

# A kinetic study of the leaching of pentlandite in acidic ferric sulphate solutions

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## SYNOPSIS

A study was made of the kinetics in the leaching of nickel from pentlandite in dilute-acidic ferric sulphate solutions as a basis for subsequent studies on bacterial leaching. The chemical leaching rate was found to be highly dependent on the temperature and the concentration of ferric ions. The proposed mechanism for the leaching process is one involving rate control by chemical processes and mass transport. Good agreement was found between the experimental data and the proposed mechanism.

## SAMEVATTING

Daar is 'n studie gemaak van die kinetika in die uitloging van nikkell uit pentlandiet in verdunde suur ferrisulfaat-oplossings as 'n basis vir later studies in verband met bakteriese uitloging. Daar is gevind dat die tempo van die chemiese uitloging in 'n baie hoë mate afhang van die temperatuur en die konsentrasie van die ferri-ione. Die voorgestelde meganisme vir die uitloogproses is een wat temperatuurkontrolle deur chemiese prosesse en massa-oordrag behels. Daar is gevind dat die eksperimentele data goed met die voorgestelde meganisme ooreenkom.

## INTRODUCTION

A previous paper<sup>1</sup> gave an account of the theory and various applications of bacterial-leaching technology, as well as reporting a study carried out at the University of New South Wales on the mechanisms involved in the bacterial leaching of a number of copper sulphides<sup>2</sup>. Indeed, at present by far the major portion of the theoretical and practical expertise available in the field of bacterial leaching is based on the treatment of copper and, to a lesser extent, zinc sulphides. Little information is available on the bacterial leaching of nickel sulphides, and a need for this information recently became clear as a result of growing interest in Southern Africa, West Australia<sup>3</sup>, and possibly elsewhere.

This need has been accentuated by the developing exploitation of nickel deposits in these localities, where the large waste dumps could perhaps yield some revenue (as in the case of copper) from the use of a treatment method such as bacterial leaching. It is rather surprising that so little information on nickel leaching under bacterial dump-leaching conditions has been published. One reason for this could well be that low ambient temperatures in places like Canada, where one would expect a keen interest in

nickel leaching, render bacterial dump-leaching unpractical.

A research programme has been conducted over the past few years with the aim of extending part of the knowledge of the bacterial leaching of copper and zinc sulphides into the leaching of nickel sulphide. A part of this programme is discussed in the present paper. It is sincerely hoped that this work will provide some useful practical information and stimulate further interest in the field of bacterial dump leaching, particularly in base-metal mining in Southern Africa.

The research programme was divided into two phases. Phase 1 dealt with the chemical leaching of nickel from a sulphide ore in a dump-leaching environment and is described in the present paper. Chemical leaching was studied both to provide information on its use as a separate process and to serve as a basis for comparison with the subsequent investigation of bacterial leaching. Phase 2 (published separately) was a bacterial leaching study of a nickel sulphide ore. For the sake of completeness, the broad overall conclusions of phase 2 are presented in the Addendum to the present paper.

## NICKEL LEACHING

Nickel sulphides are leached on a commercial scale in a large number of localities. The Sherritt-Gordon process<sup>4</sup> involves the leaching of a concentrate of nickel and cobalt

sulphides in ammoniacal solution.

Other processes for the leaching of mixed nickel sulphides in acid solution, which are discussed in most texts on hydrometallurgy<sup>5, 6</sup>, use high temperature-pressure (autoclave) conditions.

The chemical reactions by which pentlandite dissolves in acidic ferric sulphate solutions are complex, and little work on the subject has been reported in the literature. Klets *et al.*<sup>7</sup> showed that, during the leaching of a pentlandite-pyrrhotite mixture with ferric chloride solutions, elemental sulphur was formed in the surface layers. Phases such as millerite (NiS), beyrichite (NiS), and troilite (FeS) were also formed, and jarosite [KFe<sub>3</sub>(SO<sub>4</sub>)<sub>2</sub>(OH)<sub>6</sub>] was precipitated from solution at low acid concentrations. Shneerson *et al.*<sup>8</sup>, in a study of the autoclave leaching of pentlandite under oxygen pressure, found the activation energy to be 14 kcal/mol and the order with respect to oxygen pressure to be ½. Millerite was formed as an intermediate phase. The interpretation of these results is complicated by the fact that the stoichiometry of the pentlandite was not known or is not given.

## MATERIALS, METHODS, AND EQUIPMENT

### Preparation of Sulphide Minerals

A high-purity pentlandite was prepared from Shangani flotation concentrates, the composition of which is shown in Table 1A. (The Shangani nickel deposit is near

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Bulawayo, Rhodesia.) These flotation concentrates were first passed over a laboratory-size gravity-concentration table (Wilfley table) to remove most of the residual gangue and yield a sulphide-rich fraction.

This fraction was then passed through a wet magnetic separator (Sala laboratory model) to remove the magnetic pyrrhotite (FeS) fraction. Finally, the material was floated at pH 5 to remove some of

the residual pyrite (FeS<sub>2</sub>). The composition of the final pentlandite concentrate is shown in Table IB. This material was found to be about 90 per cent pentlandite (NiFeS<sub>1,8</sub>), with about 6,1 per cent pyrite.

TABLE I

DETAILS OF PENTLANDITE CONCENTRATES

A. *Low-grade Concentrate*  
Chemical assay:

	Ni	Fe	Cu	S
Total %	18,27	37,03	1,5	33,7

Mineralogical (X-ray diffractometric analysis):

Approx. %	Pentlandite	Pyrrhotite	Pyrite	Talc	Dolomite	Chlorite
	60	20	10	5	Trace	Trace

Calculated mineralogical composition:

%	Pentlandite	Pyrrhotite	Pyrite	Chalcopyrite	Gangue
	55,5	19,8	11,6	4,4	8,7

B. *High-grade Concentrate*  
Chemical assay:

	Fe	Ni	Cu	S
Total %	32,3	30,6	0,5	34,3

Mineralogical (X-ray diffractometric analysis):

Pentlandite	Pyrite	Chalcopyrite	Talc
Major	Minor	Trace	Trace

Calculated mineralogical composition:

%	Pentlandite	Pyrite	Chalcopyrite	Gangue
	90,0	6,1	1,5	2,4

Screen analysis (mesh size):

	+35	-35+48	-48+65	-65+100	-100+150	-150+200	-200+325	-325
%	0	0	0,1	2,7	8,3	19,1	32,4	37,4

## EXPERIMENTAL METHODS

### Leaching

The prepared pentlandite was screened to between 200 and 325 mesh, and just prior to use was washed in 1M H<sub>2</sub>SO<sub>4</sub> for 5 minutes and dried with acetone to remove the surface oxide layer. (This procedure, by eliminating the initial rapid release of surface nickel oxide into solution, was found to result in a more reliable leaching curve.) The pentlandite was leached in 250 ml conical flasks containing 150 ml of the appropriate leaching solution and 15 g of the mineral, the mineral being mixed as a 10 per cent slurry in the leaching solution. Samples of 1 ml were taken from the flasks at regular intervals and, after filtering, the nickel concentration was measured by atomic-absorption spectrophotometry. Five samples were usually taken over four hours but, where the leaching rates were very low, sampling was extended over a period of twenty-four hours. The curves of concentration versus time were linear (within limits of experimental errors), and the slopes of these lines, representing initial leaching rates of nickel, were computed using a linear regression programme based on a least-squares fit. Each test was done in triplicate and, if more than 20 per cent variance was obtained between two of the calculated rates, the test was repeated.

### Mineralogical Examination

Sintered discs of pentlandite concentrates and mounted polished specimens of the mineral were examined after leaching both by optical techniques and with a JEOL model JXA 3SM electron microprobe analyser. Useful information on the mineralogical and chemical transformations during leaching were obtained with these techniques.

### Chemical Assays

The leach liquors were assayed on a routine basis with a Techtron model AA5 atomic-absorption analyser. Other methods included classical wet methods and instrumental techniques.

### Mineralogical Assays

The services of the Mineralogical Section of the Johannesburg Con-

solidated Investment Co. Processing Research Laboratory were employed. The techniques included classical optical methods, X-ray diffractometric analysis, and electron-microprobe analysis.

## RESULTS AND DISCUSSION

### Factorial Leaching Experiment

The following are considered to be the most important physico-chemical parameters involved in the chemistry of heap leaching<sup>9-11</sup>:

- (a) Concentration of ferric ions (Fe<sup>3+</sup>), M
- (b) Concentration of oxygen (pO<sub>2</sub>), %
- (c) Temperature, °C
- (d) Concentration of hydrogen ions, (H<sup>+</sup>), M
- (e) Mass transport, i.e., rate of stirrer rotation, *W*, r/min.

These are not all easily controllable in a heap-leaching operation, but a knowledge of their effect on the leaching rate contributes to an overall picture of the process. There are other factors involved, but these are outside the scope of this initial investigation, which was aimed at providing a background to the studies on bacterial leaching.

A 2<sup>5</sup> factorial experiment was carried out to show the effects and interactions of the above five factors on the leaching of nickel from pentlandite in acidic ferric sulphate solutions. This was followed by a conventional kinetic investigation of the process.

The values chosen for each factor are shown in Table II, and the complete factorial design of the 2<sup>5</sup> experiment, together with the results, is shown in Table III.

TABLE II  
VALUES OF FACTORS TESTED

Factor	Level	
	0	1
Fe <sup>3+</sup> , M	0,01	0,25
pO <sub>2</sub> , %	1	100
Temperature, °C	30	80
H <sup>+</sup> , M	2 × 10 <sup>-4</sup>	2,0
Agitation rate, r/min	0	400

The measured rates of nickel leaching (shown in Table III) were processed according to the method described by Mendelowitz<sup>12</sup> to give the average effect for each factor and combination of factors.

The results of the factorial experiment can be summed up as follows.

- (1) The temperature increase from 30 to 80°C has the greatest average positive effect on the leaching rate. The average increase in the leaching rate due to this increase in temperature was 113,88 p.p.m. of Ni<sup>2+</sup> per hour.
- (2) The average effect of an increase in the concentration of ferric ions from 0,01 to 0,25 M was an increase of 95,98 p.p.m. of Ni<sup>2+</sup> per hour. This is approximately the same as the average combined effect of the increased ferric-ion concentration and the increased temperature, viz, 84,42 p.p.m. of Ni<sup>2+</sup> per hour.
- (3) Other factors and combinations showing less significant average effects are
  - (i) pO<sub>2</sub>
  - (ii) *W*
  - (iii) pO<sub>2</sub> and *W*
  - (iv) pO<sub>2</sub> and temperature.
- (4) A surprising result is the negative average effect of (H<sup>+</sup>) in the range tested.
- (5) The leaching rate is optimized under the conditions of test 24, i.e., high levels of all the factors excepting (H<sup>+</sup>). The relative importance of the factors is as follows:
  - (i) temperature positive
  - (ii) (Fe<sup>3+</sup>) positive
  - (iii) pO<sub>2</sub> positive
  - (iv) *W* positive
  - (v) (H<sup>+</sup>) negative.
- (6) All the combinations with (H<sup>+</sup>) have negative average effects. All the other combinations have positive average effects.

### Kinetic Leaching Experiment

It is well established that the leaching rates of most sulphides in acidic ferric sulphate solutions are controlled by the cathodic reactions of the electrochemical couples<sup>13</sup>. This appears to be true also for pentlandite, especially considering the large increases in leaching rate obtained with ozone as described later. In the present leaching experiments, two electron acceptors were available, viz, oxygen and ferric ions, so that the overall rate is probably composed of two separate rates:

$$R_{\text{overall}} = R_1 + R_2 \dots (1)$$

TABLE III

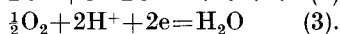
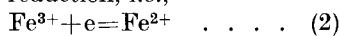
DESIGN AND RESULTS OF FACTORIAL EXPERIMENT

Test No.						Leaching rate p.p.m./h						Effect
	1	2	3	4	5		1	2	3	4	5	
1	0	0	0	0	0	0	0,80	9,89	355 25	675 19	2 067 77	129,24
2	1	0	0	0	0	0,80	9,09	345,36	319 94	1 392 58	1 375 61	85,98
3	0	1	0	0	0	2,77	130,04	19,72	837 06	559 75	896 85	56,05
4	1	1	0	0	0	6,32	215,32	300,22	555 52	815 86	409 45	25,59
5	0	0	1	0	0	0	7,42	46,92	333 13	86 37	1 822 45	113,88
6	1	0	1	0	0	130,04	12,30	790,14	226 62	810 48	1 350 77	84,42
7	0	1	1	0	0	8,29	156,15	46,13	556 62	101 61	718 41	44,90
8	1	1	1	0	0	207,03	144,07	509,39	259 24	307 84	401 97	21,12
9	0	0	0	1	0	4,25	1,19	4,35	93 57	615 97	-316 85	-19,80
10	1	0	0	1	0	3,17	45,73	328,78	-7 20	1 206 48	-403 89	-25,24
11	0	1	0	1	0	8,20	135,95	5,18	562 78	540 69	-415 85	-25,99
12	1	1	0	1	0	4,10	654,19	221,44	247 70	810 08	-298 13	-18,63
13	0	0	1	1	0	29,50	7,31	0,34	71 45	60 03	-334 93	-20,93
14	1	0	1	1	0	126,65	38,82	556,28	30 16	658 38	-409 97	-25,62
15	0	1	1	1	0	9,89	146,60	2,55	282 34	90 07	-382 97	-23,94
16	1	1	1	1	0	134,18	362,79	256,69	25 50	311 90	-302 77	-18,92
17	0	0	0	0	1	0	0,80	8,29	335 47	-35 31	717 39	44,84
18	1	0	0	0	1	1,19	3,55	85,28	280 50	-281 54	256 11	16,01
19	0	1	0	0	1	23,29	130,04	4,88	743 22	-106 51	724 11	45,26
20	1	1	0	0	1	22,44	198,74	-12,08	463 26	-297 38	206 23	12,89
21	0	0	1	0	1	0	1,08	44,54	324 43	-100 77	590 51	36,91
22	1	0	1	0	1	135,95	4,10	518,24	216 26	-315 08	269 39	16,84
23	0	1	1	0	1	116,93	97,15	31,51	555 94	-41 29	598 35	37,40
24	1	1	1	0	1	537,26	124,29	216,19	254 14	-256 84	221 83	13,86
25	0	0	0	1	1	3,02	1,19	2,75	76 99	-54 97	-246 23	-15,39
26	1	0	0	1	1	4,29	0,85	68,70	-16 96	-279 96	-190 87	-11,93
27	0	1	0	1	1	18,77	135,95	3,02	473 70	-108 17	-214 31	-13,39
28	1	1	0	1	1	20,05	420,33	27,14	184 68	-301 80	-215 55	-13,47
29	0	0	1	1	1	15,50	1,27	-2,04	65 95	-93 95	-224 99	-14,06
30	1	0	1	1	1	131,10	1,28	284,38	24 12	-289 02	-193 63	-12,10
31	0	1	1	1	1	110,85	115,60	0,01	286 42	-41 83	-195 07	-12,19
32	1	1	1	1	1	251,94	141,09	25,49	25 48	-260 94	-219 11	-13,69

where

$R_1$  = rate due to cathodic ferric reduction

$R_2$  = rate due to cathodic oxygen reduction, i.e.,



Ingraham and his co-workers studied the kinetics of leaching of a variety of copper sulphides under conditions similar to those used in the present experiments. For covellite ( $\text{CuS}$ ), these investigators found the activation energy of leaching to be 22 kcal/mol, indicating strong rate control by chemical processes<sup>9</sup>. On the other hand, for chalcocite ( $\text{Cu}_2\text{S}$ ), they found the activation energy of leaching to be 5 kcal/mol and the rate-controlling step to be diffusion of reactant through boundary layers into the solid-liquid interface<sup>10</sup>. Chalcopyrite was found to have an activation energy of leaching of 14 kcal/mol, a value lying between those for chemical processes and mass transport as rate control<sup>11</sup>. These workers postulated that, in the leaching of chalcopyrite, the mechanism involves the diffusion of reactants

through a film of surface sulphur. This sulphur is formed as a result of the leaching, and its thickness increases continually. This explained the parabolic nature of the kinetics observed. The rate-limiting step is the diffusion of ferric sulphate through the layer of sulphur. At high concentrations of ferric sulphate, the reverse diffusion of ferrous sulphate is rate limiting. Agitation was found to have no effect on the leaching rate. In many respects the process resembles pore diffusion in catalyst particles.

In the present investigation, the observed activation energy of nickel leaching was 14,5 kcal/mol (Fig. 5) — the same magnitude as observed by Ingraham and his co-workers in the leaching of chalcopyrite. However, it is not likely that the mechanisms are the same. In the leaching of pentlandite, it was found that the sulphur did not accumulate on the mineral surface, but readily detached and became suspended in the leaching solution. The observed kinetics were also linear. The value of the activation energy would then seem to indicate a 'mixed' mechanism

in which both chemical processes and mass-transport phenomena are rate controlling.

This is consistent with the postulate that the overall rate comprises two separate rates, since it is most likely that the ferric reaction is controlled by mass transport, while the cathodic oxygen reduction is controlled by chemical processes. The former reaction is known to be kinetically and thermodynamically more favourable than is the oxygen-reduction reaction in sulphide leaching. (This is also consistent with the results of the factorial experiment, where it is shown that the concentration of ferric ions has a greater positive effect on the leaching rate than oxygen concentration has.) In the rate expression, the concentration of ferric ions and agitation would be grouped together, as would the concentrations of oxygen and hydrogen ions. Thus, the following rate expression is proposed:

$$R_{\text{overall}} = K_1 (\text{Fe}^{3+})^a W^b + K_2 p\text{O}_2^c (\text{H}^+)^d \quad (4)$$

where  $K_1$  and  $K_2$  are rate constant.

*Effect of Ferric Ions*

When the effect of ferric ions on

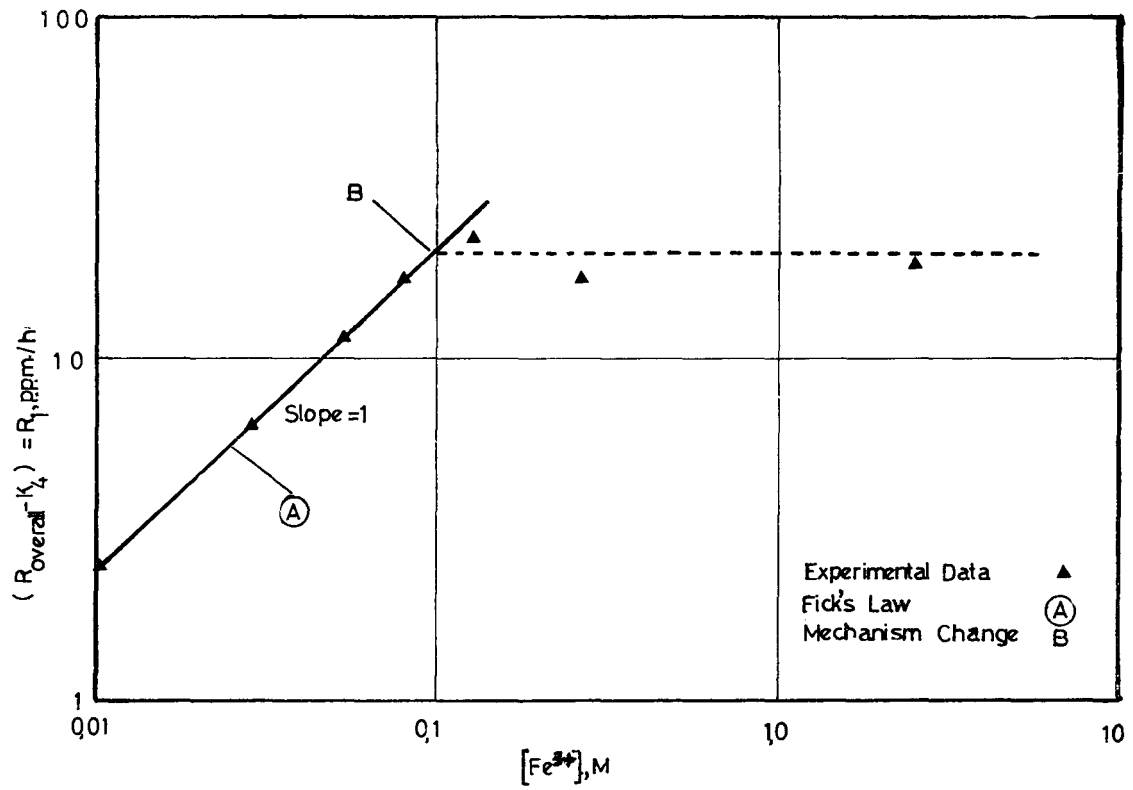


Fig. 1—Plot of  $\log R_1$  versus  $\log (\text{Fe}^{3+})$

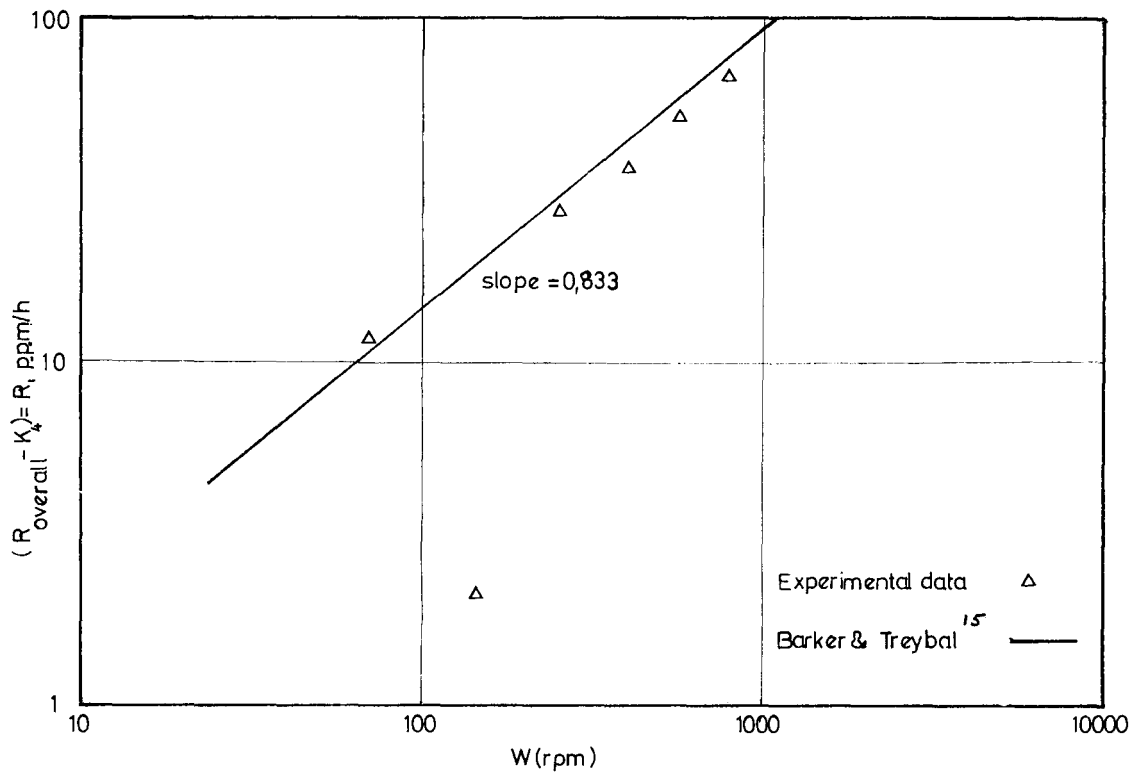


Fig. 2—Plot of  $\log R_1$  versus  $\log W$

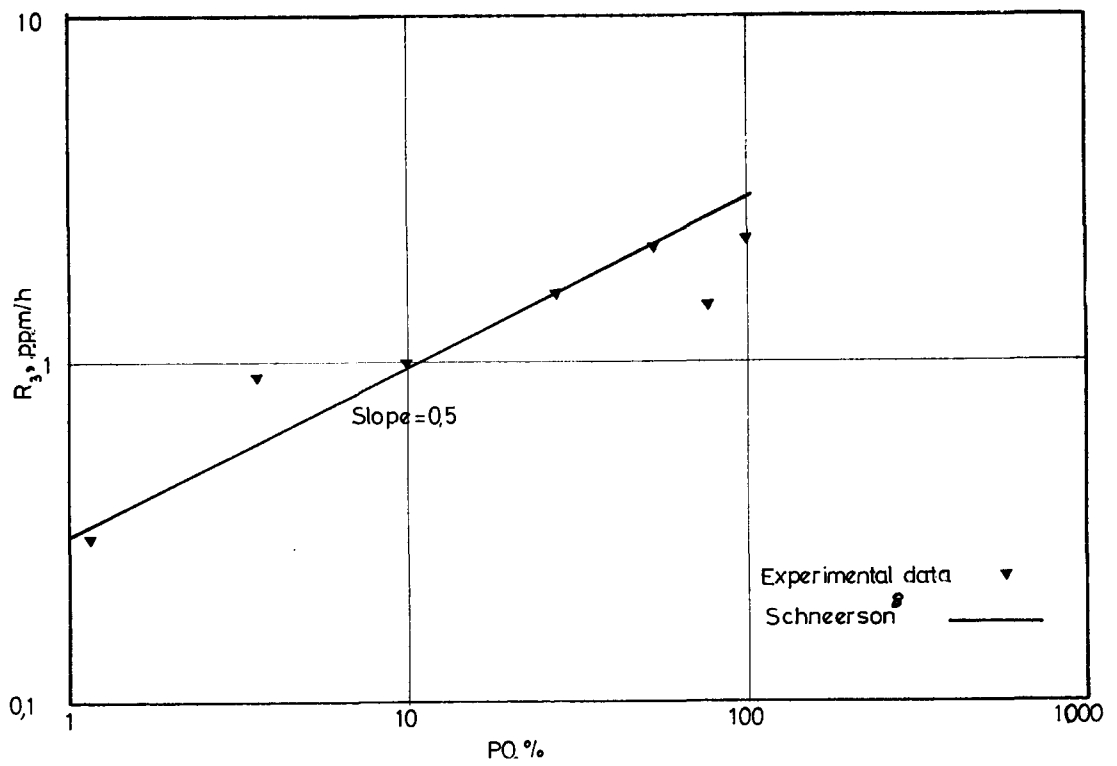


Fig. 3—Plot of  $\log R_3$  versus  $\log pO_2$

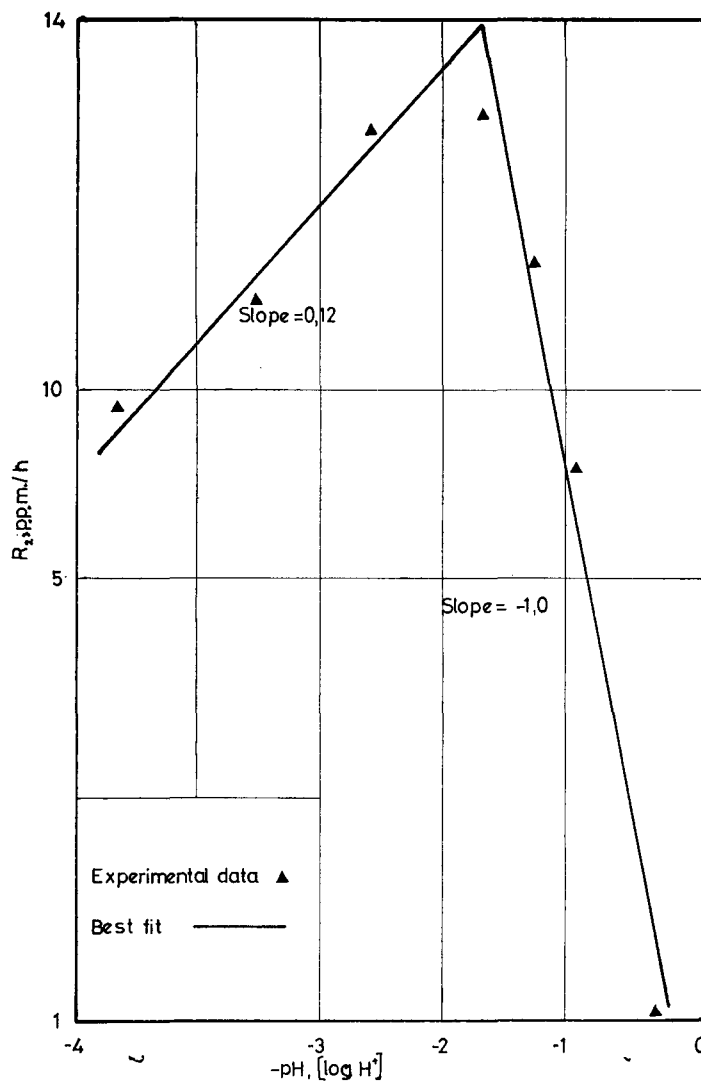


Fig. 4—Plot of  $\log R_2$  versus  $\log (H^+)$

the leaching rate was measured, the other parameters being kept constant, the rate expression could be reduced to the form

$$R_{\text{overall}} = K_3 \cdot (\text{Fe}^{3+})^a + K_4,$$

where

$$\begin{aligned} K_3 &= K_1 \cdot W^b \\ W &= 200 \text{ r/min,} \\ K_4 &= K_2 \cdot p\text{O}_2^c \cdot (\text{H}^+)^d, \\ p\text{O}_2 &= 50 \%, \\ (\text{H}^+) &= 2 \times 10^{-2} \text{ M.} \end{aligned}$$

A plot of  $\log (R_{\text{overall}} - K_4)$  versus  $\log (\text{Fe}^{3+})$  would have a slope of  $a$  and an intercept equivalent to  $K_3$ . This is shown in Fig. 1, where  $K_4$  was obtained by extrapolation to zero concentration on the plot of  $R_{\text{overall}}$  versus  $(\text{Fe}^{3+})$ .  $K_4$  was found to be equal to 23 p.p.m./h, which represents the rate of leaching when  $(\text{Fe}^{3+})=0$ ,  $p\text{O}_2=50 \%$ , and  $(\text{H}^+)=2 \times 10^{-2}\text{M}$ .

In Fig. 1 the data are compared with a line of slope 1,0 and are consistent with this line up to about 0,1 M  $\text{Fe}^{3+}$ , after which the rate appears to be independent of  $(\text{Fe}^{3+})$ . (At this point the reaction is probably controlled by the diffusion of some other reactant or product.) These data are discussed again later.

#### Effect of Agitation

Fig. 2 shows a plot of  $\log (R_{\text{overall}} - K_4)$  versus  $\log W$ , where  $K_4$  was again taken to be 23 p.p.m./h. A line of slope 0,833 was drawn through the data for purposes of the discussion later on, the data being reasonably consistent with this line.  $K_4$  was also estimated from these data by means of a linear plot of  $R_{\text{overall}}$  versus  $W$  and was found to be 23 p.p.m./h, which is in good agreement with the previously measured value.

#### Effect of Oxygen

The rate expression was reduced to  $R_{\text{overall}} = K_6 + K_7 \cdot p\text{O}_2^c$ , where  $K_6 = K_1 \cdot (\text{Fe}^{3+})^a \cdot W^b$ , which is equivalent to the rate of leaching when  $p\text{O}_2=0$ ,  $(\text{Fe}^{3+})=0,125\text{M}$ , and  $W=200 \text{ r/min}$ .

$$K_7 = K_2 (\text{H}^+)^d.$$

A plot of  $\log (R_{\text{overall}} - K_6)$  versus  $\log p\text{O}_2$  would have a slope of  $c$ . This is shown in Fig. 3.  $K_6$  was obtained from the intercept of the plot of  $R_{\text{overall}}$  versus  $p\text{O}_2$ ;  $K_6$  is estimated to be 20 p.p.m./h from this plot. The data in Fig. 3 are compared with a line of slope 0,5.

#### Effect of Hydrogen Ions

A plot of  $\log (R_{\text{overall}} - K_6)$  versus  $\log (\text{H}^+)$  would have a slope equal to  $d$ . The value of  $K_6$  measured previously was used since in practice  $(\text{H}^+)$  cannot be zero.

Fig. 4 gives the value of

$$\begin{aligned} d &= 0,1 \text{ for pH 4 to pH 0,75} \\ \text{and } d &= -1,0 \text{ for pH 0,75 to} \\ &\text{pH } -0,75. \end{aligned}$$

#### Effect of Temperature

The Arrhenius plot for the leaching of pentlandite in acid ferric sulphate

solutions is shown in Fig. 5. From the slope of this graph, the activation energy was calculated to be 14,5 kcal/mol.

#### Leaching with Ozone

Large increases in the leaching rate of nickel were obtained when ozonized oxygen was added to the leaching solution. This action of ozone supports the postulate that cathodic reactions are rate limiting under the conditions of these experiments<sup>14</sup>.

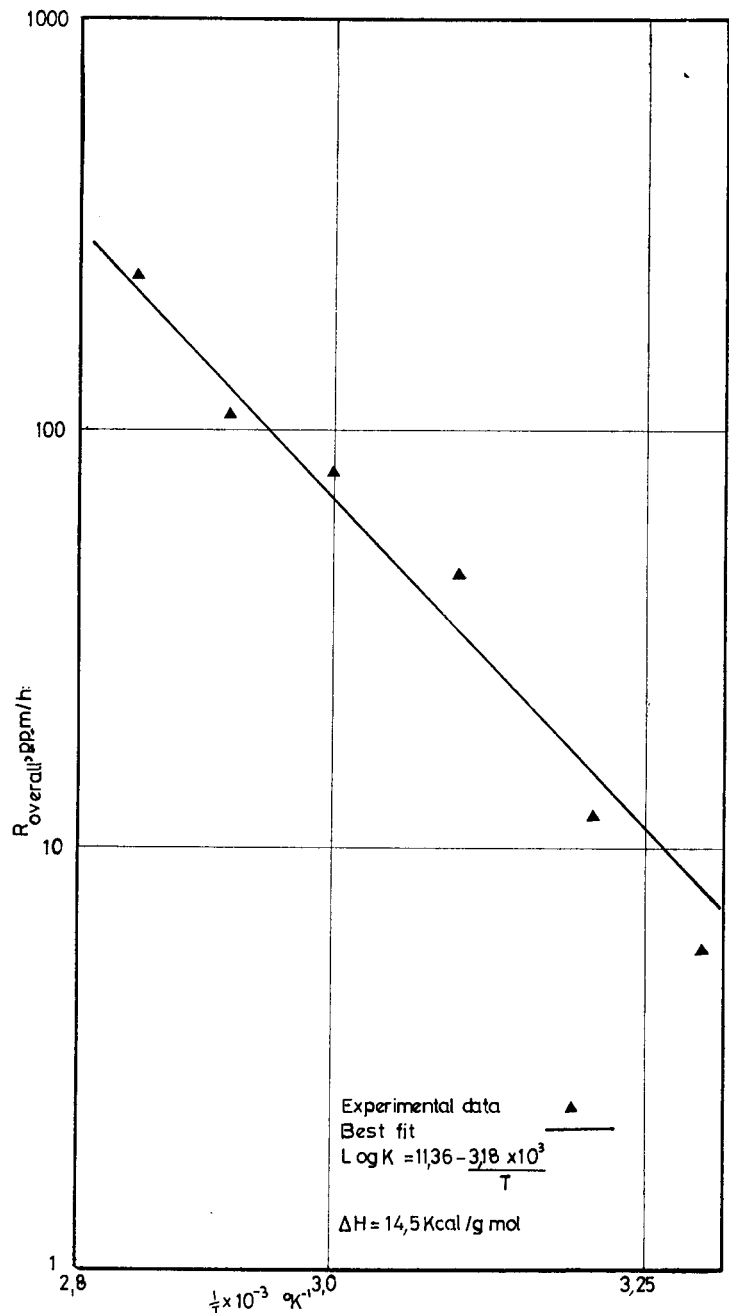
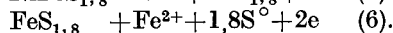
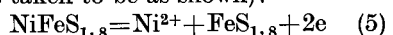


Fig. 5—Effect of temperature on the chemical leaching rate (Arrhenius plot)

### Mechanism of Chemical Leaching

Examinations of the leach residues from the present experiments by optical microscopy, X-ray diffraction, and electron-microprobe analysis showed that two intermediate phases, pyrrhotite (in small amounts) and elemental sulphur (in stoichiometric amounts), are formed. Jarosite is precipitated from solution at pH values above 4.5. The unleached pentlandite was covered with a thin, loosely bound layer containing pyrrhotite and sulphur. The leached surface was cracked and pitted, showing that dissolution occurred preferentially at regions of crystal imperfections and grain boundaries. When a sintered disc of pentlandite was electrolysed in sulphuric acid solution at pH 3 for 24 hours by maintaining a voltage of +5V on the disc with respect to a platinum electrode, the molar ratio of nickel to iron dissolved was 1.05 to 1. The disc was found to be covered with a loose layer of pyrrhotite and a small amount of sulphur. Most of the sulphur detached from the specimen and reported as an amorphous suspension in the solution.

Considered together, these results suggest that pentlandite dissolves in acidic solutions by an electrochemical mechanism with the following sequence of anodic reactions (if the stoichiometry of the pentlandite is taken to be as shown):



### DISCUSSION OF KINETIC STUDIES

It was proposed earlier that the rate of nickel leaching from pentlandite follows a rate equation of the form

$$R_{\text{overall}} + R_1 + R_2 \quad (1)$$

In this model,  $R_1$  was considered to represent the rate of leaching due to the cathodic reduction of ferric ions at the mineral surface and was represented by the term

$$K_1 \cdot (\text{Fe}^{3+})^a \cdot W^b$$

It was postulated that the rate of ferric leaching was controlled by mass transport.

$R_2$  was considered to represent the rate of leaching due to the cathodic reduction of oxygen at the

mineral surface and was represented by

$$K_2 \cdot p\text{O}_2^c \cdot (\text{H}^+)^d$$

In general terms, Fick's Law of diffusion can be written

$$V \cdot \frac{dC}{dt} = k \cdot A \cdot (C - C_i) \quad (7)$$

When applied to ferric ions,  $C_i = 0$  and  $C$  can be assumed constant equal to  $(\text{Fe}^{3+})$ , since the leaching was followed for only a relatively short time.

$$\therefore V \frac{dC}{dt} = k A (\text{Fe}^{3+}) \quad (8)$$

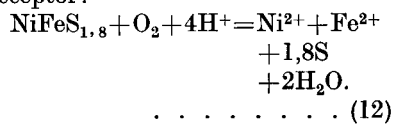
$$\text{i.e., } R_1 \propto k A (\text{Fe}^{3+}) \quad (9)$$

Barker and Treybal<sup>15</sup> have shown that mass-transfer coefficients for suspended solids dissolving in agitated liquids vary as the speed of stirrer rotation to the power 0.833, i.e.,  $k \propto W^{0.833}$  . . . . . (10)

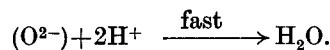
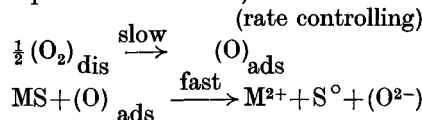
$$\therefore R_1 \propto (\text{Fe}^{3+}) W^{0.833} \quad (11)$$

Schneerson *et al.*<sup>8</sup>, in a study on the autoclave leaching of pentlandite, have shown that the rate of leaching is proportional to  $p\text{O}_2^{\frac{1}{2}}$ .

The leaching of nickel from pentlandite takes place according to the following overall reaction when oxygen is the terminal electron acceptor:



The following mechanism is proposed as representing the individual steps in this scheme. (For the sake of simplicity, pentlandite is represented as MS, where M represents the total metallic portion. This is valid, as nickel and iron were leached in equivalent amounts.)

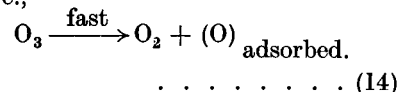


$$\text{Therefore, } \frac{d(\text{M}^{2+})}{dt} = \frac{2d(\text{Ni}^{2+})}{dt} = \frac{d(\text{O})_{\text{ads}}}{dt}$$

$$\text{i.e., } R_2 \propto p\text{O}_2^{\frac{1}{2}} \quad (13)$$

(dis=dissolved ads=adsorbed)

The mechanism of oxygen adsorption is supported by the fact that, when ozone was used in place of oxygen (as discussed previously), the leaching rates were higher. It is probable that the atomic oxygen derived from ozone is more rapidly adsorbed onto the mineral surface, i.e.,



Thus, the proposed model is

$$\begin{aligned} R_{\text{overall}} &= K_1 (\text{Fe}^{3+}) W^{0.833} \\ &+ K_2 p\text{O}_2^{\frac{1}{2}} (\text{H}^+)^{\circ} \end{aligned} \quad (15)$$

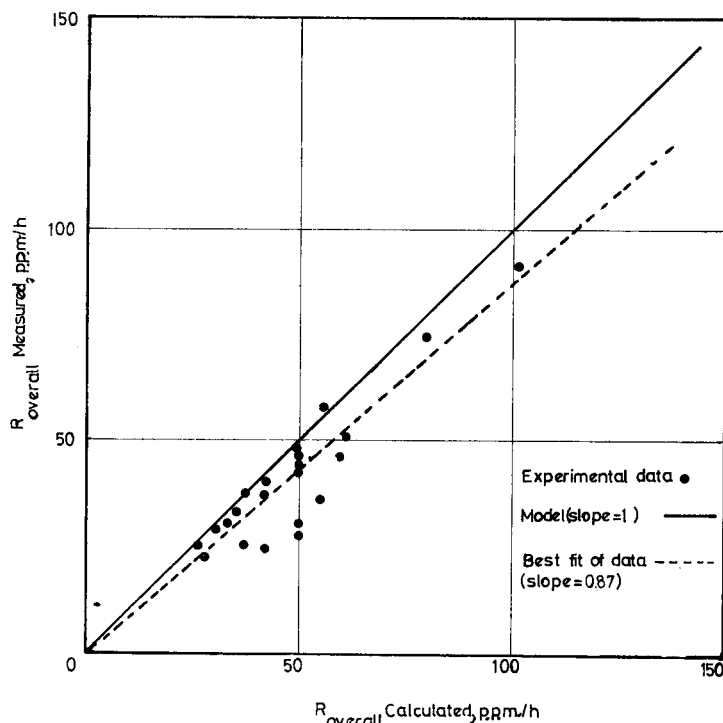


Fig. 6—Comparison of experimental data and the proposed model



This model was compared with the experimental data in Figs. 1 to 4 by superimposing lines of the appropriate slope on the experimental points. It is considered that the model is consistent with the experimental data. A comparison between the experimental data and the calculated data based on the model is given in Fig. 6. Good agreement between the model and the experimental data was found for pH values above 0,75.

### CONCLUSION

It is proposed that, during the leaching of pentlandite in acidic ferric sulphate solutions, the overall chemical leaching rate is represented by two separate rates, one controlled by mass transport and the other by chemical processes. The mass-transport mechanism is consistent with the data of Barker and Treybal<sup>15</sup> when ferric ions are the diffusing reactant. The chemical mechanism is consistent with the work of Schneerson<sup>8</sup> and can be explained in terms of the adsorption of oxygen onto the mineral surface.

### ADDENDUM

Batch tests on bacterial leaching showed a linear pattern of nickel leaching and bacterial growth, with a marked dependence on oxygen concentration and rate of agitation. In the mechanism proposed as a

result of the batch tests, the rate of bacterial leaching is proportional to the concentration of bacteria attached at the mineral surface and to the square of the oxygen concentration.

In continuous leaching, the rates were found to be higher than those predicted from the batch data, this effect being interpreted in terms of a higher specific growth rate of bacteria in continuous operation. A brief economic assessment of a process based on the continuous tests on bacterial leaching was found to show some promise.

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### REFERENCES

1. CORRANS, I. J., HARRIS, B., and RALPH, B. J. Bacterial leaching: an introduction to its application and theory, and a study on its mechanism of operation. *J. S. Afr. Inst. Min. Metall.*, vol. 72, no. 8. 1972.
2. CORRANS, I. J. Studies on the bacterial leaching of natural and synthetic iron copper sulphide minerals. University of New South Wales, M.Sc. Thesis, 1970.
3. RALPH, B. J. University of New South Wales, Personal Correspondence, 1971.
4. PEARCE, R. F., WARNER, J. P., and MACKIEV, U. N. A new method of matte refining by pressure leaching

- and hydrogen reduction. *J. Metals*, Jan. 1960.
5. HABASHI, F. Principles of extractive metallurgy. vol. 2, Hydrometallurgy. London, Gordon and Breach, 1970.
6. BURKIN, A. R. The chemistry of hydrometallurgical processes. London, E. & F. N. Spon, 1966.
7. KLETS, V. E., TSEFT, A. L., and LIOPO, V. A. Leaching of nickel from a mixture of pyrrhotite and pentlandite by an iron chloride solution. *Tr. Irkutsk. Politekhn. Inst.*, no. 27. 1966. p. 115.
8. SCHNEERSON, Y. M., LESHCH, I. Y., and FRUMINA, C. M. Role of pyrrhotite in the oxidative autoclave leaching of sulphides. *Tr. Proekt. Nauch-Issled. Inst. Giprotnickel*, no. 29. 1966. p. 24.
9. THOMAS, G., and INGRAHAM, T. R. Kinetics of dissolution of synthetic covellite in aqueous acidic ferric sulphate solutions. *Can. Metall. Q.*, vol. 6, no. 2. 1967. p. 153.
10. THOMAS, G., INGRAHAM, T. R., and MACDONALD, R. J. C. Kinetics of dissolution of synthetic digenite and chalcocite in aqueous acidic ferric sulphate solutions. *Ibid.*, vol. 6, no. 3. 1967. p. 281.
11. DUTRIZAC, J. E., MACDONALD, R. J. C., and INGRAHAM, T. R. The kinetics of dissolution of synthetic chalcocite in aqueous acidic ferric sulphate solutions. *Trans. Metall. Soc. AIME*, vol. 245. 1969. p. 955.
12. MENDELOWITZ, A. Statistical techniques in analytical research. *S. Afr. Ind. Chem.*, Aug. 1956.
13. MAJIMA, H., and PETERS, E. Electrochemical mechanisms for the decomposition of metal sulphides. University of British Columbia, School of Mineral Engineering, Research Report, 1969.
14. CORRANS, I. J. Improvements in hydrometallurgy, S. Afr. Patent No. 73/4851. Appl. Jul. 1973.
15. BARKER, J. J., and TREYBAL, R. E. Mass-transfer coefficients for solids suspended in agitated liquids. *AIChE J.*, vol. 6. 1960. p. 287