for the change in reaction rate.

For a chemically-controlled reaction then, the rate may be classified by relations of increasing complexity.

(1)

$$r = K C^n W \quad (18)$$

where r = rate of reaction

K = rate constant

C = concentration of leaching reagent

W = weight or mole concentration of reactive mineral

n = reaction order w.r.t. C

~ all in appropriate units.

This is a very simplified approach which accounts for the change in surface area only by the change in weight concentration of the species.

(2)

$$r = K C^n W^{2/3} \quad (19)$$

This is of more representative than Equation (18) since the exponent of W expresses the surface area to volume ratio. The method

is strictly accurate if the leaching particles are equi-sized spheres but the method may be useful for approximations.

$$(3) \quad r = K_v C^n W \quad (20)$$

where K_v includes the variable activation energy

The parameters included in the activation energy term must be determined by statistical analysis of experimental data.

$$(4) \quad r = K C^n A \quad (21)$$

where A = surface area for reaction

The variation in area term must be accounted for in some manner. As mentioned previously the shrinking sphere, with or without adjustment factors is often used. An empirical method accounting for the change in area is considered later in this thesis.

Even though the reaction kinetics might not be linear they may, for the purpose of analysis, be considered as linear over small ranges of variation. However analysis by this method is somewhat restrictive.

The physical motion of the system must also be considered.

Three cases are described:

(1) Static bed of solids with passage of leaching solution and possibly gas as in dump, column or in-situ leaching. A number of models of these processes have been published [50,52,53,54].

(2) Leaching where both solids and liquids are in motion.
i.e. agitation leaching

- (a) Continuous processes where phases are continually added and withdrawn from the system.
- (b) Batch leaching where the system is essentially closed during the reaction.

The object of this project is to simulate a continuous, cocurrent, agitation-leaching process. A graphical approach to predict continuous cocurrent-process behaviour from laboratory batch-extraction data is described by Jones [55]. The method is shown in Figures 9 and 10. The quantity of component dissolved, Q , in a batch test is obtained as a function of time, t , as in Figure 9. This extraction curve is analysed by practical or mathematical means and the slope, $\frac{dQ}{dt}$, is plotted against Q as shown in Figure 10. A line of slope equal to the inverse of the nominal residence time (θ) and passing through the stage input value of Q on the abscissa intersects the stage output value on the curve. This construction is continued for as many stages as desired.

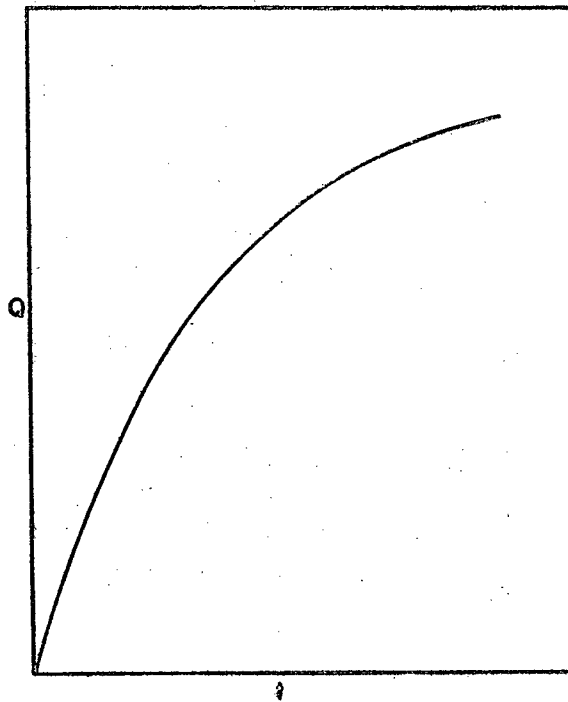


Figure 9. Typical extraction curve.

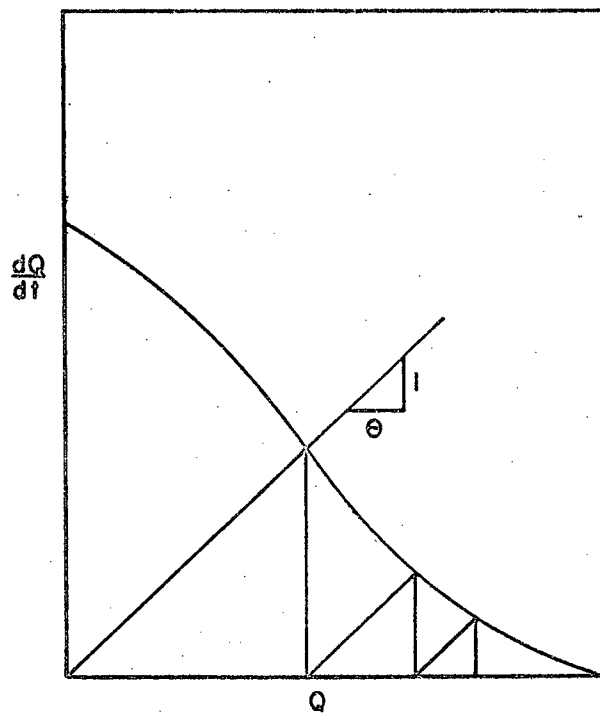


Figure 10. Rate of extraction vs. extraction showing construction for staging analysis.

Alternatively, the extractions can be determined on a trial and error basis for a particular stage configuration. Since this analysis is based only on the amount of material dissolved it is only suitable for the same initial conditions of feed solids, solution and temperature as in the batch test. It also only applies to the condition of back-mixing although this assumption is reasonable for low reaction rates, long residence times and sufficient agitation.

The general mass balance approach applied to purely backmixed reactors involves a set of component and overall mass balances with rates determined as a function of output concentrations for each vessel.

The simplified form of the solution component balance is expressed in Equation (22) for a leaching reaction

$$v C = v C_o + r V \quad (22)$$

where v = solution volumetric flow rate

C = concentration of component in outlet solution

C_o = initial concentration of component in input solution

r = rate of reaction per unit volume

V = volume of vessel

Again, the difficulty is in evaluation of the rate term and accounting for variables which affect r .

If the residence time distribution (RTD) has a significant influence on reactor performance it may have to be taken into account. For perfect backmixing the RTD is given by:

$$E(t) = \frac{1}{\bar{t}} e^{-t/\bar{t}} \quad (23)$$

where t = time

\bar{t} = nominal residence time

For non-ideal mixing the summation approach may be the most suitable i.e. ~ summing the reaction for each empirically-determined residence time range. This procedure is satisfactory for first order reactions since the rates are then independent of concentration. For non first order reactions the situation is considerably more complex. Detailed analysis of the chemical engineering principles involved are given in the references [1,2,56,57,58,59].

1.12 Modelling of other Unit Operations in Leach Circuit

1.12.1 Grinding

With the current flowsheet it is envisaged that ball milling will be used to reactivate the leach residue. The object of grinding simulation is usually to determine the product size distribution as a function of feed size distribution and mill parameters. By necessity, the modelling of grinding is extremely empirical and involves a large series of calculations to account for the complete particle size range.

A kinetic model may be used for ball milling based on the following first order assumption [60].

$$\frac{d W_i}{dt} = - K_i W_i \quad (24)$$

where W_i = amount of material in size range i

K_i = breakage constant

$\frac{d W_i}{dt}$ = rate of breakage from size range i

The complete analysis is based on the assumption of perfect backmixing, a condition which is reasonable for ball milling.

Another method for grinding simulation is the matrix model which involves a combination of classification, selection for breakage and breakage matrices to determine output size distributions [61].

A number of theoretical relations have been proposed to describe size reduction. The one which applies more closely to fine grinding is that of Rittinger.

$$d E = - \frac{C dX}{X^2} \quad (25)$$

where dE = unit energy input

C = proportionality constant

X = size dimension

Rittinger's Law states that the amount of new surface area produced in proportional to the energy input to breakage. This energy of breakage, however, represents only a small fraction of the total energy input to a mill, the rest reporting as heat and sound.

1.12.2 Flotation

It has been found that flotation often closely follows the simple first order relationship of Equation 26 [61].

$$r = K W \quad (26)$$

where r = rate of flotation

K = flotation rate constant

W = concentration of floatable component.

The flotation rate constant K may be theoretically dependent to varying degrees on a large number of variables [62]. These variables include particle size, degree of liberation, air bubble surface area, fraction of bubble surface covered with mineral and the efficiency of the froth in retaining the desired mineral. The complete characterization of all influencing variables is not possible. However, the range of some of these variables in practice may be sufficiently small that they can be assumed constant for approximations of circuit behaviour.

On the basis of Equation (26) and backmixed flotation cells it can be shown that the recovery of floatable mineral is [63]:

$$R_1 = \frac{K \theta}{1 + K \theta} \quad (27)$$

where R_1 = recovery from 1st cell

θ = cell retention time

This can be extended to recovery from the n^{th} cell in series:

$$R_n = \frac{K \theta}{1 + K \theta} \left(1 - \sum_{i=1}^{n-1} R_i \right) \quad (28)$$

Hence the total recovery from a simple series set of flotation cells is the summation of the individual cell recoveries.

$$R = \sum (R_1 + R_2 + \dots + R_n) \quad (29)$$

$$= 1 - (1 + K \theta)^{-n} \quad (30)$$

CHAPTER 2

BASIS OF THE LEACHING MODEL

The basis of the leaching model had to be established to determine the experimentation required to provide necessary data. Hence this Chapter introduces the approach to the formulation of the leaching model while complete details are presented in Chapter 4 along with the formulation of the models of the other unit operations.

2.1 Modelling by Mass Balances

Mass balancing was considered the most practical and versatile method for simulation of leaching. For the steady state conditions considered the mass balance is most simply described by Equation (31).

$$O = I \pm R \quad (31)$$

where O = rate of output

I = rate of input

R = total rate of generation (+) or consumption (-)

The mass balances are applied to active components in each phase as well the overall phases. In the flowsheet considered there are two solids streams entering the leach. These are considered as separate phases throughout the leach train for reasons enunciated later in this chapter.

It has already been shown that the reaction is relatively slow. Therefore the degree of extraction in any one stage is not likely to be very high. Hence the leaching vessels are considered to be entirely backmixed regardless of their design. The existence of the recycle solids stream validates, to an extent, the neglecting of any non-ideal residence time distribution (RTD). For example, a particle which short circuits the leach has a higher probability of re-entering the leach train earlier than a particle which has not short circuited the leach. However this does not entirely nullify the effects for a non first order reaction.

There are many possible complicating effects but these are neglected on the basis of negligible influence and the aim of maintaining model simplicity. These factors include the RTD's for the solution as well as both solids streams. As well, the RTD for the different classes of particle size may vary. Consideration of a RTD that is not ideally backmixed leads to a rapid escalation of required computations since each residence time class has to be

considered separately.

2.2 Rates of Reaction

Rates of the chemically-controlled reactions must be defined for finely divided concentrate in an aqueous medium. Two different bases are used in this model for the different minerals considered. For molybdenite the characterization of the leaching rate of a concentrate consisting of non-uniform particles is based on equation (21)

MOLYBDENITE:

$$r = K C^n A \quad (21)$$

Two other sulphide minerals are considered since they consume nitric acid and raise the impurity content of the solutions. For the concentrates used the major sulphide impurities accounted for were pyrite and chalcopyrite. Since they are present only in relatively small quantities the simplified description of Equation (19a) is used.

PYRITE, CHALCOPYRITE:

$$r = K C W^{2/3} \quad (19a)$$

For lack of information the reactions for both these minerals are considered to be first order with respect to C.

It is required not only to determine what the parameters are in these reactions but to account for the changes that may occur in them as the reactions proceed.

The importance of the analysis of both the C and the A terms is shown by a rough analysis of previous experiments (Reports 7 and 8, reference [4]). The extraction curves for as-received concentrate and concentrate that had been wet ground for one hour in a pebble mill are plotted in Figure 11. These points have been approximately fitted to power curve equations of the form $y = a t^b$. The rates of leaching as a function of time were determined by differentiation and are shown in Figure 12. Although it cannot be claimed that this analysis is accurate it still demonstrates the point that in a partially closed or bounded system the finer material will initially leach faster but will eventually leach at a slower rate due to depletion of solids and consumption of active reagent. However the net extraction will still be greater for the finer solids at any particular time up to that for complete extraction.

2.2.1 Analysis of Terms

- (1) \underline{r} - rate of leaching per unit volume of solution

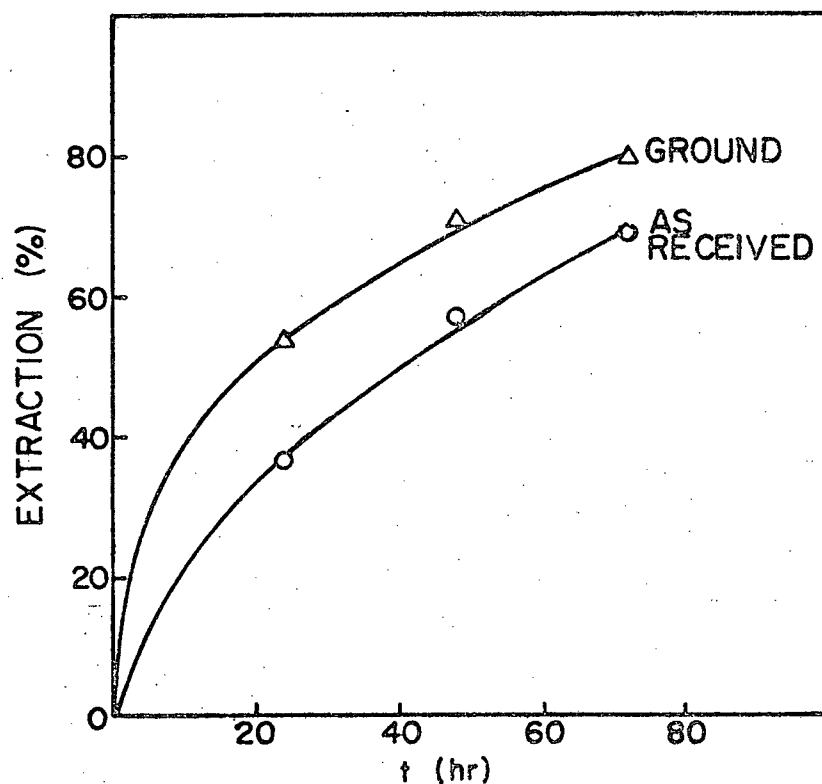


Figure 11. Extraction curves for Gibraltar molybdenite concentrate (a) as received (b) wet ground one hour in laboratory pebble mill. 49.9%Mo, initial pulp density 112 grams/litre solution, initial 4M HNO_3 , ambient temperature, atmospheric exposure. [4]

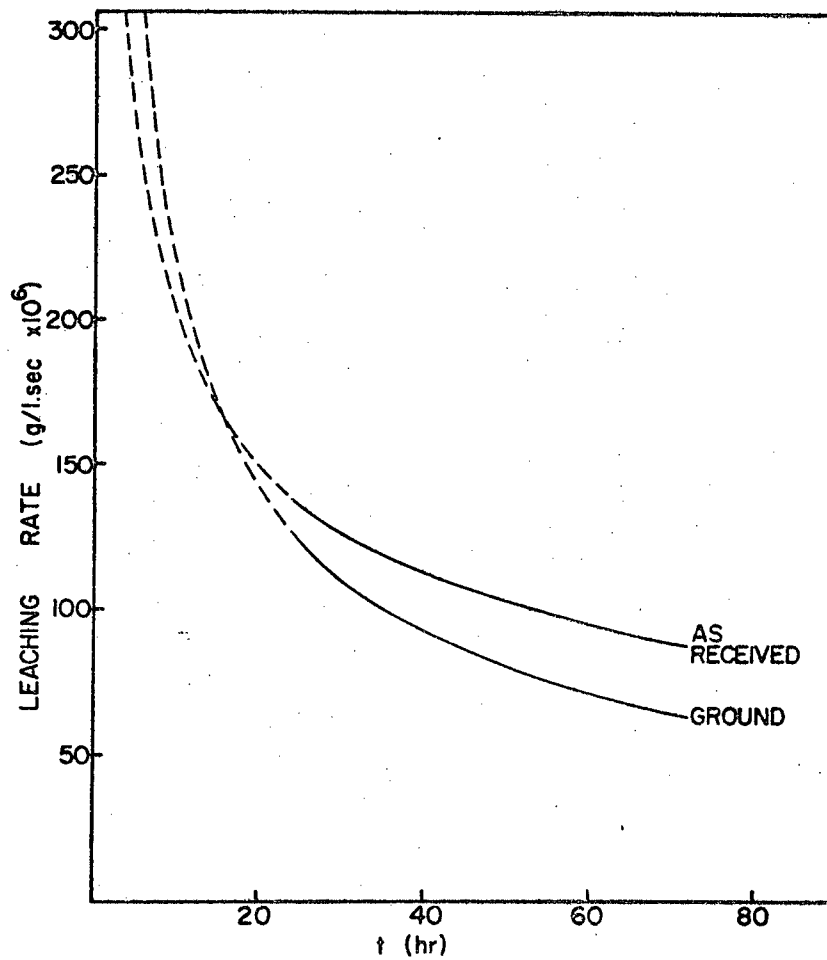


Figure 12. Leaching rates of Gibraltar molybdenite concentrate (a) as received (b) wet ground one hour. Conditions as in Figure 11.

(2) C

In the earlier discussion it was shown that the exact mechanism for leaching of sulphides by nitric acid may be quite complex. On the basis of empiricism then, the term C was taken as the "nitric acid" concentration in molar units since it could be measured and had a determinable influence on the rate of reaction.

(3) n

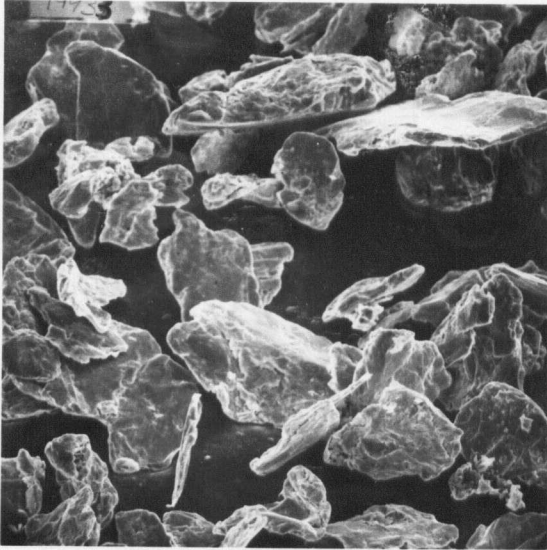
Having decided to use the nitric acid concentration as the reactant in solution the reaction order had to be determined by experiments using standard procedures.

(4) A

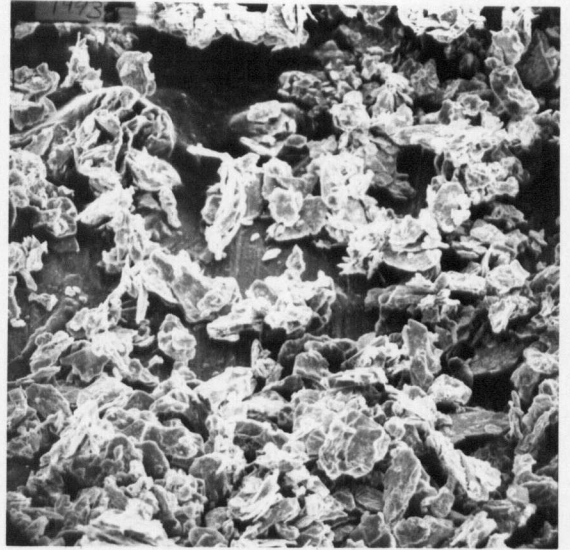
This defines the surface area of particles on which the chemical reaction occurs. It is common practice to consider a 'uniform' or 'average' particle within the bulk or particle size range for analysis of this term. Having defined the single particle the overall behaviour is described by summation over all the particles. The SEM photographs in Figure 13 show an extreme non-uniformity of size and shape characteristic of molybdenite concentrates. Accounting for the change in surface area of a molybdenite particle is also complicated by the following factors:

(i) Initial definition of A is not adequate since it cannot be determined accurately.

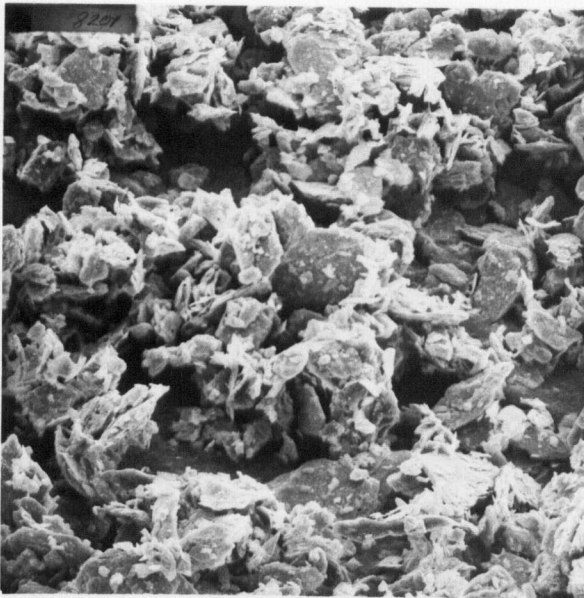
(ii) Anisotropy of leaching. Leaching is more active



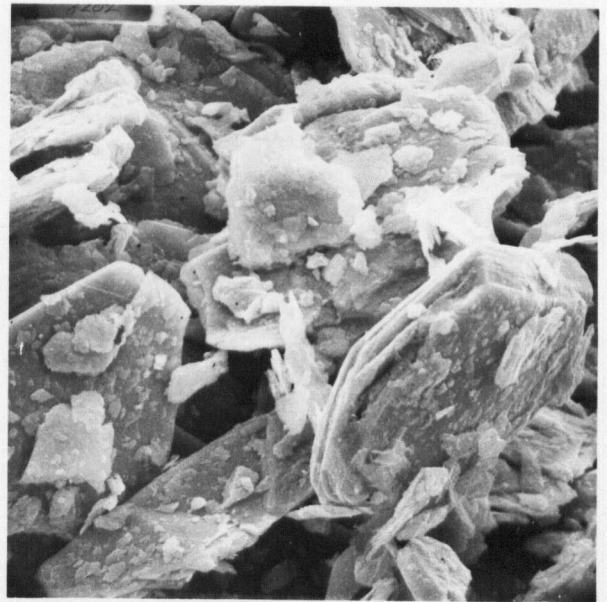
(a)



(b)



(c)



(d)

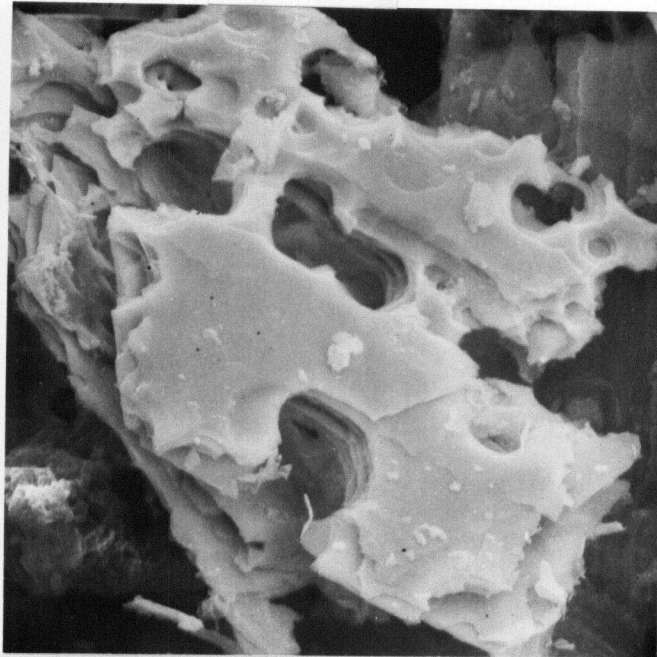
Figure 13. Molybdenite concentrates. (a) Brenda +325 mesh. (160x) (b) Brenda -400 mesh. (160x) (c) Gibraltar. (325x) (d) Gibraltar. (1600x)

at the plate edges and defects thus leading to complex effects on A (see Figure 14)

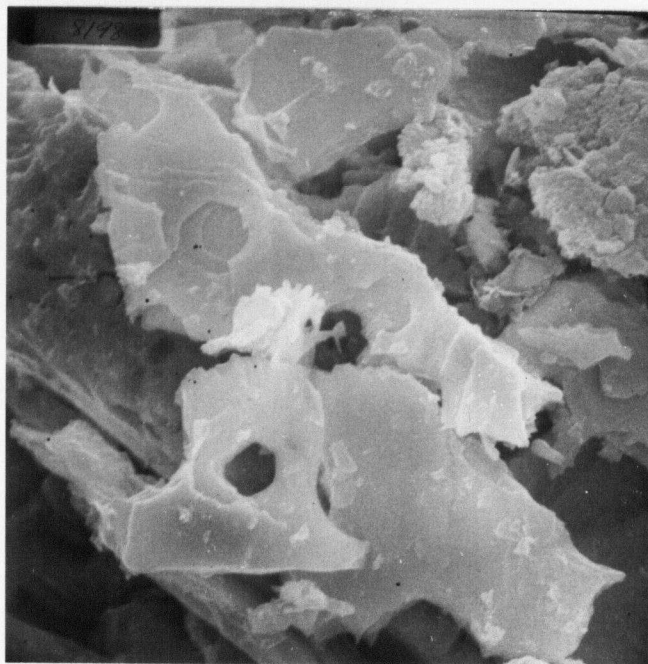
- (a) Leaching of plate edges decreases the 'active' area available for leaching since the plate is shrinking.
- (b) Leaching of defects within a plate increases the active surface area since the pits formed enlarge as the reaction proceeds.
- (iii) The plate structure of molybdenite can lead to phenomena that are difficult to take into account. The weak bonding between plates may result in the cleavage of particles, induced by agitation or by NO gas pressure where solution has penetrated between plates.
- (iv) The softness of the mineral can lead to severe physical deformation which would likely influence leaching characteristics.

The conclusion is that the single particle basis is illogical for this system. It would be more advantageous to describe the bulk properties with respect to A in order to truly describe the average behaviour.

The numerical value of A remains an undefinable term in relation to the active surface area and the manner in which it changes. An extremely approximate analysis was performed on data from reference [64] where the average particle diameter and surface area per gram



(a)



(b)

Figure 14. Leach residues. (a) Gibraltar concentrate leached 3 days, initial pulp density 168 g/l solution, initial 4M HNO_3 , 64% extraction. (2000x). (b) MoS_2 concentrate leached to 60-75% extraction. (4000x).

were determined on four different concentrates by Coulter counter and BET with krypton gas respectively. Calculations based on disc-shaped particles and the experimentally determined values show the thickness to diameter ratio to increase as the particle size decreases. (see Figure 15). The effect on surface areas is also shown. This is not conclusive evidence since the ratio will be influenced not only by the degree of grinding but also the morphology of the mineral in the ore. However it does demonstrate the complexity involved in evaluating the reactive surface area.

The problem is overcome by the following strategy using the results from batch experimentation. Equation (21) is normalized as:

$$r = K' C^n A' \quad (32)$$

where $A' = \frac{A}{A_{t=0}} = \text{area factor}$

For batch or continuous cocurrent leaching then:

$$\begin{aligned} r &= K' C^n \quad \text{at } t = 0 \\ \text{since } A' &= 1 \end{aligned} \quad (33)$$

The functional form of A' versus fraction leached (area decay curve) can be determined by curve fitting of appropriate experimental data.

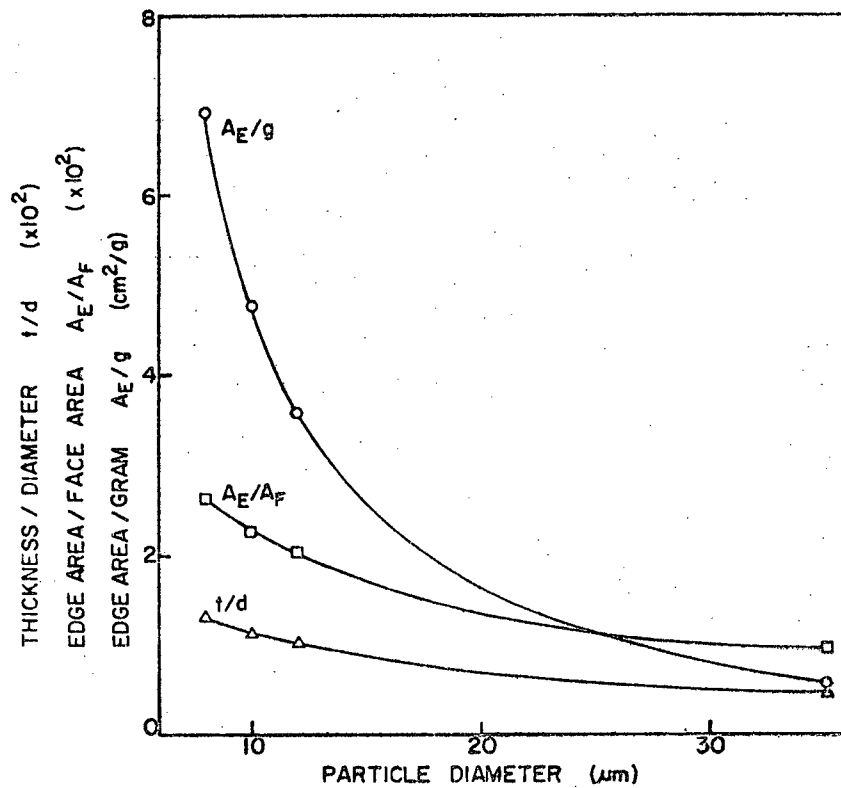


Figure 15. Approximate dimensional characteristics of four molybdenite concentrates.

This then defines the area factor in a term independent of time.

If A' is determined on a per unit weight of solid basis then an additional term has to be introduced to account for the pulp density and its change in the practical system.

$$r = K' C^n A' P' \quad (34)$$

where P = ratio of current pulp density to experimental pulp density

A linear relationship between active surface area and weight of solids is assumed. To allow for the effects of temperature the Arrhenius factor is introduced into the rate constant term.

$$K' = K'_0 e^{-E_A/RT} \quad (35)$$

where E_A = activation energy
 R = gas constant
 T = absolute temperature

For evaluation of the rates of reaction of MoS_2 the two solids streams entering the leach (new solids and recycle solids) having different analyses and particle size distributions are considered separately throughout the leach. Although bulk analysis

and initial area factor could be easily calculated by a weighted average, the properties subsequent to commencement of leaching are much more difficult if not impossible to determine. A simple analogy based on leaching of uniform spheres demonstrates this point. For a hypothetical constant leaching environment the rate of leaching depends only on the surface area. The surface areas versus fraction leached for an equal mass of spheres of 1 unit radius and 2 units radius are shown in Figure 16. Several points of equal leaching time are joined by dashed lines to show how the surface areas vary. The data is replotted in Figure 17 as surface area versus time. The total surface area for a 50 wt % initial mixture of each size is also shown. This demonstrates the complexity when considering just two particle sizes and indicates the problems when considering a continuous range of particle sizes or particle size classes.

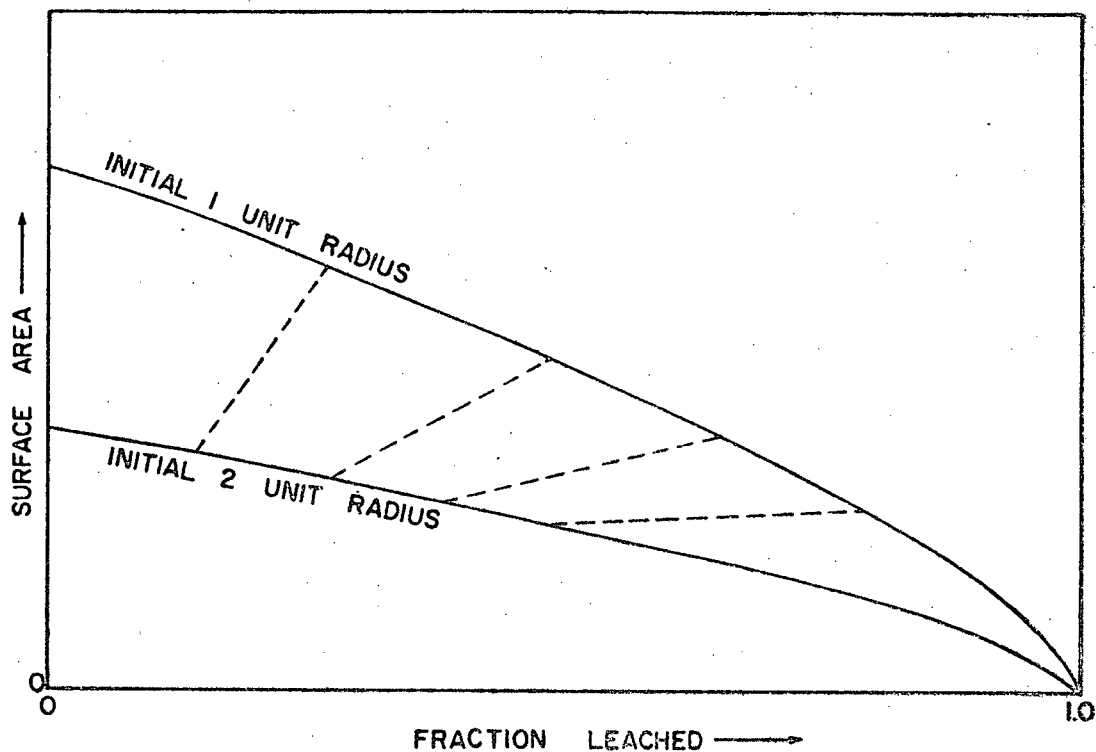


Figure 16. Surface area vs. fraction leached for initial equal masses of spheres of one unit radius and two units radius. Constant leaching environment.

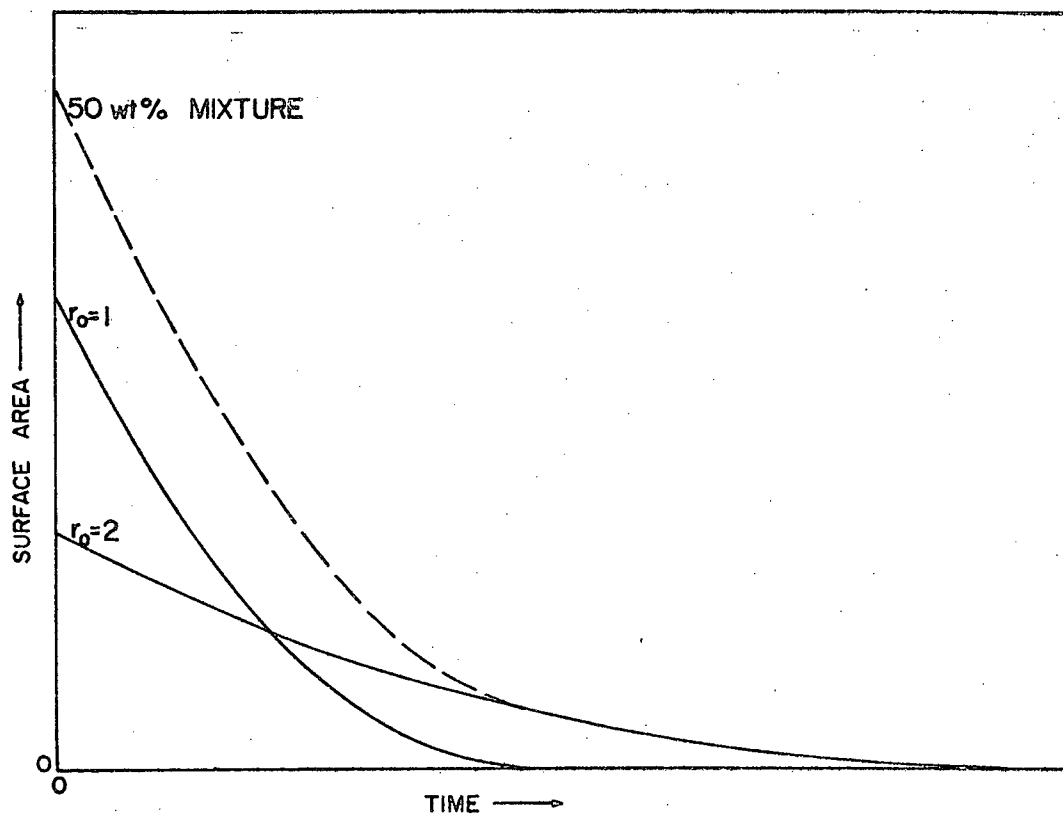


Figure 17. Surface area vs. time for initial equal masses of spheres of one unit radius and two units radius. Constant leaching environment.

CHAPTER 3

EXPERIMENTATION

The previous Chapter outlining the basis for the model formulation also indicated the type of data that would be required to operate the model. Data that were not available from the previous work, literature or by analogy were furnished by designed experiments. Most experiments involved relatively short term tests in which the effects of changing variables could be neglected or averaged.

The molybdenite concentrates used in the test work were supplied by Endako Mines Division of Canex Placer Ltd. (Sept. 1977) and Brenda Mines Ltd. (Sept. 1977) both located in British Columbia. Both concentrates were direct flotation products which had not been subjected to the purification leaches practised at each of the plants. Chemical analyses and sizings for these two concentrates are listed in Table VII.

3.1 Apparatus

The experimental apparatus is depicted in Figure 18. The leaching reactions were conducted in a standard 500 ml filtering flask

Table VII

CONCENTRATE ANALYSES AND SIZINGS

Analysis	Endako	Brenda
Mo	54.82%	55.92%
Fe	0.84	0.65
Cu	0.027	0.237
Pb	0.048	0.32
Bi	0.059	-
S	37.63*	38.36*
SiO ₂	8.0**	-
INSOL	-	1.59
Sizing	5% + 19 microns 44% + 9 microns 56% - 9 microns (~99% - 325#)	(~72% - 325#)

* by calculation on basis of MoS₂, FeS₂, CuFeS₂

** typical value

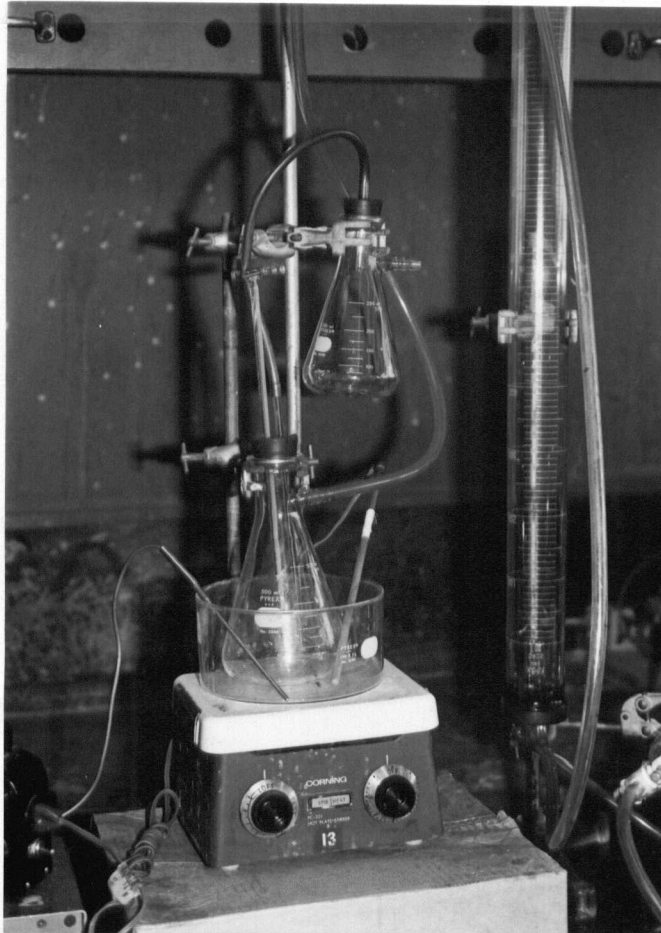
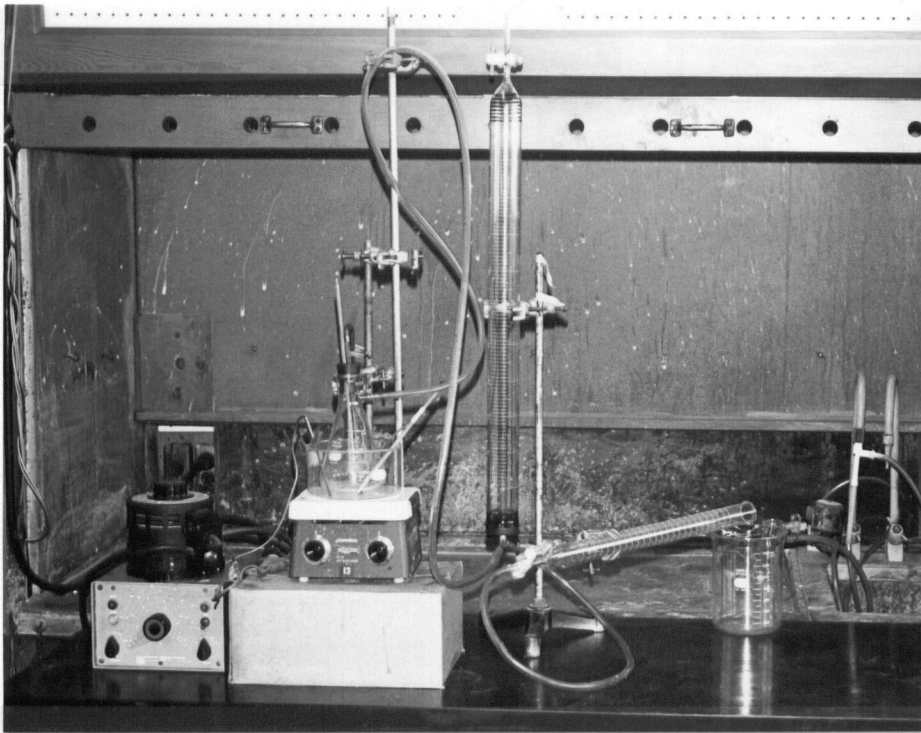


Figure 18. Experimental apparatus.

at essentially atmospheric pressure. Temperature was automatically controlled for most of the tests by a Thermistemp controller using an immersion heater located in the water bath surrounding the reaction flask. Temperature within the reaction flask was usually maintained within $\pm 0.5^{\circ}\text{C}$ of the desired set-point. Agitation was achieved by magnetic stirring.

The reaction flask was sealed during the reaction to avoid oxygen access and in-situ acid regeneration. The gas produced by the leach was trapped in a gas-collecting tube with the water being displaced through an overflow.

Before most leaching tests were performed the solution in the reaction flask was bubbled with argon and then nitric oxide produced in a gas generator by sodium nitrite and sulphuric acid. Bubbling with argon eliminated most of the air from the system while bubbling with nitric oxide attempted to duplicate the continuous system which is saturated with this gas. It was impossible to avoid some air access when opening the flask to introduce the concentrate but the effects of this were considered minimal.

3.2 Chemical Analysis

Solution analysis was chosen to gauge the extent of reaction

since changes in molybdenum concentration could be readily detected by atomic absorption techniques whereas changes in solids content was more difficult to determine and less reliable. A Perkin Elmer Model 306 Atomic Absorption Spectrophotometer was used for the analyses.

Standard solutions for molybdenum, as outlined in the operating manual, required slightly alkaline conditions. Since the leach solutions were acid and contained iron the treatment with alkali could result in hydroxide precipitation, thus necessitating filtration. The use of acid standards was investigated and found to be satisfactory. Acid standards were necessary since the use of acid test solutions and alkaline standards gave low results.

Molybdenum is known to suffer from interfering ions in AAS analysis. Suggested methods for overcoming interferences involved the additions of large quantities of particular salts such as aluminium chloride and ammonium chloride to the solutions. Additions of ammonium chloride created highly unstable readings on the AAS. To avoid effects of interferences the standard solutions were generally made with starting leach acid which already contained nitric and sulphuric acids, and dissolved iron. Testing also showed that molybdenum absorbance was relatively insensitive to nitric acid over ranges of interest in this work.

Iron and copper atomic absorption analyses were conducted with simple acid standards produced by dissolution of pure metal.

3.3 Experimentation and Analysis

The results of the experimental program, including the initial exploratory experimentation, are tabulated in Appendix B. The more important results are analysed and discussed in the remainder of this Section under the appropriate headings.

3.3.1 Reaction Order with Respect to Nitric Acid

To determine the reaction order the initial rate of reaction was determined for different initial nitric acid concentrations. Other possible variables were kept as constant as possible by the following conditions.

(1) Use of large particle sizes: Since the Brenda concentrate was the coarser of the two, the +325 mesh fraction of it was used in these tests.

(2) Termination of experiments at low degrees of extraction so that the area of reaction only changed by a negligible amount. For the different acid concentrations the tests were terminated after different times to attain similar degrees of extraction.

(3) Low pulp density tests so that there are only minor changes in solution concentrations.

Since the area of reaction is essentially constant for these reactions the area may be included within the rate constant so that the rate equation becomes pseudo-homogeneous.

$$r = K'[\text{HNO}_3]^n \quad (36)$$

Therefore the plot of $\log r$ versus $\log [\text{HNO}_3]$ has a slope equal to the reaction order as shown in Figure 19. The slope is evaluated at 1.84 for the filled points. Due to the limited experimentation the reaction order is taken as 2.0 for the model calculations.

The two high points at $1\text{M}[\text{HNO}_3]$ are neglected in the analysis since they were long-time tests and possibly subject to particle cleaving. The test involving the addition of sulphuric acid demonstrated a very minor difference from those without sulphuric acid additions.

3.3.2 Determination of Area Factor Relationship for Endako Molybdenite Concentrate

The aim of this series of experiments was to determine how

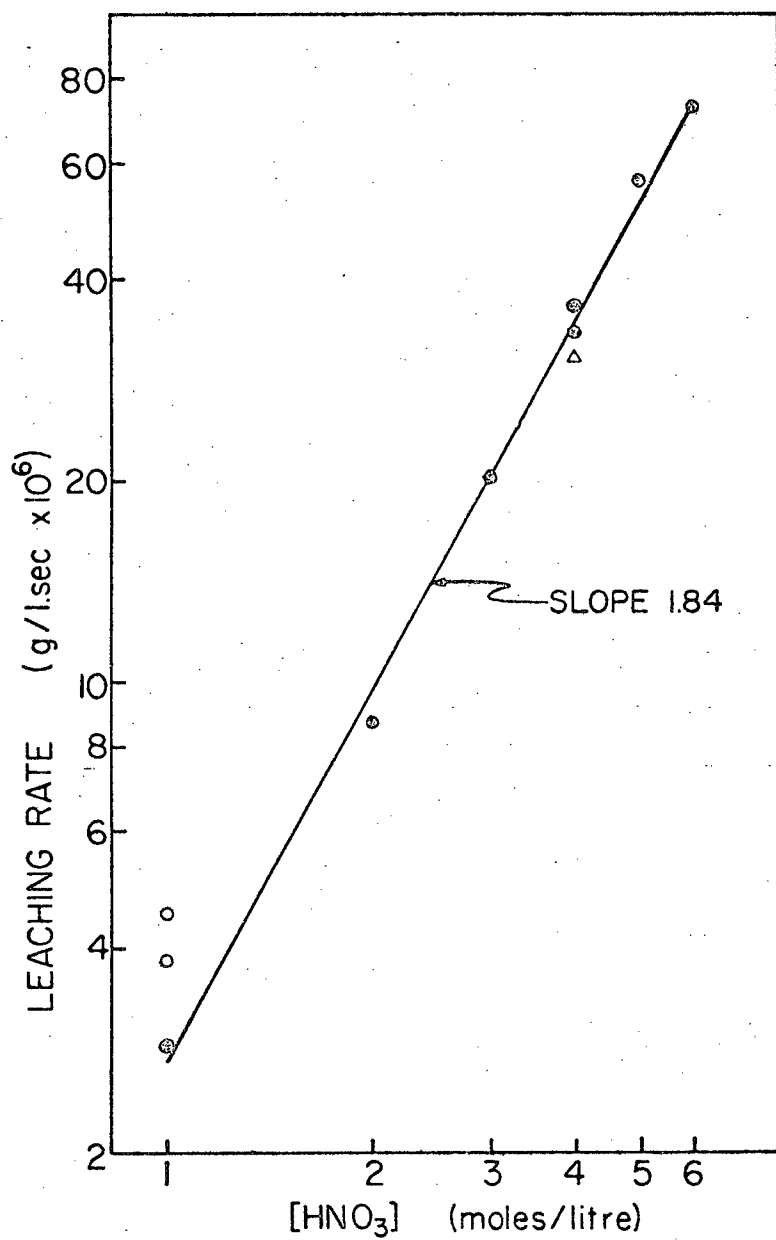


Figure 19. Log initial reaction rate vs. log initial HNO_3 for Brenda +325 mesh molybdenite concentrate.

the reactive surface area of the molybdenite changed as leaching progressed. Since the leaching rate is directly proportional to the active surface area the relative change in active surface area could be determined from controlled experiments. In these experiments the leaching conditions for each test were maintained constant. (solution composition, MoS_2 pulp density, temperature) except for the degree to which the input solids had been leached. The tests were performed in series with the residue from one test as the feed solids for the next test. The measured rates were plotted as a function of the arithmetic average of the degree leached of the input and output solids. For accuracy the degree of leaching within any particular test was kept relatively low. The results are plotted in Figure 20.

The experimental points were fitted to a three parameter exponential equation using the U.B.C. subroutine LQF [70].

$$r = 4.664 \times 10^{-3} e^{-3.3134 \phi^{0.3360}} \quad (\text{g/litre.sec}) \quad (37)$$

where ϕ = fraction of MoS_2 leached

This equation fits the points remarkably well but is unrealistic between zero extraction and the first experimental point, as well as for extractions above the final experimental value (~50%). For model

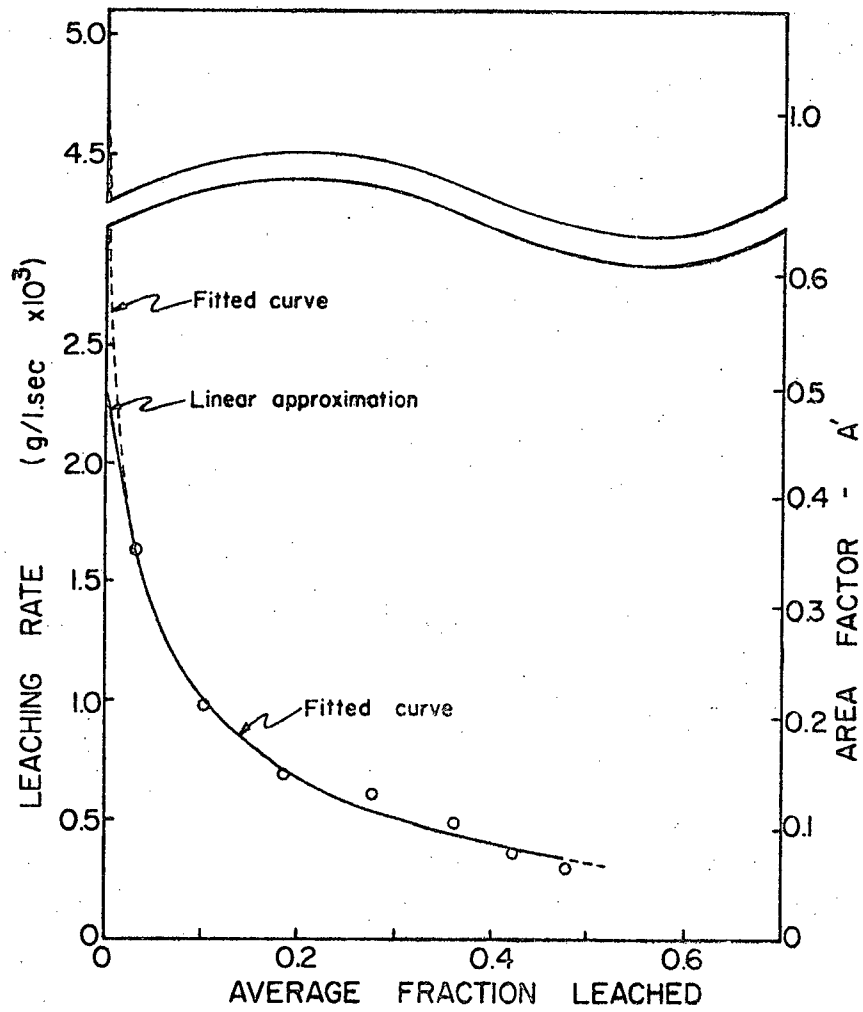


Figure 20. Leaching rate and area factor vs. fraction leached for Endako molybdenite concentrate. Constant leaching environment.

stability a separate linear relationship with an estimate of the intercept on the ordinate is assumed for the zone adjacent to zero extraction. The area factor, A' , is obtained by normalizing the experimental curve by dividing through by the extrapolated value of the rate at zero extraction. This value calculated from the curve fitting was initially employed although the use of the value from the linear approximation may be more realistic. It is not important though, since the normalizing value is only a reference point and will not influence the final results. Under this scheme the area factor relationship is given by:

$$\begin{aligned} A' &= 0.5003 - 4.586 \phi \\ \text{for } 0 &\leq \phi \leq 0.0333 \end{aligned} \quad (38)$$

and,

$$A' = e^{-3.3134 \phi^{0.3360}} \quad (39)$$

$$\text{for } 0.0333 \leq \phi \leq 0.5$$

Having calculated the value of n the effective rate constant K' can be calculated since at $t = 0$ $A' = 1$

$$r = K' [\text{HNO}_3]^2 \quad (40)$$

$$K' = 2.915 \times 10^{-4} \left(\frac{\text{g Mo}}{\text{mole Mo}} \right) \left(\frac{\text{l}}{\text{sec.mole HNO}_3} \right)$$

and
$$K'_O = 4.5359 \times 10^{10} \left(\frac{\text{g Mo}}{\text{mole Mo}} \right) \left(\frac{\ell}{\text{sec. mole HNO}_3} \right)$$

using an activation energy of 20 Kcal/mole.

This value accounts for the molar concentration of nitric acid and the mass rate of extraction of molybdenum.

By similar procedures the rate constants for pyrite and chalcopyrite in Endako concentrate were determined assuming activation energies of 10 Kcal/mole.

$$\text{Fe in FeS: } K'_O = 1.1516 \times 10^4 \left(\frac{\text{g Fe}}{\text{mole Fe}} \right) \left(\frac{\ell^{2/3} (\text{mole Fe})^{1/3}}{\text{mole HNO}_3 \cdot \text{sec}} \right)$$

$$\text{Fe in CuFeS}_2: K'_O = 2.618 \times 10^3 \left(\frac{\text{g Fe}}{\text{mole Fe}} \right) \left(\frac{\ell^{2/3} (\text{mole Fe})^{1/3}}{\text{mole HNO}_3 \cdot \text{sec}} \right)$$

$$\text{Cu in CuFeS}_2: K'_O = 2.978 \times 10^3 \left(\frac{\text{g Cu}}{\text{mole Cu}} \right) \left(\frac{\ell^{2/3} (\text{mole Cu})^{1/3}}{\text{mole HNO}_3 \cdot \text{sec}} \right)$$

CHAPTER 4

FORMULATION OF MODEL

The model is constructed on a modular basis with a main control program and separate subroutines for different real and hypothetical operations. The block diagram flowsheet on which the computer model is based is presented in Figure 21 while the flow diagram for the computer program is shown in Figure 22.

The model was developed using the computing facilities at U.B.C. Initial work was conducted on an IBM 370/168 while the latter stages involved the use of the Amdahl 470 V/6 - II. Double precision arithmetic was used for the calculations.

Initial Assumptions

(1) The feed concentrate is relatively uniform with respect to chemical analysis and partical size distribution. This is necessary since the behaviour of the model depends on parameters associated with the feed. Milling operations tend to produce a relatively consistent product despite variations in the mill heads so that a single calibration of a concentrate should be adequate.

(2) Laboratory determined parameters are assumed to apply to

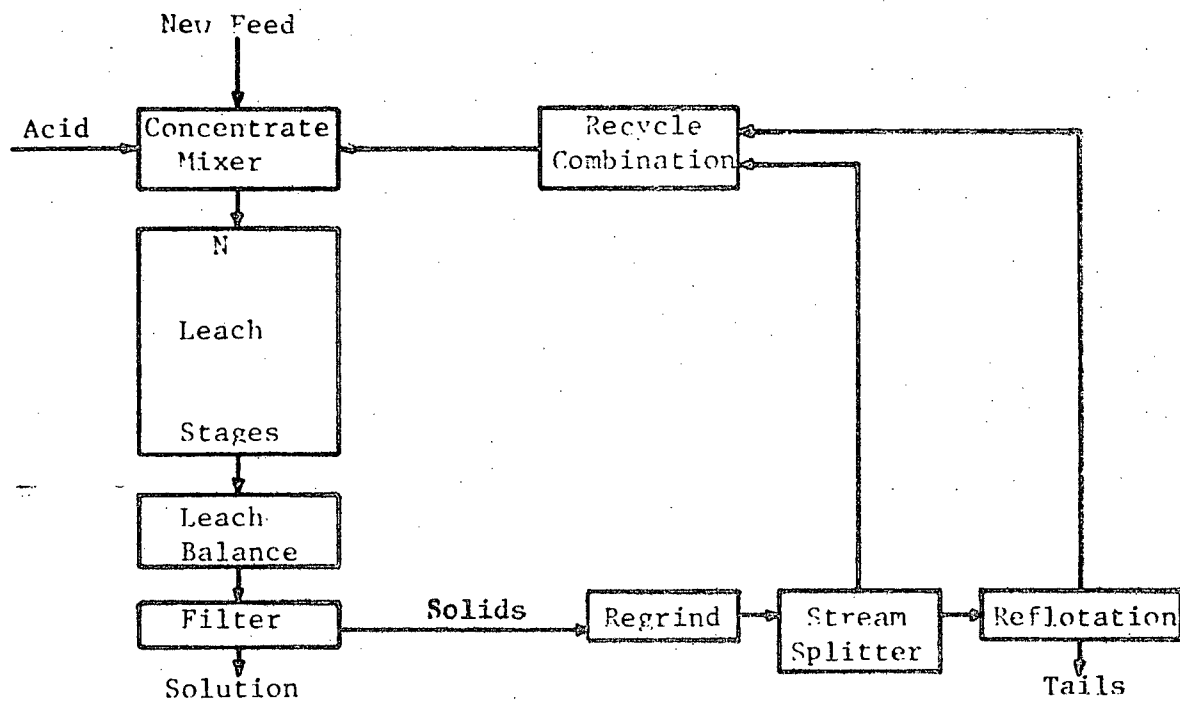


Figure 21. Model block diagram.

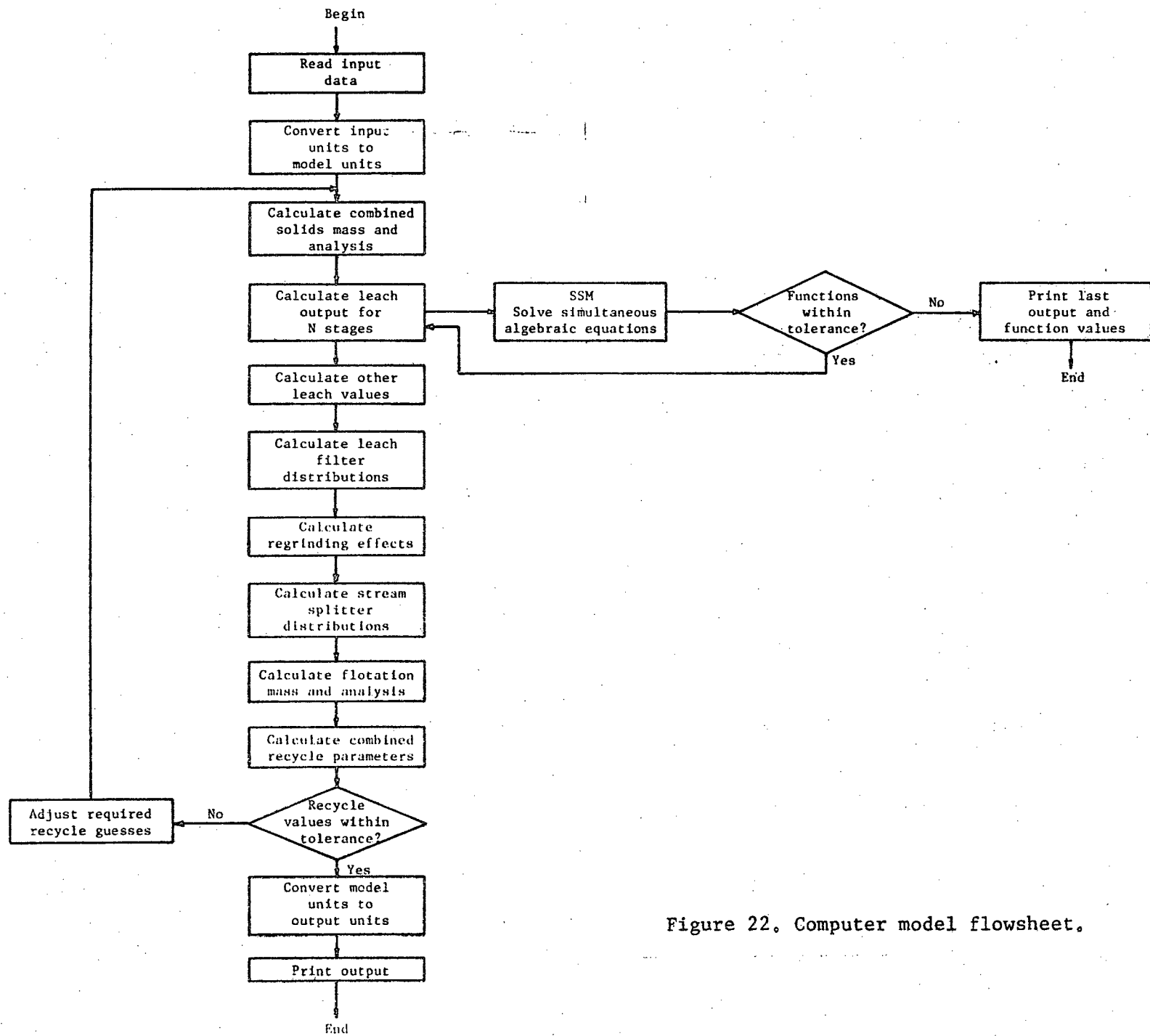


Figure 22. Computer model flowsheet.

industrial scale. This may apply reasonably well to many leaching systems but such extrapolation is less accurate in the case of grinding and to a smaller degree, flotation.

4.1 Recycle Estimates

Since there is a solids recycle stream in the flowsheet realistic estimates have to be made for the parameters associated with this stream in order to commence calculations. On passing through the entire cycle these recycle parameters are calculated and compared to the initial estimates. If the guessed and calculated values are not within a specified tolerance the guesses are adjusted and the calculations redone. The adjustment criterion is a modified Wegstein method which uses secant techniques. Two sets of guessed and calculated values are required to operate the secant method. The sets are produced by a small perturbation in the guessed variable for the first time it does not fall within tolerance. Subsequent new guesses are produced by the following relation

$$X_{k+1} = X_k - (X_k - XC_k)R \quad (41)$$

where X = estimated value

XC = calculated value

k = iteration number

R = multiplying factor defined by:

$$R = (X_k - X_{k-1}) / (X_k - X_{k-1} - XC_k + XC_{k-1}) \quad (42)$$

Subject to $R \leq R_{\max}$

This convergence algorithm is performed by the main program on recycle parameters that are initially out of tolerance or stray out of tolerance due to variations in other parameters.

4.2 Concentrate Mixer

This hypothetical unit combines the new solids and recycle solids to determine the bulk analysis of the total feed to the leach train. In reality new and recycle solids streams would be fed separately to the leach train with adequate mixing occurring quite rapidly in the first stage.

For the purpose of simplifying calculations the pyrite and chalcopryite in the recycle solids are transferred to the new solids stream.

4.3 Leaching

Assumptions

- (1) All leaching reactors operate at the same temperature.
(by controlled cooling)
- (2) Each reactor is backmixed.
- (3) The volume occupied by solids and gas in the slurry is small and relatively constant. For the model calculations the solids and gas are considered to occupy 8% of the total slurry volume.
- (4) Solution volume is assumed constant with variations occurring in density as the reaction proceeds.
- (5) All reacted sulphide is considered to dissolve as sulphate on the basis of the long contact times and the minor concentrations of chalcopyrite.
- (6) Negligible frothing occurs in the reactors.
- (7) Iron and copper are in the form of pyrite and chalcopyrite.
- (8) The leach is operated at approximately atmospheric pressure.

Since the reactors are backmixed the rates of reactions are dependent on the output concentrations of the influencing variables.

Hence the set of equations describing the leach must be solved simultaneously. A set of eighteen equations, fourteen of which are non-linear are established to simulate the leaching system.

Nomenclature for Leach Equations

Subscripts

i = input
o = output
R = recycle solids

Variables

v = volumetric flow rate of leach solution
 ρ = density of solution
w = mass flow rate of solids
X = mass fraction of component in phase
V = reactor volume
 R_g = rate of generation of component in phase per vessel
 R_c = rate of consumption of component in phase per vessel
 A' = area factor for new solids relative to standard pulp density
 A'_R = area factor for recycle solids relative to standard pulp density
 P' = ratio of current pulp density of new solids to

experimental pulp density used for determination of

K'_{Mo}

P'_R = ratio of current pulp density of recycle solids to
experimental pulp density used for determination
of K'_{Mo}

K'_{Mo} = rate constant for molybdenum leaching*

K'_{Fe} = rate constants for iron leaching*

K'_{Cu} = rate constant for copper leaching*

ϕ = fraction leached

LEACH EQUATIONS

Component Balances (g/s)

Liquid (Mo, Fe, Cu, HNO_3)

$$v \rho X_i - v \rho_o X_o + R_g - R_c = 0 \quad (43)$$

Solids (New Mo, Recycle Mo, Fe, Cu)

$$w_i X_i - w_o X_o + R_g - R_c = 0 \quad (44)$$

* based on 1 litre of solution.

Overall Mass Balances (g/s)

Liquid

$$v \rho_i - v \rho_o + \Sigma R_g - \Sigma R_c = 0 \quad (45)$$

Solids (New solids, Recycle Solids)

$$w_i - w_o + \Sigma R_g - \Sigma R_c = 0 \quad (46)$$

RATE EQUATIONS (New Mo, Recycle Mo, Fe, Cu, HNO₃) (g/s)

$$\text{New Mo } R_{\text{NMo}} = K'_{\text{Mo}} [\text{HNO}_3]^2 A' P' V \quad (47)$$

where A' is determined by interpolation of experimental results and P' by extrapolation based on a linear relationship between surface area and mass of solids.

$$\text{Recycle Mo } R_{\text{RMo}} = K'_{\text{Mo}} [\text{HNO}_3]^2 A'_R P'_R V \quad (48)$$

$$\text{Fe } R_{\text{Fe}} = K'_{\text{Fe}} [\text{HNO}_3] W^{2/3} V \quad (49)$$

In the model this rate is considered in two parts: that from FeS₂ and that from CuFeS₂.

$$\text{Cu } R_{\text{Cu}} = K'_{\text{Cu}} [\text{HNO}_3] W^{2/3} V \quad (50)$$

HNO₃

$$R_{\text{HNO}_3} = 3.9412R_{\text{Mo}} + 5.6419R_{\text{Fe}} + 0.6611R_{\text{Cu}} \quad (51)$$

where the constants are based on the stoichiometry of leaching of MoS₂, FeS₂, CuFeS₂.

AREA FACTORS (New Mo, Recycle Mo)

$$\text{New Mo } A' = e^{-a_2\phi^{a_3}} \quad (52)$$

where a₂, a₃ are empirically determined constants.

$$\text{Recycle Mo } A'_R = b_1 e^{-b_2 b_3 \phi_R} \quad (53)$$

where b₁ and b₂ are parameters conditioned by the regrinding step and b₃ is a constant.

The solution of such a set of non-linear and linear equations is a formidable task. Several subroutines are available at U.B.C. to solve these equations but the subroutine SSM (see U.B.C. NLE) was chosen since it was quoted as the most "robust" [67,68]. The equations are programmed in the following form:

Non-Linear

$$F_x = 0 \quad (54)$$

Linear

$$A_x = B \quad (55)$$

Basically this is a secant method which requires an initial set of output guesses to commence computations. Hence guesses have to be provided for each leaching stage.

4.4 Leach Balance

The purpose of this subroutine is to calculate final stage leach output values that are not determined by the solution of the simultaneous equations. Values calculated are:

- (1) Total solids flow rate - sum of new and recycle solids.
- (2) Molybdenum content of combined solids.
- (3) Siliceous insoluble content of solids by mass balance since this component is unaffected by the leach.
- (4) Sulphur contents of combined solids and of liquid by stoichiometric balance.
- (5) Calculation of the weighted-average area factor of solids exiting the leach.
- (6) Total fraction of molybdenum leached from new and recycle input solids.

4.5 Filter

The filter subroutine performs the solid/liquid separation on the leached slurry. At present it allows for 100% of the solids

to pass to the regrind operation but was included for future expansion of the program. The main factor to consider in filtration would be the loss of filtrate in the filter cake rather than loss of solids.

4.6 Regrind

The regrind operation not only increases the absolute value of the area factor but also increases the curvature of the remaining composite area decay curve. From Figure 20 it can be seen that the area decay curve approaches linearity after a relatively low degree of leaching. Regrinding would increase the curvature but probably not to the same extent as the initial concentrate. In the process of milling the original ore numerous size reduction steps are involved, all having the potential to produce fines. The size reduction steps are listed in Table VIII.

Table VIII

SIZE REDUCTION STEPS IN NORMAL MILLING OPERATIONS

1	Primary Crushing
2	Secondary Crushing
3	Tertiary Crushing
4	Rod Milling
5	Ball Milling
6	Regrind Ball Milling (may be more than one regrind mill)

Particles may bypass or be recycled through some size reduction steps by classifiers operated in closed circuit. Since the regrind step in the current flowsheet involves one single-pass operation before returning to the leach it is probable that the "fines" content is not as great as in the new concentrate. Hence the area factor relationship for the recycle concentrate will differ from that for the new concentrate and is assumed to follow the relationship in Equation (53). The recycle area parameters are determined as follows:

$$b_1 = A'_L + k_g t_g \quad (56)$$

where A'_L = composite area factor value at leach exit

b_1 = area factor value at grind exit.

k_g = grind constant (t^{-1})

t_g = mean residence time in grinding mill.

$k_g t_g$ = incremental new surface area factor created.

But k_g cannot be determined directly by experimentation.

$$\therefore b_1 = A'(1 + k'_g t_g) \quad (57)$$

since $k_g = k'_g A'$

where k'_g is determined experimentally (see Appendix D)

No information was available on the form of the exponential portion of Equation (53). To avoid undue complexity in view of the uncertainty surrounding this expression the relationship is simply assumed as:

$$b_2 = 1 + k'_g t_g \quad (58)$$

and b_3 = an appropriate constant which influences the shape of the recycle area decay plot.

4.7 Stream Splitter

The stream splitter divides the mass flow from the regrind mill to the flotation section or directly back to the leach according to a predetermined ratio.

Assumption

The stream splitting is assumed to be unbiased so that the chemical analysis and surface area parameters associated with the two separate streams are the same as those for the reground solids.

4.8 Flotation

Assumptions

- (1) Flotation rates are considered as first order with respect to mineral concentration in the pulp.
- (2) The flotation rates of each mineral are described by separate single rate constants.
- (3) The pulp residence time in each cell is only significantly influenced by the flotation of the dominant component (molybdenite).
- (4) Cell volume is 25% air in pulp during operation [69].
- (5) A simple series of flotation cells is used with no pulp recycle.

Nomenclature for Flotation

- R_i = fractional mineral recovery from i^{th} cell ($i=1$ to n)
- K = flotation rate constant
- θ_i = pulp residence time in i^{th} cell
- u = pulp volumetric flow into bank of cells
- m = mass flow rate of floatable component into cell
- α = factor which converts mass of floated solids to volume of flotation pulp (50 wt % H_2O)
- V = volume of deaerated pulp in cell.

The pulp residence time in the first cell based on the tailings flow is:

$$\theta_1 = \frac{V}{u - \alpha m R_1} \quad (59)$$

Since θ is variable with cell number the total recovery cannot be obtained from a simple series summation as when θ is assumed constant. Hence the recovery of MoS_2 is determined on a cell-by-cell basis. For the n^{th} cell:

$$R_n = \frac{K\theta_n}{1 + K\theta_n} \left(1 - \sum_{i=1}^{n-1} R_i\right) \quad (60)$$

and

$$\theta_n = \frac{V}{u - \alpha m \left(R_n + \sum_{i=1}^{n-1} R_i\right)} \quad (61)$$

$$= \frac{V}{u - \alpha m \sum_{i=1}^n R_i} \quad (62)$$

By substituting Equation (61) into Equation (60) and rearranging:

$$\alpha m R_n^2 - \left(u - \alpha m \sum_{i=1}^{n-1} R_i + KV\right) R_n + \left(1 - \sum_{i=1}^{n-1} R_i\right) KV = 0$$

which is a quadratic equation and can be solved for the root $0 < R_n < 1$.

$$R_n = \frac{(u - \alpha m \sum_{i=1}^{n-1} R_i + KV) - \sqrt{(u - \alpha m \sum_{i=1}^{n-1} R_i + KV)^2 - 4\alpha m(1 - \sum_{i=1}^{n-1} R_i)KV}}{2\alpha m}$$

(63)

Equations (63) and (62) are solved sequentially for each flotation cell with the overall recovery of molybdenite given by the summation of the individual cell recoveries. Then equations of the same form as Equation (60) are used for the recoveries of the other minerals using the cell residence times already established by the molybdenite flotation.

4.9 Recycle Combination

This hypothetical unit is used to determine the calculated recycle parameters of mass flow, chemical analysis (5 components) and area factor parameters for comparison to the estimated values. The mass flow and analysis are determined by a mass balance on the solids recycling directly after grinding and those in the refloatation concentrate.

Assumption

The refloat product is assumed to have the same area factor parameters as the solids which are reground only. The error introduced

by this simplification is negligible since there is a very high recovery of molybdenite during refloatation.

4.10 Input/Output Routines

The functions of these routines are:

- (1) a. Convert input units to model units
b. Convert model units to output units
when convergence of recycle parameters has been successful.
- (2) Control converged output printing with additional overall calculations.

CHAPTER 5

MODEL EVALUATION AND DISCUSSION

Although some aspects of the overall model are still subject to uncertainty the simulation was partially evaluated in the current form. Complete validation is not possible until a continuous plant is constructed although model viability could likely be improved with further laboratory experimentation, particularly with respect to grinding and flotation.

Model results were obtained for a moderately-sized plant with the calibrated Endako concentrate as the plant feed. Since the system operates under steady-state conditions the response of most interest was the solids recycle ratio. The recycle ratio would be subject to some maximum limit depending on the initial solids feed rate and the maximum pulp density under which the leach can continue to operate satisfactorily. With any steady-state model caution should be exercised in relating model values to plant values where fluctuations occur. In a relatively slow leaching system such as this, fluctuations should occur with low frequency. Attainment of steady state after adjusting some variable should similarly take considerable time.

In interpreting the behaviour of such a system it should be

remembered that the C and A terms in Equation (21), describing the basic rate relationship, are not purely independent variables. The new input values are independent to the extent of possible plant operations but interact in arriving at the steady state values operating in each leaching vessel. The relationship is further complicated by the presence of the solids recycle stream.

The model calculations were based on a chosen standard condition and the effects of individually varying particular plant or process variables. The standard conditions are outlined in Table IX.

Table IX

STANDARD CONDITION OF LEACH PROCESS

Vessels - 2 cocurrent at 120,000 litres each

New Feed - 10.8 tonnes/day Endako MoS_2 (as calibrated)

Solution - 87.8 litres/min.

- 252.1 grams HNO_3 /litre (4 M)

Leach Temperature - 35°C

Approximate Leach Stage Residence Time - 19.5 hr.

Grinding Mill Solids Hold Up - 800 kg

Fraction of Recycle Bypassing Flotation - 0.5

Flotation Cells - 4 x 150 litres

This choice is not necessarily an optimum but allows the determination of the influences on the process of particular variables. Trends which result in a decreasing recycle ratio, and hence lower input pulp density, show the potential for increased throughput while still operating below the maximum allowable pulp density.

For this study a tolerance of 0.25% was used on the recycle parameters. (absolute value of difference of estimated and calculated value divided by the average of the two and multiplied by 100). This would lead to a tolerance on the calculated molybdenum extraction versus the steady state extraction of less than about 1.8%.

Tolerance error is the cause of the small scatter in the following graphs. In these graphs each point represents individual model determinations.

5.1 Stability and Convergence

Stability

The problems of instability arise in the solution of the simultaneous equations describing each leaching stage. Instability in such a set of equations becomes more likely as the equations become increasingly complex and non-linear. This requires greater emphasis

on the choice or calculation of initial estimates to commence model runs and to continue calculations until a specified convergence criterion on the recycle stream is satisfied.

Failure of the leach-solving subroutine to converge within its specified tolerance can be attributed to two general reasons:

(1) Failure of the algorithm by its inability to determine an independent set of directions for the variables. Hence the guesses for the stage output were in excessive error.

(2) Convergence of the leach algorithm was not achieved within the maximum number of internal iterations specified (set at 150). This also indicates bad guessing and may further result in failure by (1) if a greater number of iterations was specified.

Once computations have commenced stability is enhanced by basing new estimates on previous calculations. The guess criteria are outlined as follows where:

$X_{k,j}$ = estimated value

$XC_{k,j}$ = calculated value

G_F = guess factor for stage 2 based on stage 1 output

k = leaching stage counter

j = cycle iteration counter

(1) 1st stage output guesses:

(a) Initial guess for $j = 1$

$$X_{1,1}$$

(b) For $j > 1$

$$X_{1,j} = X_{C,1,j-1} \quad (64)$$

(2) 2nd stage output guesses:

(a) Initial guess for $j = 1$

$$X_{2,1} = G_F X_{C,1,1} \quad (65)$$

(b) For $j > 1$

$$X_{2,j} = \frac{X_{C,2,j-1}}{X_{C,1,j-1}} \cdot X_{C,1,j} \quad (66)$$

(3) 3rd stage output guesses

(a) Initial guess for $j = 1$

$$X_{3,1} = \frac{X_{C,2,1}}{X_{C,1,1}} \cdot X_{C,2,1} \quad (67)$$

except for rate equations where

$$X_{3,1} = M \cdot \frac{X_{C,2,1}}{X_{C,1,1}} \cdot X_{C,2,1} \quad (68)$$

where M is taken as 1.5

(b) For $j > 1$

$$X_{3,j} = \frac{XC_{3,j-1}}{XC_{2,j-1}} \cdot XC_{2,j} \quad (69)$$

(4) 4th stage or greater output guesses:

(a) Initial guess for $j = 1$

$$X_{k,j} = \frac{XC_{k-1,j}}{XC_{k-2,j}} \cdot XC_{k-1,j} \quad (70)$$

(b) For $j > 1$

$$X_{k,j} = \frac{XC_{k,j-1}}{XC_{k-1,j-1}} \cdot XC_{k-1,j} \quad (71)$$

Mathematical instability could also arise within the system of algebraic equations since the solving routine is unconstrained. In searching for the true values certain variables may cause instabilities or impossibilities in particular equations as follows:

(1) A negative number to a fractional power

(2) Negative concentration or flow rate

In most cases when this condition arises, mathematical and physical stability is maintained by using an alternate equation where the appropriate term is set to zero. In one case stability is maintained by setting the term to zero in the original equation.

Convergence

Convergence of the eight recycle parameters within a specified

tolerance is required before the complete output is printed. Convergence is attained by the previously defined adjustment criterion, but to maintain the leach calculation stability, the step sizes must be less than current critical values.

Since the step size is relative to the difference between the estimated value and calculated value the approach to convergence would decelerate as the true value is approached. Hence the fractional adjustment is increased as the tolerance becomes smaller with model stability maintained since the absolute variation is still small.

It was apparent from the early model work that the mass flow rate of recycle solids created more sensitivity to instability. Therefore, for high calculated tolerance values, the fractional adjustment to this particular variable is less than for the others. For low tolerance values high fractional adjustments are operative for all recycle parameters.

Under this convergence scheme all parameters that are not within tolerance are continually adjusted until tolerance is achieved or the computer run terminated. Some recycle parameters such as molybdenum and sulphur contents are quite predictable and experience only small variations. Convergence is therefore quite rapid for these variables.

The recycle parameters are not entirely independent variables.

Hence variations in one parameter can cause alterations in other parameters. This can lead to a floating effect on some variables particularly those that are more highly dependent on each other such as recycle solids flow rate and area factor parameters. With different degrees of interdependency and different adjustment factors convergence is approached by at least one variable while the other(s) may 'float'. Once the first has converged the other(s) begin converging.

For economical convergence the estimates for the recycle parameters should not be grossly in error. Guesses that are highly in error will lead to excessive computation times.

For concentrates containing relatively small amounts of iron and copper the convergence criterion becomes superfluous for these two elements. Since they are leached to extremely low levels (essentially zero), tolerance adjustments are not necessary after the recycle values for these two elements have been set to appropriately low levels.

Aborted Runs

Once instability or lack of convergence of the leach sub-routines has occurred the computer run is terminated. Often the printed output can be helpful for subsequent runs since, although failure has occurred, many variables have approached their converged values. The

terminated values for the first stage output guesses, the recycle parameters and guess factors if necessary, except for those in obvious error, can be used for the subsequent run. The more erroneous values should be altered slightly in the appropriate direction. The direction can be ascertained from a knowledge of the variables involved and the form of the equation in the model (ie. $Fx = 0$).

To date most errors have been associated with the rate equations. Hence if model failure does occur success can be achieved with an interactive procedure, often within one or two attempts.

5.2. Model Results

5.2.1 New Solids Flow Rate

This variable determines the production of the leaching process since, at steady state, the input of new feed must be balanced by the extraction of the same amount of material to the appropriate exit streams. The range of the new solids flow rate is subject to constraints of maintaining physical stability of the system, particularly with respect to the maximum operable pulp density within the leach.

Figure 23 demonstrates how the recycle ratio increases at an increasing rate as the new solids feed rate is raised. The graph will

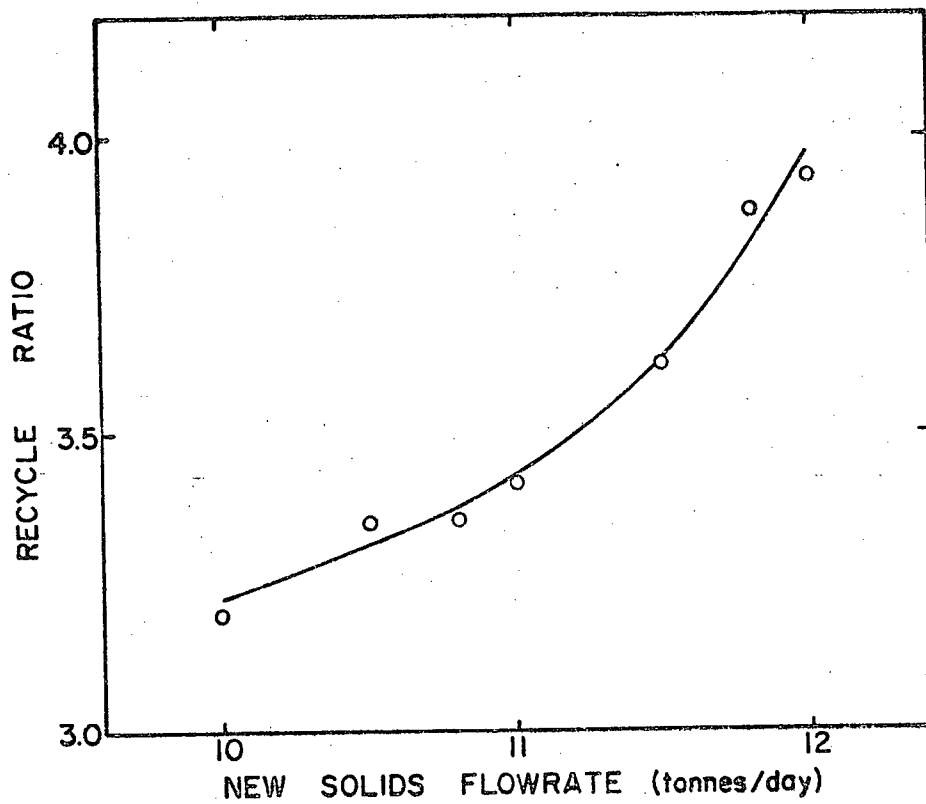


Figure 23. Solids recycle ratio vs. new solids flowrate. Other conditions standard.

approach an asymptotic limit as the stoichiometric balance of leachable minerals and nitric acid approaches complete consumption of the nitric acid for steady state conditions. Under most leaching conditions the maximum pulp density restrictions will likely be encountered before this limit is reached. The impact of the greater new solids input and correspondingly greater recycle solids flow rate is to lower the solution reactivity in each leaching stage. This shown in Figure 24 where the nitric acid concentration in each stage is plotted as a function of the new solids feed rate. Figure 24 also shows the variation in other factors which affect the overall rate of molybdenum extraction to solution. The total input pulp density is raised as a consequence of increases in both the new and recycle solids streams. The operating area factors for both the new and recycle solids are greater for increased solids input since both are leached to lesser degrees on passing through the leach.

For increased new solids flow rate there is a greater input of molybdenum to solution. Hence for constant solution flow rate the net gain in molybdenum concentration is greater. This point is confirmed by Figure 25 where the difference between the pregnant solution and recycle solution molybdenum contents is plotted against new solids feed rate.

The lowering of the percent molybdenum extraction per pass as the new solids feed rate is increased is shown in Table X. The

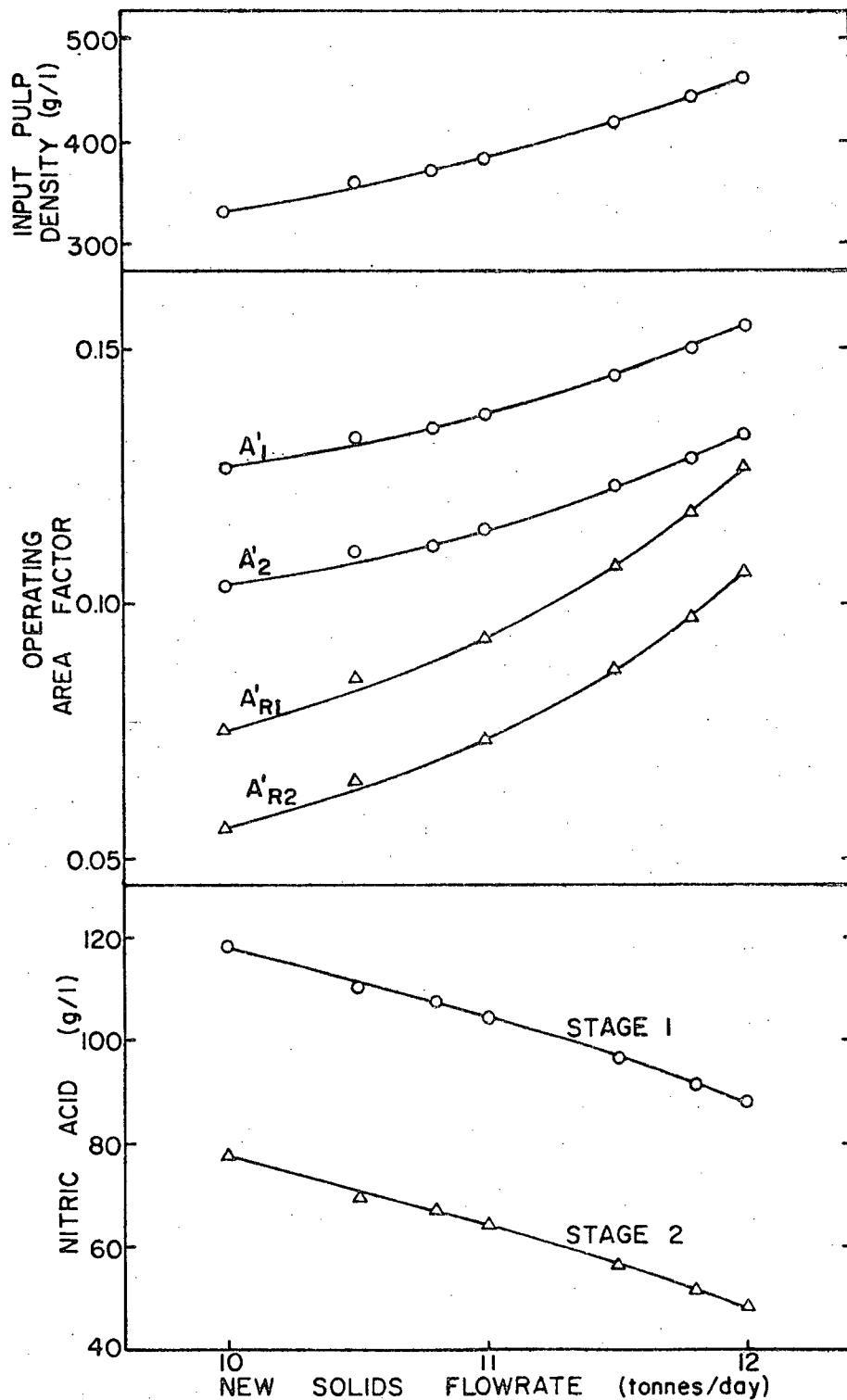


Figure 24. Total input pulp density, operating area factors and operating nitric acid concentrations vs. new solids flowrate. Other conditions standard.

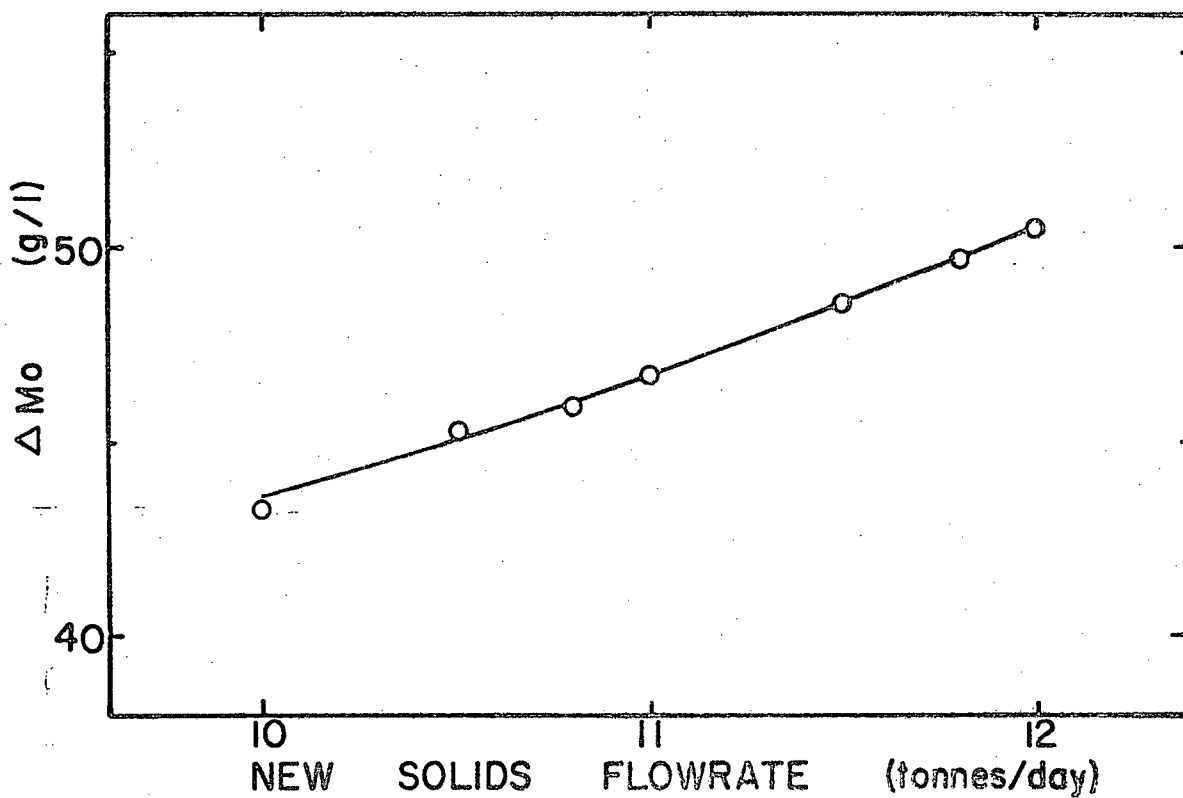


Figure 25. Gain in solution molybdenum concentration vs. new solids flowrate. Other conditions standard.

total input solids signify new and recycle concentrates.

Table X

EXTRACTION FROM TOTAL INPUT SOLIDS ON EACH PASS
FOR DIFFERENT NEW SOLIDS FLOW RATES(%)

New Solids Flow Rate (tonne/day)	Stage 1	Stage 2	Stage 1+2
10.0	18.2	5.6	23.8
10.5	17.7	5.2	22.8
10.8	17.5	5.0	22.5
11.0	17.2	4.9	22.1
11.5	16.7	4.4	21.1
11.8	16.3	4.1	20.4
12.0	16.0	3.9	19.9

It is also evident that the proportion of extraction work done by the leach vessels shifts slightly more in favour of the first stage.

5.2.2 Initial Acid Strength

The initial acid strength is similarly subject to stoichiometric restrictions. Figure 26 shows how the recycle ratio increases as the initial nitric acid concentration is decreased, again approaching

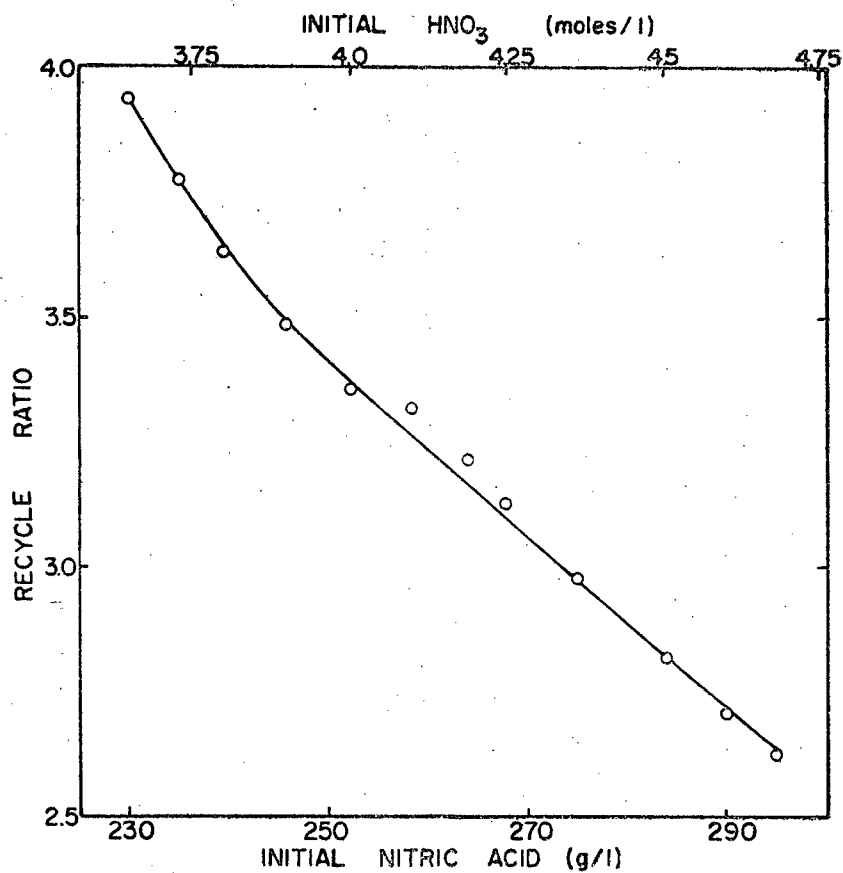


Figure 26. Solids recycle ratio vs. initial nitric acid concentration. Other conditions standard.

an asymptotic limit due to depletion of nitric acid under steady operations. This result indicates the advantage of using as high an initial nitric acid concentration as possible, subject to practical limitations. As shown earlier, the extent to which molybdenum can be precipitated from solution is subject to pH. On a plant scale there may be an optimum balance between leaching rate and the recycle of soluble molybdenum for different operating acidity levels. The earlier laboratory work on the process did show some slight discolouration of the hemi-hydrate when using high initial nitric acid concentrations ($\sim 6M$). The cause and extent of this was not fully determined although product purity was still high.

With higher initial nitric acid concentrations each leaching vessel operates at higher nitric acid levels, as demonstrated by Figure 27. The increased leaching rates result in a greater degree of reaction of the solids and hence operation at lower area factor values. Figure 27 shows how the operating area factors vary as a function of initial nitric acid concentration. The decrease in input pulp density as a function of initial nitric acid results from the lower solids recycle. This is also shown in Figure 27.

Since the mass flow of new solids and volumetric flow of solution are constant for this series of runs the gain in solution molybdenum concentration is consistent at the steady state level. Hence,

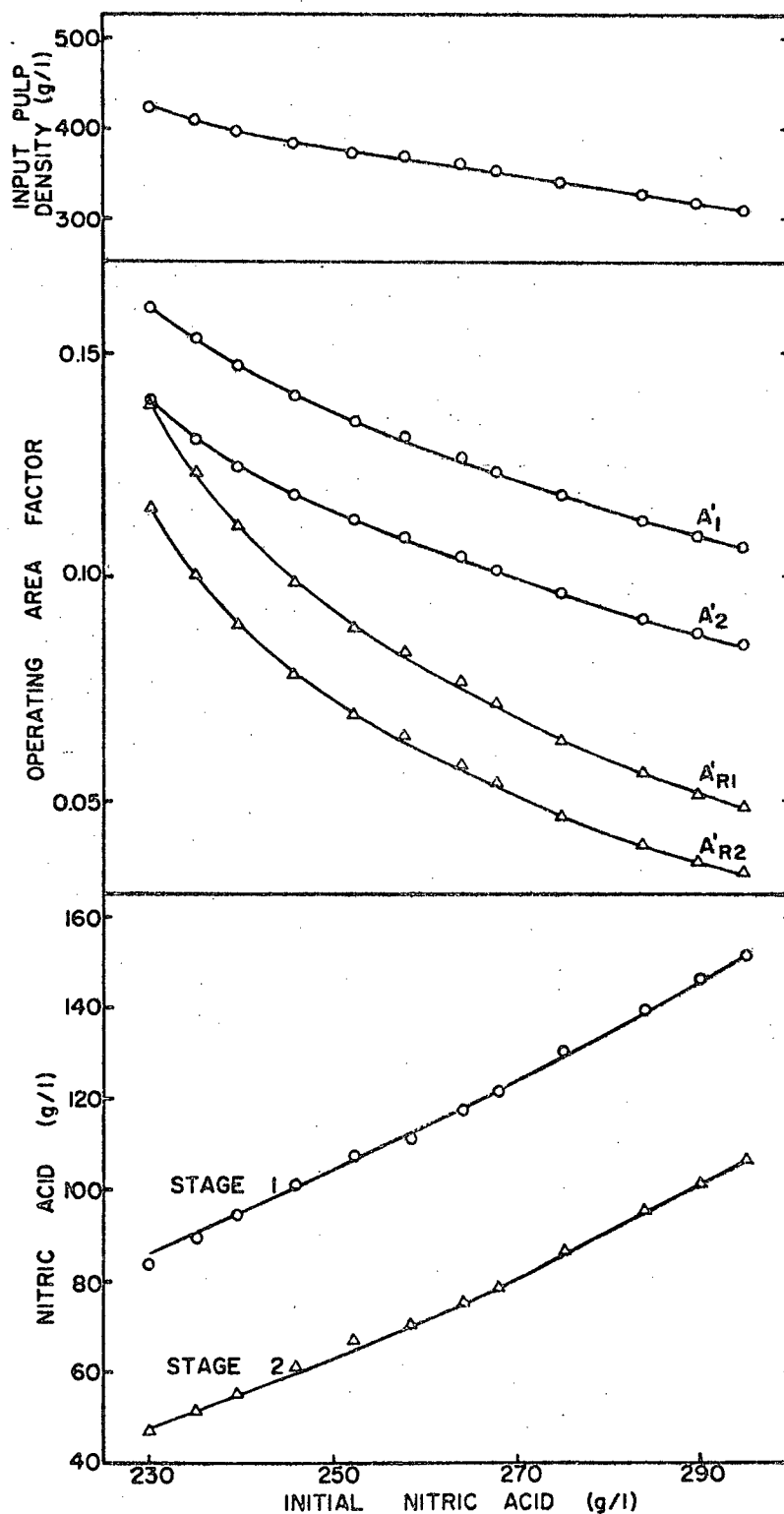


Figure 27. Total input pulp density, operating area factors and operating nitric acid concentrations vs. initial nitric acid concentration. Other conditions standard.

there is no increase in the molybdenum content of the pregnant solution to offset the higher solubility limits at pH's less than the isoelectric point. However, increased input acid levels will allow a greater treatment rate of new molybdenite concentrate thus producing a richer pregnant solution while still operating below the maximum pulp density.

The greater leaching rates result in higher operating siliceous insoluble concentrations in solids throughout all phases of the leaching operation. The operating concentrations for leach residue, refloatation product and recycle solids are graphed against initial nitric acid in Figure 28. This trend applies to variations in all parameters which lead to increased instantaneous reaction rates.

The percent extractions from total solids input of Table XI naturally show increases as the initial nitric acid concentration is raised.

5.2.3 Solution Flow Rate

The variation of solution flow rate has a similar effect on the solids recycle ratio as changes in initial nitric acid concentration. This follows from the stoichiometric balance since a lower solution flow rate of the same acid concentration results in fewer moles of acid

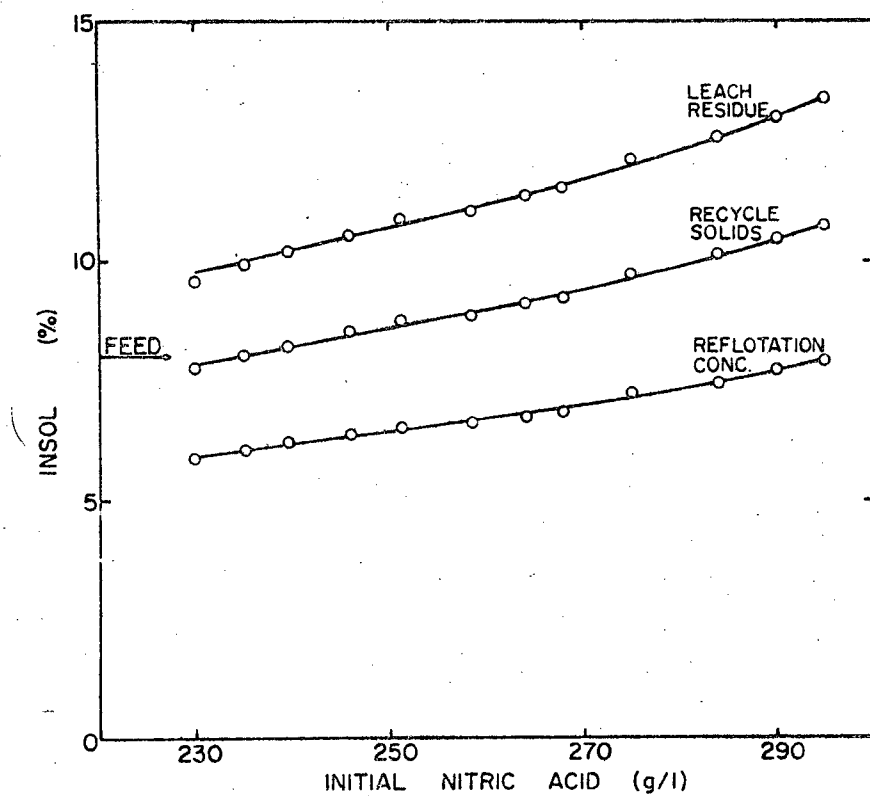


Figure 28. Insol content of leach residue, reflation concentrate and recycle solids vs. initial nitric acid concentration. Other conditions standard.

Table XI

EXTRACTION FROM TOTAL INPUT SOLIDS ON EACH PASS
FOR DIFFERENT INITIAL NITRIC ACID CONCENTRATIONS(%)

Initial HNO_3 (g/l)	Stage 1	Stage 2	Stage 1+2
230	15.6	3.9	19.5
235	16.0	4.2	20.2
239.5	16.4	4.5	20.9
245.8	17.0	4.8	21.7
252.1	17.5	5.0	22.5
258.4	17.8	5.2	23.0
264	18.3	5.4	23.7
667.8	18.6	5.6	24.2
275	19.3	6.0	25.2
284	20.0	6.4	26.4
290	20.6	6.6	27.2

The gain in percent extraction for the first stage outweighs the gain in the second stage extraction.

available for the same quantity of solids. The solids recycle ratio versus solution flow rate is graphed in Figure 29. Again it can be seen that the recycle ratio rises to an asymptotic limit as the solution flow rate is decreased.

The factors influencing the rate of reaction are plotted in Figure 30. With increasing solution flowrate the solution has less residence time to react and therefore operates at higher nitric acid levels in each leaching stage. With higher solution reactivity the recycle ratio and hence input pulp density are lowered. The greater degree of reaction similarly results in operation at lower levels of area factor.

Despite the increased solution reactivity the lower residence time and steady-state operation result in a lower gain in molybdenum concentration in solution, as shown in Figure 31. The net quantity of dissolved molybdenum is still the same since the volume flow of solution is greater. With similar total acidity the molybdenum precipitated per litre in subsequent processing will be less but this would be compensated by higher volumetric throughput.

A greater percentage extraction per pass through the leach is obtained as the solution flow rate is increased. The values in Table XII

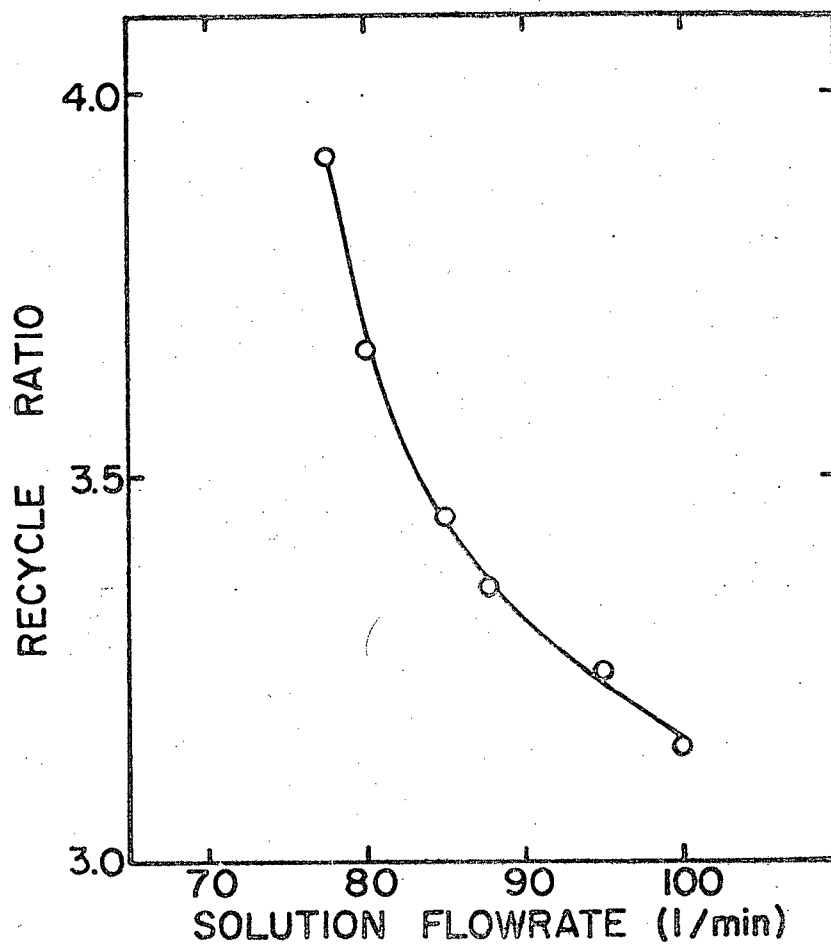


Figure 29. Solids recycle ratio vs. solution flowrate. Other conditions standard.

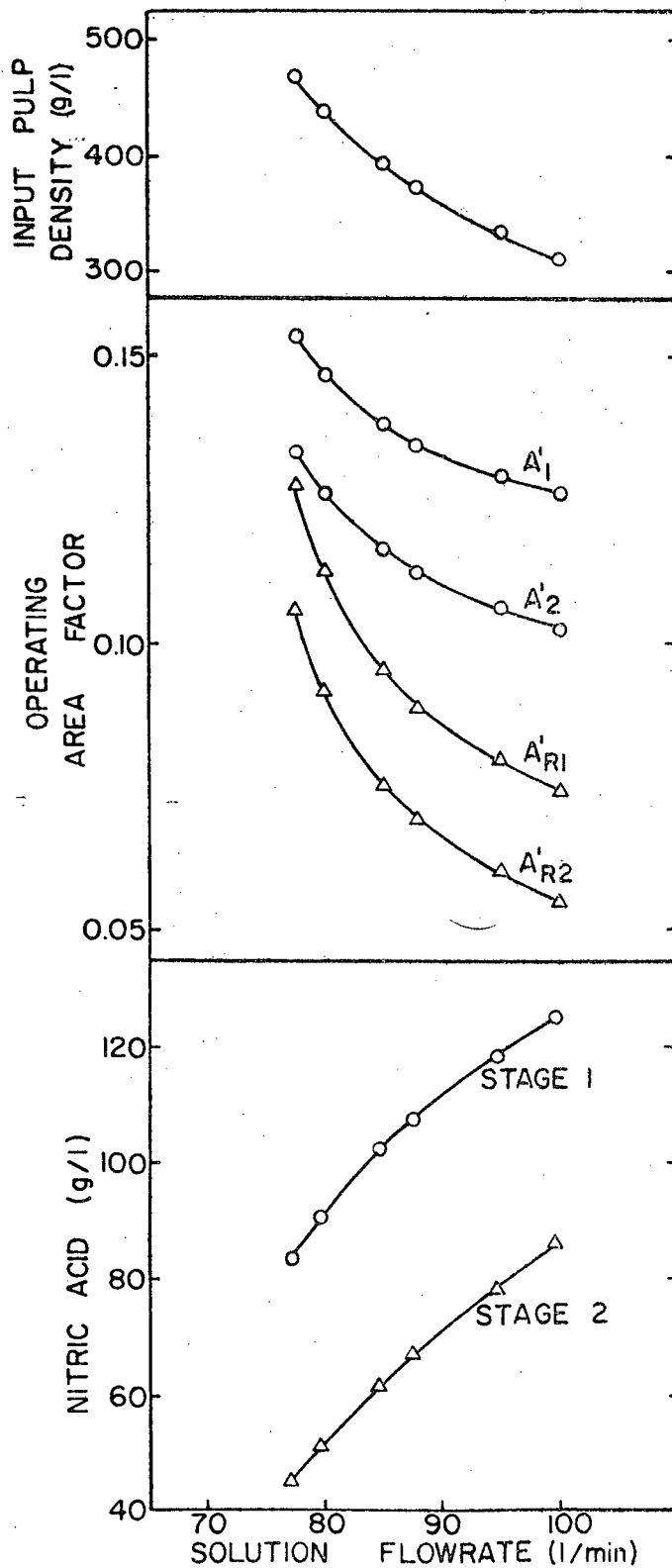


Figure 30. Total input pulp density, operating area factors and operating nitric acid concentrations vs. solution flowrate. Other conditions standard.

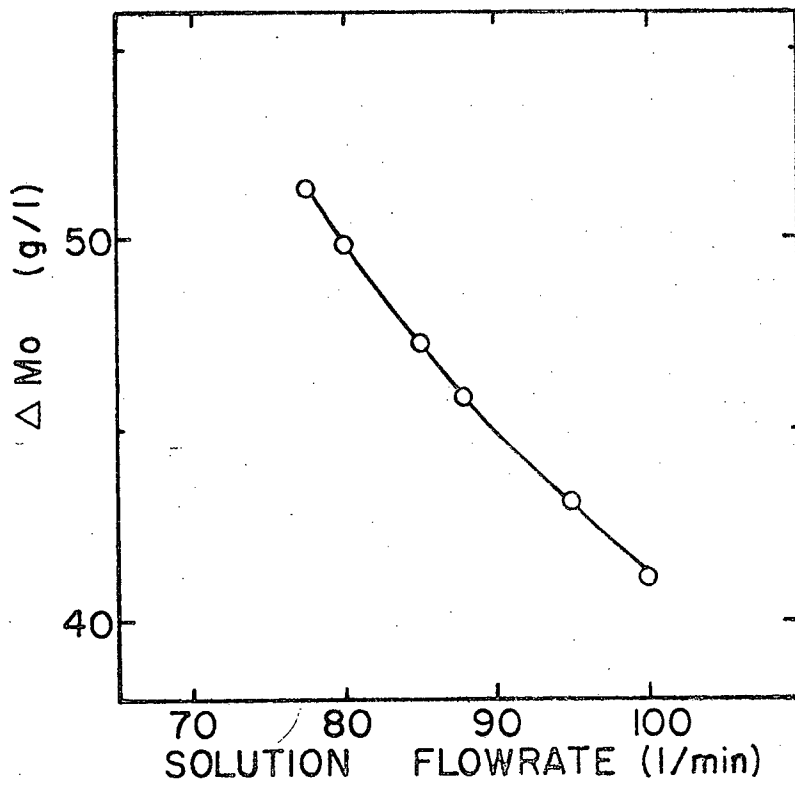


Figure 31. Gain in solution molybdenum concentration vs. solution flowrate. Other conditions standard.

also show only a very slight change in the work distribution between stages with the second stage exhibiting a marginally greater gain in percent extraction than the first.

Table XII

EXTRACTION FROM TOTAL INPUT SOLIDS ON EACH PASS
FOR DIFFERENT SOLUTION FLOW RATES(%)

Solution Flow Rate (ℓ/min)	Stage 1	Stage 2	Stage 1+2
77.5	16.2	3.8	20.0
80.0	16.6	4.2	20.8
85.0	17.2	4.7	21.9
87.8	17.5	5.0	22.5
95.0	17.9	5.6	23.5
100.0	18.2	6.0	24.1

5.2.4 Leach Temperature

As with any thermally-activated process the instantaneous reaction rate increases exponentially with temperature. As Figure 32 shows, the recycle ratio diminished as the leaching temperature was raised. Over the temperature range examined there was a slight indication of curvature in the anticipated direction.

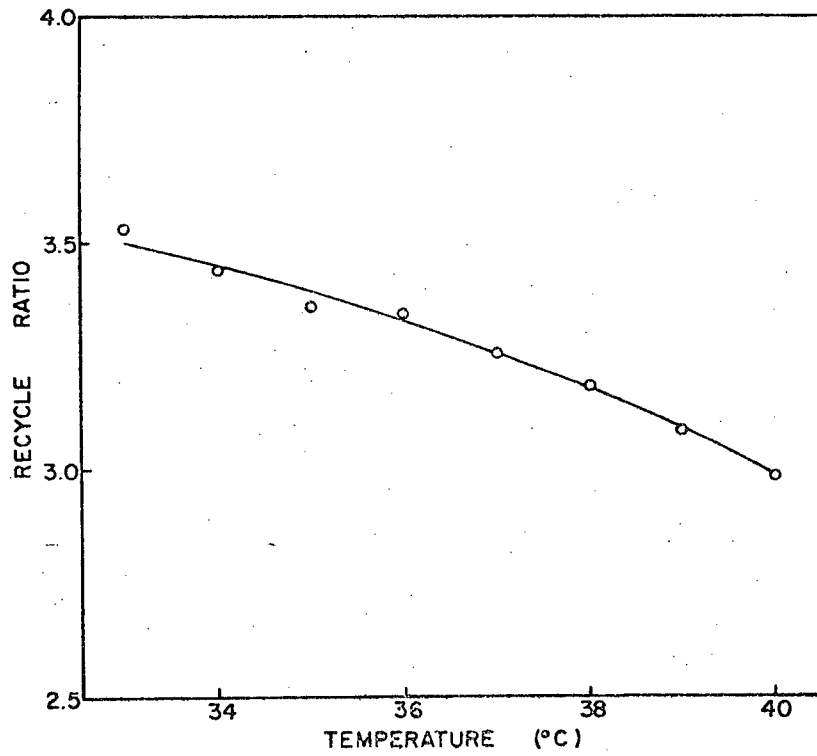


Figure 32. Solids recycle ratio vs. leach temperature. Other conditions standard.

Figure 33 shows that the input pulp density and operating area factors are at lower levels for higher temperatures. Any change in operating nitric acid levels was not significant within the tolerance limits used. With constant new solids and solution input the steady state operations result in a constant gain in molybdenum concentration in the pregnant solution.

Changes in the leaching temperature result in a slight alteration in the distribution of leaching work done by each stage as can be seen in Table XIII.

Table XIII

EXTRACTION FROM TOTAL INPUT SOLIDS ON EACH PASS
FOR DIFFERENT LEACH TEMPERATURES (%)

Temp (°C)	Stage 1	Stage 2	Stage 1+2
33	16.6	4.9	21.6
34	17.0	5.0	22.0
35	17.5	5.0	22.5
36	17.8	5.0	22.8
37	18.3	5.1	23.4
38	18.7	5.2	23.9
39	19.2	5.3	24.5
40	19.8	5.4	25.2

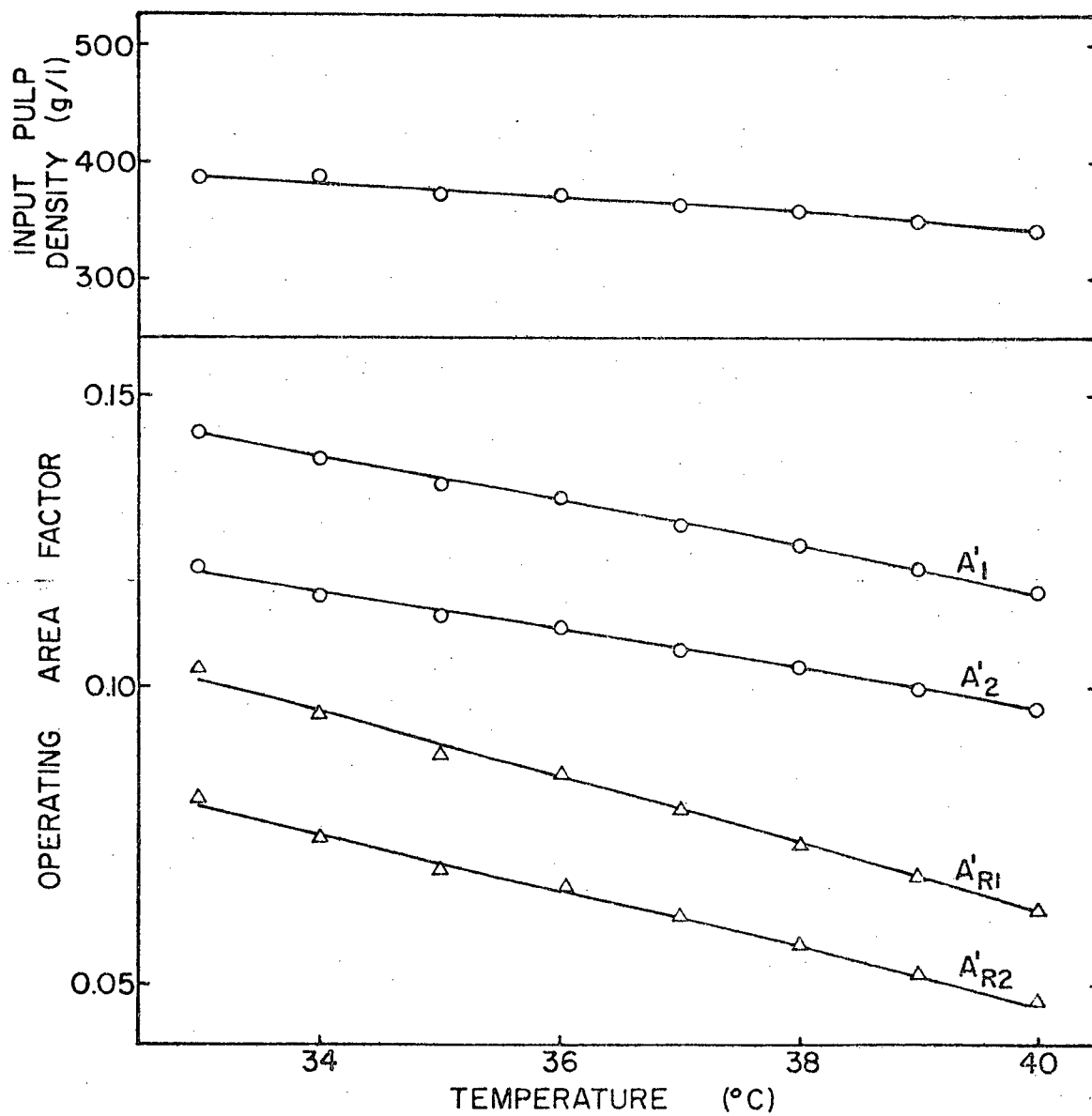


Figure 33. Total input pulp density and operating area factors vs. leach temperature. Other conditions standard.

These results show that increasing reactivity by raising the leach temperature leads to a slight increase in the proportion of leaching performed by the first stage.

5.2.5 Partial Bypassing of Flotation

Since the purpose of reflation is to eliminate insoluble gangue the increased bypassing of this step leads to higher operating levels of siliceous minerals in all the solids streams. The effect of bypassing on the insol contents of the leach residue, reflation concentrate and recycle solids is shown in Figure 34. The insol levels rise at an increasing rate as the effect of recycling the siliceous components compounds itself.

At recycle solids insol levels less than that of the new feed there is a negligible effect on the total mass of the recycle flow. However, the solids recycle ratio is significantly increased as the reflation bypass is raised to levels which result in higher operating insol contents of the solids streams. This point is shown in Figure 35.

At this stage of development the flotation section only provides an indication of behaviour since the flotation rate constants were essentially estimated. This does not necessarily detract from the leaching model since preliminary test work has revealed high recoveries.

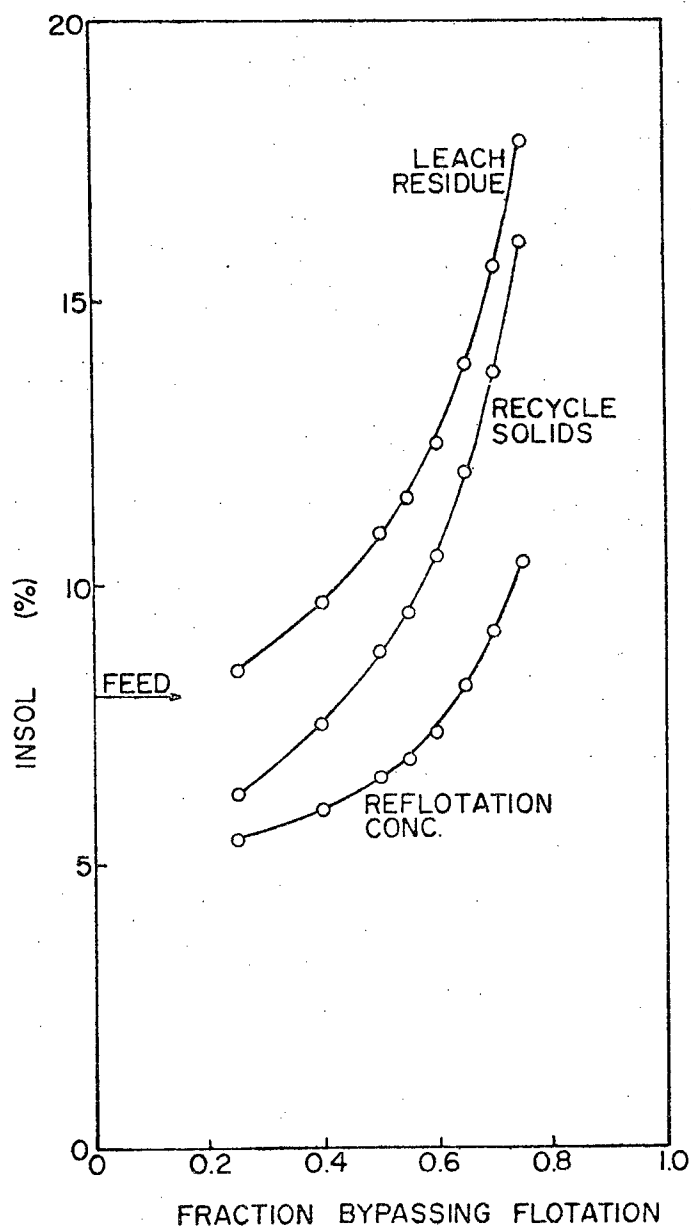


Figure 34. Insol content of leach residue, reflation concentrate and recycle solids vs. fraction bypassing flotation. Other conditions standard.

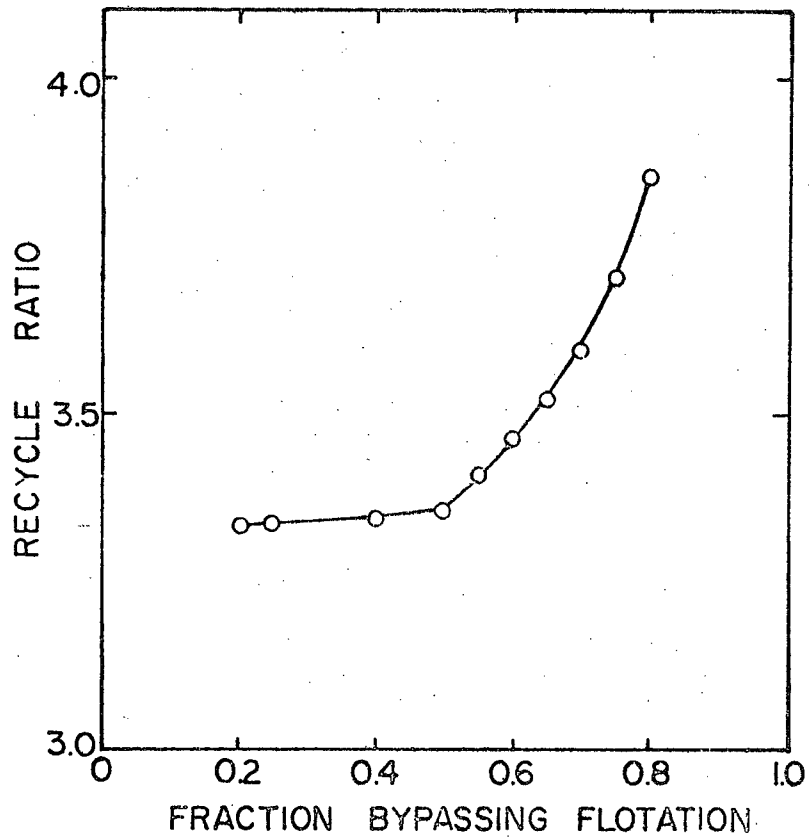


Figure 35. Solids recycle ratio vs. fraction bypassing flotation. Other conditions standard.

A major concern in the flotation section is the mass of molybdenum lost to the tails. Although the model was not run under optimum flotation conditions the results show a decreasing loss of molybdenum to the tails as the flotation bypass is increased above about 0.5. The results should be treated with caution, however, since the water flow rate to flotation was not adjusted in accordance with the solid flow rate to maintain similar pulp densities.

Although the model does not account for the analysis of the solids in the effect of grinding this may have some influence. With higher degrees of flotation bypass the grinding mill treats material with higher concentrations of harder siliceous minerals. As well as affecting the grinding of molybdenite this would also lead to increased consumption of grinding media.

5.2.6 Leach Vessel Volume

The effect of the leach vessel volume on the solids recycle ratio is shown for the case of two equi-sized stages in Figure 36. Although the recycle ratio decreases as the vessel size increases the change is not drastic when considering the range of vessel sizes investigated. Hence the use of extremely large vessels is not warranted for the small additional benefits gained.

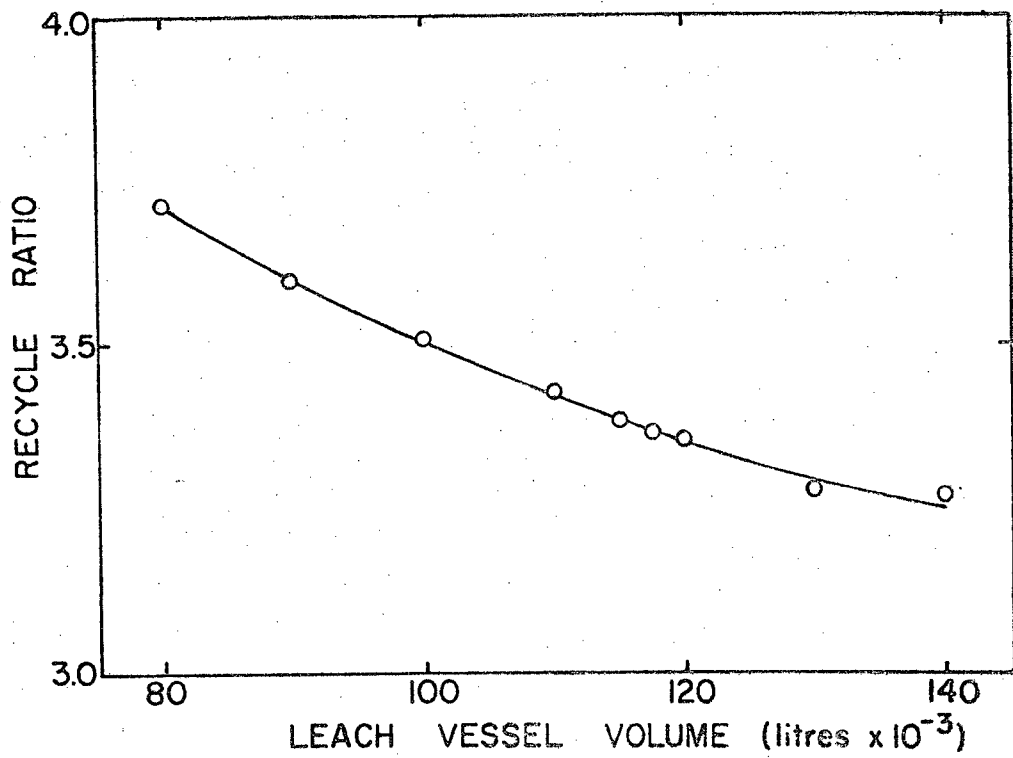


Figure 36. solids recycle ratio vs.leach vessel volume. Other conditions standard.

The input pulp density and operating area factors both decrease as the vessel volume is increased. This can be seen in Figure 37. The operating nitric acid levels, however, did not show significant variation under the tolerance limits used.

The net decrease in physical factors which affect the reaction rate is more than compensated for by the longer residence times which increase in an approximately linear fashion with vessel volume.

The effect of two-stage leaching but with different vessel volumes was briefly investigated. No difference in recycle ratio was detected (within the tolerance limits) for leaching with stage 1 at 100,000 litres and stage 2 at 140,000 litres. A slight increase in recycle ratio to 3.46 was calculated when stage one was set at 80,000 litres and stage 2 at 160,000. This can only be casually compared to the case for a pure, second-order reaction where a shallow minimum in total reactor volume for a given degree of reaction occurs where the volume of stage 1 is 70% of stage 2.

The slight possible advantages of using different reactor sizes would therefore not compensate for the additional cost of such a configuration.

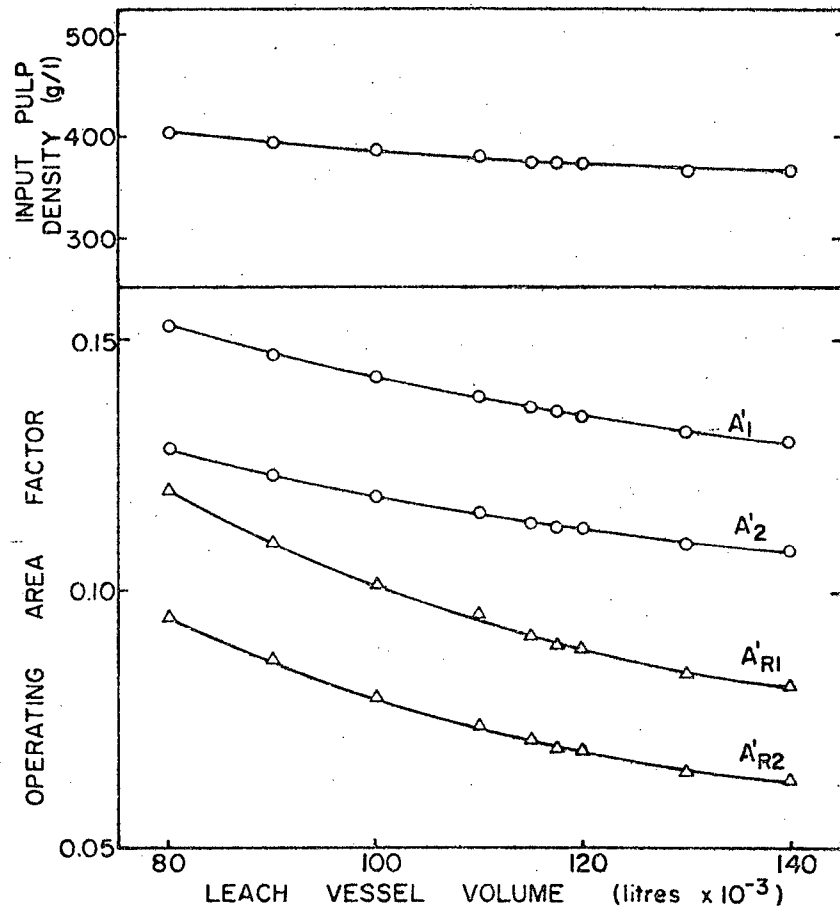


Figure 37. Total input pulp density and operating area factors vs. leach vessel volume. Other conditions standard.

5.2.7 Number of Leaching Stages

Figure 38 shows the solids recycle ratio as a function of the number of leaching vessels for constant vessel volume. The effect of "adding" cocurrent stages for the standard operating conditions indicate a marked decrease in recycle ratio from one to two stages with much less improvement from two stages to three. Additional staging in this manner above two or three vessels may not be justified when considering the increased capital costs and molybdenum inventory. Table XIV lists the extraction from the total input solids for one, two and three stages under the same conditions pertaining to Figure 38.

Table XIV

EXTRACTION FROM TOTAL INPUT SOLIDS

ON EACH PASS FOR DIFFERENT NUMBER OF STAGES (%)*

Stages	Stage 1	Stage 2	Stage 1+2	Stage 3	Stage 1+2+3
1	16.5	-	-	-	-
2	17.5	5.0	22.5	-	-
3	17.8	5.7	23.6	2.8	22.4

For three-stage leaching the distribution of leaching work between stages

* constant stage volume

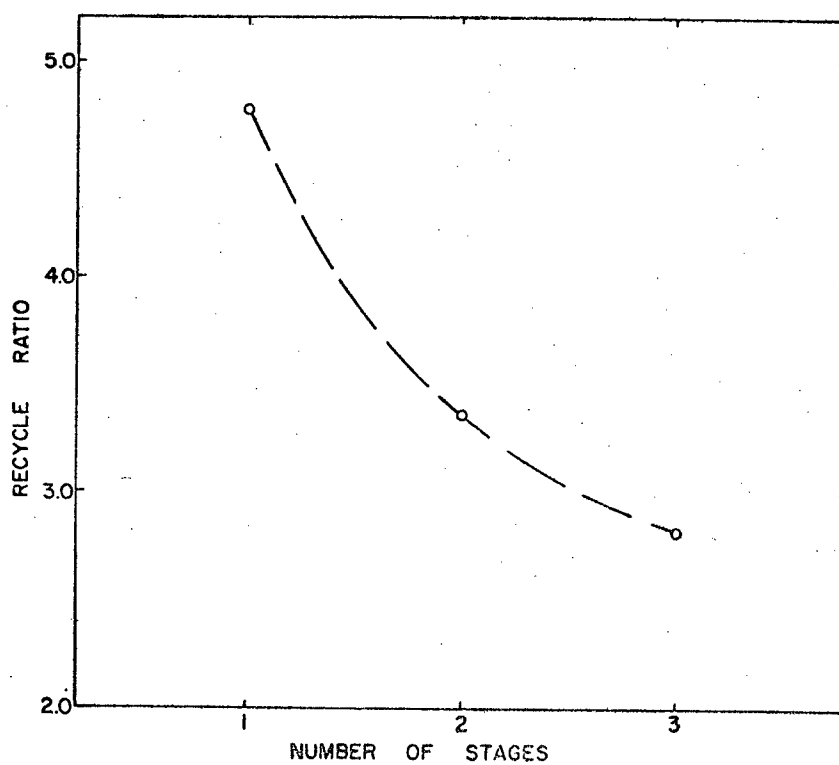


Figure 38. Solids recycle ratio vs. number of leach stages. Constant stage volume. Other conditions standard.

one, two and three is in the ratio 1 : 0.32 : 0.16.

The results of the one-stage simulation did show a small, but detectable, concentration of iron and copper in the recycle solids.

The effect of multiple staging when considering constant total volume is shown in Table XV.

Table XV

SOLIDS RECYCLE RATIO AS A FUNCTION OF NUMBER OF
STAGES (CONSTANT TOTAL VOLUME)

No. of Stages	Vol. Per Stage(l)	Recycle Ratio
2	120,000	3.35
3	80,000	3.22
4	60,000	3.08

The division of leaching vessel volume into a greater number of stages lowers the solids recycle ratio but the additional expense involved with increased staging may again not be justified.

5.2.8 Grinding

Since the grinding section of the model was the most suspect part some study was conducted on the effects of changing grinding parameters. With the uncertainty in the exponential portion of Equation (53) the value of the multiplying factor, b_3 , was examined over a small range. The influence of this term on the recycle area factor as a function of fraction leached is plotted in Figure 39. For the model calculations a value of 2.0 was chosen for b_3 . Although this choice cannot be validated at this stage extremely rough calculations on the previous grinding work show the resulting exponential value to be in the appropriate range.

There is no doubt that some error is associated with this section. However it is likely that the error is not extreme and would mean rather minor changes in the sizing of relatively small-scale equipment to produce approximately equivalent practical results.

The influence of grinding mill size on the recycle solids area factor relationship is presented in Figure 40. It can be seen that the plot is raised and the curvature is increased as the grinding mill size is increased. However, the solids recycle ratio becomes

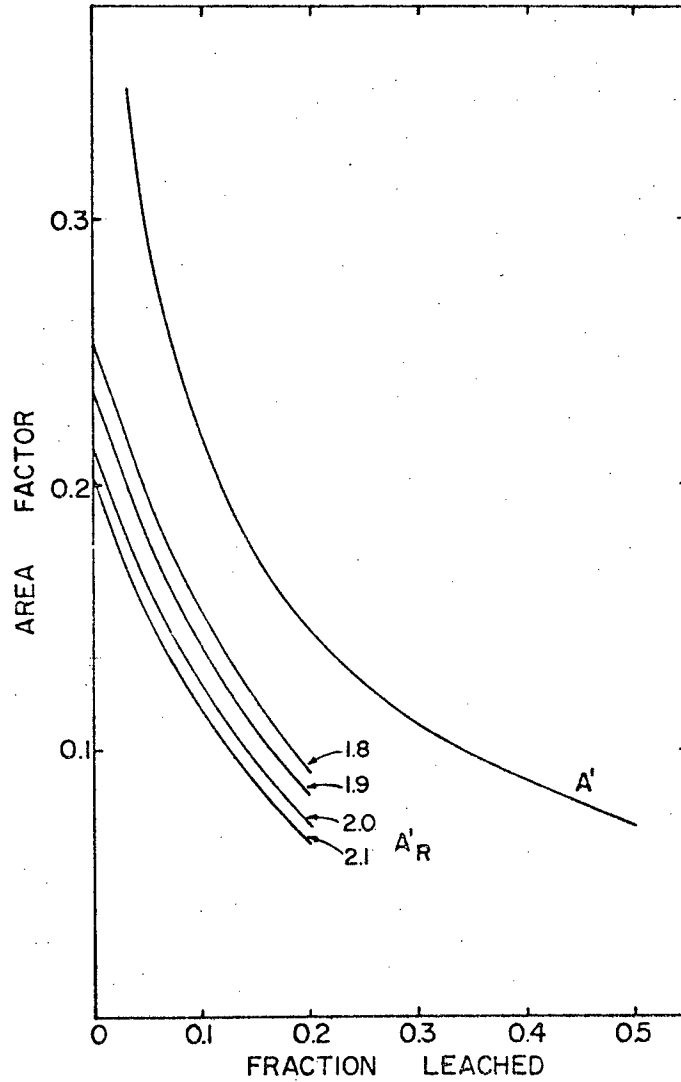


Figure 39. Recycle area factor vs. fraction leached for different values of b_3 . Standard conditions.

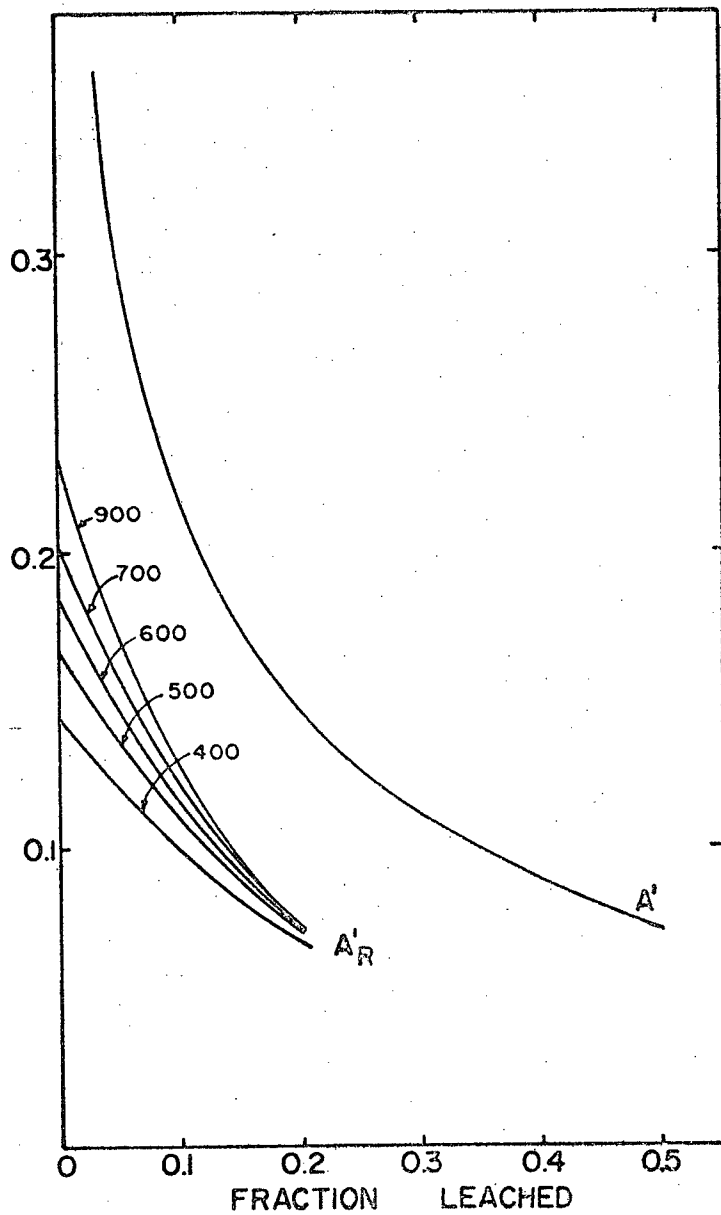


Figure 40. Recycle area factor vs. fraction leached for different grinding mill sizes. Standard conditions. (Grinding mill size units - kilograms solids holdup)

relatively insensitive to grinding mill size for higher mill sizes.

This is, at least in part, due to the choice of equation but may also indicate the interactive effects of mineral surface area and reagent concentration in such a partially bounded system.

This section of the model does demonstrate the logical trends but further work is definitely required to verify the results.

CHAPTER 6

CONCLUSIONS

A steady state mathematical model of a major section of a proposed molybdenite leaching process has been developed from a relatively limited amount of available data. A significant feature of the leaching model for molybdenite is the bulk empirical determination of the change in active mineral surface area as leaching progresses. This is achieved by interpolation and extrapolation from batch experimentation. The method avoids vague assumptions on particle shape, with or without correction factors, and also allows for other influences such as particle non-uniformity and particle cleavaging which are extremely difficult to quantify. The number of mathematical calculations are also somewhat reduced by elimination of the necessity to consider particle size classes.

In its current form the model accounts for numerous plant and operating variables as follows:

- (1) Number, size and distribution of leaching vessels.
- (2) Size of grinding mill.
- (3) Number and size of flotation cells.
- (4) Variation in new solids feed rate and analysis.

- (5) Variation in solution flow rate and nitric acid strength.
- (6) Influence of partially bypassing flotation.
- (7) Effect of leaching temperature

The model cannot be considered as complete at this stage since some sections are subject to uncertainty and total verification is not possible at this time. The main points of uncertainty in the formulation are listed as:

- (1) Accounting for the regrind step, particularly with the exponential part of Equation (53).
- (2) Use of laboratory-determined batch grinding data and extrapolating to continuous plant-scale operations.
- (3) Use of constant, estimated flotation rate constants.
- (4) Approximation of the operating active surface area of solids in the leach based on averaging of effects in batch experimentation and the neglecting of the solids residence time distribution in the leaching model.

Although some aspects of the model require further clarification this current type of formulation should be adequate for future work. At the current stage of process development a more rigorous or thorough, and thus more difficult and expensive model is not justified.

Although no detailed economic study was performed the previous work and the results of this model indicate the feasibility of the process. However, further evaluation is required to ascertain the viability of using the process.

The formulation of a mathematical model does not eliminate the necessity of piloting a process which has not previously been tested on a pilot or commercial scale. The model can be utilized in the design of such a plant which can then, in turn, provide verification or indicate required adjustments to the formulation.

Industrial piloting is essential for revealing other possible unknown influences on the smooth operation of the process. A model, such as this one, is based on a relatively few number of small-scale observations. Other factors which could influence the performance may not be taken directly into account by the model. Some may impose limits on the process but these limits could possibly be determined by separate experimentation. Another aspect to consider is the frequency and amplitude of fluctuations that might occur on an industrial scale.

Although this model has been developed for a specific process the basis of formulation may prove useful in evaluation of other similar systems. This applies particularly to the leach simulation.

CHAPTER 7

RECOMMENDATIONS

Further work is warranted on this system and may be summarized as follows:

- (1) Further evaluation of effects of grinding.
- (2) Experimental studies on refloatation of leached and ground residues.
- (3) Increase model stability, e.g. attempt partial linearization.
- (4) Further test and develop (if necessary) the chalcopryrite and pyrite leaching equations.
- (5) Test the model on other molybdenite concentrates.
- (6) Evaluation of hemihydrate precipitation behaviour with a view to optimizing the leach/precipitation system.
- (7) Investigate the effects of pressure on leaching rates.
- (8) Investigate NO_2 as a substitute for HNO_3 in first-stage leaching.

REFERENCES

1. D.M. Himmelblau and K.B. Bischoff: Process Analysis and Simulation - Deterministic Systems, John Wiley & Sons Inc. N.Y. 1968.
2. D.M. Himmelblau: Process Analysis by Statistical Methods, John Wiley & Sons Inc. N.Y. 1970.
3. E. Peters and A. Vizsolyi: Hydrometallurgical Treatment of Molybdenite Concentrates, research proposal, University of British Columbia, 1974.
4. E. Peters and A. Vizsolyi: Hydrometallurgical Treatment of Molybdenum Concentrates, Series of 12 monthly reports provided under contract with Placer Development Ltd., University of British Columbia, Aug. 1974 - June 1975.
5. E. Peters and A. Vizsolyi: Cominco Contract Research, University of British Columbia, 1972.
6. M. Pourbaix and N. De Zoubov: Atlas of Electrochemical Equilibria in Aqueous Solutions, Pergamon, London, 1966.
7. D.S. Davies, R.E. Lueders, R.A. Spitz and T.C. Fraciewicz: Nitric-Sulfuric Leach Process Improvements, presented at AIME 107th Annual Meeting, Denver, Colorado, Feb. 27, 1978.
8. A.I. Busev: Analytical Chemistry of Molybdenum, Ann Arbor-Humphrey Science Publishers, Ann Arbor, 1969.
9. M.M. Jones, J. Am. Chem. Soc., 1954, 76, 4233.
10. P.E. Churchward and J.B. Rosenbaum: Unit Processes in Hydrometallurgy, Met. Soc. Conf., Vol. 24, pp. 441-52, AIME, Dallas, Texas, 1963.
11. J.Y. Lee, D.H. Reynolds and R.B. Bhappu: Continuous Processing and Process Control, Met. Soc. Conf., Vol. 49, pp. 105-24, Philadelphia, Pennsylvania, 1966.
12. H.H. Read: Rutley's Element of Mineralogy, 25th Edition pp. 459-61, Thomas Murby and Co., London, 1967.

13. A. Sutulov: Molybdenum Extractive Metallurgy, University of Concepción, Chile, 1965.
14. A. Sutulov: Molybdenum and Rhenium Recovery from Porphyry Coppers, University of Concepción, Chile, 1970.
15. A. Sutulov: Copper Porphyries, University of Utah Printing Services, Salt Lake City, Utah, 1974.
16. A. Kuklis: Molybdenum, preprint from Bulletin 667, U.S. Dept. of Interior, Bureau of Mines, pp. 1-16.
17. A. Sutulov: World Mining, 1978, Vol. No. 3, pp. 73-75.
18. J.W. Goth: E/MJ, 1977, Vol. 178, No. 3, pp. 88-92.
19. J.A. Butterfield and J.A. Ganshorn: Molybdenum Supply and Demand Forecast, presented at CIM Conference of Metallurgists, Vancouver, B.C., Aug. 21-24, 1977.
20. A. Bouchard and R.F. Johnson: Can. Min. J., 1978, Vol. 99, No.2, pp. 116-118.
21. D.G. Lindsay: Endako Roasting Practice, presented at CIM Conference of Metallurgists, Vancouver, B.C., Aug. 21-24, 1977.
22. P.H. Jennings, R.W. Stanley and H.L. Ames: International Symposium on Hydrometallurgy, pp. 868-883, AIME, 1973.
23. E. Gratch and R. Bradburn: Molybdenite Concentrate Production at Brenda Mines Ltd., presented at CIM Conference of Metallurgists, Vancouver, B.C., Aug. 21-24, 1977.
24. Brenda Mines Ltd., Company Brochure.
25. Anonymous: J.O.M., 1977, Vol. 29, No. 10, pp. 9-12.
26. L.F. McHugh, J. Godschalk and M. Kuzior: Climax Conversion Practice III, presented at CIM Conference of Metallurgists, Vancouver, B.C., Aug. 21-24, 1977.
27. G.R. Grimes and G. Witkamp: J.O.M., 1971, Vol. 23, No. 2, pp.17-24.
28. L. White: E/MJ, 1977, Vol. 178, No. 5, pp. 80-81.

29. P.A. Butters: Mineral Processing and Extractive Metallurgy, Proc. 9th Comm. Min. and Met. Cong., Vol. 3, IMM, London, 1970.
30. A.N. Zelikman: Molybdenum, pp. 439, Metallurgiya, Moscow, U.S.S.R., 1970.
31. G. Björling and G.A. Kolta: VII International Mineral Processing Congress, Vol. 1, 1964.
32. J.G. Posel: U.S. Patent 3,965,239, June 22, 1976.
33. J.G. Posel, G.P. Williams and N. Nilsen: U.S. Patent 3,966,462, June 29, 1976.
34. A.N. Zelikman, L.V. Belyaevskaya and T.E. Prosenkova: Chem. Abs. 72:81734 d.
35. I.P. Smirnov, V.I. Zyurkalov and N.I. Chuikina: Tsvetn. Metally, 1975, No. 2, pp. 44-45, (Russ.).
36. O.V. Fedulov, B.I. Taranenko, V.D. Ponomarev and L.V. Svechkova: Chem. Abs., 68:32601 n.
37. D.G. Kerfoot and R.W. Stanley: U.S. Patent 3,988,418, Oct. 26, 1976.
38. Zh.G. Gukasyan and R.K. Arustamyan: Prom-St. Arm, 1974, No. 9, pp. 68-70, (Russ.).
39. J.D. Prater, P.B. Queneau and T.J. Hudson: Trans. SME-AIME, 1973, Vol. 254, pp. 117-22.
40. P.B. Queneau and J.D. Prater: U.S. Patent 3,793,429, Feb. 19, 1974.
41. F. Habashi: Trans. SME-AIME, 1973, Vol. 254, pp. 224-27.
42. G. Bjorling, J. Faldt, E. Lindgren and I. Toromanov: Extractive Metallurgy of Copper, Vol. II, Hydrometallurgy and Electrowinning, Int. Symp. AIME, Las Vegas, Nevada, 1976.
43. H.M. Brennecke et al: The Nitric Sulfuric Leach Process for Recovery of Copper from Concentrate, presented at AIME 107th Annual Meeting, Denver, Colorado, Feb. 27, 1978.
44. R.A. Hard: U.S. Patent 3,910,636, Oct. 7, 1975.

45. F. Habashi: Trans. SME-AIME, 1974, Vol. 254, pp. 228-30.
46. R. Ouellet, A.E. Torma and J.P. Bolduc: Can. Met. Q., 1975, Vol. 14, No.4, pp. 339-43.
47. G. Bjorling and W. Mulak: Trans. IMM, 1976, Vol. 85, pp. C98-C101.
48. P. Fossi, L. Gandon, C. Bozec and J.M. Demarthe: CIM Bull., 1977, Vol. 70, No. 783, pp. 188-97.
49. B.W. Madsen, M.E. Wadsworth and R.D. Groves: Trans. SME-AIME, 1975, Vol. 258, pp. 69-74.
50. R.L. Braun, A.E. Lewis and M.E. Wadsworth: Solution Mining Symposium, pp. 295-323, AIME, N.Y., 1974.
51. M.I. Brittan: Int. J. of Min. Proc., 1975, No. 2, pp. 321-31.
52. J.A. Harris: Proc. Aust. Inst. Min. and Met., 1969, No. 230, pp. 81-91.
53. R.J. Roman, B.R. Benner, G.W. Becker: Trans. SME-AIME, 1974, Vol. 256, pp. 247-52.
54. L.M. Cathles and J.A. Apps: Met. Trans. B, 1975, Vol. 6B, pp. 617-24.
55. R.W. Jones: Chem. Eng. Prog., Jan. 1951, pp. 46-8.
56. O. Levenspiel: Chemical Reaction Engineering, 2nd Edition, John Wiley & Sons Inc., N.Y., 1972.
57. K.G. Denbigh and J.C.R. Turner: Chemical Reactor Theory, 2nd edition, Cambridge, 1971.
58. A. Cooper and G. Jeffreys: Chemical Kinetics and Reactor Design, Prentice-Hall Inc., 1973.
59. R.H. Perry and C.H. Chilton (eds): Chemical Engineers' Handbook, 5th edition, pp. 4-1 to 4-43, McGraw-Hill Book Co., N.Y., 1973.
60. A. Mular: Mechanistic and Empirical Modelling of Mineral Processes, Mineral Engineering 575, University of British Columbia.
61. A. Mular and W.R. Bull (eds): Mineral Process: Their Analysis, Optimization and Control, pp. 168-352, 1969-1973.

62. R.P. King, E.M. Buchalter: NIM Report No. 1573, Johannesburg, South Africa, Feb. 20, 1974.
63. N. Arbiter and C.C. Harris: Froth Flotation, pp. 215-46, AIME, N.Y., 1962.
64. I.A. Wilkomersky, A.P. Watkinson and J.K. Brimacombe: Trans. IMM, 1975, Vol. 84, pp. C197-C205.
65. F.E. Pawlek: Extractive Metallurgy of Copper, Vol. II, pp. 690-705, Hydrometallurgy and Electrowinning, Int. Symp. AIME, Las Vegas, Nevada.
66. F.C. Bond: Crushing and Grinding Calculations, Allis-Chalmers Manufacturing Co., Milwaukee, Wisconsin, 1961.
67. W.B. Gragg and G.W. Stewart: A Stable Variant of the Secant Method for Solving Non-Linear Equations, Carnegie-Mellon University, Pittsburgh, Pennsylvania, April 1974.
68. C. Moore Lee, U.B.C. NLE. Zeros of Non-Linear Equations, Computing Centre, University of British Columbia, Feb., 1977.
69. I.J.T. Hopkins: Modification of a Copper Flotation Circuit, Dept. of Mineral Engineering, University of British Columbia, May, 1975.
70. J. Streat and C. Moore Lee, U.B.C. Curve: Curve Fitting Techniques, Computing Centre, University of British Columbia, March, 1976.

APPENDIX A

CONSUMPTION OF MOLYBDENUM BY CATEGORY

	1976*	1977(est.) [18]
Alloy Steels	50.7%	49%
Stainless Steels	13.4%	20%
Tool Steels	5.3%	9%
Cast Irons	7.9%	7%
Superalloys and Other Special Alloys	7.6%	3%
Molybdenum Metal	6.6%	3%
Chemicals	7.3%	8%
Other	1.2%	1%

* USBM Statistics - January to September, 1976.

APPENDIX B
EXPERIMENTAL RESULTS

Run	Solution	Solution Vol. (ml)	Initial Solids (g)	Pulp Density (g.solid/l.solution)	Leach Time (min)	Ave.Temp. (°C)	Mo Leached (g)	Ave. Leach Rate (gMo/l.sec.x10 ³)
L1	3.94M HNO ₃	128	16.16 E	126.3	79	24	0.6847	1.13
L2	3.94M HNO ₃	200	25.30 E	126.0	45	35	1.3506	2.50
L3	3.94M HNO ₃	200	46.48 E	232.4	32	35.5	1.4723	3.83
L4	3.94M HNO ₃	250	31.50 E	126.0	12.5	35	0.7099	3.79
L5	L4 leach solution	200	25.30 E	126.0	59	35	1.2133	1.71
L6	3.6M HNO ₃	200	25.20 E	126.0	45	35	1.2201	2.26
	7.4g/2Fe(NO ₃) ₃ ·9H ₂ O							
L7	3.94M HNO ₃	200	25.20 E	126.0	43	35.5	1.1976	2.32
L8	3.94M HNO ₃	200	25.2 L4 res	126.0	45	35	1.0800	2.00
L9	3.94M HNO ₃	250	15.00 E	60.0	16	35	0.3550	1.48
					35	35	1.1800	2.25
L10	4.0M HNO ₃	245	12.00 B+325#	49.0	30	35	0.0162	0.0364
					138.5	35	0.0946	0.0465
L11	5.0M HNO ₃	250	12.00 B+325#	48.0	11.2	35	0.0095	0.0565
					45.8	35	0.0420	0.0611
					75.2	35	0.0780	0.0691
					105.2	35	0.1255	0.0795
L12	5.0M HNO ₃	250	12.00 B+325#	48.0	9.6	35	0.0080	0.0556
					70.2	35	0.0720	0.0684
					130.5	35	0.1460	0.0746
					190.4	35	0.2310	0.0809
L13	5.0M HNO ₃	250	12.00 B+325#	48.0	19.4	35	0.0165	0.0567
L14	4.0M HNO ₃	250	12.00 B+325#	48.0	30.1	35	0.0150	0.0332
L15	3.0M HNO ₃	250	12.00 B+325#	48.0	65.2	35	0.0200	0.0204

E - Endako

B - Brenda

APPENDIX B

(Continued)

Run	Solution	Solution Vol. (ml)	Initial Solids (g)	Pulp Density (g.solids/l.solution)	Leach Time (min)	Ave.Temp. (°C)	Mo Leached (g)	Ave.Leach Rate (gMo/l.sec.x10 ³)
L16	1.0M HNO ₃	250	12.00 B+325#	48.0	481	35	0.0325	0.00450
L17	2.0M HNO ₃	250	12.00 B+325#	48.0	120.5	35	0.0158	0.00874
L18	6.0M HNO ₃	250	12.00 B+325#	48.0	13.4	35	0.0145	0.0721
L19	1.0M HNO ₃	250	12.00 B+325#	48.0	480	35	0.0275	0.00382
L20	1.0M HNO ₃	250	12.00 B+325#	48.0	90.1	35	0.0039	0.00289
L21	4.0M HNO ₃	250	12.00 B+325#	48.0	30.1	35	0.0138	0.0306
L22	1.0M H ₂ SO ₄ 4.0M HNO ₃ 3 g/l Fe ³⁺ 5.2 g/l SO ₄ ²⁻	450	25.00 E	55.6	20.8	35	0.9135	1.627
L23	4.0M HNO ₃ 3 g/l Fe ³⁺ 5.2 g/l SO ₄ ²⁻	420	22.85 L22 res	54.4	40.5	35	0.9996	0.9794
L24	4.0M HNO ₃ 3 g/l Fe ³⁺ 5.2 g/l SO ₄ ²⁻	387	20.80 L23 res	53.7	80.2	35	1.2694	0.6817
L25	4.0M HNO ₃ 3 g/l Fe ³⁺ 5.2 g/l SO ₄ ²⁻	345.5	18.25 L24 res	52.8	100.9	35	1.2680	0.6062
L26	4.0M HNO ₃ 3 g/l Fe ³⁺ 5.2 g/l SO ₄ ²⁻	303.8	15.79 L25 res	51.97	109.8	35	0.9789	0.4891
L27	4.0M HNO ₃ 3 g/l Fe ³⁺ 5.2 g/l SO ₄ ²⁻	271.5	13.88 L26 res	51.12	119.9	35	0.7113	0.3642
L28	4.0M HNO ₃ 3 g/l Fe ³⁺ 5.2 g/l SO ₄ ²⁻	248.3	12.31 L27 res	49.57	179.7	35	0.8060	0.3011

E - Endako

B - Brenda

APPENDIX C

SOURCE LISTING OF COMPUTER PROGRAM

NOMENCLATURE

- A (M,I) =COEFFICIENTS OF LINEAR EQUATIONS
- ACIDN =MOLAR CONCENTRATION OF NITRIC ACID
- ARCUCP =ARRHENIUS FACTOR FOR CU (CUFES2)
- ARFEPY =ARRHENIUS FACTOR FOR FE (FES2)
- ARFECF =ARRHENIUS FACTOR FOR FE (CUFES2)
- ARRMO =ARRHENIUS FACTOR FOR MO (MOS2)
- B (I) =R.H.S. OF LINEAR EQUATIONS
- CSF (K,I) =CALCULATED STAGE FACTORS
- CSFPIT (K,I) =CALCULATED STAGE FACTORS FOR PREVIOUS ITERATION
- CUDIS =COPPER DISSOLVED IN LEACH
- EXTRN =LEACH MO EXTRACTION
- F (I) =NONLINEAR FUNCTIONS IN LEACH ALGORITHM
- FC (I) =FLOTATION RATE CONSTANTS
- PEPDIS =IRON AS PES2 DISSOLVED IN LEACH
- FLOW =WATER FLOWRATE INTO FLOTATION CELLS
- FRACL =FRACTION OF NEW FEED MOS2 LEACHED
- FRACLR =FRACTION OF RECYCLE MOS2 LEACHED
- PTX (I) =REFLOTATION TAILING VARIABLES
- FX (I) =LEACH FILTER OUTPUT
- G (I) =GUESSED OUTPUT FROM STAGE 1
- GC (I) =GRIND CONSTANTS
- GF (I) =GUESS FACTORS FOR STAGE 2
- GFX (I) =REGRIND TO REFLOAT VARIABLES
- GX (I) =GRINDING MILL OUTPUT
- IT =SPECIFIED NUMBER OF ITERATIONS
- ITPRNT =PRINTING CONTROLLER
- J =CYCLE ITERATION COUNTER
- K =LEACH STAGE COUNTER
- KK =PRINTING VARIABLE - EVERY 'KK'TH ITERATION
- L (I) =RECYCLE ADJUSTMENT COUNTER
- LC (I) =LEACH CONSTANTS
- LL =PRINTING CONTROLLER
- MODIS =MOLYBDENUM DISSOLVED IN LEACH
- MONEW =NEW MOLYBDENUM INPUT
- MOREC =RECYCLE MOLYBDENUM INPUT
- MOTOL =TOLERANCE ON MOLYBDENUM EXTRACTION
- N =NUMBER OF LEACH STAGES
- NF =NUMBER OF FLOTATION CELLS
- PFLOW =PULP FLOW INTO FLOTATION CELLS
- PULPD =INPUT PULP DENSITY TO LEACHING
- R (I) =RECYCLE VARIABLE MULTIPLIERS
- RCPY (I) =FLOTATION STAGewise CUFES2 RECOVERY
- RDIV =DIVISOR FOR R (1)
- RECCPY =FLOTATION RECOVERY OF CUFES2
- RECMO =FLOTATION RECOVERY OF MOS2
- RECPY =FLOTATION RECOVERY OF PES2
- RECRAT =RATIO OF RECYCLE SOLIDS/NEW SOLIDS
- RECSIL =FLOTATION RECOVERY OF SILICEOUS GANGUE
- RFX (I) =REFLOTATION CONCENTRATE VARIABLES
- RGX (I) =DIRECT REGRIND TO RECYCLE VARIABLES
- RMAX =INITIAL INPUT MAXIMUM ADJUSTMENT FACTOR ON RECYCLE
- RMO (I) =FLOTATION STAGewise MCS2 RECOVERY
- RPY (I) =FLOTATION STAGewise PES2 RECOVERY
- RR (I) =MAXIMUM SPECIFICATION ON R (I)
- RSIL (I) =FLOTATION STAGewise INSOL RECOVERY
- RX (I) =SOLIDS RECYCLE ESTIMATES
- RXC (I) =CALCULATED RECYCLE VARIABLES
- RXCOLD (I) =PREVIOUS CALCULATED RECYCLE VARIABLES

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RXOLD(I)	=PREVIOUS ESTIMATE OF RECYCLE VARIABLES
RXX(I)	=INPUT RECYCLE PARAMETERS FOR EACH LEACH STAGE
SNR(I)	=STAGEWISE OVERALL MO RECOVERY FROM NEW FEED
SPLIT	=PROPORTION OF REGRIND OUTPUT BYPASSING REFLOTATION
SR(I)	=STAGEWISE OVERALL MO RECOVERY
SRR(I)	=STAGEWISE OVERALL MO RECOVERY FROM RECYCLE SOLIDS
SULDIS	=SULPHUR DISSOLVED IN LEACH
SX(K,I)	=STORAGE OF LEACH OUTPUT FOR EACH STAGE
T	=LEACH TEMPERATURE
TOL	=TOLERANCE LIMIT ON RECYCLE VARIABLES
TOLC(I)	=CALCULATED TOLERANCE ON RECYCLE VARIABLES
TGRND	=MEAN RESIDENCE TIME IN GRINDING MILL (SEC)
TMGRND	=MEAN RESIDENCE TIME IN GRINDING MILL (MIN)
V(I)	=INPUT VARIABLES
VL(I)	=COMBINED INPUT VARIABLES
VOL(K)	=LEACH VESSEL VOLUMES
VOLFL	=VOLUME OF INDIVIDUAL FLOTATION CELLS
VV(I)	=STORAGE OF INPUT VARIABLES
WTRCPY	=WGT. OF CUFES2 TRANSFERRED FROM RECYCLE TO NEW SOLIDS
WTRCU	=WGT. OF CU TRANSFERRED FROM RECYCLE TO NEW SOLIDS
WTRFEP	=WGT. OF FE(FES2) TRANSFERRED FROM RECYCLE TO NEW SOLIDS
WTRPY	=WGT. OF FES2 TRANSFERRED FROM RECYCLE TO NEW SOLIDS
X(I)	=LEACHING OUTPUT VARIABLES
XFEPY	=LEACH STAGE OUTPUT SOLID FE CONC. AS FES2
XX(I)	=OVERALL LEACH OUTPUT VARIABLES CALCULATED SEPARATELY

 C STEADY-STATE COMPUTER SIMULATION OF MOLYBDENITE/NITRIC ACID
 C LEACHING PROCESS INVOLVING MULTI-STAGE COCURRENT LEACHING,
 C GRINDING AND FLOTATION

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IMPLICIT REAL*8 (A-H,O-Z)
REAL*8 MONEW,MOREC,LC,MGTOL
EXTERNAL FCN
DIMENSION X(18),P(14),V(13),VV(13)
DIMENSION RX(8),RXX(2)
DIMENSION LC(15),VOL(9)
DIMENSION VL(6),XX(7),FX(7),GX(8),GC(2),RGX(6),GFX(6),RFX(6)
DIMENSION FTX(3),RXC(8),PC(4)
DIMENSION SNR(9),SRR(9),SR(9)
DIMENSION SX(9,18)
DIMENSION G(18),GF(18),CSF(9,18)
DIMENSION R(8),RR(8),RXOLD(8),RXCOLD(8),TOLC(8),L(8)
LOGICAL SWCHA
COMMON/AREA1/V,VL,RX,RXX
COMMON/AREA2/MONEW,MOREC,LC
COMMON/AREA3/VOL,T,K
COMMON/AREA4/X,XX
COMMON/AREA5/FX,GX
COMMON/AREA6/GC,SPLIT
COMMON/AREA7/RGX,GFX
COMMON/AREA8/RFX,FTX,RXC
COMMON/AREA9/PC
COMMON/AREA10/VOLFL,FLOW,NF
COMMON/AREA11/N,LL,J
COMMON/AREA12/SNR,SRR,SR,SX
COMMON/AREA13/EXTRN,RECRAT,PULPD,MOTOL
COMMON/AREA14/RECMO,RECPY,RECCPY,RECSIL
COMMON/AREA15/TMGRND
COMMON/AREA16/FRACL,FRACLR
COMMON/AREA17/G,GF
COMMON/AREA18/CSF
COMMON/AREA19/VV
COMMON/AREA20/ARRMO,ARFECF,ARFEPY,ARUCUP
COMMON/AREA21/SWCHA
COMMON/SESSOM/A(20,22),B(20),Y(22,21)
NAMELIST/LISTI/J,TOLC,R,L
NAMELIST/LISTRX/RX
NAMELIST/LISTV/V
NAMELIST/LISTG/G
NAMELIST/LISTGF/GF
NAMELIST/LISTLC/LC
NAMELIST/LISTT/T
NAMELIST/LISTGC/GC,SPLIT
NAMELIST/FLOTN/NF,VOLFL,FLOW,FC
NAMELIST/LISRX/RXC
NAMELIST/LISCON/TOL,IT,RMAX,ITPRNT,KK
READ(5,102) (V(I),I=1,13)
WRITE(6,500)
500 FORMAT('0','NEW SOLIDS INPUT')
WRITE(6,501)
501 FORMAT('+' , '-----')
WRITE(6,502) V(1)
502 FORMAT('NEW SOLIDS FLOWRATE (TONNES/DAY) =',F8.3)
WRITE(6,503)
503 FORMAT('0','NEW SOLIDS INPUT ANALYSIS (WGT%)')
WRITE(6,504) V(2),V(3),V(4),V(5),V(6)

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504  FORMAT('MO=',F7.3,2X,'FE=',F7.3,2X,'CU=',F7.3,2X,
1  'INSOL=',F7.3,2X,'S=',F7.3)
    WRITE(6,505)
505  FORMAT('O','INPUT SOLUTION')
    WRITE(6,506)
506  FORMAT('+', '-----')
    WRITE(6,507) V(7),V(8)
507  FORMAT('SOLUTION FLOWRATE (L/MIN)=',F7.2,4X,'DENSITY (G/L)=',F8.2)
    WRITE(6,508)
508  FORMAT('O','LEACH SOLUTION ANALYSIS (G/L)')
    WRITE(6,509) V(9),V(11),V(12),V(10),V(13)
509  FORMAT('MO=',F8.3,3X,'FE=',F8.3,3X,'CU=',F8.3,3X,'S=',F8.3,3X,
1  'HNO3=',F8.3)
    READ(5,102) (RX(I),I=1,8)
    READ(5,102) (LC(I),I=1,15)
    WRITE(6,LISTLC)
    READ(5,102) T
    WRITE(6,LISTT)
102  FORMAT(8G10.5)
    READ(5,100) N
100  FORMAT(I1)
    K=1
300  CONTINUE
    IF(K.GT.N) GO TO 302
    READ(5,101) NSV,VOLUME
101  FORMAT(I1,9X,G10.1)
    J=1
301  VOL(K)=VOLUME
    WRITE(6,120) K,VOL(K)
120  FORMAT('O','STAGE NUMBER',I2,5X,'----',F12.1,2X,'LITRES')
    J=J+1
    K=K+1
    IF(J.GT.NSV) GO TO 300
    GO TO 301
302  CONTINUE
    READ(5,102) (G(I),I=1,18)
    WRITE(6,LISTG)
    READ(5,102) (GF(I),I=1,18)
    WRITE(6,LISTGF)
    READ(5,102) (GC(I),I=1,2)
    READ(5,102) SPLIT
    WRITE(6,LISTGC)
    READ(5,465) NF
    READ(5,464) VOLFL,FLOW
    READ(5,464) (PC(I),I=1,4)
    WRITE(6,FLOTN)
    VOLFL=0.75D0*VOLFL
465  FORMAT(I1)
464  FORMAT(8G10.4)
    READ(5,103) IT
103  FORMAT(I2)
    READ(5,102) TOL
    READ(5,102) RMAX
    READ(5,100) ITPRNT
    READ(5,100) KK
    WRITE(6,LISCON)
    SWCHA=.TRUE.
    IF(ITPRNT.EQ.0) SWCHA=.FALSE.
    CALL INPUT
    DO 290 I=1,13

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290 VV(I)=V(I)
CONTINUE
BT=1.9871D0*T
ARRMO=DEXP(-LC(5)/RT)
ARFECF=DEXP(-LC(6)/RT)
ARFEPY=DEXP(-LC(7)/RT)
ARUCP=DEXP(-LC(8)/RT)
MCNEW=V(2)*V(1)
DO 298 K=1,N
VOL(K)=0.92D0*VOL(K)
298 CONTINUE
DO 292 I=1,8
L(I)=1
292 CONTINUE
RDIV=2.0
DO 296 J=1,IT
M=J/KK
LL=KK*M
MOBEC=RX(1)*RX(2)
RXX(1)=RX(1)
RXX(2)=RX(2)
CALL CONMIX
DO 324 K=1,N
IF(K.NE.1) GO TO 282
DO 281 I=8,13
V(I)=VV(I)
281 CONTINUE
282 CONTINUE
CALL LEACH(&299)
324 CONTINUE
CALL LEABAL
CALL FILTER
CALL REGR
CALL REGRSP
CALL REFLOT
CALL RECYC
IF(J.EQ.1) WRITE(6,LISTRX)
IF(LL.LT.J) GO TO 285
WRITE(6,LISTRX)
285 CONTINUE
C TOLERANCE AND ITERATION ADJUSTMENT CALCULATIONS
DO 293 I=1,8
R(I)=0.D0
TOLC(I)=DABS(2.D0*(RX(I)-RXC(I)))/(RX(I)+RXC(I))
IF(TOLC(I).LT.TOL) GO TO 293
IF(L(I).NE.1) GO TO 295
RXCLD(I)=RX(I)
RXCLD(I)=RXC(I)
RX(I)=0.999D0*RX(I)
L(I)=L(I)+1
GO TO 293
295 CONTINUE
R(I)=(RX(I)-RXOLD(I))/(RX(I)-RXC(I)-RXOLD(I)+RXCOLD(I))
IF(I.NE.3) GO TO 278
IF(RXC(I).LT.1.D-05) R(I)=0.D0
278 CONTINUE
IF(I.NE.4) GO TO 277
IF(RXC(I).LT.1.D-05) R(I)=0.D0
277 CONTINUE
IF(DABS(R(I)).LT.RMAX) GO TO 294

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RR(I)=RMAX
IF (I.EQ.1) GO TO 279
IF (TOLC(I).LT.0.05.AND.TOLC(I).GT.0.02) RR(I)=RMAX+RMAX/3.0
IF (TOLC(I).LT.0.02) RR(I)=RMAX+(2.0*RMAX/3.0)
IF (TOLC(I).LT.0.0075) RR(I)=0.75
279 CCNTINUE
IF (I.NE.1) GO TO 280
RR(I)=RMAX/RDIV
IF (TOLC(I).LT.0.0075) RR(I)=0.9D0
IF (TOLC(I).LT.0.05.AND.TOLC(I).GT.0.015) RDIV=1.5
IF (TOLC(I).LT.0.015) RDIV=1.0
280 CCNTINUE
IF (RR(I).GT.0.6) RR(I)=0.6
IF (R(I).LT.0.) R(I)=-RR(I)
IF (R(I).GE.0.) R(I)=RR(I)
294 CCNTINUE
RXCLD(I)=RX(I)
RXCLD(I)=RXC(I)
RX(I)=RX(I)-(RX(I)-RXC(I))*R(I)
L(I)=L(I)+1
293 CCNTINUE
IF (LL.LT.J) GO TO 284
WRITE(6,LISTI)
284 CCNTINUE
IF (J.NE.1) GO TO 286
LSUM=0
DO 287 I=1,8
LSUM=LSUM+L(I)
287 CCNTINUE
IF (J.EQ.1) WRITE(6,LISTI)
IF (LSUM.EQ.8) GO TO 288
GO TO 296
286 CCNTINUE
SUMR=0.D0
DO 289 I=1,8
SUMR=SUMR+DABS(R(I))
289 CCNTINUE
IF (SUMR.EQ.0.) GO TO 288
296 CCNTINUE
DO 291 I=1,8
IF (TOLC(I).GT.TOL) GO TO 299
291 CCNTINUE
288 CCNTINUE
WRITE(6,LISTG)
WRITE(6,LISTRX)
RX(1)=RX(1)/11.57D0
DO 276 I=2,6
RX(I)=100.D0*RX(I)
276 CCNTINUE
WRITE(6,LISTRX)
WRITE(6,LISTI)
CALL OUTPUT
CALL OUTPRT
299 CCNTINUE
WRITE(6,LISTI)
WRITE(6,LISRX)
WRITE(6,LISTRX)
STOP
END

```

SUBROUTINE CONMIX

C COMBINATION OF NEW AND RECYCLE SOLIDS STREAMS

IMPLICIT REAL*8 (A-H,O-Z)

DIMENSION V (13), VL (6), RX (8), RXX (2), VV (6)

COMMON/AREA1/V, VL, RX, RXX

COMMON/AREA19/VV

NAMELIST/LISTVL/VL

VL (1)=VV (1)+RX (1)

DO 180 I=2,6

VL (I)=(VV (I)*VV (I)+RX (I)*RX (I))/VL (1)

180 CONTINUE

C TRANSFER ALL FES2 AND CUPES2 IN RECYCLE SOLIDS TO NEW SOLIDS

WTRCU=RX (4)*RX (1)

WTRFEP=RX (3)*RX (1)-0.8790D0*WTRCU

WTRPY=2.1482D0*WTRFEP

WTRCPY=2.8885D0*WTRCU

V (1)=VV (1)+WTRCPY+WTRPY

V (2)=VV (2)*VV (1)/V (1)

V (3)=(VV (3)*VV (1)+RX (3)*RX (1))/V (1)

V (4)=(VV (4)*VV (1)+WTRCU)/V (1)

V (5)=VV (5)*VV (1)/V (1)

V (6)=(VV (6)*VV (1)+0.3494D0*WTRCPY+0.5345D0*WTRPY)/V (1)

RETURN

END

C *****

SUBROUTINE LEACH (*)

C SUBROUTINE TO SET UP LEACH CONDITIONS FOR EACH STAGE AND

C CALL SOLVING SUBROUTINE

IMPLICIT REAL*8 (A-H,O-Z)

REAL*8 MONEW, MOREC, LC

EXTERNAL FCN

DIMENSION X (18), F (14), V (13)

DIMENSION RX (8), RXX (2)

DIMENSION LC (15), VOL (9)

DIMENSION VL (6)

DIMENSION XX (7)

DIMENSION SNR (9), SRR (9), SR (9)

DIMENSION G (18), GF (18), CSF (9, 18)

DIMENSION SX (9, 18), CSFPIT (9, 18)

COMMON/AREA1/V, VL, RX, RXX

COMMON/AREA2/MONEW, MOREC, LC

COMMON/AREA3/VOL, T, K

COMMON/AREA4/X, XX

COMMON/AREA11/N, LL, J

COMMON/AREA12/SNR, SRR, SR, SX

COMMON/AREA16/FRACL, FRACL

COMMON/AREA17/G, GF

COMMON/AREA18/CSF

COMMON/SE\$SOM/A (20, 22), B (20), Y (22, 21)

NAMELIST/LISTX/X

NAMELIST/LISTP/F

IF (K.EQ.1) GO TO 325

V (1)=X (1)

V (2)=X (2)

V (3)=X (13)

V (4)=X (14)

V (8)=X (5)

V (9)=X (3)

V (11)=X (15)

V (12)=X (16)

V(13)=X(4)
RXX(1)=X(9)
RXX(2)=X(10)

```

325  CONTINUE
C   COEFFICIENTS FOR LINEAR EQUATIONS - 1:OVERALL LIQUID MASS BALANCE
C   2:NEW SOLIDS MASS BALANCE  3:RECYCLE SOLIDS MASS BALANCE
C   4:RATE EQUATION-HNO3
      DO 322 I=1,19
      DO 323 M=1,19
      A(I,M)=0.D0
323  CONTINUE
322  CONTINUE
      A(1,5)=-V(7)
      A(1,6)=1.6683D0
      A(1,7)=-0.4762D0
      A(1,12)=1.6683D0
      A(1,17)=2.1481D0
      A(1,18)=0.9999D0
      A(2,1)=1.D0
      A(2,6)=1.6683D0
      A(2,17)=2.1481D0
      A(2,18)=0.9999D0
      A(3,9)=1.D0
      A(3,12)=1.6683D0
      A(4,6)=3.9412D0
      A(4,7)=-1.D0
      A(4,12)=3.9412D0
      A(4,17)=5.6419D0
      A(4,18)=0.6611D0
      B(1)=-V(7)*V(8)
      B(2)=V(1)
      B(3)=RXX(1)
      B(4)=0.D0
      IF(K.NE.1) GO TO 326
      DO 350 I=1,18
      Y(I,1)=G(I)
350  CONTINUE
      GO TO 333
326  CONTINUE
      IF(K.GT.2) GO TO 352
      DO 351 I=1,18
      Y(I,1)=GF(I)*X(I)
351  CONTINUE
      GO TO 353
352  CONTINUE
      IF(J.NE.1) GO TO 318
      IF(K.NE.3) GO TO 313
      CSF(K-1,6)=1.5D0*CSF(K-1,6)
      CSF(K-1,7)=1.5D0*CSF(K-1,7)
      CSF(K-1,12)=1.5D0*CSF(K-1,12)
      CSF(K-1,17)=1.5D0*CSF(K-1,17)
      CSF(K-1,18)=1.5D0*CSF(K-1,18)
313  CONTINUE
      DO 354 I=1,18
      Y(I,1)=CSF(K-1,I)*X(I)
354  CONTINUE
      GO TO 317
318  CONTINUE
      DO 316 I=1,18
      Y(I,1)=CSFPIT(K,I)*X(I)

```

```

316 CONTINUE
317 CCNTINUE
333 CONTINUE
353 CONTINUE
    DO 327 I=2,15
    DO 340 M=1,18
340 Y(M,I)=Y(M,1)
327 Y(I,I)=Y(I,I)*1.001D0
C CALL TC SUBROUTINE TO SOLVE SIMULTANEOUS ALGEBRAIC EQUATIONS
  CALL SSM(X,P,14,4,5.D-03,150,PCN,.TRUE.,.TRUE.,.TRUE.,IFAIL,&328)
  IF(X(13).LT.0.) X(13)=1.D-07
  IF(X(14).LT.0.) X(14)=1.D-07
  IF(K.NE.1) GO TO 335
  DO 336 I=1,18
  G(I)=X(I)
336 CONTINUE
335 CCNTINUE
328 CONTINUE
  IF(IFAIL.NE.0) GO TO 329
  DO 330 I=1,18
  SX(K,I)=X(I)
330 CONTINUE
  IF(K.EQ.1) GO TO 355
  DO 356 I=1,18
  CSF(K,I)=SX(K,I)/SX(K-1,I)
356 CONTINUE
  IF(K.EQ.1) GO TO 315
  DO 314 I=1,18
  CSFPIT(K,I)=SX(K,I)/SX(K-1,I)
314 CCNTINUE
315 CONTINUE
  IF(K.NE.2) GO TO 320
  DO 319 I=1,18
  GF(I)=CSF(K,I)
319 CONTINUE
320 CONTINUE
355 CONTINUE
  SNE(K)=100.D0*(MONEW-X(1)*X(2))/MONEW
  SRR(K)=100.D0*(MOREC-X(9)*X(10))/MOREC
329 CCNTINUE
  WRITE(6,331) K,IFAIL
331 FORMAT('0','LEACH FAIL CODE FOR STAGE (' ,I1,' )=' ,I10)
  IF(J.EQ.1) WRITE(6,LISTX)
  IF(LL.LT.J) GO TO 321
  WRITE(6,LISTX)
321 CONTINUE
  IF(IFAIL.EQ.0) GO TO 334
  IF(J.NE.1) WRITE(6,LISTX)
  X(1)=X(1)/11.57D0
  X(2)=100.D0*X(2)
  X(3)=X(5)*X(3)
  X(4)=X(5)*X(4)
  X(9)=X(9)/11.57D0
  X(10)=100.D0*X(10)
  X(13)=100.D0*X(13)
  X(14)=100.D0*X(14)
  X(15)=X(5)*X(15)
  X(16)=X(5)*X(16)
  WRITE(6,LISTX)
  WRITE(6,LISTF)

```

RETURN 1

334 CONTINUE

RETURN

ENE

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C *****

SUBROUTINE FCN (X,F)

C SUBROUTINE CONTAINING THE SET OF NONLINEAR ALGEBRAIC EQUATIONS

IMPLICIT REAL*8 (A-H,O-Z)

REAL*8 MONEW,MOREC,LC

DIMENSION X(18),F(14),V(13)

DIMENSION RX(8),RXX(2)

DIMENSION LC(15),VOL(9)

DIMENSION VL(6)

COMMON/AREA1/V,VL,RX,RXX

COMMON/AREA2/MONEW,MOREC,LC

COMMON/AREA3/VOL,T,K

COMMON/AREA16/FRACL,FRACLR

COMMON/AREA20/ARRMO,ARFECF,ARFEPY,ARCUCP

FRACL=(MONEW-X(1)*X(2))/MONEW

IF (FRACL.LT.0.) FRACL=1.D-09

FRACLR=(MOREC-X(9)*X(10))/MOREC

IF (FRACLR.LT.0.) FRACLR=0.D0

ACIDN=X(4)*X(5)/63.02D0

C LIQUID COMPONENT BALANCES - MO,FE,CU,HNO3

F(1)=V(7)*V(8)*V(9)-V(7)*X(5)*X(3)+(X(6)+X(12))

F(2)=V(7)*V(8)*V(11)-V(7)*X(5)*X(15)+X(17)

F(3)=V(7)*V(8)*V(12)-V(7)*X(5)*X(16)+X(18)

F(4)=V(7)*V(8)*V(13)-V(7)*X(5)*X(4)-X(7)

C SOLID COMPONENT BALANCES - MO-NEW,MO-RECYCLE,FE,CU

F(5)=V(1)*V(2)-X(1)*X(2)-X(6)

F(6)=RXX(1)*RXX(2)-X(9)*X(10)-X(12)

F(7)=V(1)*V(3)-X(1)*X(13)-X(17)

F(8)=V(1)*V(4)-X(1)*X(14)-X(18)

C RATE EQUATIONS - MO-NEW,MO-RECYCLE,FE,CU

IF (X(1).LE.0.) GO TO 15

F(9)=X(6)-LC(1)*VOL(K)*X(8)*ACIDN**2

1*(1.6683D0*X(2)*X(1)/(LC(15)*V(7)))*ARRMO

IF (X(9).LT.0.) GO TO 17

F(10)=X(12)-LC(1)*VOL(K)*X(11)*ACIDN**2

1*(1.6683D0*X(10)*X(9)/(LC(15)*V(7)))*ARRMO

GO TO 18

17 CONTINUE

F(10)=X(12)-0.D0

18 CONTINUE

XFEFY=X(13)-0.8790D0*X(14)

IF (XFEFY.LT.0.) XFEFY=0.D0

IF (X(14).LT.0.) GO TO 13

F(11)=X(17)-LC(2)*ACIDN*VOL(K)*ARFEPY

1*(0.8790D0*X(14)*X(1)/(55.85D0*V(7)))*(2./3.)

2-LC(3)*ACIDN*VOL(K)*ARFECF*(XFEFY*X(1)/(55.85D0*V(7)))*(2./3.)

F(12)=X(18)-LC(4)*ACIDN*VOL(K)*ARCUCP

1*(X(14)*X(1)/(63.54D0*V(7)))*(2./3.)

GO TO 14

13 CONTINUE

F(11)=X(17)-0.D0

2-LC(3)*ACIDN*VOL(K)*ARFECF*(XFEFY*X(1)/(55.85D0*V(7)))*(2./3.)

F(12)=X(18)-0.D0

14 CONTINUE

GO TO 16

15 CONTINUE

```

F(9)=X(6)-0.D0
IF(X(9).LT.0.) GO TO 19
F(10)=X(12)-LC(1)*VOL(K)*X(11)*ACIDN**2
1*(1.6683D0*X(10)*X(9)/(LC(15)*V(7)))*ARRMO

```

```

GO TO 20
19 CONTINUE
F(10)=X(12)-0.D0
20 CONTINUE
F(11)=X(17)-0.D0
F(12)=X(18)-0.D0
16 CONTINUE
C SURFACE AREA FACTOR TERMS - MOS2-NEW,MOS2-RECYCLE
IF(FRACL.LT.LC(13)) GO TO 11
F(13)=X(8)-DEXP(-LC(9)*(FRACL**LC(10)))
GO TO 12
11 CONTINUE
F(13)=X(8)-LC(11)+LC(12)*FRACL
12 CONTINUE
F(14)=X(11)-RX(7)*DEXP(-RX(8)*LC(14)*FRACL)
RETURN
END

```

```

C *****
SUBROUTINE LEABAL
C CALCULATION OF VARIABLES NOT DIRECTLY DETERMINED BY
C THE LEACH EQUATIONS
IMPLICIT REAL*8 (A-H,O-Z)
DIMENSION V(13),VL(6),X(18),XX(7)
DIMENSION RX(8),RXX(2)
LOGICAL SWCHA
COMMON/AREA1/V,VL,RX,RXX
COMMON/AREA4/X,XX
COMMON/AREA21/SWCHA
NAMELIST/LISTXX/XX
REAL*8 MODIS
C CALCULATE FINAL STAGE OUTPUT VALUES - 1:TOTAL SOLIDS FLOW RATE
C 2:MO IN SOLIDS 3:SIO2 IN SOLIDS 4:S IN SOLIDS 5:S IN LIQUID
C 6:WEIGHTED AVERAGE AREA FACTOR 7:TOTAL FRACTION OF MO LEACHED
XX(1)=X(1)+X(9)
XX(2)=(X(2)*X(1)+X(10)*X(9))/XX(1)
XX(3)=VL(5)*VL(1)/XX(1)
MODIS=VL(2)*VL(1)-XX(2)*XX(1)
CUDIS=VL(4)*VL(1)-X(14)*X(1)
FEEDIS=(VL(3)*VL(1)-X(13)*X(1))-0.8790D0*CUDIS
SULDIS=0.6683D0*MODIS+1.0091D0*CUDIS+1.1481D0*FEEDIS
XX(4)=(VL(6)*VL(1)-SULDIS)/XX(1)
XX(5)=(V(10)*V(8)*V(7)+SULDIS)/(V(7)*X(5))
XX(6)=(X(8)*X(1)+X(11)*X(9))/XX(1)
XX(7)=(VL(2)*VL(1)-XX(2)*XX(1))/(VL(2)*VL(1))
IF(SWCHA) WRITE(6,LISTXX)
RETURN
END

```

```

C *****
SUBROUTINE FILTER
IMPLICIT REAL*8 (A-H,O-Z)
DIMENSION X(18),XX(7),FX(7),GX(8)
COMMON/AREA4/X,XX
COMMON/AREA5/FX,GX
NAMELIST/LISTFX/FX
C FILTER - SOLIDS/LIQUID SEPARATION AFTER FINAL LEACHING STAGE
C 1:TOTAL SOLIDS MASS FLOW 2:MO 3:FE 4:CU 5:SIO2 6:S 7:A0

```

```

FX(1)=XX(1)
FX(2)=XX(2)
FX(3)=X(13)*X(1)/XX(1)
FX(4)=X(14)*X(1)/XX(1)
FX(5)=XX(3)
FX(6)=XX(4)
FX(7)=XX(6)
RETURN
END

```

C *****

SUBROUTINE REGR

C DETERMINE EFFECT OF REGRINDING ON RECYCLE SOLIDS

C AREA FACTOR PARAMETERS

```

IMPLICIT REAL*8 (A-H,O-Z)
DIMENSION GC(2),FX(7),GX(8)
COMMON/AREA5/FX,GX
COMMON/AREA6/GC,SPLIT
COMMON/AREA15/TMGRND
NAMELIST/LISTGX/GX
TGRIND=GC(1)/FX(1)
DO 370 I=1,6
GX(I)=FX(I)
370 CONTINUE
GX(7)=FX(7)*(1.DO+GC(2)*TGRIND)
GX(8)=1.DO+GC(2)*TGRIND
TMGRND=TGRIND/60.DO
RETURN
END

```

C *****

SUBROUTINE REGRSP

C CALCULATE DISTRIBUTION OF SOLIDS MASS FLOWRATE TO REFLOTATION

C AND DIRECTLY TO THE LEACH

```

IMPLICIT REAL*8 (A-H,O-Z)
DIMENSION FX(7),GX(8),RGX(6),GFX(6)
DIMENSION GC(2)
COMMON/AREA5/FX,GX
COMMON/AREA6/GC,SPLIT
COMMON/AREA7/RGX,GFX
NAMELIST/LISRGX/RGX
NAMELIST/LISGFX/GFX
DO 380 I=2,6
RGX(I)=FX(I)
GFX(I)=FX(I)
380 CONTINUE
RGX(1)=SPLIT*FX(1)
GFX(1)=(1.DO-SPLIT)*FX(1)
RETURN
END

```

C *****

SUBROUTINE REPLOT

C FLOTATION MODEL TO CALCULATE RECOVERIES, MASS FLOWRATES AND

C ANALYSES. MOS2, CUFES2, FES2, INSOL

```

IMPLICIT REAL*8 (A-H,O-Z)
DIMENSION GFX(6),FC(4),RMO(9),RPY(9),RCPY(9),RSIL(9),RT(9)
DIMENSION RFX(6),FTX(3)
DIMENSION RGX(6),RXC(8)
LOGICAL SWCHA
COMMON/AREA7/RGX,GFX
COMMON/AREA8/RFX,FTX,RXC
COMMON/AREA9/FC

```


COMMON/AREA10/VOLFL, FLOW, NF
 COMMON/AREA14/RECMO, RECPY, RECCPY, RECSIL
 COMMON/AREA21/SWCHA
 NAMELIST/RECOVS/RECMO, RECPY, RECCPY, RECSIL
 NAMELIST/FLOTS/RFX
 NAMELIST/TAILS/FTX

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GFX(2)=1.6683D0*GFX(2)*GFX(1)
 GFX(3)=2.1482D0*(GFX(3)-0.8790D0*GFX(4))*GFX(1)
 GFX(4)=2.8885D0*GFX(4)*GFX(1)
 GFX(5)=GFX(5)*GFX(1)
 RECMC=0.D0
 PFLOW=FLOW+GFX(1)/4.5D+03
 DO 460 I=1, NF
 RMO(I)=(PFLOW-0.12128D-02*GFX(2)*RECMO+FC(1)*VOLFL)-DSORT((PFLOW-
 10.12128D-02*GFX(2)*RECMO+FC(1)*VOLFL)**2.D0-0.48512D-02*GFX(2)*
 2(1.D0-RECMO)*FC(1)*VOLFL))/(0.24256D-02*GFX(2))
 RECMC=RECMO+RMO(I)
 RT(I)=VOLFL/(PFLOW-0.12128D-02*GFX(2)*RECMO)
 460 CONTINUE
 RECPY=0.D0
 DO 461 I=1, NF
 RPY(I)=(FC(2)*RT(I)/(1.D0+FC(2)*RT(I)))*(1.D0-RECPY)
 RECPY=RECPY+RPY(I)
 461 CCNTINUE
 RECCPY=0.D0
 DO 462 I=1, NF
 RCPY(I)=(FC(3)*RT(I)/(1.D0+FC(3)*RT(I)))*(1.D0-RECCPY)
 RECCPY=RECCPY+RCPY(I)
 462 CONTINUE
 RECSIL=0.D0
 DO 463 I=1, NF
 RSIL(I)=(FC(4)*RT(I)/(1.D0+FC(4)*RT(I)))*(1.D0-RECSIL)
 RECSIL=RECSIL+RSIL(I)
 463 CONTINUE
 RFX(1)=GFX(2)*RECMO+GFX(3)*RECPY+GFX(4)*RECCPY+GFX(5)*RECSIL
 RFX(2)=0.5994D0*GFX(2)*RECMO/RFX(1)
 RFX(3)=(0.4655D0*GFX(3)*RECPY+0.3043D0*GFX(4)*RECCPY)/RFX(1)
 RFX(4)=(0.3462D0*GFX(4)*RECCPY)/RFX(1)
 RFX(5)=GFX(5)*RECSIL/RFX(1)
 RFX(6)=0.6683D0*RFX(2)+1.0091D0*RFX(4)+1.1481D0*(RFX(3)-0.8790D0
 1*RFX(4))
 FTX(1)=GFX(1)-RFX(1)
 FTX(2)=(0.5994D0*GFX(2)-RFX(2)*RFX(1))/FTX(1)
 FTX(3)=(GFX(5)-RFX(5)*RFX(1))/FTX(1)
 IF(SWCHA) WRITE(6, RECOVS)
 IF(SWCHA) WRITE(6, FLOTS)
 IF(SWCHA) WRITE(6, TAILS)
 RETURN
 END

C *****

SUBROUTINE RECYC

C COMBINATION OF REFLOTATION CONCENTRATE AND SOLIDS DIRECTLY
 C RECYCLED FROM REGRINDING

IMPLICIT REAL*8(A-H,O-Z)
 DIMENSION RXC(8), RGX(6), GX(8), RFX(6), FTX(3), FX(7)
 DIMENSION GFX(6)
 COMMON/AREA5/FX, GX
 COMMON/AREA7/RGX, GFX
 COMMON/AREA8/RFX, FTX, RXC
 COMMON/AREA11/N, LL, J

NAMLIST/LISRXC/RXC

RXC(1)=RGX(1)+RFX(1)

DO 390 I=2,6

RXC(I)=(RGX(1)*RGX(I)+RFX(1)*RFX(I))/RXC(1)

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390 CONTINUE

RXC(7)=GX(7)

RXC(8)=GX(8)

IF(J.EQ.1) WRITE(6,LISRXC)

IF(LL.LT.J) GO TO 391

WRITE(6,LISRXC)

391 CONTINUE

RETURN

END

C *****

SUEROUTINE INPUT

C CONVERSION OF INPUT UNITS TO MODEL UNITS

IMPLICIT REAL*8 (A-H,O-Z)

DIMENSION V(13),VL(6),RX(8),RXX(2)

DIMENSION GC(2),G(18),GF(18),FC(4),VOL(9)

COMMON/AREA1/V,VL,RX,RXX

COMMON/AREA3/VOL,T,K

COMMON/AREA6/GC,SPLIT

COMMON/AREA9/FC

COMMON/AREA10/VOLFL,FLOW,NF

COMMON/AREA17/G,GF

V(1)=11.57D0*V(1)

DO 900 I=2,6

V(I)=V(I)/100.D0

900 CONTINUE

V(7)=V(7)/60.D0

DO 902 I=9,13

V(I)=V(I)/V(8)

902 CONTINUE

RX(1)=11.57D0*RX(1)

DO 901 I=2,6

RX(I)=RX(I)/100.D0

901 CONTINUE

T=T+273.15

G(1)=11.57D0*G(1)

G(2)=G(2)/100.D0

G(3)=G(3)/G(5)

G(4)=G(4)/G(5)

G(9)=11.57D0*G(9)

G(10)=G(10)/100.D0

G(13)=G(13)/100.D0

G(14)=G(14)/100.D0

G(15)=G(15)/G(5)

G(16)=G(16)/G(5)

GC(1)=1.D03*GC(1)

GC(2)=GC(2)/60.D0

DO 903 I=1,4

FC(I)=FC(I)/60.D0

903 CONTINUE

FLCW=FLOW/60.D0

RETURN

END

C *****

SUEROUTINE OUTPUT

C CONVERSION OF MODEL UNITS TO OUTPUT UNITS PLUS ADDITIONAL

C CALCULATIONS

```

IMPLICIT REAL*8 (A-H,O-Z)
REAL*8 MONEW,MOREC,LC,MOTOL
DIMENSION VL(6),XX(7),FX(7),GX(8),GC(2),RGX(6),GFX(6),RFX(6)
DIMENSION PFX(3),RXC(8),FC(4),LC(15),VOL(9),X(18)
DIMENSION SNR(9),SRR(9),SR(9),V(13),VV(13),RX(8),RXX(2) - 177 -
DIMENSION SX(9,18)
COMMON/AREA1/V,VL,RX,RXX
COMMON/AREA2/MONEW,MOREC,LC
COMMON/AREA3/VOL,T,K
COMMON/AREA4/X,XX
COMMON/AREA5/FX,GX
COMMON/AREA7/RGX,GFX
COMMON/AREA8/RFX,PFX,RXC
COMMON/AREA11/N,LL,J
COMMON/AREA12/SNR,SRR,SR,SX
COMMON/AREA13/EXTRN,RECRAT,PULPD,MOTOL
COMMON/AREA14/RECNO,RECPY,RECCPY,RECSIL
COMMON/AREA19/VV

```

C LEACH CALCULATIONS

C STAGewise NO RECOVERIES

```

DO 705 K=1,N
TMCIN=MONEW+MOREC
SR(K)=(TMOIN-((SX(K,1)*SX(K,2))+(SX(K,9)*SX(K,10))))/TMOIN
1*100.DO

```

```

705 CONTINUE
EXTRN=86.40D-02*(SNR(N)*MONEW+SRR(N)*MOREC)
RECRAT=11.57D0*RX(1)/VV(1)
PULPD=(11.57D0*RX(1)+VV(1))/VV(7)
DO 700 K=1,N
SX(K,1)=0.8640D-01*SX(K,1)
SX(K,2)=100.DO*SX(K,2)
SX(K,3)=SX(K,3)*SX(K,5)
SX(K,4)=SX(K,4)*SX(K,5)
SX(K,9)=0.8640D-01*SX(K,9)
SX(K,10)=100.DO*SX(K,10)
SX(K,13)=100.DO*SX(K,13)
SX(K,14)=100.DO*SX(K,14)
SX(K,15)=SX(K,15)*SX(K,5)
SX(K,16)=SX(K,16)*SX(K,5)

```

700 CONTINUE

C LEACH CALCULATIONS

```

XX(1)=0.8640D-01*XX(1)
XX(2)=100.DO*XX(2)
XX(3)=100.DO*XX(3)
XX(4)=100.DO*XX(4)
XX(5)=XX(5)*SX(N,5)
XX(7)=100.DO*XX(7)

```

C FILTER CALCULATIONS

```

FX(1)=0.8640D-01*FX(1)
DO 701 I=2,6
FX(I)=100.DO*FX(I)

```

701 CONTINUE

C REGRIND CALCULATIONS

```

GX(1)=0.8640D-01*GX(1)
DO 702 I=2,6
GX(I)=100.DO*GX(I)

```

702 CONTINUE

C REGRIND SPLIT CALCULATIONS

```

RGX(1)=0.8640D-01*RGX(1)
GFX(1)=0.8640D-01*GFX(1)

```

```
C REFLOTATION CALCULATIONS
  RECMO=100.D0*RECMO
  RECPY=100.D0*RECPY
  RECCPY=100.D0*RECCPY
  RECSIL=100.D0*RECSIL
  RFX(1)=0.8640D-01*RFX(1)
  DO 703 I=2,6
  RFX(I)=100.D0*RFX(I)
703  CCNTINUE
  FTX(1)=0.8640D-01*FTX(1)
  FTX(2)=100.D0*FTX(2)
  FTX(3)=100.D0*FTX(3)

C MOLYBDENUM TOLERANCE CALCULATIONS
  MONEW=86.40D0*MONEW
  MOTOL=(10.D0*FTX(1)*FTX(2)+EXTRN-MONEW)/MONEW

C RECYCLE COMBINATION CALCULATIONS
  RXC(1)=0.8640D-01*RXC(1)
  DO 704 I=2,6
  RXC(I)=100.D0*RXC(I)
704  CCNTINUE
  RETURN
  END

C *****
  SUBROUTINE OUTPRT
C  CONTRCL CONVERGED OUTPUT PRINTING
  IMPLICIT REAL*8 (A-H,O-Z)
  REAL*8 MONEW,MOTOL
  DIMENSION XX(7),FX(7),GX(8),GC(2),RGX(6),GFX(6),RFX(6)
  DIMENSION FTX(3),RXC(8),FC(4),VOL(9),X(18),LC(15)
  DIMENSION SX(9,18),CSF(9,18)
  DIMENSION SNR(9),SRR(9),SR(9)
  DIMENSION V(13),VL(6),RX(8),RXX(2)
  COMMON/AREA1/V,VL,RX,RXX
  COMMON/AREA2/MONEW,MOREC,LC
  COMMON/AREA3/VOL,T,K
  COMMON/AREA4/X,XX
  COMMON/AREA5/PX,GX
  COMMON/AREA7/RGX,GFX
  COMMON/AREA8/RFX,FTX,RXC
  COMMON/AREA11/N,LL,J
  COMMON/AREA12/SNR,SRR,SR,SX
  COMMON/AREA13/EXTRN,RECRAT,PULPD,MOTOL
  COMMON/AREA14/RECMO,RECPY,RECCPY,RECSIL
  COMMON/AREA15/TMGRND
  COMMON/AREA18/CSF
  WRITE(6,801) N
801  FORMAT('0','FINAL LEACHING STAGE(','I1,') OUTPUT')
  WRITE(6,807)
807  FORMAT('+' , ' ' )
  WRITE(6,843) EXTRN
843  FORMAT('EXTRACTION OF MO TO SOLUTION (KG/DAY)=' ,F7.1)
  WRITE(6,854) MONEW
854  FORMAT('NEW INPUT MOLYBDENUM TO LEACH(KG/DAY)=' ,F7.1)
  WRITE(6,855) MOTOL
855  FORMAT('MOLYBDENUM FRACTIONAL TOLERANCE=' ,F8.5)
  WRITE(6,850) RECRAT
850  FORMAT('0','SOLIDS RECYCLE RATIO=' ,F7.3)
  WRITE(6,851) PULPD
851  FORMAT('0','STAGE 1 INPUT PULP DENSITY (G/L)=' ,F7.2)
  IF(PULPD.LT.550.0) GO TO 852
```

```

853 WRITE(6,853)
853 FORMAT('WARNING:INPUT PULP DENSITY HIGH')
852 CONTINUE
      WRITE(6,802)
802 FORMAT('0','LEACH SOLIDS RESIDUE FLOWRATE (TONNES/DAY)')
      WRITE(6,803) XX(1),SX(N,1),SX(N,9)
803 FORMAT('TOTAL SOLIDS=',F8.3,'NEW SOLIDS=',F8.3,'RECYCLE SOLIDS=',
1F8.3)
      WRITE(6,804)
804 FORMAT('0','TOTAL OUTPUT SOLIDS ANALYSIS (WGT%)')
      WRITE(6,805) XX(2),FX(3),FX(4),XX(3),XX(4)
805 FORMAT('MO=',F7.3,2X,'FE=',F7.3,2X,'CU=',F7.3,2X,'INSOL=',F7.3
1,2X,'S=',F7.3)
      WRITE(6,806)
806 FORMAT('0','NEW SOLIDS OUTPUT ANALYSIS (WGT%)')
      WRITE(6,808) SX(N,2)
808 FORMAT('MO=',F7.3)
      WRITE(6,809)
809 FORMAT('0','RECYCLE SOLIDS OUTPUT ANALYSIS (WGT%)')
      WRITE(6,810) SX(N,10)
810 FORMAT('MO=',F7.3)
      WRITE(6,839)
839 FORMAT('0','OUTPUT LEACH SOLUTION')
      WRITE(6,840) SX(N,5)
840 FORMAT('SOLUTION DENSITY (G/L)=',F8.2)
      WRITE(6,841)
841 FORMAT('0','LEACH SOLUTION ANALYSIS (G/L)')
      WRITE(6,842) SX(N,3),SX(N,15),SX(N,16),XX(5),SX(N,4)
842 FORMAT('MO=',F8.3,3X,'FE=',F8.3,3X,'CU=',F8.3,3X,'S=',F8.3,3X,
1'HNO3=',F8.3)
      WRITE(6,811)
811 FORMAT('0','STAGE CUMULATIVE RECOVERIES OF MO (%MO DISSOLVED)')
      WRITE(6,813)
813 FORMAT(10X,'TOTAL',10X,'NEW SOLIDS',10X,'RECYCLE SOLIDS')
      DO 812 K=1,N
      WRITE(6,814) K,SR(K),SNR(K),SRR(K)
814 FORMAT('STAGE',I1,3X,F7.3,10X,F7.3,14X,F7.3)
812 CONTINUE
      WRITE(6,844)
      IF(N.EQ.1) GO TO 848
844 FORMAT('0','CALCULATED STAGE FACTORS - FOR STAGES 2 TO N')
      DO 845 K=2,N
      WRITE(6,847) K
847 FORMAT('STAGE',I1)
      WRITE(6,849) (CSF(K,I),I=1,18)
849 FORMAT(18F5.2)
845 CONTINUE
848 CONTINUE
      WRITE(6,815)
815 FORMAT('0','REGRIND PARAMETERS')
      WRITE(6,816)
816 FORMAT('0','REGRIND PARAMETERS')
      WRITE(6,817) TMGRND
817 FORMAT('0','MEAN RESIDENCE TIME IN GRINDING MILL(MINUTES)=',F7.2)
      WRITE(6,818)
818 FORMAT('0','RECYCLE AREA FACTOR PARAMETERS')
      WRITE(6,819) GX(7),GX(8)
819 FORMAT('B1=',F8.5,'B2=',F8.5)
      WRITE(6,820)
820 FORMAT('0','STREAM SPLIT - SOLIDS FLOWRATES (TONNES/DAY)')

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821 WRITE(6,821) RGX(1),GFX(1)
822 FORMAT('DIRECT GRIND TO RECYCLE=',F8.3,'GRIND TO FLOTATION=',F8.3)
823 WRITE(6,822)
824 FORMAT('0','FLOTATION RESULTS')
825 WRITE(6,823)
826 FORMAT('+' , '-----')
827 WRITE(6,824)
828 FORMAT('0','MINERAL RECOVERIES (%)')
829 WRITE(6,825) RECMO,RECPY,RECCPY,RECSIL
830 FORMAT('MOS2=',F7.3,'FES2=',F7.3,'CUFES2=',F7.3,'INSOL=',F7.3)
831 WRITE(6,826) RFX(1)
832 FORMAT('0','MASS FLOWRATE OF CONCENTRATE (TONNES/DAY)=',F8.3)
833 WRITE(6,827)
834 FORMAT('0','FLOTATION CONCENTRATE ANALYSIS (WGT%)')
835 WRITE(6,828) RFX(2),RFX(3),RFX(4),RFX(5),RFX(6)
836 FORMAT('MO=',F7.3,'FE=',F7.3,'CU=',F7.3,'INSOL=',F7.3,'S=',F7.3)
837 WRITE(6,829) PTX(1)
838 FORMAT('0','MASS FLOWRATE OF FLOTATION TAILS (TONNES/DAY)=',F8.3)
839 WRITE(6,830)
840 FORMAT('0','FLOTATION TAILS ANALYSIS (WGT%)')
841 WRITE(6,831) PTX(2)
842 FORMAT('MO=',F7.3)
843 WRITE(6,832)
844 FORMAT('0','CALCULATED VALUES FOR RECYCLE SOLIDS')
845 WRITE(6,833)
846 FORMAT('+' , '-----')
847 WRITE(6,834) RXC(1)
848 FORMAT('0','RECYCLE SOLIDS MASS FLOWRATE (TONNES/DAY)=',F8.3)
849 WRITE(6,835)
850 FORMAT('0','RECYCLE SOLIDS ANALYSIS (WGT%)')
851 WRITE(6,836) RXC(2),RXC(3),RXC(4),RXC(5),RXC(6)
852 FORMAT('MO=',F7.3,'FE=',F7.3,'CU=',F7.3,'INSOL=',F7.3,'S=',F7.3)
853 WRITE(6,837)
854 FORMAT('0','RECYCLE AREA FACTOR PARAMETERS')
855 WRITE(6,838) RXC(7),RXC(8)
856 WRITE(6,838) RX(7),RX(8)
857 FORMAT('B1=',F8.5,'B2=',F8.5)
858 DC 856 K=1,N
859 WRITE(6,857) K
860 FORMAT('0','STAGE(' ,I1,') X VALUES')
861 DO 858 I=1,18
862 WRITE(6,859) SX(K,I)
863 FORMAT(G12.5)
864 CONTINUE
865 CONTINUE
866 RETURN
867 END

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APPENDIX D

OTHER SPECIFIC PARAMETERS USED IN MODEL

(1) Grind Constant $k'_g = 0.0570 \text{ sec}^{-1}$

- by analysis of Report 7 and 8 data [4]
using initial calculated rates of reaction.

A' = area factor for grinding mill input

A'' = area factor for ground solids

Initial leach rates (at 1 min.)

$$r' \propto A'$$

$$r'' \propto A''$$

Ratio:

$$\frac{r''}{r'} = \frac{A''}{A'} = \frac{A' + k_g t_g}{A'} = 4.43$$

$$\therefore k_g t_g = 3.43 A'$$

$$k_g = \frac{3.43 A'}{t_g}$$

$$= k'_g A'$$

$$= 0.0570 A'$$

(2) Flotation rates constants:

$$\text{MoS}_2 = 1.0 \text{ min}^{-1}$$

$$\text{FeS}_2 = 0.5^*$$

$$\text{CuFeS}_2 = 0.5^*$$

$$\text{Insol} = 0.10$$

* estimates - may be some control depending on desirability of recycling FeS_2 and CuFeS_2 .