

Experimental and modelling studies of the kinetics in the leaching of pyrolusite

by J.C. ZACHARIADES* and D.M. FRASER*

SYNOPSIS

The leaching of pyrolusite in acidic ferrous sulphate solution was studied so that the important factors governing the kinetics of the reaction could be determined. The reaction is very rapid, and was monitored by continuous measurement and logging of the redox potential in solution by use of a microcomputer. The relationship between redox potential and manganese extraction was established empirically for each set of conditions by the use of a technique in which a calibration run was conducted in parallel with each leaching run. The study involved a number of batch leaching runs, and demonstrated that, of the variables investigated, only the initial ferrous ion concentration and the reaction temperature affect the rate of manganese extraction. The final extraction did not vary. The reaction was modelled from the results by use of the shrinking-core model and Brittan's activation-energy model. The latter was found to provide a significantly better fit to the data.

SAMEVATTING

Die loging van pirolusiet in suur ferrosulfaatoplossing is bestudeer ten einde die belangrike faktore wat die kinetika van die reaksie beheer, te bepaal. Die reaksie is baie vinnig en is gemoniteer deur die deurlopende meting en aantekening van die redokspotensiaal in oplossing met gebruik van 'n mikrorekenaar. Die verhouding tussen die redokspotensiaal en mangaanekstraksie is vir elke stel toestande empiries bepaal volgens 'n tegniek waar daar 'n kalibreerloop parallel met elke loogloop uitgevoer is. Die studie het 'n aantal groepslooglope behels en het getoon dat van die veranderlikes wat ondersoek is, net die aanvanklike ferroioonkonsentrasie en die reaksietemperatuur die tempo van mangaanekstraksie raak. Die eindekstraksie het nie gewissel nie. Die reaksie is aan die hand van die resultate gemodelleer met gebruik van die krimpendekernmodel en Brittan se aktiveringsenergiemodel. Daar is gevind dat laasgenoemde 'n beduidend beter passing by die data gee.

Introduction

Many leaching systems are characterized by non-linear leaching behaviour, in which the initial and final rates cannot be fitted simultaneously by the use of a single rate constant in classical generalized models such as the shrinking-core model¹. The object of the present study was to characterize such a non-linear leaching system, in terms both of actual leaching rates and of a suitable model to account for the non-linear behaviour.

The system chosen for this study was the leaching of pyrolusite in an acidic ferrous medium. In this system, leaching is rapid, approaching maximum extraction within five minutes. This precluded monitoring of the progress of the reaction by conventional sample extraction and analysis. A method involving continuous measurement of the redox potential of the leaching solution, with parallel calibration of the redox potential versus the manganese extraction, was therefore applied.

The first section of the paper deals with the kinetics of the reaction background information, experimental procedure (including validation of the technique used), and the results of the leaching experiments.

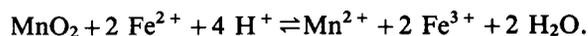
The second section is a comparison of the results achieved in the application of two models to the pyrolu-

site leaching data: the shrinking-core model, and Brittan's activation-energy model.

Experimental Determination of Leaching Kinetics

Selection of Method

The reaction studied was the reductive leaching of manganese dioxide in pyrolusite by use of an acidic ferrous sulphate solution. The reaction in its basic form is



As the reaction progresses, both the solution pH and redox potential can be expected to increase.

The reductive leaching of manganese dioxide has been studied by several workers, the most thorough attempts at explaining the kinetic behaviour being those of Cornelius and Woodcock², Koch³, and Majima *et al.*⁴. Their findings were similar in most respects: pH affected the rate only when it was too high to prevent the precipitation of ferric hydroxide, although the addition of acid did not always eliminate this; the initial concentration of ferric ions had no effect on the rate, and the increase in rate with temperature indicated an activation energy slightly higher than is normally associated with diffusion control. These workers differed about the dependence of the reaction rate on the initial concentration of ferrous ions: Cornelius and Woodcock, using an ore containing 50 per cent manganese, found first-order dependence, whereas Majima *et al.*, using a lower-grade ore, observed a reaction order of 0,85. Koch reported zero-order de-

* Department of Chemical Engineering, University of Cape Town, Private Bag, Rondebosch, 7700 Cape Province.

© The South African Institute of Mining and Metallurgy, 1991. SA ISSN 0038-223X/3.00+0.00. Paper received 20th Aug., 1990; modified paper received 20th Nov., 1990.

pendence in the leaching of a pure synthetic manganese dioxide provided the ferrous concentration was greater than 0,01 M. Koch also found that the initial concentration of manganous ions had no effect on the leaching rate, while Cornelius and Woodcock's study showed no change in rate when the leaching solution became saturated with manganous ions.

The speed of the leaching was such that continuous monitoring of the rate had to be adopted. Given the involvement of the ferrous-ferric couple in the reaction, the use of redox potential as an indicator of leaching progress suggested itself. Koch, in fact, employed a technique based on redox measurement.

To make use of the redox potential of the solution for this purpose required the adoption of a method for relating the redox measurements to the extraction of manganese from the ore, possibly via the ratio of ferrous to ferric ions. Ferrous and ferric ions in an acidic sulphate solution form a complex ionic system⁵, with a number of complexes of these ions co-existing with uncomplexed ions. These equilibria are complicated, and depend on pH, ionic strength, temperature, and other factors.

In the work done by Koch, pure synthetic manganese dioxide was used. The relationship between the redox potential and the manganese extraction was established empirically in a calibration run conducted together with each leaching run. The method entailed the incremental addition of small amounts of manganese dioxide to a solution identical to that used for each leaching run; once equilibrium had been reached, redox measurements were made after each addition of ore, and samples were withdrawn for manganese analysis. The desired relationship was then derived from the measured redox potentials and manganese concentrations.

Two other approaches to the establishment of this relationship were considered for the present work. One was to develop correlations from redox measurements on solutions of ferrous and ferric sulphate. The other was to use the model developed by Dry⁵, which is based on correlations between ionic equilibria and Debye-Hückel activity. However, neither of these was regarded as satisfactory in view of the relatively low accuracy obtainable and the possible involvement of other ionic species in the solution potential.

The method used by Koch therefore appeared to be the best suited to this work. However, it required some validation since this study would be using pyrolusite ore containing iron and other gangue material. The ore used had a manganese dioxide content of 29 per cent, a total manganese content of 26 per cent, and a considerable amount of iron (18 per cent). It was therefore possible that other components would be leached, and that the change in redox potential during the course of a batch leaching run would not be exclusively due to the reduction of manganese dioxide.

Experimental Details

Materials and Equipment

Analytical-grade chemicals were used throughout, and the solutions were made up in distilled water.

The pyrolusite, which was supplied by Mintek, assayed total manganese 26 per cent, manganese dioxide 29 per cent, and iron 18 per cent, with a negligible amount of

sulphur. The particle size of the ore was 90 per cent smaller than 24 μm , with a d_{50} of 10 μm .

The leaching tests were carried out in a 1-litre round-bottomed glass vessel supported in a thermostatically-controlled water bath. The vessel was fitted with a set of baffles and with an impeller having a variable-speed drive. The baffles and impeller, which were constructed of stainless steel, ensured good mixing of the vessel's contents.

The solution pH and redox potential were measured by means of two electrodes immersed in the leaching solution. The instruments used were a Radiometer Copenhagen PHM83 digital pH meter and a Metrohm redox meter. Both electrodes had combined measuring and reference assemblies; the reference electrodes were silver/silver chloride in saturated potassium chloride, allowing operation at temperatures of up to 100 °C.

The data-logging equipment comprised a voltage amplifier, a serial interface, and a microcomputer. This equipment was used to measure the pH and redox potential, the readings being averaged over intervals of one second and the digital data being stored on disk. Software was used in the calibration of the probes and subsequent conversion of the stored data to pH and redox values.

Procedure

The batch leaching runs were carried out in pairs, with continuous measurement and logging of the solution pH and redox potential. The results from one run of each pair, referred to as the *dynamic* run, were used for redox-time curves, from which the leaching kinetics would be determined. The other run, referred to as the *calibration* run, involved incremental addition of the ore to establish the relationship between the measured redox potential and the manganese extraction.

The solution was made up in a quantity of 2 litres to ensure that the dynamic and calibration runs would have identical starting conditions; 900 ml of solution was placed in the glass vessel, the stirrer was started, and the solution was allowed to reach constant temperature in the water bath.

The redox electrode, having been cleaned with optical polishing powder, and the pH electrode, having been calibrated for the reaction temperature, were placed in the solution and monitored until steady readings were obtained, at which stage the data-logging program was initiated. After 100 seconds, 5,00 g of pyrolusite was added, and the reaction was monitored for approximately 30 minutes. Fig. 1 is a plot of the raw redox-potential data obtained in this way. A sample of liquid was taken before the ore was added, and another sample was taken and filtered after 30 minutes, when leaching was complete. Both samples were stored for later analysis.

The identical start-up procedure was followed in the calibration runs but the ore was added in steps, two increments of 0,5 g and four of 1,0 g being used. Approximately 10 minutes were allowed after each addition for leaching to be completed, after which a 20 ml sample was taken, filtered, and stored for analysis, and the next increment of ore added.

The data from the calibration runs were converted to redox units and used to establish the equilibrium redox potential for each stage of ore addition. An example of

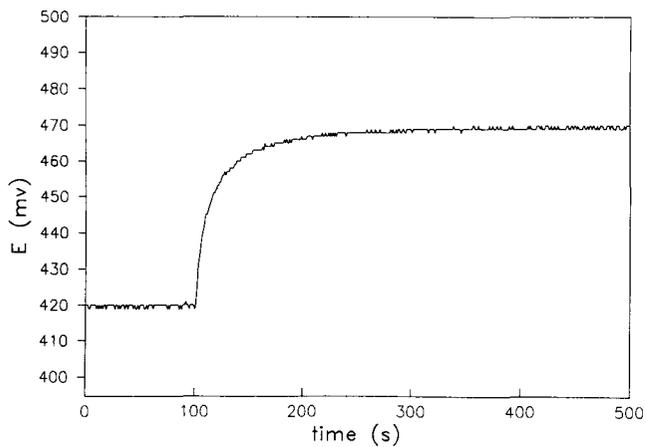


Fig. 1—Increase in redox potential during leaching

the logged readings for a calibration run is given in Fig. 2. All the samples were analysed for manganese (by atomic-absorption spectrometry), and for Fe^{2+} , Fe^{3+} , and H_2SO_4 (by titration).

The data thus obtained were used in the plotting of curves for

- concentration of manganese against ore added
- redox potential against concentration of manganese
- concentrations of Fe^{2+} , Fe^{3+} , and H_2SO_4 against ore added.

Curves were fitted to the data for redox potential versus manganese concentration from the calibration runs, regression techniques being used with either polynomial or log functions. In all cases, the regression coefficient, r^2 , was better than 0,996.

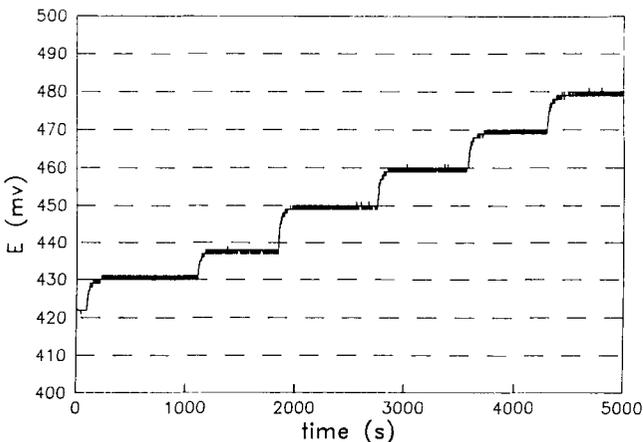


Fig. 2—Redox values recorded during a calibration run

Curves for two runs are shown in Fig. 3. The second curve is derived from the run carried out with no initial ferric sulphate. The shape of the two curves reflects the response to the change in the ferric:ferrous ratio as manganese extraction occurs; the change in redox potential is most rapid when the ratio is either very low or very high, a trend that is predicted by the Nernst equation^{6,7}.

Once the logged readings for the kinetic runs had been converted to redox and pH units, the above relationships were used in the data-conversion program to convert the readings of redox potential to manganese concentrations, which were then plotted against time.

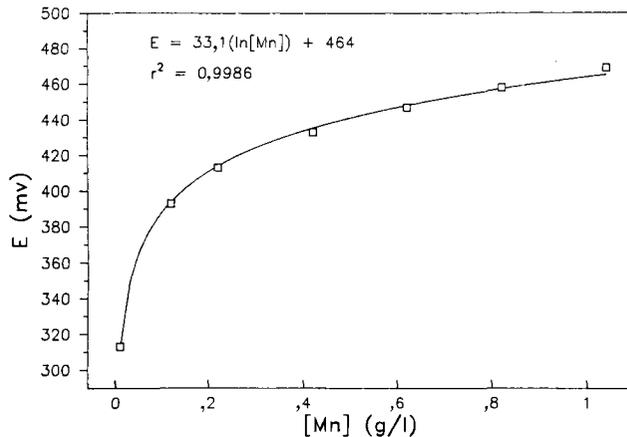
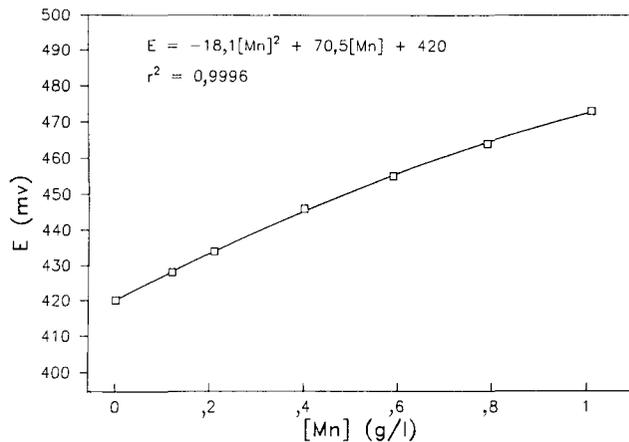


Fig. 3—Relationship between redox potential and manganese concentration in solution
(a) Initial $[\text{Fe}^{3+}] = 0,01 \text{ M}$
(b) No initial $[\text{Fe}^{3+}]$

Aspects Examined

The various aspects that were examined included reproducibility, electrode response, stirrer speed, concentrations of interest, and reaction temperatures.

Duplicate tests performed under identical solution conditions and additions of ore showed that the reproducibility of the results was excellent.

Tests were done to establish the response speeds of the redox electrode since the change in redox potential is rapid at the start of a run. The results of a typical step-change test carried out by the addition of concentrated ferric solution to the initial leaching solution is shown in Fig. 4.

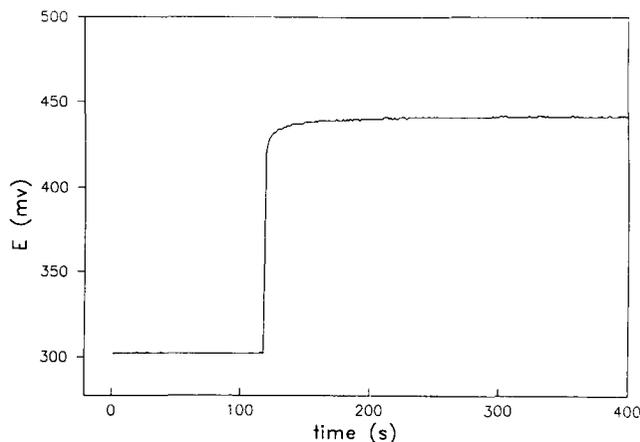


Fig. 4—Response of measured redox potential to a step change

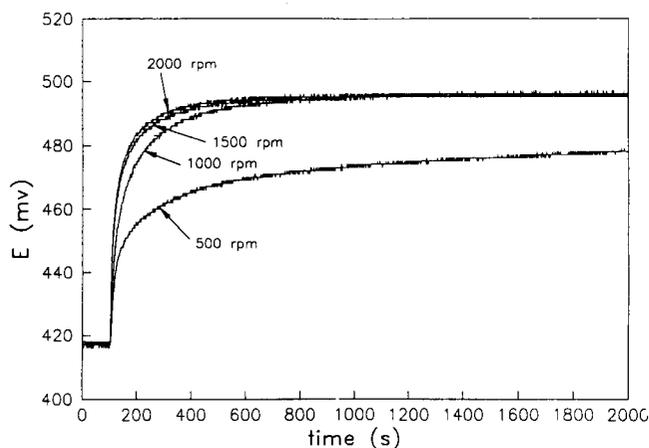


Fig. 5—Effect of stirrer speed on leaching rate

The electrode response is initially first-order with a time constant of 1 second, but then slows down to an equivalent time constant of 3 seconds. Compared with 20 seconds for leaching, this shows that the redox electrode response was significantly faster than the rate of change of redox potential during leaching.

The effect of stirrer speed on the leaching rate was investigated for stirrer speeds between 500 and 2000 r/min. The results are given in Fig. 5, which shows that speeds below 1000 r/min were insufficient for proper mixing, with slight increases in rate from 1000 to 2000 r/min (the maximum stirrer speed). All the runs were therefore performed at 2000 r/min to ensure that bulk mass-transfer effects were minimized.

The study of factors affecting the leaching rate involved ten runs, each with its associated calibration run. The parameters investigated were the initial concentrations of manganese, ferrous ions, ferric ions, and acid, and the reaction temperature.

The conditions used for the experiments are summarized in Table 1. The base conditions for the comparison of results (Run 1) were a temperature of 25 °C, an FeSO_4 concentration of 20 g/l (0,07 M), an $\text{Fe}_2(\text{SO}_4)_3$ concentration of 3 g/l (0,01 M), and an H_2SO_4 concentration of 5 g/l (0,05 M).

TABLE I
CONDITIONS USED IN THE LEACHING-RATE EXPERIMENTS

Run no.	Temp °C	FeSO_4 g/l	$\text{Fe}_2(\text{SO}_4)_3$ g/l	H_2SO_4 ml/l	MnSO_4 g/l
1	25	20,0	3,0	5,0	0,0
2	25	20,0	3,0	12,5	0,0
3	25	20,0	3,0	2,0	0,0
4	25	40,0	3,0	5,0	0,0
5	25	10,0	3,0	5,0	0,0
6	25	20,0	6,0	5,0	0,0
7	25	20,0	0,0	5,0	0,0
8	25	20,0	3,0	5,0	10,0
9	40	20,0	3,0	5,0	0,0
10	60	20,0	3,0	5,0	0,0

Validation of the Calibration Technique

As mentioned previously, the nature of the ore was such that the method of using a calibration run to determine the relationship between redox potential and manganese dioxide concentration had to be validated. If other

components in the ore were being leached at rates different from that at which the manganese dioxide was being leached, a relationship obtained from equilibrium data would not be applicable to the dynamic situation prevailing during leaching.

Because the time required for collecting and filtering samples during leaching was long (30 seconds) in relation to the rapidity of the reaction, it was not possible to obtain samples reflecting the solution composition at a given time. It was possible, however, to take samples and to filter and analyse them in order to establish redox-extraction values during the course of a run. A comparison of these values with those for a calibration run would demonstrate whether they showed the same relationship.

A pair of runs was accordingly carried out: the first was a normal calibration run and the second a dynamic run, during which three samples were taken and analysed for redox potential and manganese extraction. The first sample was taken before the ore was added, the second shortly after the addition of the ore, and the third after about 90 seconds. The last two samples were filtered rapidly to stop leaching. The redox values for the filtered samples were obtained by placing them in a water-bath at the temperature used for the run. Duplicate runs were also done as a check on the reproducibility.

The results for one pair of runs is shown in Fig. 6. It is clear that the redox-extraction values for the samples taken during leaching fall on the line derived from the calibration run. This indicates that the use of equilibrium relationships established from calibration runs in the determination of the manganese extraction during leaching runs is valid.

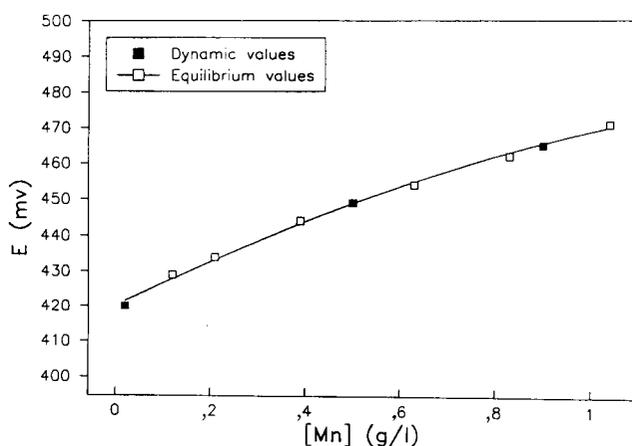


Fig. 6—Comparison of redox-extraction under dynamic and equilibrium conditions

Results and Discussion

Two aspects of the results are considered here:

- the relationships between the species produced (Mn , Fe^{3+}) and consumed (Fe^{2+} , H_2SO_4), and a comparison with stoichiometric values
- the effects of the various parameters on the extraction rate, by comparison of the leaching-rate curves for runs 2 to 10, expressed as manganese concentration versus time, with that drawn for run 1 (the base conditions).

Relationships between the Species

From the equation for the reduction of manganese di-

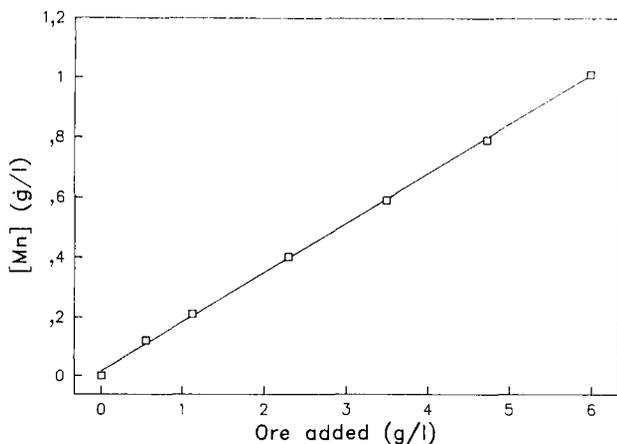


Fig. 7—Manganese extraction versus ore added in a typical calibration run

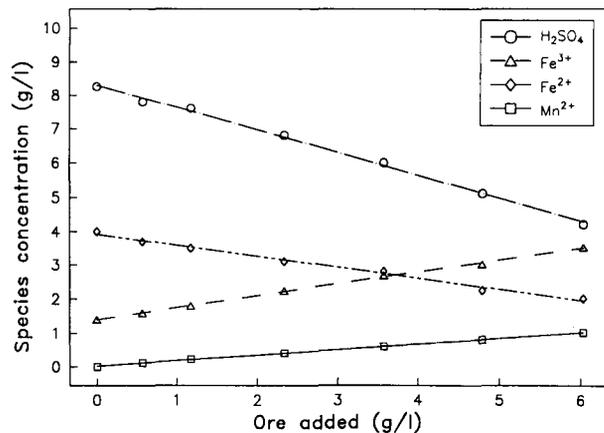
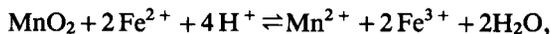
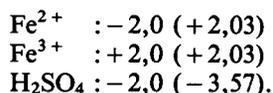


Fig. 8—Species concentration versus ore added in a typical calibration run

oxide in acidic ferrous solution,



the molar ratios (mass ratios in brackets) for each mole of Mn^{2+} produced are calculated:



Sample plots derived from the calibration runs are shown in Fig. 7 for manganese, and in Fig. 8 for all species. The experimental mass ratios derived from an analysis of the samples taken from the calibration runs are shown in Table II.

The results are in good agreement with the theoretical values, and there are no clearly identifiable trends for any of the species. The manganese extraction ranged from 0,164 to 0,183 g per gram of ore added. The manganese dioxide content of the ore is 29 per cent, and the total manganese content is 26 per cent. If the manganese appearing in solution was derived solely from the manganese dioxide, as can be deduced from the observed consumption and production of iron species, the extraction ranged from 90 to 100 per cent, with most runs giving an extraction of 90 to 93 per cent. The consumption of sulphuric acid was always higher than expected from the stoichiometry, and this can be attributed to some consumption by other materials in the ore.

TABLE II
MEASURED RATIOS OF SPECIES CONSUMED:PRODUCED

Run	$\text{Fe}^{2+}:\text{Mn}^{2+}$	$\text{Fe}^{3+}:\text{Mn}^{2+}$	$\text{H}_2\text{SO}_4:\text{Mn}^{2+}$
Theory	-2,03	2,03	-3,57
1	-2,16	2,13	-3,92
2	-1,98	2,08	-3,80
3	-2,02	2,04	-3,97
4	-2,03	2,07	-4,16
5	-2,07	2,07	-3,72
6	-2,01	2,13	-4,06
7	-2,11	2,01	-4,09
8	-1,96	1,91	-3,77
9	-2,11	2,16	-3,88
10	-1,93	2,20	n/a
Average	-2,04	2,08	-3,93

The good agreement between the amount of manganese extracted and the change in iron species in solution indicates that the dominant leaching reaction is the reduction of manganese dioxide. This conclusion is further borne out by the fact that the iron concentration in solution, calculated as the sum of the ferrous and ferric readings, remains virtually constant. These results help explain the good correspondence of the redox-extraction relationships for dynamic and equilibrium conditions, and serve to reinforce the validity of the calibration-curve technique.

Rate Studies

The conditions used for each of the ten leaching-rate runs performed are summarized in Table 1. The manganese concentrations for each of these runs were plotted against time and compared. The effects of the parameters that were varied are discussed below. No comparative leaching curves are shown where they were found to be equivalent.

Ferrous concentration. The initial concentration of ferrous ions had a strong influence on the rate of leaching, as shown in Fig. 9, where the effect of initial ferrous ion concentrations of 0,04 M, 0,07 M, and 0,14 M are compared. It is clear from Fig. 9 that increasing ferrous ion concentrations increased the rate of leaching but not the final extraction. Cornelius and Woodcock² reported first-order behaviour, and Majima *et al.*⁴ used a reaction order

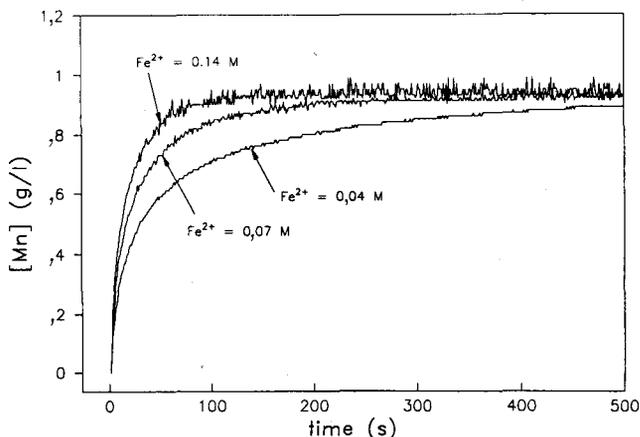


Fig. 9—Effect of initial ferrous ion concentration on leaching rate

of 0,85 to explain the dependence on ferrous ion concentration.

Acid strength. An increase in the acid strength from 0,05 M to 0,12 M resulted in no apparent increase in the leaching rate. Halving the strength to 0,02 M also did not show any significant change, although there was a slight apparent reduction in the final extraction. This was partly due to the extreme flattening of the redox-extraction calibration curve at low acid concentrations, which also accounts for the large signal noise observed. This flattening is due to the fact that, at higher pH values (higher than 2), ferric ions are increasingly bound up in hydrated complexes⁵ and therefore contribute less to the redox potential. These results agree with those of Cornelius and Woodcock² and of Koch³.

Ferric ion concentration. The initial ferric ion concentration was varied from 0,01 M (base condition) to 0,03 M and also to 0,0 M. No difference in the leaching rates was observed, which was in accordance with previous findings.

Manganese ion concentration. The use of a starting solution of 0,05 M in manganous ion produced no significant effect on the extraction rate compared with that measured in the absence of added manganese. This is in agreement with the findings of Koch³.

Temperature. An increase in the temperature to 40 °C, and again to 60 °C, produced increases in the leaching rates, with a marginal increase in the final extraction. A comparative plot for these temperatures is given in Fig. 10.

Almost identical leaching curves were obtained for various acid, ferric, and manganous ion concentrations despite the sometimes large differences in shape and position of the redox-extraction calibration curves. This provides further evidence to justify the choice of method for monitoring the reaction and converting the redox readings to manganese concentrations.

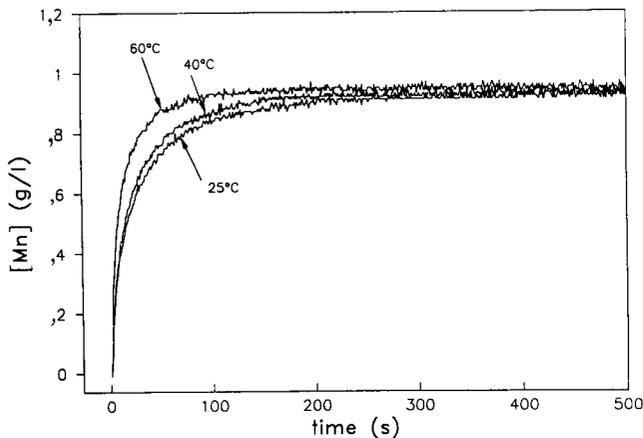


Fig. 10—Effect of temperature on leaching rate

Modelling of the Leaching Kinetics

The experimental results were used in a comparison of two models: the shrinking-core model and Brittan's activation-energy model^{1,8}. The latter is a model with a distributed rate constant in which the magnitude of the rate constant is related to conversion by means of a variable activation energy. The shrinking-core model provides a basis for comparison with Brittan's model.

Of the variables examined in the experimental work, only the ferrous ion concentration and the reaction temperature were shown to have an effect on the rate of manganese extraction. Consequently, only the data from runs 1, 4, 5, 9, and 10, in which these quantities were varied, were used in the modelling.

The raw results were in the form of the averaged values recorded for each second of the reaction. Although the noise on the readings was low, smooth curves were drawn through plots of the measured values and, in order to obtain a limited number of data points for modelling purposes, twelve values were taken for each run. The data used are listed in Table III.

TABLE III
EXPERIMENTAL DATA USED IN THE MODELLING

Time s	Run no.	Mn ²⁺ concentration in solution				
		1	4	5	9	10
Ferrous concn (g/l)		20	40	10	20	20
Temperature (°C)		25	25	25	40	60
0		0,0	0,0	0,0	0,0	0,0
12,5		0,43	0,50	0,34	0,47	0,65
25,0		0,59	0,69	0,47	0,63	0,77
50,0		0,73	0,83	0,59	0,77	0,88
75,0		0,81	0,89	0,66	0,84	0,91
100,0		0,84	0,92	0,71	0,87	0,92
150,0		0,88	0,93	0,77	0,91	0,94
200,0		0,90	0,93	0,80	0,93	0,94
250,0		0,91	0,93	0,84	0,93	0,94
300,0		0,91	0,94	0,85	0,93	0,94
400,0		0,92	0,94	0,87	0,93	0,94
500,0		0,93	0,94	0,89	0,93	0,94

The extraction data were converted to values of manganese remaining in the ore (as moles of manganese per litre), use being made of the assay value for manganese dioxide in the unleached ore. Allowance was made for incomplete extraction (the maximum extraction was 93 per cent) by the use of a 'refractory' component to account for a small amount of residual manganese dioxide once leaching had ceased.

The Shrinking-core Model

The shrinking-core is the most commonly used simple model to describe heterogeneous reaction behaviour in its application to several leaching systems.

The model is well-known and requires only limited description. Three resistances to reaction are identified: liquid-film diffusion, solid-layer diffusion, and surface reaction. These act in series on an initially non-porous spherical particle. The resistances may be unequal in magnitude to the extent that one resistance may be dominant; alternatively, each may contribute significantly to an overall resistance, and mixed kinetics are said to apply⁹⁻¹¹.

For the purposes of this work, mixed kinetics were employed. In addition, owing to the batch nature of the leaching experiments, a term accounting for the decreasing ferrous ion concentration, which was shown experimentally to follow the reaction stoichiometry very closely, was incorporated. The notation used by Wadsworth¹⁰ was followed.

The form of the model relating conversion to time was, thus,

$$\frac{d\alpha}{dt} = \frac{3VC_{ferr}}{r_{film} + r_{ash} + r_{react}}$$

The terms in this expression are

$$C_{ferr} = C_0(1 - \sigma b \alpha) \dots\dots\dots \text{Ferrous concentration}$$

Resistances

$$r_{film} = \frac{\sigma \delta r_0}{D_s} \dots\dots\dots \text{Liquid-film diffusion}$$

$$r_{ash} = \frac{r_0^2 \sigma [1 - (1 - \alpha)^{1/3}]}{D_e (1 - \alpha)^{1/3}} \dots\dots \text{Solid-layer diffusion}$$

$$r_{react} = \frac{r_0}{k_s (1 - \alpha)^{2/3}} \dots\dots\dots \text{Reaction}$$

The variables used are as follows:

- α Fractional conversion of MnO_2 ($0 < \alpha < 1$)
- t Leaching time (s)
- V Molar volume of MnO_2 in ore (cm^3/mol)
- C_0 Initial Fe^{2+} concentration (mol/cm^3)
- σ $Fe^{2+}:MnO_2$ stoichiometric ratio
- b Initial reactant:solid ratio
- δ Liquid-film thickness (cm)
- r_0 Initial particle radius (cm)
- D_s Solution diffusion coefficient (cm^2/s)
- D_e Solid-layer diffusion coefficient (cm^2/s)
- k_s First-order rate constant (cm/s).

The diffusion coefficients and the reaction rate constant are governed by separate Arrhenius relationships:

$$D_s = D'_s e^{-E_d/RT} \text{ and } k_s = k'_s e^{-E_r/RT},$$

where E_d and E_r are the activation energies for diffusion and reaction respectively.

The solid-layer diffusion coefficient is related to the solution diffusion coefficient by a proportionality constant, since pore diffusion is simplified in the case of liquids¹¹. Thus,

$$D_e = aD_s.$$

The constants V , C_0 , σ , b , δ , and r_0 were set from values determined from the ore characteristics and experimental conditions, or from the literature. A single particle radius of $5 \mu m$, corresponding to the d_{50} value of the ore, was used.

The other constants (D'_s , E_d , k'_s , E_r , a) were regarded as unknowns, and the model was implemented and fitted to the data by means of a FORTRAN program employing a NAG optimization routine (EO4JAF)¹² to solve for the unknown parameters, which were treated as bounded variables. Initial estimates and limits were derived from the literature^{5,10}.

The magnitude of the overall discrepancy between the experimental data and the values predicted by the model was calculated as the square root of the mean square relative error:

$$\text{Error} = \sqrt{\frac{\sum (y-f)^2}{N y^2}}$$

where y = observed value for data point
 f = function value for corresponding point
 N = total number of data points.

The results are shown graphically in Figs. 11 and 12 for Fe^{2+} and temperature variation respectively. The modelling error, as the r.m.s. relative error, is 0,23. In terms of the model, the solid-layer diffusion accounts for over 95 per cent of the resistance, with the activation energy for this term (22 kJ/mol) accounting well for the temperature dependency observed. The variation with ferrous ion concentration is relatively poor, and cannot be improved by alteration of the reaction order since the reaction term is small (the model is based on first-order kinetics). The shape of the curves obtained is fair, but it can be seen that the slowing-down of the rate after the initial fast extraction is not reproduced particularly well.

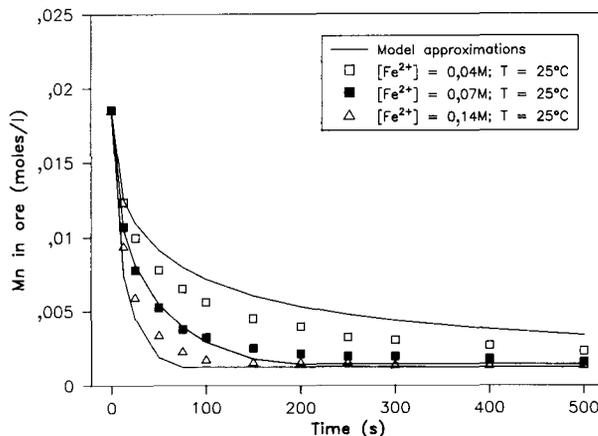


Fig. 11—The modelling of Fe^{2+} effects—the shrinking-core model

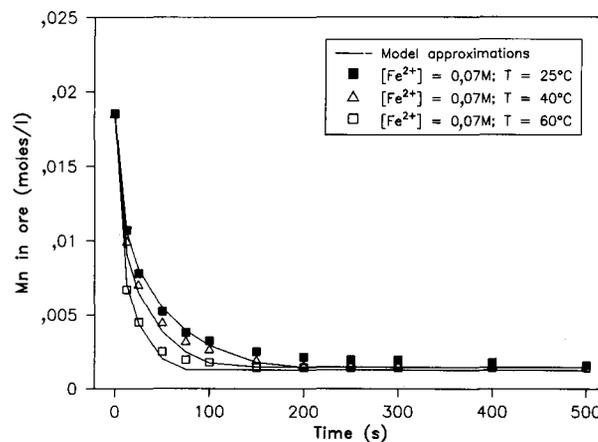


Fig. 12—The modelling of temperature effects—the shrinking-core model

In the light of the above, given the dominance of the solid-layer diffusion term, little accuracy is sacrificed by the modelling of the reaction from this term alone (error = 0,24).

Brittan's Activation-energy Model

Brittan's model¹ has been applied with considerable success to the segregation of copper and the leaching of gold.

The basic premise of the model is that, in the absence

of detailed knowledge of the leaching mechanism, rate-limiting factors can be lumped together as an overall resistance expressed in terms of an activation-energy barrier. This 'activation energy' (E) increases as leaching progresses: there is a linear dependence of E on the residual metal concentration (C_m) in the ore:

$$E = E_0(1 - \alpha[C_m])$$

(where α is a constant).

So, the rate constant, k , is

$$k = Ae^{-E/RT},$$

with E as defined above. With appropriate substitution,

$$k = e^{\left(\frac{a[C_m]-b}{T} + c\right)}$$

This rate constant can be used together with a suitable mass-action term to provide a rate expression for a reaction.

The experimental work with pyrolusite provided guidelines for the design of a rate expression. Of the parameters varied, only the ferrous ion concentration and the reaction temperature affected the rate. In the light of this, the following expression was designed for testing:

$$\frac{d[Mn]}{dt} = -k[Mn]^p[Fe^{2+}]^q.$$

In this equation,

$[Mn]$ is the concentration of manganese remaining in the ore at any time (mol/l).

$[Fe^{2+}]$ is the concentration of ferrous ions in solution (mol/l).

p is the reaction order with respect to manganese, and was assigned one of two values: 1 or 2/3. A value of 1 would imply that the mixture is effectively homogeneous with respect to MnO_2 . A value of 2/3, from simple geometric considerations for a single particle size, would allow for surface-area control to be accounted for⁸.

q is the reaction order with respect to Fe^{2+} , and was included as a variable since its value was not apparent from the data or from the literature. Other researchers have given values of 1 and under.

k is as defined earlier, and incorporates the effect of temperature.

The variables manipulated were the reaction orders with respect to manganese and Fe^{2+} as specified before, as well as the three constants involved in the activation-energy expression (a , b , and c).

A FORTRAN program was used to solve the model for given parameter estimates and to perform regressions on the data to find values for a , b , and c that yielded the closest fit. Optimization was performed according to an algorithm used by Brittan, which performed a Newton-Raphson type of procedure^{13,14}. Values for the reaction-order terms were varied from run to run, and were not included in the regression. This was done by simply taking a value for p , the manganese term, as either

1 or 2/3, and progressively varying the value of q , the Fe^{2+} term. For each pair of values, a regression was carried out to optimize the values of the rate-constant parameters.

The best fit to all sets of data was obtained when values of 1 for p and 0,7 for q were used. The r.m.s. relative error in this case was approximately 0,08—one-third that for the shrinking-core model. The use of these values, together with the values determined by regression for a , b , and c , gave an excellent approximation to all five sets of data.

The results are presented in Figs. 13 and 14, where the effects of varying temperature and ferrous ion concentration are illustrated. It will be noted how well the predicted curves follow the experimental data, compared with those for the shrinking-core model, especially as far as the variation in ferrous ion concentration is concerned.

The final form of the rate expression was thus

$$\frac{d[Mn]}{dt} = -e^{\left(\frac{a[Mn]-b}{T} + c\right)} [Mn][Fe^{2+}]^{0,7}$$

with parameters $a = 29\ 825$

$$b = 2\ 630$$

$$c = 6,52.$$

The concentrations are expressed in moles per litre, with the temperatures in Kelvin.

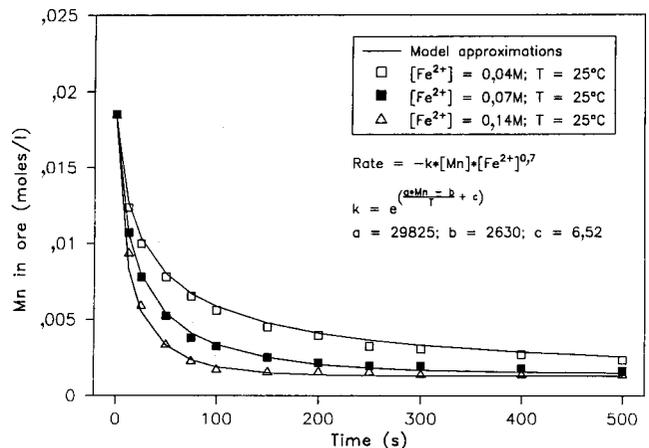


Fig. 13—The modelling of Fe^{2+} effects—Brittan's model

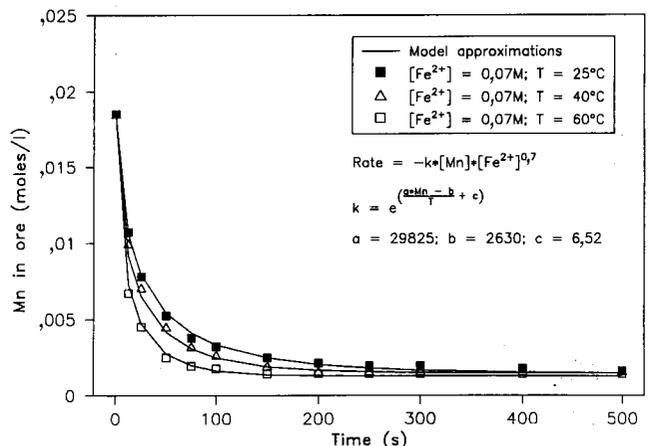


Fig. 14—The modelling of temperature effects—Brittan's model