

poor predictions, but the "empirical" Nernst equation and the "best straight line" give average and maximum errors of about 9 and 16 millivolts - a slight improvement over the use of the total concentration ratio. Allowing for the complexes FeHSO_4^{2+} and FeHSO_4^+ as well as FeSO_4^+ , HSO_4^- and FeSO_4^0 gives slightly better average and maximum errors of 8 and 15 millivolts. Including the species $\text{FeHSO}_4\text{SO}_4^0$ and $\text{Fe}(\text{SO}_4)_2^-$ causes poorer predictions of the redox potential - see Appendix III for the relevant printouts.

The results in Figure 5.6 were obtained by allowing for the complex species FeSO_4^+ , HSO_4^- and FeSO_4^0 , and minimising the sum of the squared differences between the measured redox potential values and the "theoretical" Nernst equation predictions, using the values of the three stability quotients as independent variables. This resulted in average and maximum errors of 5,4 and 9,1 millivolts - a significant improvement over the results in Figure 5.5. Unfortunately the values of the stability quotients arising from this regression are not realistic. The regression and literature values of these quotients are as follows:

Species	Value of concentration quotient		
	Value ex regression	Literature values	
		Quotient	Ionic strength
FeSO_4^+	555	228 to 84	0,15 to 2,67
HSO_4^-	16,5	35 to 8	0,1 to 3,0
FeSO_4^0	88,0	17* to 1,7	0,15 to 3,4

(*Estimated - see section 4.2.3 and Appendix V)

The calculated ionic strengths, allowing for the above complexes, ranged between 0,2 and 2,66, therefore the stability quotients should be inside the above ranges of literature values. This is only true for HSO_4^- . The stability quotients of FeSO_4^+ and FeSO_4^0 from the regression are well above the expected ranges. These concentration quotient values, therefore, should not be taken as physically significant. They are merely fitted values which result in reasonable redox

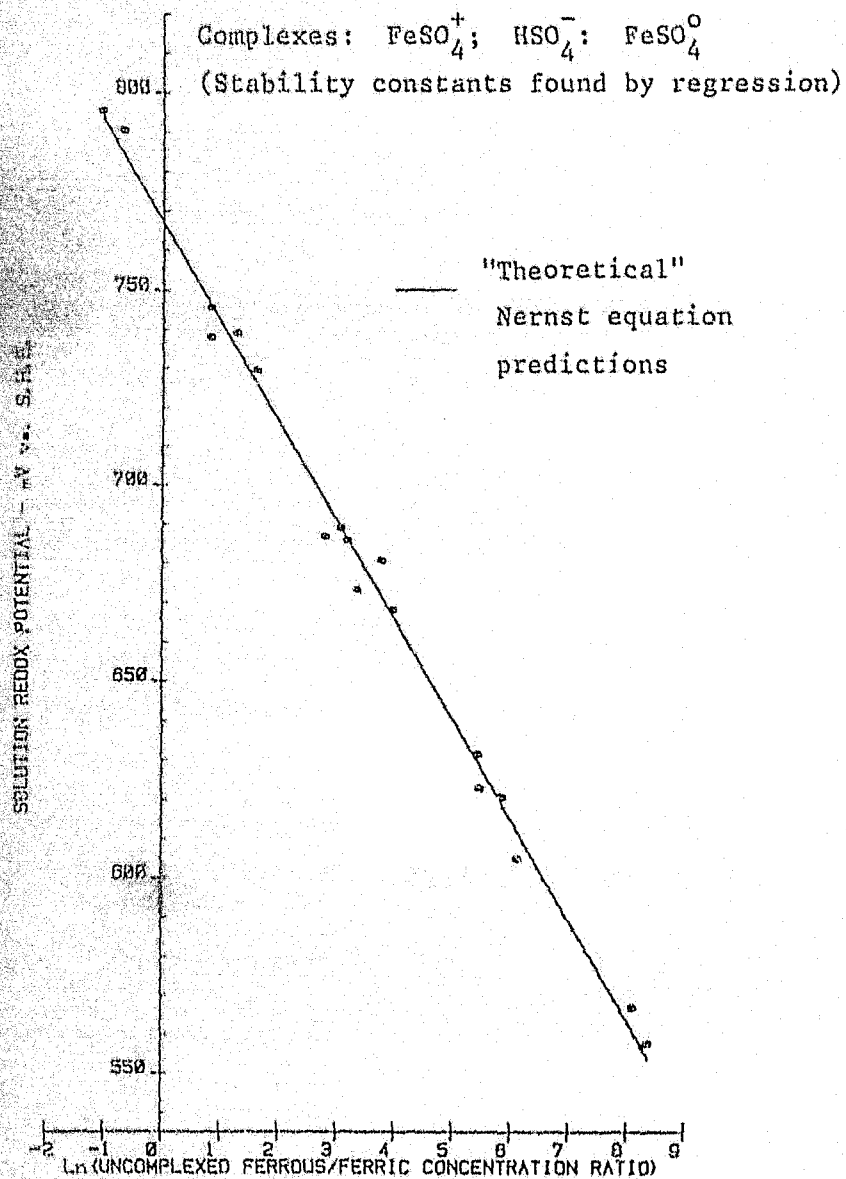


Fig. 5.6

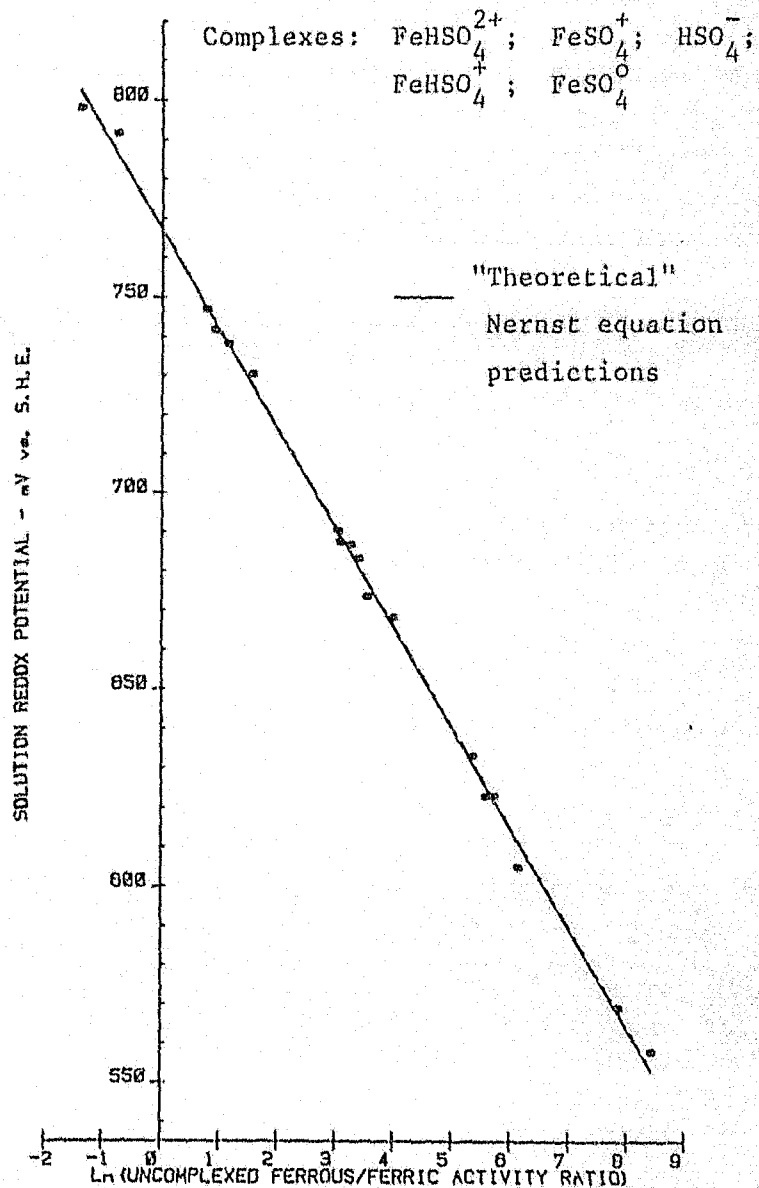


Fig. 5.7

potential predictions.

c) Individual activity coefficients

Allowing for the existence of complex species and using Debye-Hückel individual activity coefficients in the calculation of the species distribution in solution and the ferrous/ferric activity ratio, gives the results shown in Figure 5.7. The complexes allowed for are FeHSO_4^{2+} , FeSO_4^+ , HSO_4^- , FeSO_4^0 and FeHSO_4^+ . This is in agreement with the work of Sapienszko *et al* (48), who found the only ferric species in acid sulphate solution to be FeSO_4^+ , FeHSO_4^{2+} and uncomplexed Fe^{3+} . Beukenkamp and Herrington (21) found the ferrous sulphate complexes to be FeSO_4^0 and FeHSO_4^+ . The removal of FeHSO_4^{2+} and FeHSO_4^+ from the species present, or the inclusion of $\text{FeHSO}_4\text{SO}_4$ and $\text{Fe}(\text{SO}_4)_2^-$, both result in poorer redox potential predictions - see Appendix III.

The stability constants at zero ionic strength and 25°C for FeHSO_4^{2+} , FeSO_4^+ , FeSO_4^0 and FeHSO_4^+ , were assigned the following values:

Species	Stability constant at 25°C	
	This work	Literature values
FeHSO_4^{2+}	2306	1900 to 4900**
FeSO_4^+	10640	8710 to 13800
FeSO_4^0	161	158 ± 18*
FeHSO_4^+	513	400**

* Uncertainty in the stability constant of FeSO_4^0 estimated from data in Smith and Martell for similar species

** Values estimated from data at non-zero ionic strength (see section 4.2.3 - pages 75-77)

The stability constant values for FeHSO_4^{2+} , FeSO_4^+ and FeSO_4^0 are within the ranges of published values, and can thus be accepted as reasonable, physically significant constants. The value - estimated from

Beukenkamp and Herrington(31) - from the literature for the stability constant of FeHSO_4^+ is about 400. Beukenkamp and Herrington did not control their ionic strength, nor do they give a specific temperature at which their measurements were made, thus one must presume that room temperature was used. The value of 400 is therefore unlikely to be the exact value of this constant. If similar uncertainty is assumed for the FeHSO_4^+ as for the ferric analogue (FeHSO_4^{2+}), the literature value becomes 400 ± 176 , and the value from this work of 513 is inside this range, and can thus also be accepted as reasonable.

5.2.2 Redox potential at elevated temperature

The redox potential measurements made at 90°C, as well as values reported by Verbaan(38), were correlated by means of the "theoretical" Nernst equation (section 4.2.1) using individual Debye-Hückel activity coefficients and allowing for the species FeHSO_4^{2+} , FeSO_4^+ , HSO_4^- , FeSO_4^0 and FeHSO_4^+ in solution. The resultant predictions and measurements are shown in Figure 5.8. At 90°C, 52°C and 22°C, good predictions of the solution redox potential were obtained. Two of Verbaan's(38) data points at 50°C lie a little further away from the "theoretical" Nernst equation predictions than the rest of the data points. Verbaan plotted his measured redox potential values against the ferric/ferrous concentration ratio:

$$\left[\text{Fe}^{3+}\right]^{0,4} / \left[\text{Fe}^{2+}\right]^{0,25}$$

At 75°C and 90°C he obtained straight lines, while at 50°C and 25°C he obtained curved plots. However, if one neglects the two data points further from the Nernst equation predictions (Figure 5.8) at 50°C, and plots the remaining three points (against the above ratio) as before, Verbaan's results give a straight line, as for his results at 75°C and 90°C. Verbaan's results at 25°C can be fitted by a straight line with accuracy similar to the results for 75°C and 90°C. The deviation of some of Verbaan's results at 50°C from the theory presented in this work may be due to a measurement error in Verbaan's work, since his results at 50°C differ from his results at other temperatures. Alternatively, the activity ratio between ferrous and ferric ions in solution may be a much more complex function than has been assumed in this work. Since the results obtained in this work

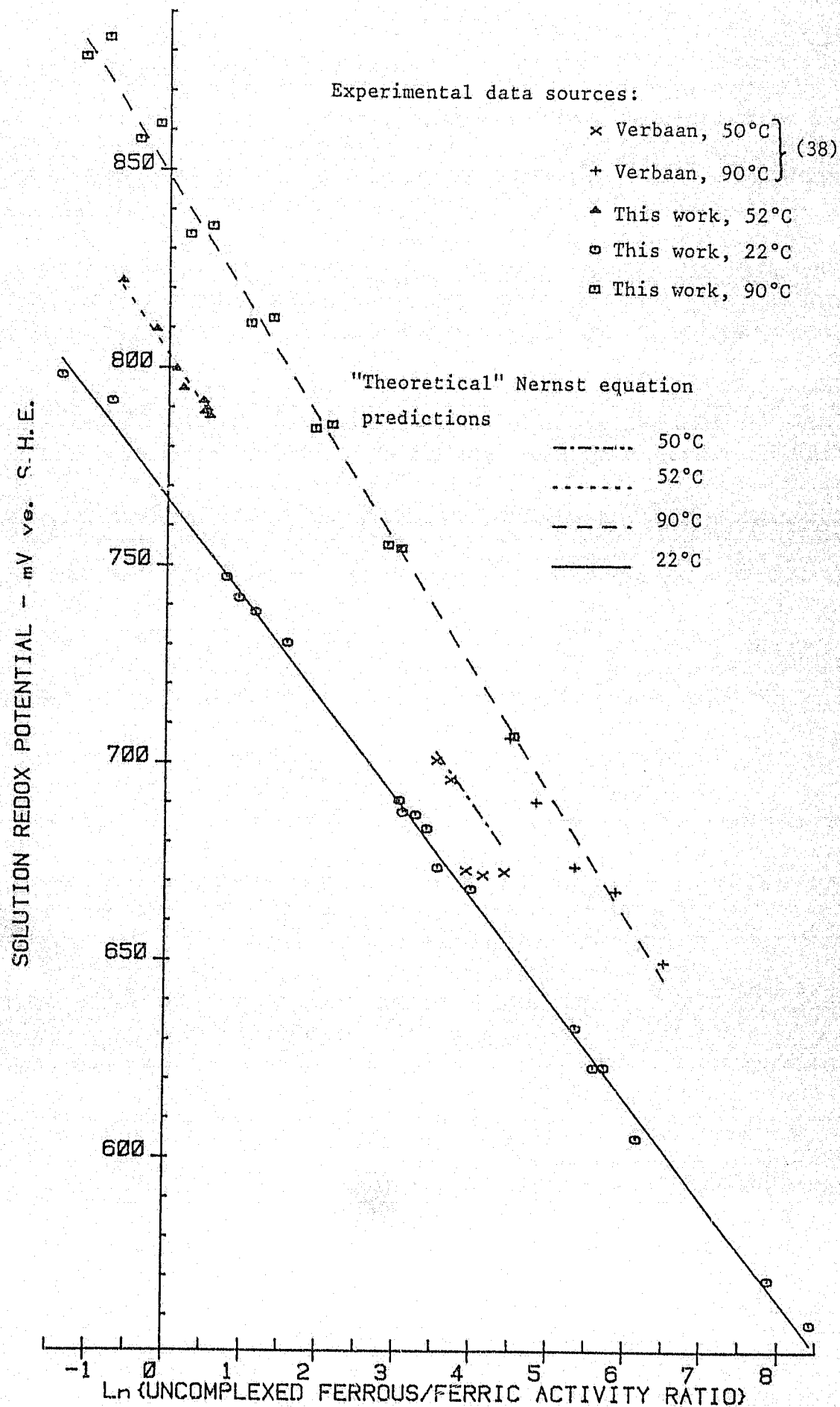


Fig. 5.8

span a much greater range of the ferrous/ferric ratio than Verbaan's results, and good predictions of the redox potential have been obtained, except for Verbaan's two points, it seems likely that some measurement error gave rise to the larger deviations of these points from the theory. In any event, the maximum error was less than 20 millivolts, which is not disastrous.

The stability constants (at zero ionic strength) for the various complexes were calculated at the higher temperatures by means of their values at ambient temperature and the well known equation (39):

$$\frac{d(\ln K)}{dT} = \frac{\Delta H}{RT^2}$$

Where: ΔH = Heat of reaction for complex formation
 T = Absolute temperature
 R = Universal gas constant
 K = Stability constant

For the complexes FeHSO_4^{2+} , FeHSO_4^+ and FeSO_4^0 , the assumption of constant heat of reaction (ΔH) gave satisfactory results over the temperature range studied. These values were found by trial and error (on the accuracy of redox potential predictions) to be as follows:

Species	Heat of reaction, kJ/mol		References
	This work	Literature	
FeHSO_4^{2+}	63,4	75*	5
FeHSO_4^+	60,6	70*	6
FeSO_4^0	6,5	6,7 ; 2,3	47 ; 76

*These values were estimated, not measured

These heats of reaction are of the same order of magnitude as the values in the literature, and can therefore be accepted as reasonable.

The temperature dependence of the stability constant of HSO_4^- is accounted for in Pitzer's sulphuric acid correlation(22), as described in section 4.2.2(b). This correlation was used at all temperatures,

therefore a separate heat of reaction for HSO_4^- formation is not required.

The assumption of constant heat of reaction for the formation of FeSO_4^+ did not give satisfactory redox potential predictions at elevated temperatures. Instead, this heat of reaction was assumed to be a linear function of temperature, i.e., the specific heats of the FeSO_4^+ , Fe^{3+} and SO_4^{2-} were assumed to be constant over the temperature range studied(39). This gave rise to the following expression for the stability constant as a function of temperature:

$$\ln K^0 = A + B/T + C \ln T$$

Where: K^0 = Stability constant of FeSO_4^+

T = Absolute temperature

A, B, C = Constants

Differentiating the above equation gives the heat of reaction for the formation of FeSO_4^+ as:

$$\Delta H = RT^2 \frac{d(\ln K^0)}{dT}$$

Therefore: $\Delta H = RT^2 \frac{d}{dT} (A + B/T + C \ln T)$

Therefore: $\Delta H = R(C \cdot T - B)$

The values of the constants A , B , and C were found by trial and error (on the accuracy of the redox potential predictions) to be:

$$A = -900,421$$

$$B = 39110,926$$

$$C = 136,626$$

(The large number of digits is required for accurate exponentiation)

The results of Sapiieszko *et al*(48) can be used to check the reasonableness of the above values. They measured the stability constant of FeSO_4^+ at 25°C, 55°C and 80°C, and their values for this constant cannot be accurately represented by an equation of the form: $\ln K = A + B/T$ (i.e., constant heat of reaction). An equation of the form: $\ln K = A + B/T + C \ln T$ (as in this work) is capable of accurately representing their data. Using this form of equation, and the stability constant values (at an ionic strength of 2,67) from Sapiieszko *et al*(48) results in the following values for the heat of reaction, as

compared to the values from the present work:

Temperature	Heat of reaction, kJ/mol	
	This work	Sapieszko <i>et al</i>
25°C	13,5	15,4
55°C	47,6	43,5
80°C	76,0	67,0

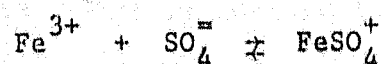
The values from this work are similar to those ex Sapieszko *et al*(48), and can therefore be accepted as reasonable.

5.2.3 Discussion

The objective of this part of the work was to calculate the solution redox potential in acid ferric-ferrous sulphate solution. Figure 5.8 shows that this can be done.

The results summarised in Figure 5.8 cover a range of ionic strength from about 0,1 to almost 4. Strictly speaking the use of Debye-Hückel activity coefficients is not justified in this range of ionic strength(7). However, various workers (43,44) have found that the Debye-Hückel predictions, when coupled with complex formation, give reasonable results at concentrations far in excess of those for which the use of the Debye-Hückel equation is accepted as justified. The following analysis also serves to justify the use of the Debye-Hückel activity coefficients in the range of ionic strength used in this work:

Consider the equilibrium:



The thermodynamic equilibrium constant (or the concentration quotient at zero ionic strength) is given by:

$$K = \frac{\gamma_{\text{FeSO}_4^+}}{\gamma_{\text{Fe}^{3+}} \gamma_{\text{SO}_4^=}} \frac{[\text{FeSO}_4^+]}{[\text{Fe}^{3+}] [\text{SO}_4^=]}$$

$$\text{or: } \log K = \log \left\{ \frac{[\text{FeSO}_4^+]}{[\text{Fe}^{3+}][\text{SO}_4^{=}]}\right\} + \log \left\{ \frac{\gamma_{\text{FeSO}_4^+}}{\gamma_{\text{Fe}^{3+}}\gamma_{\text{SO}_4^{=}}}\right\}$$

Where: $[]$ = species concentration
 γ = activity coefficient

The above equilibrium can also be represented at a specific ionic strength by a concentration quotient, i.e.:

$$\log K' = \frac{[\text{FeSO}_4^+]}{[\text{Fe}^{3+}][\text{SO}_4^{=}]} \quad \text{at a given ionic strength}$$

Values are quoted in the literature for the concentration quotient at various ionic strengths (including zero). The effect of activity coefficient changes can thus be extracted from the literature as follows:

$$\log K = \log K' + \log \left\{ \frac{\gamma_{\text{FeSO}_4^+}}{\gamma_{\text{Fe}^{3+}}\gamma_{\text{SO}_4^{=}}}\right\}$$

$$\text{Therefore } \log \left\{ \frac{\gamma_{\text{FeSO}_4^+}}{\gamma_{\text{Fe}^{3+}}\gamma_{\text{SO}_4^{=}}}\right\} = \log(K/K')$$

Figure 5.9 was constructed by the above method for the stability quotients of FeSO_4^+ and FeSO_4^0 . The symbols represent data points calculated from values quoted in the literature. The solid lines represent activity coefficient corrections calculated using the Debye-Hückel equation for individual ionic activity coefficients, at the ionic strengths indicated. For FeSO_4^+ values from the literature were used. For FeSO_4^0 no consistent values at non-zero ionic strengths were found, therefore a number of bivalent metal sulphates were used to generate data points. This is justified because the bivalent metal sulphate complexes are all outer-sphere complexes(49), thus the major effect influencing their stability constants is electrostatic attraction between the metal and sulphate ions(50).

Figure 5.9 shows that the use of the Debye-Hückel equation for individual ionic activity coefficients results in reasonable corrections for ionic strength to the thermodynamic stability constants. Therefore the use of the Debye-Hückel equation is considered to be acceptable at the ionic strengths used in this work, when coupled with complex formation.

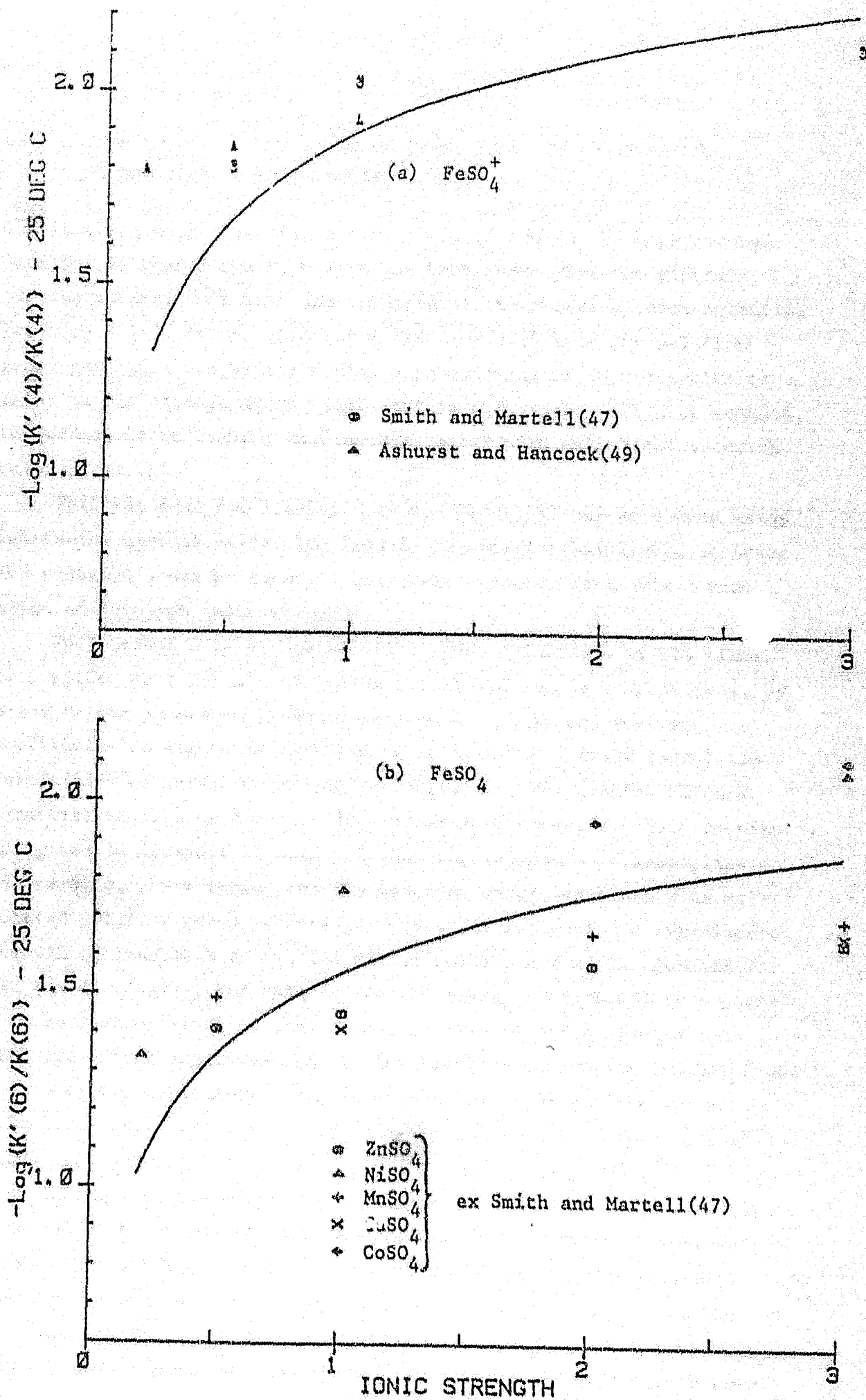


Fig. 5.9 Effect of ionic strength on equilibrium constants

5.3 Combination of the leaching model with the calculation of solution redox potential

The leaching model has been successfully fitted to the experimental data for leaches 7 and 8, and it has been shown that the mineral surface potential is best approximated by the solution redox potential (section 5.1). It was also shown (section 5.2) that the solution redox potential can be calculated with an error of 10 millivolts or less, in the concentration range used in this work. All that remains, therefore, is to combine the leaching model with calculated solution redox potential.

This was done for leaches 3 to 6. These leaches were done using increasing amounts of ferrous iron in the initial solutions, to lower the solution redox potential. This gave leaching data over a wide range of solution redox potential.

For leaches 3 to 6, the solution redox potentials at the times of sampling were calculated, using the liquid sample compositions, by means of the equations given in section 4.2, with the modified equilibrium constants as detailed in section 5.2. These calculated potential-time curves were used to approximate the mineral surface potential in leaches 3 to 6. The computer printouts of these results are given in Appendix IX, and the leaching results are summarised in Figure 5.10, which shows that the leaching model, combined with calculated solution redox potentials, correctly predicts the experimental results of leaches 3 to 6. The fit is not as good as for leaches 7 and 8 individually, but this is not surprising. Leaches 3 to 6 cover a larger potential range and up to four sets of extraction vs time data are fitted simultaneously by leaches 3 to 6, whereas leaches 7 and 8 were fitted separately. The calculated redox potentials may also cause a slightly worse fit, due to small differences between actual and calculated potential values.

In summary, therefore, the leaching model has been successfully combined with the theoretical calculation of the solution redox potential. This means that the leaching of the matte can now be predicted, and thus the leaching model can be used as a design tool in scaling-up the leaching of this matte. The effect of high concentrations of nickel, copper and cobalt on the solution redox potential would have

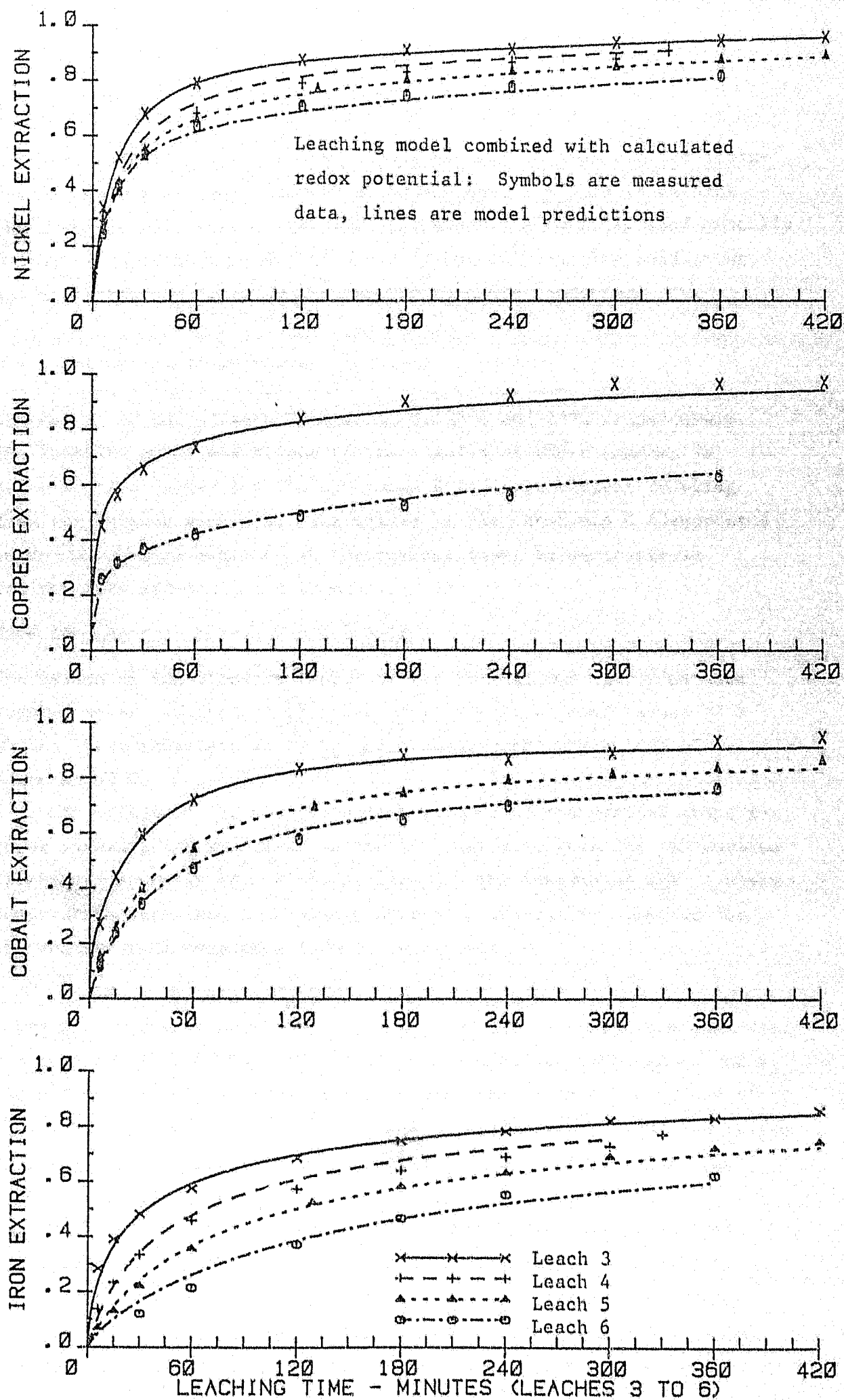


Fig. 5.10

to be evaluated before the model could be used to simulate the leaching of the matte under industrial conditions, but this is outside the scope of this work. Nevertheless, since the model is fundamentally based, it could be expanded to cover industrial leaching conditions, and to extrapolate small-scale results to plant conditions.

5.4 Effect of temperature

Leaches 9, 10 and 11 were done at 52°C, 25°C and 28°C respectively. The leaching model was fitted to the results of these leaches in order to find values for the constants K for each element leaching from the various minerals. The values of the constants k (dependence on potential) were assigned at the various lower temperatures as follows (see section 4.1.1.3 and 5.1.2.):

From the theory, $k = (1 - \beta_1) F/(RT)$

The values of the symmetry factor β_1 for the various reactions were assumed to be independent of temperature. This allowed values of k at the lower temperatures to be calculated, using the values of β_1 found at 90°C.

The values of the various rate constants at the various temperatures investigated are given in the computer printouts for the various leaches in Appendix IX. Plots of $\ln(K)$ vs the inverse of the absolute temperature were used to evaluate Arrhenius activation energies for the various rate constants from the equation:

$$K = K' \exp\{-E_a/(RT)\}$$

where K is the rate constant, K' is a frequency factor, R the universal gas constant ($R = 8,314 \text{ g mol}^{-1} \text{ K}^{-1}$), T the absolute temperature and E_a the activation energy. Figure 5.11 shows typical examples of the plots obtained. All the plots are presented in Appendix XI. From the slopes of these plots, the activation energies were calculated. The values found are given in Table 5.3

In his study of the diffusivity of the ferric ion, Madson(45) found that the effect of temperature on the ferric ion diffusivity in concentrated sulphate solution gave rise to an apparent activation energy of 22.4 kJ/mol. Madsen stated that, for reactions controlled by liquid phase diffusion, the apparent activation energy is generally

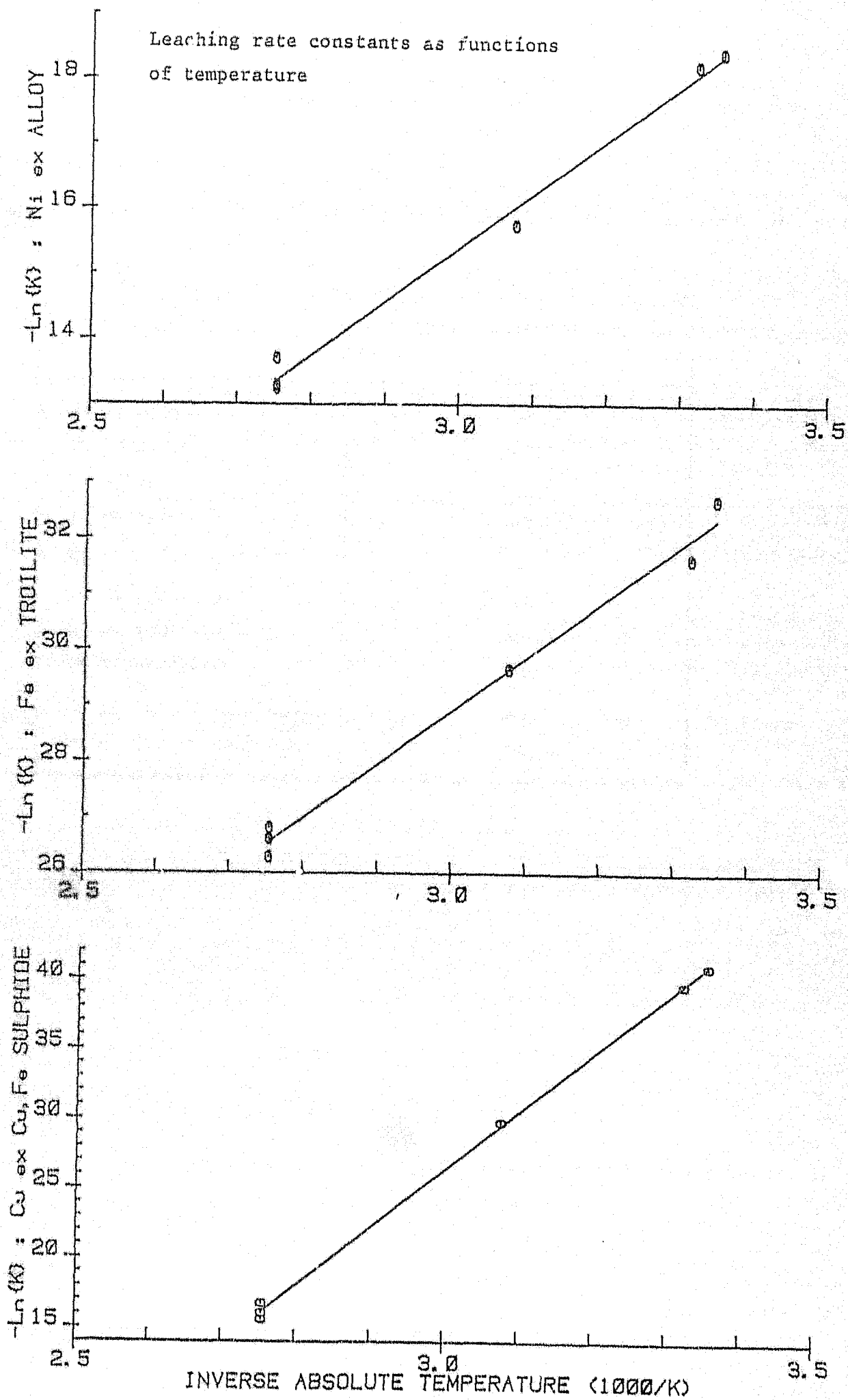


Fig. 5.11

TABLE 5.3

Values of the activation energy of the various leaching rate constants

Rate constant	Activation energy, kJ/mol
Ni ex alloy	68,7
Cu ex alloy	68,7
Co ex alloy	69,6
Fe ex alloy	68,7
Ni ex troilite	80,7
Cu ex troilite	77,8
Co ex troilite	102,2
Fe ex troilite	80,0
Cu ex Cu, Fe sulphide	344,5
Fe ex Cu, Fe sulphide	344,5

between 8 and 25 kJ/mol. The activation energies in Table 5.3 are far above 25 kJ/mol, thus the assumption made in section 4.1(a), namely that at no stage does liquid phase diffusion control the leaching rate, is justified. The high values of the activation energies found indicate that the leaching rates are controlled by chemical kinetics.

5.5 Dependence of the leaching rate on the unleached mineral remaining

In section 4.1(f) the assumption was made that the alloy and copper, iron sulphide phases, which exist as inclusions in the troilite, leach according to shrinking particle mathematics. The dependence of the leaching rate of an element m can be expressed as:

$$-\frac{dm}{dt} \propto m^x$$

where $x = 2/3$ for a shrinking particle model, $x = \text{zero}$ for leaching in a cylindrical pore, and $x = \text{some other value}$ for intermediate leaching models.

The effect of the value of x on the fit of the leaching model to the experimental results was examined for leach 9 (52°C) and leaches 7 and 8 (90°C). Various values of x were inserted into the model for the leaching of nickel from the alloy phase, and copper from the copper, iron sulphide phase. Table 5.4 lists the various values of x used, and shows the fit of the model to the data, in terms of total squared errors, for the various values of x used. The various printouts are shown in Appendix IX. In the case of copper, the value of x has no effect on the fit of the model to the data. For nickel at 90°C, x has a very small effect while at 52°C (leach 9) the effect is larger than at 90°C (leaches 7 and 8), but is still not significant, as examination of the relevant printouts in Appendix IX shows. From these results, therefore, it seems that no significant penalty is incurred by the assumption of shrinking particle mathematics for the alloy and copper, iron sulphide phases in this particular matte.

TABLE 5.4

Effect of x on overall squared errors

a) Leaching of Ni ex alloy:

x	Total squared errors	
	Leach 9	Leaches 7 and 8
2/3	$5,9 \cdot 10^{-4}$	$1,9 \cdot 10^{-3}$
0,6	$5,1 \cdot 10^{-4}$	$1,8 \cdot 10^{-3}$
0,5	$3,8 \cdot 10^{-4}$	$1,7 \cdot 10^{-3}$
0,4	$2,9 \cdot 10^{-4}$	$1,7 \cdot 10^{-3}$
0,3	$1,9 \cdot 10^{-4}$	$1,7 \cdot 10^{-3}$
0,2	$1,2 \cdot 10^{-4}$	$1,8 \cdot 10^{-3}$
0,1	$1,3 \cdot 10^{-4}$	$2,1 \cdot 10^{-3}$
0,05	$1,5 \cdot 10^{-4}$	$2,3 \cdot 10^{-3}$

b) Leaching of Cu ex Cu, Fe sulphide:

x	Total squared errors	
	Leach 9	Leaches 7 and 8
2/3	$1,7 \cdot 10^{-3}$	$3,0 \cdot 10^{-3}$
0,5	$1,7 \cdot 10^{-3}$	$3,0 \cdot 10^{-3}$
0,25	$1,7 \cdot 10^{-3}$	$3,0 \cdot 10^{-3}$
0,1	$1,7 \cdot 10^{-3}$	$3,0 \cdot 10^{-3}$

6. CONCLUSIONS

The following conclusions are drawn from this work:

- a) The leaching of the low grade matte is electrochemical in nature.
- b) The leaching mechanism for galena (PbS) fits the experimental results for the leaching of this matte, which is mainly troilite (FeS).
- c) The leaching of the matte can be modelled by a shrinking particle model, along with an electrochemical rate expression. Because the model uses the measured quantitative matte composition (alloy, troilite, copper, iron sulphide and magnetite phases), it is fundamentally sound, and should be able to be applied elsewhere with confidence.
- d) The matte surface potential during leaching is best approximated by the solution redox potential.
- e) The solution redox potential can be calculated from the Nernst equation, using Debye-Hückel activity coefficients, if the various sulphate complexing equilibria are taken into account.
- f) The leaching model has been successfully combined with calculated solution redox potentials, to predict leaching rates.
- g) The elemental sulphur formed on the matte particles during leaching does not affect the leaching rate.

APPENDIX I

Print-outs of results of matte phase calculations

- a) X-ray diffraction data
- b) Individual microtrac particle size analyses
- c) Printouts of the results of the matte phase calculations

X-ray diffraction data

The X-ray diffraction measurements were done on a Phillips X-ray diffraction unit, using powdered matte samples. The X-ray patterns obtained were compared with those of known minerals. These reference patterns were taken from the "Powder Diffraction File" (Inorganic Centre for Diffraction Data, 1601 Park Lane, Swarthmore, P.A. 19801, U.S.A.)

Similar results were obtained for all the matte fractions ex the Warman cyclosizer. Tables 1.1 and 1.2 give the measured interplanar spacings and X-ray peak intensities for cyclosizer fractions 6 and 2 (i.e. coarse and fine fractions) respectively. Figures 1.1 and 1.2 give the same information in graphical form, along with the X-ray diffraction patterns for troilite (FeS : card 24 - 80 of the Powder Diffraction File) and two types of pyrrhotite (Fe_{1-x}S : cards 79 - 723 and 79 - 723A of the Powder Diffraction File; and Fe_7S_8 : card 24 - 79 of the Powder Diffraction File). The matte X-ray diffraction patterns in Figures 1.1 and 1.2 are very similar, which shows that the same phases are present in the coarse and the finer size ranges represented.

For both types of pyrrhotite, there are significant X-ray diffraction peaks at interplanar spacings of 5,7 and 5,8 angstroms. These peaks do not appear in the patterns for troilite and the matte. This implies that the matte does not contain pyrrhotite, since two significant pyrrhotite peaks are missing from its X-ray diffraction pattern. The similarity between the matte and troilite patterns indicates that the matte contains troilite. Figure 1.3 shows a part of the X-ray diffraction patterns for the matte, and troilite and pyrrhotite, on a longer interplanar spacing axis. For pyrrhotite, there are multiple peaks at interplanar spacings of about 2,1 and 2,6 angstroms. At these interplanar spacings, the matte and troilite only have single peaks, which is a further indication that the matte contains troilite and not pyrrhotite as the major phase.

The other phases present (iron-nickel alloy, copper iron sulphide and magnetite) were identified by means of the smaller matte X-ray diffraction peaks, and the electron microprobe analyses given in section 2.1.

TABLE 1.1

X-ray diffraction data for the matte-cyclosizer fraction 6

Interplanar spacing, Angstroms	Relative intensity, %	Interplanar spacing, Angstroms	Relative intensity, %
0,99493	1	1,48	1
1,0499	1	1,50	1
1,0532	2	1,62	1
1,0784	1	1,63	3
1,0821	1	1,7168	32
1,0842	1	1,745	3
1,086	1	1,75	3
1,088	1	1,79	2
1,093	1	1,80	2
1,1078	2	1,93	3
1,1159	3	1,94	1
1,126	1	2,09	100
1,1315	1	2,15	3
1,1809	1	2,52	4
1,1826	1	2,66	48
1,1853	1	2,92	3
1,224	1	2,98	32
1,2684	1	3,35	1
1,2711	1	4,731	1
1,31	2	5,04	1
1,33	4		
1,44	2		
1,46	3		

TABLE 1.2

X-ray diffraction data for the matte-cyclosizer fraction 2

Interplanar spacing, Angstroms	Relative intensity, %	Interplanar spacing, Angstroms	Relative intensity, %
0,925	1	1,325	5
0,927	1	1,33	5
0,976	1	1,34	1
0,992	1	1,42	1
0,994	1	1,44	2
1,02	1	1,46	2
1,03	1	1,48	2
1,049	1	1,51	1
1,0527	2	1,63	3
1,10	2	1,72	30
1,11	3	1,74	3
1,13	1	1,78	1
1,16	1	1,93	4
1,17	1	2,09	100
1,1809	1	2,146	4
1,1853	1	2,47	2
1,19	1	2,52	5
1,22	1	2,65	40
1,26	1	2,984	30
1,28	1	3,33	3
1,31	2	4,71	2

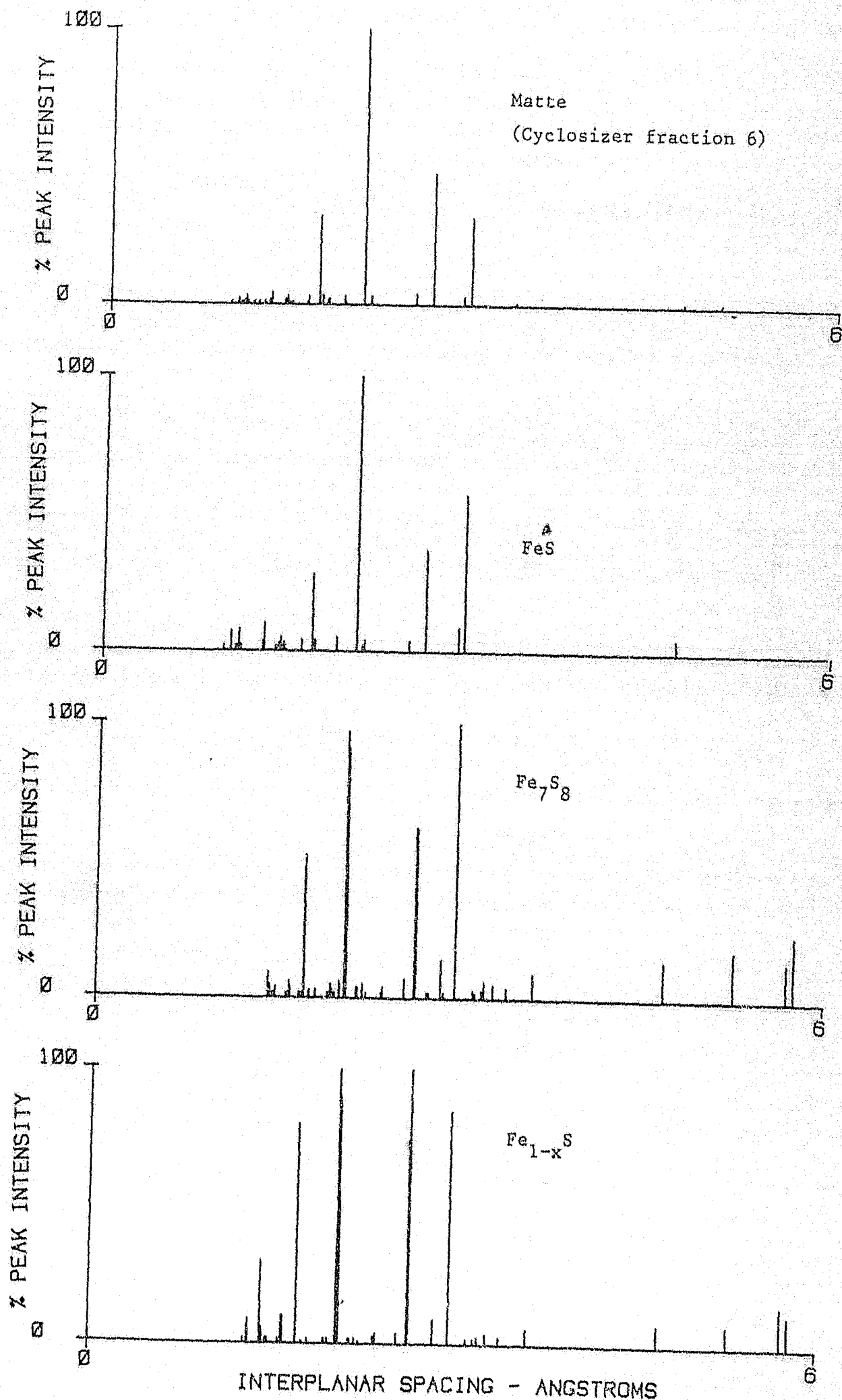


Fig. 1.1: X-ray diffraction data

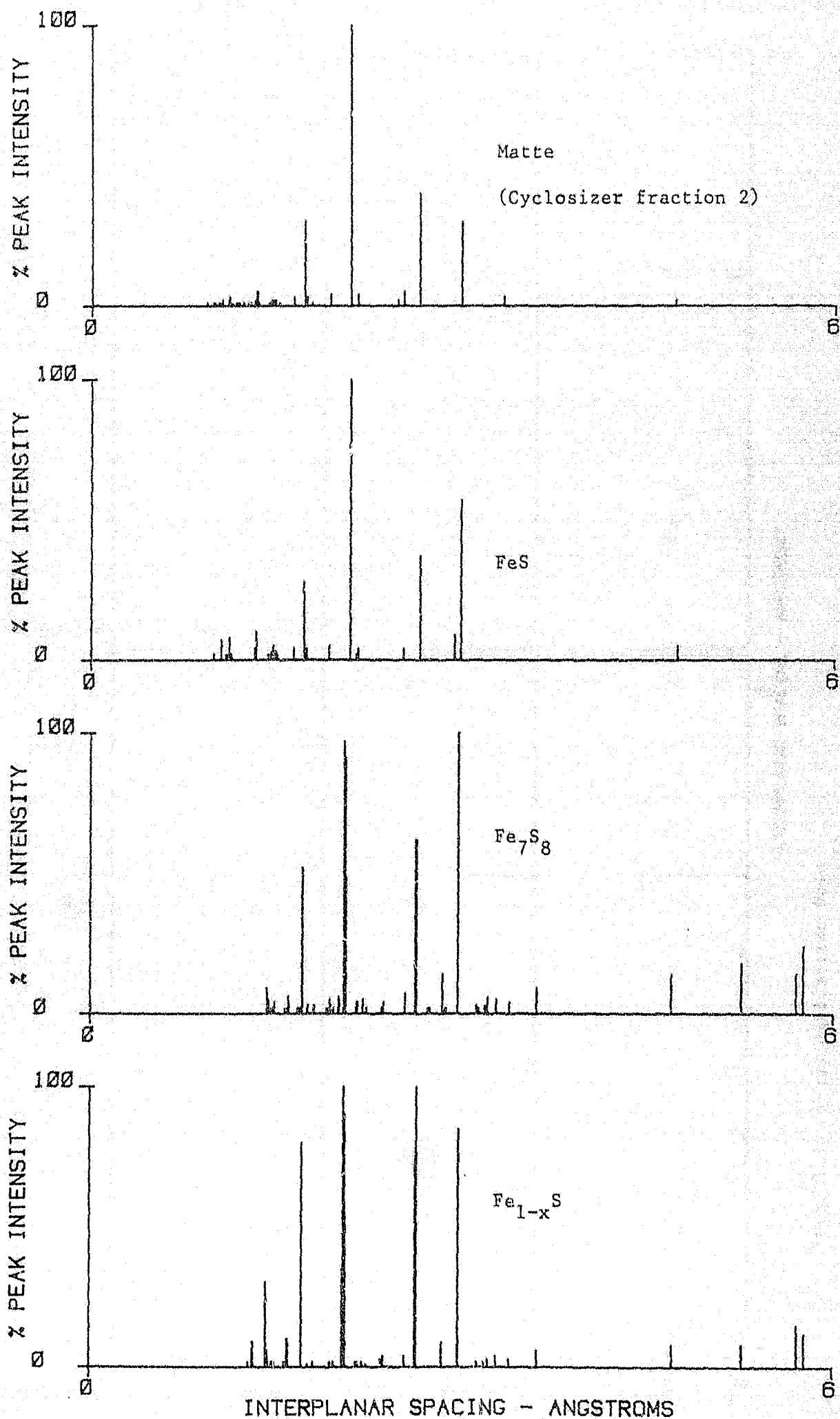


Fig. 1.2: X-ray diffraction data

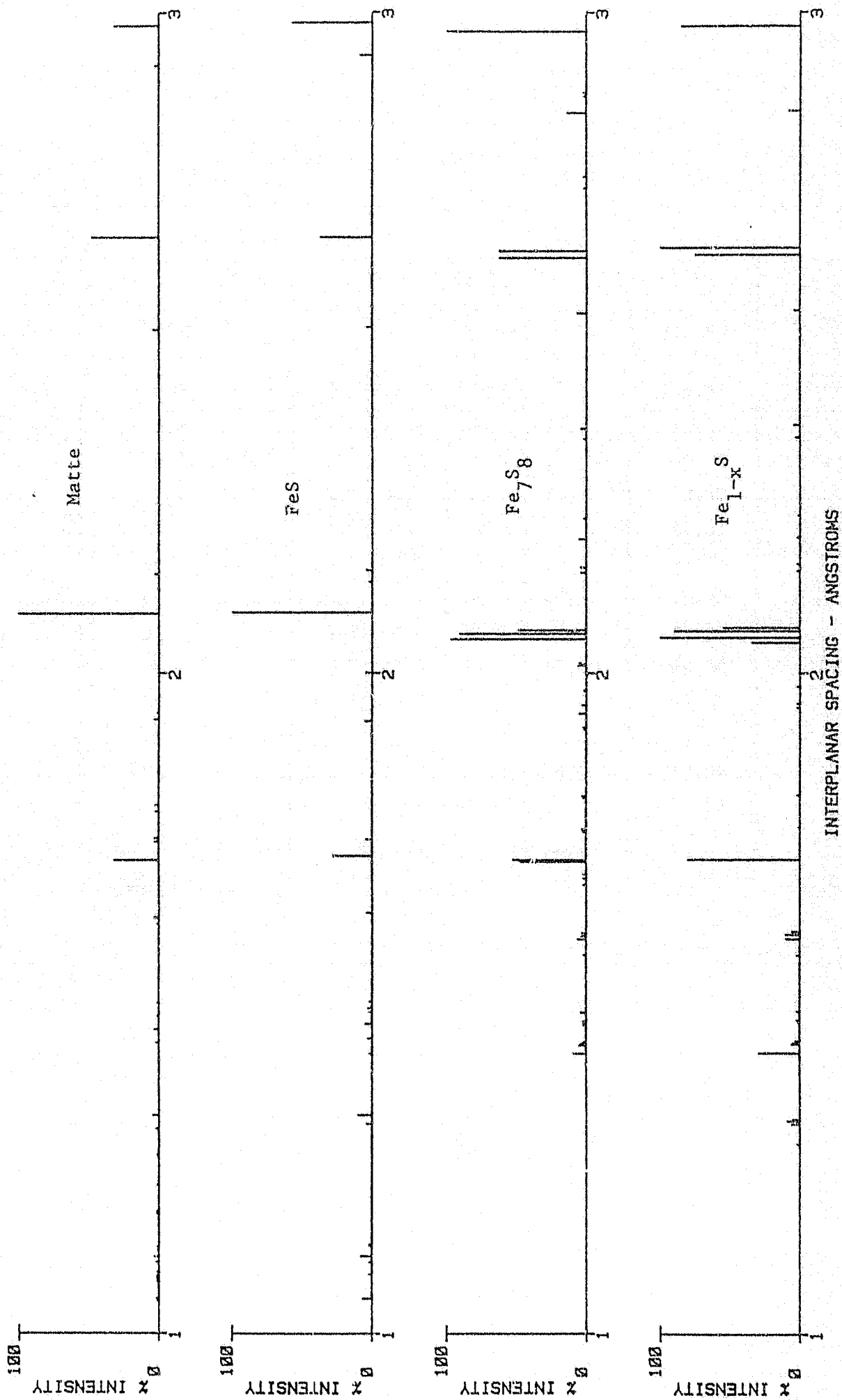


Fig. 1.3: X-ray diffraction data

MATTE SIZE DISTRIBUTION : MICROTRAC ANALYSES

Particle size, microns	Percentage smaller (cumulative)				
	Individual samples				Average
2,8	7,2	5,4	7,2	7,5	6,83
3,9	13,4	14,4	14,3	12,4	13,63
5,5	23,4	24,6	26,4	21,9	24,08
7,8	35,9	32,3	33,3	34,1	33,90
11	41,9	38,9	42,3	41,5	41,15
16	55,2	54,1	55,2	52,5	54,25
22	63,5	61,0	61,3	61,9	61,93
31	70,2	67,0	74,5	69,5	70,30
44	79,5	83,5	89,4	81,1	83,38
62	89,5	86,4	91,7	86,1	88,43
88	100	95,0	91,7	93,2	94,98
125	100	100	95,3	99,9	98,80
176	100	100	100	99,9	99,98

PHASE COMPOSITIONS

X = 40.370
Y = 1.900
Z = .000

ESQ = 4.542E-01

CALCULATED FRN COMPOSITIONS

FRN	MASS % (C)	MASS % (M)
1	5.25	5.12
2	3.43	3.40
3	3.18	3.10
4	3.53	3.02
5	2.63	2.77
6	1.47	1.88

STOP

ZIN PHASES.

ALLOY	TROILITE	MAGNETITE
68.46	31.53	.00
49.43	50.57	.00
45.67	54.33	.00
31.95	68.05	.00
36.79	63.21	.00
16.48	83.52	.00

Ni

PHASE COMPOSITIONS

X = 1.200
Y = 1.500
Z = 5.577

ESQ = 2.660E-01

CALCULATED FRN COMPOSITIONS

FRN	MASS % (C)	MASS % (M)
1	1.64	1.94
2	1.67	1.74
3	1.71	1.84
4	1.80	2.01
5	1.90	2.17
6	2.92	2.73

STOP

)

Cu

%IN PHASES.

ALLOY	TROILITE	MAGNETITE
6.53	79.84	13.63
3.02	81.96	15.02
2.53	79.86	17.62
1.73	75.43	23.24
1.55	69.14	29.34
.35	33.22	66.53

PHASE COMPOSITIONS

X = 2.500
Y = .400
Z = .000

ESR = 4.390E-01

CALCULATED FRN COMPOSITIONS

FRN	MASS % (C)	MASS % (M)
1	.57	.25
2	.47	.18
3	.45	.16
4	.41	.15
5	.41	.14
6	.27	.12

STOP

)

Co

ZIN PHASES.

ALLOY	TROILITE	MAGNETITE
38.97	61.03	.00
22.33	77.67	.00
19.82	80.18	.00
12.14	87.86	.00
14.62	85.38	.00
5.49	94.51	.00

PHASE COMPOSITIONS

X = 62.617
Y = 59.000
Z = 49.982

ESR = 6.150E-01

CALCULATED FRN COMPOSITIONS

FRN	MASS % (C)	MASS % (M)
1	58.96	59.30
2	58.75	58.60
3	58.64	58.10
4	58.40	58.00
5	58.19	58.30
6	55.88	56.00

STOP

>

Fe

XIN PHASES

ALLOY	TROILITE	MAGNETITE	
9.45	87.16	0.20	3.39
4.48	91.69	0.23	3.83
3.84	91.55	0.18	4.60
3.14	91.44	0.30	6.42
2.58	88.83	0.51	8.59
.67	68.20	1.88	31.13

LEACHABLE IRON

APPENDIX II

Results of leaching experiments for leaches 1 to 8.

Raw data:

- i) Experimental measurements
- ii) Mass balances
- iii) Extractions vs time data

Raw data for leach: 1 (Liquids)

Time, mins.	Sample vol., ml.	Assay, g/l			Assay, mg/l		
		Fe ³⁺	Fe ²⁺	SO ₄ ⁼	Ni	Cu	Co
0		101,2	0,0		22	1	5
6	26	99,6	3,65		112	63	9
15	26	98,2	4,90		158	77	11
30	26	97,4	6,05		196	90	13
60	23	97,0	7,29		225	100	14
120	25	96,1	8,48		243	112	15
180	23	95,9	9,34		251	118	16
240	25	95,5	9,83		256	123	16
300	23	95,0	10,19		265	127	17
360	25	95,1	10,50		265	130	17
420	25	95,1	10,70		269	133	17
Preg.		94,8	10,80		268	133	17
Wash A		4,02	0,12		3,3	1,5	0,1

Volume of liquid into leach : 1,5 litres
 Volume of liquid ex leach : 1,22 litres
 Wash water volume (Wash A) : 2,84 litres
 Wash water volume (Wash B) -

Raw data for leach: 1 (Solids)

Solid	Assay, mass %			
	Ni	Cu	Co	Fe
Matte into leach:	3,97	2,07	0,19	59,1
Solids ex preg. liq.:	0,62	0,28	<0,05	23,0
Solids ex samples:	1,32	0,73	0,08	38,6
Misc. solids out:	1,41	0,77	0,09	42,6

Masses recorded:

Matte into leach : 10,00 grams
Solids ex preg. liq.: 2,66 grams
Solids ex samples : 0,82 grams
Misc. solids out : 0,47 grams

Mass balance for leach: 1

Into leach

Matte in

Liquor in

Therefore: total in

Ex leach

Solids ex preg. liq.

Solids ex samples

Misc. solids out

Pregnant liquor

Wash A liquor

Wash B liquor

Samples

Therefore: total out

Mass balance, % (Out/In)

% extraction

Mass, mg			Mass, g
Ni	Cu	Co	Fe
397	207	19	5,9
33	1,5	7,5	151,8
430	208,5	26,5	157,7
16,5	7,4	<1,3	0,6
10,8	6,0	0,7	0,3
6,6	3,6	0,4	0,2
327	162,3	20,7	128,8
9,4	4,3	0,3	11,8
55,0	26,4	3,6	25,8
425,3	210,0	<27,0	167,5
98,9	100,7	<102	106,2
95,3	95,6	> 94,1	91,0

Extraction vs. time data for leach: 1

Time, mins.	Per cent extraction			
	Ni	Cu	Co	Fe
0	0	0	0	0
6	34,7	44,9	31,6	28,3
15	52,4	55,1	47,4	39,0
30	67,0	64,5	63,2	48,2
60	78,2	71,7	71,1	57,3
120	85,2	80,4	79,0	68,4
180	88,2	84,8	86,9	74,6
240	90,2	88,4	86,9	78,2
300	93,6	91,3	94,8	82,1
360	93,6	93,5	94,8	82,8
420	95,2	95,6	94,8	85,7

Raw data for leach: 2 (Liquids)

Time, mins.	Sample vol., ml.	Assay, %/l			Assay, mg/l		
		Fe ³⁺	Fe ²⁺	SO ₄ ⁼	Ni	Cu	Co
0		102,7	0,00		22,8	1,92	4,90
6	17	98,9	3,79		116	67,9	9,11
15	20	97,2	5,20		171	86,2	11,8
30	22	97,3	6,25		204	97,5	13,3
60	25	96,9	7,39		230	108	14,8
120	26	96,1	8,68		251	121	16,2
180	20	95,2	9,41		256	127	16,5
240	28	95,3	9,88		261	130	16,9
300	23	94,4	10,23		265	133	17,2
360	24	94,8	10,51		266	136	17,2
420	22	93,7	10,76		270	138	17,8
Preg.		93,9	10,74		270	137	17,8
Wash A		0,95	0,14		3,92	2,07	<1
Wash B		0,70	0,10		4,23	3,74	<1

Volume of liquid into leach : 1,5 litres
Volume of liquid ex leach : 1,23 litres
Wash water volume (Wash A) : 1,29 litres
Wash water volume (Wash B) : 1,56 litres

Raw data for leach: 2 (Solids)

Solid	Assay, mass %			
	Ni	Cu	Co	Fe
Matte into leach:	4,01	2,06	0,19	58,8
Solids ex preg. liq.:	0,51	0,19	<0,05	18,0
Solids ex samples:	1,35	0,73	0,08	38,6

Masses recorded:

Matte into leach : 10,00 grams
Solids ex preg. liq.: 2,68 grams
Solids ex samples : 1,58 grams
Misc. solids out : zero

Mass balance for leach: 2

Into leach

Matte in

Liquor in

Therefore: total in

Ex leach

Solids ex preg. liq.

Solids ex samples

Misc. solids out

Pregnant liquor

Wash A liquor

Wash B liquor

Samples

Therefore: total in

Mass balance, % (Out/In)

% extraction

Mass, mg			Mass, g
Ni	Cu	Co	Fe
401	206	19	5,88
34,2	2,9	7,35	154,05
435,2	208,9	26,35	159,93
13,7	5,1	<1,3	0,48
21,3	11,5	1,26	0,61
332,1	168,5	21,89	128,66
5,1	2,7	0,34	1,41
6,6	5,8	0,43	1,24
53,0	26,4	3,48	22,05
431,8	220,0	<28,7	154,45
99,2	105,3	<109	96,6
96,1	97,1	97,1	91,8

Extraction vs. time data for leach: 2

Time, mins.	Per cent extraction			
	Ni	Cu	Co	Fe
0	0	0	0	0
6	36,1	47,4	31,1	31,2
15	57,4	60,6	51,0	42,5
30	70,2	68,7	62,0	51,2
60	80,3	76,3	73,1	60,7
120	88,4	85,6	83,5	71,7
180	90,3	89,9	85,7	78,0
240	92,3	92,1	88,6	82,1
300	93,8	94,2	90,8	85,1
360	94,2	96,4	90,8	87,5
420	95,8	97,8	95,3	89,6

Raw data for leach: 3 (Liquids)

Time, mins.	Sample vol., ml.	Assay, g/l			Assay, mg/l		
		Fe ³⁺	Fe ²⁺	SO ₄ ⁼	Ni	Cu	Co
0		101,3	0,00		22,8	1,88	4,99
6	24	98,1	3,65		112	66,8	8,64
15	30	96,7	5,05		160	83,4	11,0
30	23	95,4	4,25		202	97,0	13,1
60	26	94,5	7,41		230	108	14,8
120	24	95,1	8,80		252	123	16,3
180	23	94,6	9,58		262	132	17,0
240	26	93,5	10,01		263	135	16,8
300	24	93,5	10,50		269	141	17,1
360	22	93,3	10,59		271	141	17,7
420	25	93,3	10,94		274	142	17,9
Preg.		93,8	10,80		271	140	17,9
Wash A		0,87	0,13		3,48	1,70	<1
Wash B		0,67	0,10		3,32	1,29	<1

Volume of liquid into leach : 1,5 litres
Volume of liquid ex leach : 1,21 litres
Wash water volume (Wash A) : 1,51 litres
Wash water volume (Wash B) : 1,49 litres

Raw data for leach: 3 (Solids)

Solid	Assay, mass %			
	Ni	Cu	Co	Fe
Matte into leach:	3,98	2,02	0,19	58,9
Solids ex preg. liq.:	0,63	0,27	<0,05	23,4
Solids ex samples:	1,38	0,75	0,09	39,3
Misc. solids out:				

Masses recorded:

Matte into leach : 10,00 grams
Solids ex preg. liq.: 3,15 grams
Solids ex samples : 1,22 grams
Misc. solids out : zero

Mass balance for leach: 3

Into leach

Matte in

Liquor in

Therefore: total in

Ex leach

Solids ex preg. liq.

Solids ex samples

Misc. solids out

Pregnant liquor

Wash A liquor

Wash B liquor

Samples

Therefore: total out

Mass balance, % (Out/In)

% extraction

Mass, mg			Mass, g
Ni	Cu	Co	Fe
398	202	19	5,89
34,2	2,8	7,49	151,95
432,2	204,8	26,49	157,84
19,8	8,5	<1,6	0,74
16,8	9,2	1,10	0,48
327,9	169,4	21,66	126,57
5,3	2,6	0,35	1,51
4,9	1,9	0,32	1,15
56,3	28,7	3,69	25,44
431,0	220,3	28,72	155,89
99,7	107,6	<108,4	98,8
94,4	95,3	96,2	84,6

Extraction vs. time data for leach: 3

Time, mins.	Per cent extraction			
	Ni	Cu	Co	Fe
0	0	0	0	0
6	33,7	44,8	26,8	28,3
15	51,9	56,2	44,1	39,0
30	67,8	65,6	59,4	48,2
60	78,4	73,2	71,9	57,3
120	86,7	83,6	82,9	68,4
180	90,5	89,8	88,0	74,6
240	90,9	91,9	86,6	78,2
300	93,1	96,0	88,8	82,1
360	93,9	96,0	93,2	82,8
420	95,0	96,7	94,6	85,7

Raw data for leach: 4 (Liquids)

Time, mins.	Sample vol., ml.	Assay, g/l			Assay, mg/l		
		Fe ³⁺	Fe ²⁺	SO ₄ ⁼	Ni	Cu	Co
0		102,9	6,94		31,1	1,46	6,43
6	25	98,2	8,90		110	59,0	9,45
15	24	97,3	10,20		146	70,7	11,1
30	20	96,0	11,50		178	82,0	12,9
60	24	94,7	13,13		214	95,7	15,0
120	29		14,63		243	110	16,9
180	27	93,5	15,50		254	120	17,7
240	23	93,6	16,18		264	130	18,4
300	23	92,7	16,64		267	137	18,7
Preg.		93,5	17,20		275	143	19,2
Wash A		1,27	0,26		4,60	2,27	<1
Wash B		1,37	0,23		4,79	2,47	<1

Volume of liquid into leach : 1,5 litres
Volume of liquid ex leach : 1,265 litres
Wash water volume (Wash A) : 0,99
Wash water volume (Wash B) : 1,20 litres

Raw data for leach: 4 (Liquids)

Time, mins.	Sample vol., ml.	Assay, g/l			Assay, mg/l		
		Fe ³⁺	Fe ²⁺	SO ₄ ⁼	Ni	Cu	Co
0		102,9	6,94		31,1	1,46	6,43
6	25	98,2	8,90		110	59,0	9,45
15	24	97,3	10,20		146	70,7	11,1
30	20	96,0	11,50		178	82,0	12,9
60	24	94,7	13,13		214	95,7	15,0
120	29		14,63		243	110	16,9
180	27	93,5	15,50		254	120	17,7
240	23	93,6	16,18		264	130	18,4
300	23	92,7	16,64		267	137	18,7
Preg.		93,5	17,20		275	143	19,2
Wash A		1,27	0,26		4,60	2,27	<1
Wash B		1,37	0,23		4,79	2,47	<1

Volume of liquid into leach : 1,5 litres
Volume of liquid ex leach : 1,265 litres
Wash water volume (Wash A) : 0,99
Wash water volume (Wash B) : 1,20 litres

Raw data for leach: 4 (Solids)

Solid	Assay, mass %			
	Ni	Cu	Co	Fe
Matte into leach:	3,94	2,10	0,19	58,1
Solids ex preg. liq.:	0,86	0,70	<0,05	27,2
Solids ex samples:	1,81	1,12	0,11	43,8
Ferrous sulphate in:	<0,1	<0,1	<0,05	20,15

Masses recorded:

Ferrous sulphate in : 50 grams
Matte into leach 10,00 grams
Solids ex preg. liq.: 4,42 grams
Solids ex samples : 1,13 grams
Misc. solids out : zero

Mass balance for leach: 4

Into leach

Matte in
Liquor in
Ferrous sulphate in

Ex leach

Solids ex preg. liq.
Solids ex samples
Misc. solids out
Pregnant liquor
Wash A liquor
Wash B liquor
Samples

Therefore: total out

Mass balance, % (Out/In)

% extraction

Mass, mg			Mass, g
Ni	Cu	Co	Fe
394	210	19	5,81
46,7	2,2	9,65	154,28
			10,15
440,7	212,2	28,65	170,24
38,0	30,9	<2,21	1,20
20,5	12,7	1,24	0,49
347,9	180,9	24,29	139,97
4,6	2,2	0,31	1,51
5,7	3,0	0,43	1,92
41,1	19,7	2,94	21,13
457,8	249,4	31,42	166,22
103,9	117,5	109,7	97,6
89,1	-	-	77,0

Extraction vs. time data for leach: 4

Time, mins.	Per cent extraction			
	Ni	Cu	Co	Fe
0	0	0	0	0
6	29,2			13,8
15	42,5			23,5
30	54,4			33,4
60	67,7			45,8
120	78,4			57,2
180	82,5			63,9
240	86,2			69,1
300	87,3			72,7

Raw data for leach: 5 (Liquids)

Time, mins.	Sample vol., ml.	Assay, g/l			Assay, mg/l		
		Fe ³⁺	Fe ²⁺	SO ₄ ⁼	Ni	Cu	Co
0		96,6	18,69		33,7	3,75	7,61
6	24	95,8	19,65		94,6	52,8	9,52
15	26	95,0	20,40		128	62,4	10,8
30	26	94,0	21,44		158	71,3	12,6
60	25	93,6	22,96		190	83,1	14,4
129	20	93,0	24,83		216	98,5	16,3
180	23	91,9	25,50		224	106	16,9
240	23	91,7	26,05		232	114	17,5
300	19	91,4	26,70		236	122	17,8
360	24	90,7	27,03		241	129	18,1
420	23	90,9	27,30		245	135	18,4
Preg.		90,5	27,24		248	137	18,5
Wash A		1,11	0,41		4,34	2,71	<1
Wash B		1,29	0,36		3,91	1,54	<1

Volume of liquid into leach : 1,5 litres
 Volume of liquid ex leach : 1,27 litres
 Wash water volume (Wash A) : 1,06 litres
 Wash water volume (Wash B) : 1,75 litres

Raw data for leach: 5 (Solids)

Solid	Assay, mass %			
	Ni	Cu	Co	Fe
Matte into leach:	3,96	2,12	0,19	58,7
Solids ex preg. liq.:	1,05	0,93	0,06	33,7
Solids ex samples:	1,90	1,20	0,12	49,6
Misc. solids out:				

Masses recorded:

Matte into leach : 10,00 grams
Solids ex preg. liq.: 3,53 grams
Solids ex samples : 1,29 grams
Misc. solids out : zero

Mass balance for leach: 5

Into leach

Matte in
Liquor in (+FeSO₄)
Therefore total in

Ex leach

Solids ex preg. liq.
Solids ex samples
Misc. solids out
Pregnant liquor
Wash A liquor
Wash B liquor
Samples

Therefore: total out

Mass balance, % (Out/In)

% extraction

Mass, mg			Mass, g
Ni	Cu	Co	Fe
396	212	19	5,87
50,6	5,6	11,42	172,94
446,6	217,6	30,42	178,81
37,1	32,8	2,12	1,19
24,5	29,4	1,55	0,64
315,0	174,0	23,50	149,53
4,6	2,87	0,36	1,61
6,8	2,7	0,46	2,89
45,2	22,4	3,51	27,24
433,2	264,2	31,50	183,1
97,0	121,4	103,6	102,4
89,6	-	86,9	73,7

Extraction vs. time data for leach: 5

Time, mins.	Per cent extraction			
	Ni	Cu	Co	Fe
0	0	0	0	0
6	25,5		15,2	7,1
15	39,4		25,5	13,3
30	52,0		39,8	22,3
60	65,3		54,2	35,7
129	76,2		69,3	52,4
180	79,6		74,1	58,4
240	82,9		78,9	63,3
300	84,6		81,3	69,1
360	86,7		83,7	72,0
420	88,3		86,1	74,4

Raw data for leach: 6 (Liquids)

Time, mins.	Sample vol., ml.	Assay, g/l			Assay, mg/l		
		Fe ³⁺	Fe ²⁺	SO ₄ ⁼	Ni	Cu	Co
0		93,3	33,63		37,8	4,33	9,14
6	24	93,4	33,88		96,6	41,5	10,6
15	25	92,4	34,25		138,0	49,6	12,1
30	23	92,0	35,26		166,2	57,0	13,4
60	27	91,1	36,31		189,2	64,6	15,0
120	21	90,2	38,00		205,6	74,0	16,3
180	24	89,3	39,03		215,3	79,6	17,2
240	21	89,0	39,95		222,8	84,7	17,8
360	24	89,1	40,69		231,6	94,7	18,6
Preg.		88,3	41,14		234,9	111,5	18,8
Wash A		1,66	0		3,99	2,29	<1
Wash B		1,00	0		2,15	0,55	<1

Volume of liquid into leach : 1,6 litres
Volume of liquid ex leach : 1,38 litres
Wash water volume (Wash A) : 1,06 litres
Wash water volume (Wash B) : 1,36 litres

Raw data for leach: 6 (Solids)

Solid	Assay, mass %			
	Ni	Cu	Co	Fe
Matte into leach:	4,00	2,18	0,20	58,9
Solids ex preg. liq.:	1,28	1,10	0,09	35,7
Solids ex samples:	1,89	1,36	0,13	51,8
Misc. solids out:				

Masses recorded:

Matte into leach : 10,00 grams
Solids ex preg. liq.: 4,62 grams
Solids ex samples : 1,09 grams
Misc. solids out : zero

Mass balance for leach: 6

Into leach

Matte in

Liquor in (+ FeSO₄O

Therefore: total in

Ex leach

Solids ex preg. liq.

Solids ex samples

Misc. solids out

Pregnant liquor

Wash A liquor

Wash B liquor

Samples

Therefore: total out

Mass balance, % (Out/In)

% extraction

Mass, mg			Mass, g
Ni	Cu	Co	Fe
400	218	20	5,89
60,5	6,9	14,6	203,0
460,5	224,9	34,6	208,89
59,1	50,8	4,16	1,65
20,6	14,8	1,42	0,56
324,2	153,9	25,94	178,57
4,2	2,4	< 1,06	1,76
2,9	0,7	< 1,38	1,36
34,4	12,8	2,85	24,2
445,4	235,4	<36,81	208,10
96,7	104,7	<106,4	99,6
82,3	74,7	75,9	65,9

Extraction vs. time data for leach: 6

Time, mins.	Per cent extraction			
	Ni	Cu	Co	Fe
0	0	0	0	0
6	24,6	25,9	11,8	-
15	41,8	31,6	23,8	-
30	53,5	36,7	34,3	12,2
60	63,2	42,0	47,2	21,6
120	70,1	48,6	57,7	37,2
180	74,1	52,5	64,9	46,7
240	77,2	56,0	69,7	55,3
360	80,9	63,0	76,2	62,0

Raw data for leach: 7 (Liquids)

Time, mins.	Sample vol., ml.	Assay, g/l			Assay, mg/l		
		Fe ³⁺	Fe ²⁺	SO ₄ ⁼	Ni .	Cu	Co
0		99,8	0,03	292	33,7	1,42	7,80
6	23,1	99,4	2,50	297	122	61,6	10,8
16	16,0	98,0	3,75	300	169	75,5	13,0
30	25,3	97,5	4,70	301	200	84,9	14,5
60	24,4	97,0	5,80	298	222	94,1	15,8
120	21,8	95,9	6,90	296	236	105	16,9
182	23,1	96,1	7,65	293	244	112	17,5
240	21,3	94,2	8,05	294	248	114	17,8
300	17,3	96,4	8,50	299	253	118	18,2
360	21,3	96,2	8,90	305	256	121	18,4
420	20,9	96,0	9,20	289	260	124	18,8
Preg.		95,7	9,15	284	258	122	18,6
Wash A		1,10	0	0	2,69	1,52	0,08
Wash B		1,04			5,18	1,98	0,26

Volume of liquid into leach : 1,635 litres

Volume of liquid ex leach : 1,345 litres

Wash water volume (Wash A) : 1,010 litres

Wash water volume (Wash B) : 1,355 litres

Raw data for Leach: 7 (Potential)

Time, Mins.	Electrode potential, mV		
	Platinum	Matte	Residue
0	733	465	
6	587	447	
16	576	450	
30	568	454	
60	560	457	
120	556	471	
182	552	466	
240	552	455	
300	548	446	
360	547	436	
420	546	434	

All potentials are vs. S.C.E.

Raw data for leach: 7 (Solids)

Solid	Assay, mass %			
	Ni	Cu	Co	Fe
Matte into leach:	4,00	2,16	0,197	58,4
Solids ex preg. liq.:	1,34	0,751	0,083	33,5
Solids ex samples:	1,51	1,05	0,092	36,9
Misc. solids out:				

Masses recorded:

Matte into leach : 10,00 grams
Solids ex preg. liq.: 2,78 grams
Solids ex samples : 1,42 grams
Misc. solids out : zero

Mass balance for leach: 7

Into leach

Matte in

Liquor in

Therefore: total in

Ex leach

Solids ex preg. liq.

Solids ex samples

Misc. solids out

Pregnant liquor

Wash A liquor

Wash B liquor

Samples

Therefore: total out

Mass balance, % (Out/In)

% extraction

Mass, mg			Mass, g
Ni	Cu	Co	Fe
400	216	19,7	5,84
55,1	2,3	12,75	166,61
455,1	218,3	32,45	172,45
37,3	20,9	2,31	0,93
21,4	14,9	1,31	0,52
347,0	164,1	25,02	140,96
2,7	1,5	0,08	1,11
7,0	2,7	0,35	1,41
47,3	21,6	3,46	22,14
462,7	225,7	32,53	167,07
101,7	103,4	100,2	96,9
89,1	88,7	86,3	80,3

Extraction vs. time data for leach: 7

Time, mins.	Per cent extraction			
	Ni	Cu	Co	Fe
0	0	0	0	0
6	34,8	43,6	23,6	18,6
16	53,2	53,6	40,8	28,3
30	65,4	60,4	52,6	35,7
60	74,1	67,0	62,7	44,6
120	79,6	74,9	71,4	53,6
182	82,8	80,0	76,1	59,7
240	84,4	81,5	78,5	63,1
300	86,3	84,4	81,6	66,8
360	87,5	86,5	83,2	70,1
420	89,1	88,7	86,3	72,5

Extraction vs. time data for leach: 7

Time, mins.	Per cent extraction			
	Ni	Cu	Co	Fe
0	0	0	0	0
6	34,8	43,6	23,6	18,6
16	53,2	53,6	40,8	28,3
30	65,4	60,4	52,6	35,7
60	74,1	67,0	62,7	44,6
120	79,6	74,9	71,4	53,6
182	82,8	80,0	76,1	59,7
240	84,4	81,5	78,5	63,1
300	86,3	84,4	81,6	66,8
360	87,5	86,5	83,2	70,1
)	89,1	88,7	86,3	72,5

Raw data for leach: 8 (Liquids)

Time, mins.	Sample vol., ml.	Assay, g/l			Assay, mg/l		
		Fe ³⁺	Fe ²⁺	SO ₄ ⁼	Ni	Cu	Co
0		99,8	0,03	292	33,7	1,42	7,80
6	20,9	99,4	2,93	355,7	119,6	64,1	12,0
15	18,2	99,7	4,20	364,8	162,0	78,9	13,9
30	22,3	97,6	5,30	359,9	194,1	91,6	15,5
60	19,1	97,8	6,30	369,8	216,4	101,8	17,0
120	19,5	96,8	7,55	368,3	231,2	114,8	18,1
180	18,6	96,3	8,40	355,0	241,1	123,7	18,9
240	21,8	97,6	8,95	365,3	246,6	130,9	19,2
300	21,8	96,3	9,48	312,8	255,9	123,5	19,3
360	19,1	96,5	9,95	390,9	256,6	143,2	19,9
420	18,2	96,1	10,15	403,8	259,9	145,9	20,2
1440	19,1	95,0	11,90	390,4	285,0	160,3	21,7
Preg.		93,9	11,7	377,6	278,5	154,1	21,4
Wash A		0,376			1,10	0,531	<0,2
Wash B		0,444			1,95	0,449	<0,2

Volume of liquid into leach : 1,5 litres
Volume of liquid ex leach : 1,23 litres
Wash water volume (Wash A) : 3,00 litres
Wash water volume (Wash B) : 2,5 litres

Raw data for leach: 8 (Potential

Time, mins.	Electrode potential, mV		
	Platinum	Matte	Residue
0	700	505	516
6	579	497	498
15	571	496	493
30	563	493	478
60	556	487	455
120	550	475	436
180	546	463	424
240	544	454	417
300	543	450	413
360	540	441	409
420	538	438	407
1440	530	397	382

All potentials are vs. S.C.E.

Raw data for leach: 8 (Solids)

Solid	Assay, mass %			
	Ni	Cu	Co	Fe
Matte into leach:	4,00	2,21	0,197	58,5
Solids ex preg. liq.:	1,71	0,893	0,097	40,7
Solids ex samples:	1,79	1,14	0,108	52,8
Misc. solids out:				

Masses recorded:

Matte into leach : 10,00 grams
Solids ex preg. liq.: 0,44 grams
Solids ex samples : 1,20 grams
Misc. solids out : zero

Mass balance for leach: 8

Into leach

Matte in

Liquor in

Therefore: total in

Ex leach

Solids ex preg. liq.

Solids ex samples

Misc. solids out

Pregnant liquor

Wash A liquor

Wash B liquor

Samples

Therefore: total out

Mass balance, % (Out/In)

% extraction

Mass, mg			Mass, g
Ni	Cu	Cc	Fe
400	221	19,7	5,85
50,6	2,1	11,7	149,70
450,6	223,1	31,4	155,55
7,52	3,93	0,43	0,18
21,48	13,68	1,30	0,63
342,56	189,54	26,32	129,89
3,30	1,59	<0,6	1,13
4,88	1,12	<0,5	1,11
48,93	25,30	3,88	22,93
428,67	235,16	31,93	155,87
95	105	<105	100,2
97,6	98,0	97,5	95,3

Extraction vs. time data for leach: 8

Time, mins.	Per cent extraction			
	Ni	Cu	Co	Fe
0	0	0	0	0
6	33,4	38,7	29,5	22,5
15	49,8	47,8	42,8	32,5
30	62,3	55,6	54,0	41,2
60	71,0	61,9	64,5	49,2
120	76,7	69,9	72,2	59,5
180	80,6	75,4	77,9	66,5
240	82,7	79,9	80,0	71,1
300	86,3	75,3	80,7	75,6
360	86,6	87,5	84,9	79,3
420	87,9	89,1	87,0	80,9
1440	97,6	98,0	97,5	95,3

Raw data for leach: 9 (Liquids)

Time, mins.	Sample vol., ml.	Assay, g/l			Assay, mg/l		
		Fe ³⁺	Fe ²⁺	SO ₄ ⁼	Ni	Cu	Co
0	-	118	0	351	11,9	1,33	2,82
12	15,0	111	1,5	339	41,7	29,8	3,58
30	15,8	116	2,2	346	67,2	33,7	4,72
63	14,6	115	2,75	343	97,6	38,3	5,85
122	16,7	115	3,40	353	131	45,1	7,54
180	17,9	115	3,75	343	155	50,9	8,62
240	16,7	115	4,04	345	171	54,7	9,31
307	16,7	114	4,30	350	182	57,8	9,95
368	16,7	114	4,40	347	191	60,7	10,2
Preg	-	117	4,42	351	193	62,5	10,5
Wash	-	4,43	-	14,2	6,50	2,20	3,76

Volume of liquid into leach : 1,5 litres
Volume of liquid ex leach : 1,280 litres
Wash water volume : 1,045 litres

Raw data for leach: 9 (Potential)

Time, mins.	Redox potential, mV vs S C E
0	757
6	607
12	593
30	581
63	571
122	566
180	563
240	561
307	560
367	559

Raw data for leach: 9 (Solids)

Solid	Assay, mass %			
	Ni	Cu	Co	Fe
Matte into leach	3,58	2,13	0,20	59,3
Solids ex preg. liq.	1,57	1,30	0,11	49,7
Solids ex samples	2,26	1,56	0,14	52,0

Masses recorded:

Matte into leach : 10,00
 Solids ex preg. liq. : 6,06
 Solids ex samples : 1,01

Sulphur analyses (mass %)

	Total S	Elemental S
Matte into leach	30,4	0
Solids ex preg. liq.	39,8	13,4

Mass balance for leach: 9

Into leach:

Matte in

Liquor in

Therefore: total in

Ex leach:

Solids ex preg. liq.

Solids ex samples

Misc. solids out

Pregnant liquor

Wash liquor

Samples

Therefore: total out

Mass balance, % (Out/In)

Per cent extraction

Mass, mg			Mass, g
Ni	Cu	Co	Fe
358	213	20	5,93
17,9	2,0	4,23	177,0
375,9	215	24,23	182,9
91,1	78,8	6,67	3,0
22,8	15,8	1,41	0,5
-	-	-	-
247,0	80,0	13,44	154,9
6,8	2,3	3,93	4,6
17,2	6,1	0,99	15,3
388,9	183,0	26,44	178,3
103,5	85,1	109,1	97,5
70,9	49,6	59,6	44,4

Extraction vs time data for leach: 9

Time, mins.	Per cent extraction			
	Ni	Cu	Co	Fe
0	0	0	0	0
12	11,7	23,1	5,9	15,6
30	21,6	26,2	14,7	22,8
63	33,6	30,0	23,5	28,3
122	46,6	35,5	36,6	34,7
180	56,0	40,2	45,0	38,0
240	62,3	43,3	50,4	40,8
307	66,6	45,8	55,3	43,4
368	70,1	48,1	57,3	44,3

Raw data for leach: 10 (Liquids)

Time, mins.	Sample vol., ml.	Assay, g/l			Assay, mg/l		
		Fe ³⁺	Fe ²⁺	SO ₄ ⁼	Ni	Cu	Co
0		118	0	361	12,4	2,24	3,15
6	23,3	118	0,04	364	13,5	21,8	2,93
15	18,3	117	0,11	361	15,8	23,8	3,22
31	18,8	117	0,40	361	19,4	26,0	3,24
61	14,6	118	0,79	366	26,7	29,8	3,57
119	21,3	117	1,10	370	36,0	31,7	3,86
173	22,1	117	1,18	370	43,0	32,7	4,14
242	18,8	117	1,33	373	53,4	34,2	4,34
305	26,7	117	1,35	379	56,8	33,4	4,28
380	16,7	118	1,45	366	65,3	33,8	4,63
Preg.	-	115	1,53	351	66,4	33,6	4,44
Wash	-	3,04	-	9,31	21,0	1,75	2,73

Volume of liquid into leach : 1,5 litres

Volume of liquid ex leach : 1,25 litres

Wash water volume : 1,19 litres

Raw data for leach: 10 (Liquids)

Time, mins.	Sample vol., ml.	Assay, g/l			Assay, mg/l		
		Fe ³⁺	Fe ²⁺	SO ₄ ⁼	Ni	Cu	Co
0		118	0	361	12,4	2,24	3,15
6	23,3	118	0,04	364	13,5	21,8	2,93
15	18,3	117	0,11	361	15,8	23,8	3,22
31	18,8	117	0,40	361	19,4	26,0	3,24
61	14,6	118	0,79	366	26,7	29,8	3,57
119	21,3	117	1,10	370	36,0	31,7	3,86
173	22,1	117	1,18	370	43,0	32,7	4,14
242	18,8	117	1,33	373	53,4	34,2	4,34
305	26,7	117	1,35	379	56,8	33,4	4,28
380	16,7	118	1,45	366	65,3	33,8	4,63
Preg.	-	115	1,53	351	66,4	33,6	4,44
Wash	-	3,04	-	9,31	21,0	1,75	2,73

Volume of liquid into leach : 1,5 litres

Volume of liquid ex leach : 1,25 litres

Wash water volume : 1,19 litres

Raw data for leach: 10

Time, mins.	Redox potential, mV vs S C E
0	737
6	640
15	620
31	600
61	580
119,	571
173	566
242	565
305	563
380	562

Raw data for leach: 10 (Solids)

Solid	Assay, mass %			
	Ni	Cu	Co	Fe
Matte into leach	3,55	2,13	0,20	59,1
Solids ex preg. liq. }	2,83	1,62	0,18	56,4
Solids ex samples }				

Masses recorded:

Matte into leach : 10,00 grams
 Solids ex preg. liq. : } 8,94 grams
 Solids ex samples : }

Mass balance for leach: 10

Into leach:

Matte in

Liquor in

Therefore: total in

Ex leach:

Solids ex preg. liq. }
Solids ex samples }

Pregnant liquor

Wash liquor

Samples

Therefore: total out

Mass balance, % (Out/In)

Per cent extraction

Mass, mg			Mass, g
Ni	Cu	Co	Fe
355	213	20	5,91
18,6	3,36	4,73	177,0
373,6	216,4	24,73	182,9
253,0	144,8	16,09	5,04
83,0	42,0	5,55	146,3
25,0	2,08	3,25	3,6
6,7	5,36	0,69	21,3
367,7	194,2	25,58	176,2
94,4	89,8	103,4	96,4
21,1	21,3	9,1	14,7

Extraction vs time data for leach: 10

Time, mins.	Per cent extraction			
	Ni	Cu	Co	Fe
0	0	0	0	0
6	0,4	13,3	0	0
15	1,3	14,6	0,4	0,7
31	2,7	16,1	0,6	3,7
61	5,6	18,7	2,6	7,7
119	9,2	20,0	4,4	10,8
173	12,0	20,7	6,1	11,4
242	16,0	21,7	7,3	12,8
305	17,3	21,2	6,9	13,0
380	20,7	21,4	9,1	13,9

Raw data for leach: 11

Time, mins.	Sample vol., ml.	Assay, g/l			Assay, mg/l		
		Fe ³⁺	Fe ²⁺	SO ₄ ⁼	Ni	Cu	Co
0		101	0	302	8,21	1,21	2,02
15	18,3	79,7	0,05	245	9,37	21,5	0,952
30	18,8	78,4	0,40	241	12,1	22,7	1,01
60	17,9	77,9	0,87	235	18,7	26,2	1,25
120	19,6	77,7	1,64	242	29,3	28,6	1,59
180	18,8	77,7	1,98	236	38,1	30,7	2,22
240	19,2	77,2	2,25	243	45,8	31,8	2,52
300	16,3	77,3	2,43	237	53,2	32,9	2,92
362	18,8	77,6	2,55	237	59,1	32,3	2,74
440	17,9	77,8	2,62	240	67,0	33,2	3,08
Preg		79,4	2,65	247	70,1	35,0	3,39
Wash		1,84		5,37	6,79	0,446	2,66

Volume of liquid into leach : 1,5 litres

Volume of liquid ex leach : 1,30 litres

Wash water volume : 1,10 litres

Raw data for leach: 11

Time, mins.	Sample vol., ml.	Assay, g/l			Assay, mg/l		
		Fe ³⁺	Fe ²⁺	SO ₄ ⁼	Ni	Cu	Co
0		101	0	302	8,21	1,21	2,02
15	18,3	79,7	0,05	245	9,37	21,5	0,952
30	18,8	78,4	0,40	241	12,1	22,7	1,01
60	17,9	77,9	0,87	235	18,7	26,2	1,25
120	19,6	77,7	1,64	242	29,3	28,6	1,59
180	18,8	77,7	1,98	236	38,1	30,7	2,22
240	19,2	77,2	2,25	243	45,8	31,8	2,52
300	16,3	77,3	2,43	237	53,2	32,9	2,92
362	18,8	77,6	2,55	237	59,1	32,3	2,74
440	17,9	77,8	2,62	240	67,0	33,2	3,08
Preg		79,4	2,65	247	70,1	35,0	3,39
Wash		1,84		5,37	6,79	0,446	2,66

Volume of liquid into leach : 1,5 litres

Volume of liquid ex leach : 1,30 litres

Wash water volume : 1,10 litres

Raw data for leach: 11

Time, mins.	Redox potential, mV vs S C E
0	705
6	619
15	598
30	576
60	555
120	540
180	535
240	532
300	531
362	530
440	529

Raw data for leach: 11

Time, mins.	Redox potential, mV vs S C E
0	705
6	619
15	598
30	576
60	555
120	540
180	535
240	532
300	531
362	530
440	529

Raw data for leach: 11 (Solids)

Solid	Assay, mass %			
	Ni	Cu	Co	Fe
Matte into leach	3,59	2,13	0,20	59,3
Solids ex preg. liq.	3,10	1,64	0,18	55,1
Solids ex samples	3,01	1,75	0,18	53,6

Masses recorded:

Matte into leach : 10,00
Solids ex preg. liq. : 7,62
Solids ex samples : 0,79

Mass balance for leach: 11

Into leach:

Matte in

Liquor in

Therefore: total in

Ex leach:

Solids ex preg. liq.

Solids ex samples

Pregnant liquor

Wash liquor

Samples

Therefore: total out

Mass balance, % (Out/In)

Per cent extraction

Mass, mg			Mass, g
Ni	Cu	Co	Fe
359	213	20	5,93
11,4	1,8	2,51	119,6
370,4	214,8	22,51	125,5
236,2	125,0	13,72	4,20
23,8	13,8	1,42	0,42
91,1	45,5	4,41	106,6
7,5	2,9	0,49	2,0
6,1	4,8	0,33	39,7
364,7	192,0	20,37	126,4
98,5	89,4	90,5	100,7
25,6	26,0	14,0	19,9

Extraction vs time data for leach: 11

Time, mins.	Per cent extraction			
	Ni	Cu	Co	Fe
0	0	0	0	0
15	0,5	16,5	0	0,1
30	1,6	17,5	0,4	2,9
60	4,3	20,3	1,7	6,5
120	8,7	22,3	3,7	12,5
180	12,4	24,0	7,3	15,1
240	15,5	24,9	9,0	17,1
300	18,6	25,8	11,3	18,4
362	21,0	25,3	10,3	19,3
440	24,3	26,0	12,2	19,7

APPENDIX III

Results of redox potential measuring experiments.

- a) Raw data
- b) Printouts of measured vs predicted values

a) Raw data

Experiment A (90°C)

Measured potential, mV	Total concentrations, gmol l^{-1}			
	Fe^{3+}	Fe^{2+}	H^+	$\text{SO}_4^{=}$
630	1,703	0,013	1,757	3,446
609	1,692	0,026	1,764	3,446
585	1,678	0,050	1,779	3,456
563	1,692	0,099	1,637	3,456
537	1,694	0,197	1,457	3,467
508	1,642	0,383	1,324	3,508

Experiment B (90°C)

Measured potential, mV	Total concentrations, gmol l^{-1}			
	Fe^{3+}	Fe^{2+}	H^+	$\text{SO}_4^{=}$
636	1,866	0,014	1,286	3,456
614	1,828	0,029	1,412	3,477
588	1,794	0,057	1,457	3,477
565	1,764	0,117	1,408	3,467
538	1,683	0,235	1,456	3,487
507	1,552	0,458	1,442	3,508
460	1,223	0,951	1,404	3,487

Redox potential measurements at 22°C

Solution compositions and measured potentials

Solution	Concentration, gmol/litre				Redox potential, mV
	Fe ³⁺	H ⁺	SO ₄ ⁼	Fe ²⁺	
A1	0,010	0,204	0,127	0,010	435
A2	0,099	0,204	0,260	0,010	487
A3	0,990	0,204	1,597	0,010	542
A4	0,010	0,204	0,215	0,099	372
A5	0,099	0,204	0,350	0,099	423
A6	0,990	0,204	1,686	0,099	481
A7	0,010	0,204	1,107	0,990	310
A8	0,099	0,204	1,241	0,990	357
A9	0,990	0,204	2,578	0,990	420
B1	0,010	2,041	1,045	0,010	427
B2	0,099	2,041	1,178	0,010	484
B3	0,990	2,041	2,515	0,010	539
B4	0,010	2,041	1,134	0,099	370
B5	0,099	2,041	1,268	0,099	425
B6	0,990	2,041	2,605	0,099	483
B7	0,010	2,041	2,025	0,990	311
B8	0,099	2,041	2,159	0,990	365
B9	0,990	2,041	3,496	0,990	428

PREDICTED AND CALCULATED SOLUTION MEMOX POTENTIALS

PUMP	MEASURED	LIN. JR.	CORRECTED	EMIAL. RATIO	BEST LINE	WEKNST EDN. (EMPIRICAL)	WEKNST EDN. (THEORETICAL)	IONIC STRENGTH
1	601.	7.	686.	.000	683.	683.	161.	.42
2	733.	6.	739.	-2.293	741.	741.	825.	1.09
3	708.	1.	790.	-4.595	800.	799.	884.	7.77
4	610.	6.	624.	2.293	624.	623.	709.	.77
5	609.	5.	673.	.000	683.	683.	767.	1.45
6	727.	1.	724.	-2.303	742.	741.	825.	8.13
7	550.	3.	559.	4.545	505.	506.	650.	4.34
8	603.	2.	606.	2.303	624.	624.	708.	5.01
9	600.	0.	607.	.000	683.	683.	767.	11.69
10	673.	22.	695.	.000	683.	683.	767.	3.18
11	730.	21.	731.	-2.293	741.	741.	825.	3.84
12	705.	10.	881.	-4.595	800.	799.	884.	10.53
13	610.	22.	637.	2.293	624.	625.	709.	5.53
14	671.	21.	642.	.000	683.	683.	767.	4.20
15	724.	16.	745.	-2.303	742.	741.	825.	10.88
16	557.	18.	575.	4.545	565.	566.	650.	7.10
17	611.	18.	629.	2.303	624.	624.	708.	7.76
18	674.	14.	688.	.000	683.	683.	767.	14.45

EQUATIONS FITTED TO THE EXPERIMENTAL RESULTS :

	INTERCEPT, MILLIVOLTS	SLOPE, MILLIVOLTS	AVE. ERROR MILLIVOLTS	MAX. ERROR MILLIVOLTS
BEST STRAIGHT LINE :	602.7	-25.36	9.7	18.1
EMPIRICAL NERNST EQUATION :	602.7	-25.39	9.6	18.5
THEORETICAL NERNST EQUATION :	606.0	-25.39	84.0	102.6

TOTAL CONCENTRATION RATIO USED (22 °C)

PREDICTED AND CALCULATED SOLUTION REDOX POTENTIALS

POINT	MEASURED	LIN. JN.	CORRECTED	INITIAL RATIO	BEST LINE	NERNST EON. (EMPIRICAL)	NERNST EON. (THEORETICAL)	IONIC STRENGTH
1	661.	7.	686.	.000	683.	683.	767.	.42
2	733.	6.	734.	-2.293	741.	741.	825.	1.09
3	788.	1.	790.	-4.595	800.	799.	884.	7.77
4	618.	6.	624.	2.243	624.	625.	709.	.77
5	609.	5.	675.	.000	683.	683.	767.	1.45
6	727.	1.	724.	-2.303	742.	741.	825.	8.13
7	556.	3.	554.	4.545	565.	566.	650.	4.34
8	603.	2.	606.	2.303	624.	624.	708.	5.01
9	666.	0.	667.	.000	683.	683.	767.	11.69
10	673.	22.	645.	.000	683.	683.	767.	3.18
11	730.	21.	751.	-2.293	741.	741.	825.	3.84
12	765.	16.	801.	-4.595	800.	799.	884.	10.53
13	610.	22.	637.	2.243	624.	625.	709.	4.53
14	671.	21.	642.	.000	683.	683.	767.	4.20
15	724.	16.	745.	-2.303	742.	741.	825.	10.88
16	557.	18.	575.	4.545	565.	566.	650.	7.10
17	611.	18.	624.	2.303	624.	624.	708.	7.76
18	674.	14.	686.	.000	683.	683.	767.	14.45

EQUATIONS FITTED TO THE EXPERIMENTAL RESULTS :

	INTERCEPT, MILLIVOLTS	SLOPE, MILLIVOLTS	AVE. ERROR MILLIVOLTS	MAX. ERROR MILLIVOLTS
BEST STRAIGHT LINE :	662.7	-25.36	4.7	18.1
EMPIRICAL NERNST EQUATION :	662.7	-25.34	4.6	18.5
THEORETICAL NERNST EQUATION :	766.6	-25.34	84.6	102.6

TOTAL CONCENTRATION RATIO USED (22 °C)

CONCENTRATIONS IN SOLUTION, GMOL/LITRE

POINT	FE(3+)	H+	SO4(2-)	FE(2+)	FEHSO4SO4	FEHSO4(2+)	FEHSO4SO4-	FEHSO4+	HSO4-	FEHSO4	FEHSO4+
1	.0100	.2040	.1270	.0100	.0000	.0000	.0000	.0000	.0000	.0000	.0000
2	.0990	.2040	.2600	.0100	.0000	.0000	.0000	.0000	.0000	.0000	.0000
3	.9900	.2040	1.5970	.0100	.0000	.0000	.0000	.0000	.0000	.0000	.0000
4	.0100	.2040	.2150	.0990	.0000	.0000	.0000	.0000	.0000	.0000	.0000
5	.0990	.2040	.3500	.0990	.0000	.0000	.0000	.0000	.0000	.0000	.0000
6	.9900	.2040	1.6860	.0990	.0000	.0000	.0000	.0000	.0000	.0000	.0000
7	.0100	.2040	1.1070	.9900	.0000	.0000	.0000	.0000	.0000	.0000	.0000
8	.0990	.2040	1.2410	.9900	.0000	.0000	.0000	.0000	.0000	.0000	.0000
9	.9900	.2040	2.5780	.9900	.0000	.0000	.0000	.0000	.0000	.0000	.0000
10	.0100	2.0410	1.0450	.0100	.0000	.0000	.0000	.0000	.0000	.0000	.0000
11	.0990	2.0410	1.1780	.0100	.0000	.0000	.0000	.0000	.0000	.0000	.0000
12	.9900	2.0410	2.5150	.0100	.0000	.0000	.0000	.0000	.0000	.0000	.0000
13	.0100	2.0410	1.1340	.0990	.0000	.0000	.0000	.0000	.0000	.0000	.0000
14	.0990	2.0410	1.2680	.0990	.0000	.0000	.0000	.0000	.0000	.0000	.0000
15	.9900	2.0410	2.6050	.0990	.0000	.0000	.0000	.0000	.0000	.0000	.0000
16	.0100	2.0410	2.0250	.9900	.0000	.0000	.0000	.0000	.0000	.0000	.0000
17	.0990	2.0410	2.1540	.9900	.0000	.0000	.0000	.0000	.0000	.0000	.0000
18	.9900	2.0410	3.4960	.9900	.0000	.0000	.0000	.0000	.0000	.0000	.0000

VALUES OF EQUILIBRIUM CONSTANTS USED

TEMPERATURE : 22.066 C

REACTION 1 : 0.000E-01
 REACTION 2 : 0.000E-01
 REACTION 3 : 0.000E-01
 REACTION 4 : 0.000E-01
 REACTION 5 : 0.000E-01
 REACTION 6 : 0.000E-01
 REACTION 7 : 0.000E-01

TOTAL CONCENTRATION RATIO USED (22 °C)

PREDICTED AND CALCULATED SOLUTION REDOX POTENTIALS

POINT	MEASURED	LIO. JN.	CORRECTED	LN(ACT. RATIO)	BEST LINE	NERNST EQN. (EMPIRICAL)	NERNST EQN. (THEORETICAL)	IONIC STRENGTH
1	661.	0.	667.	1.025	703.	704.	726.	.24
2	733.	5.	736.	-0.320	752.	753.	775.	.39
3	788.	2.	791.	-1.481	781.	783.	804.	1.63
4	610.	4.	623.	4.372	634.	634.	656.	.48
5	669.	4.	673.	2.300	686.	687.	708.	.61
6	727.	2.	730.	.859	723.	723.	745.	1.81
7	556.	1.	557.	1.134	550.	549.	570.	2.16
8	603.	1.	604.	5.473	607.	606.	628.	2.25
9	666.	1.	667.	3.393	659.	659.	681.	3.15
10	673.	17.	689.	2.081	692.	692.	714.	1.24
11	730.	16.	746.	-0.148	748.	749.	771.	1.34
12	765.	11.	796.	-1.918	792.	794.	816.	2.18
13	616.	16.	631.	4.464	632.	632.	653.	1.42
14	671.	15.	686.	2.233	688.	688.	710.	1.51
15	729.	10.	739.	.433	733.	734.	756.	2.33
16	557.	9.	565.	1.396	558.	557.	579.	2.92
17	611.	8.	619.	5.138	615.	614.	636.	2.99
18	674.	0.	680.	3.115	686.	686.	688.	3.65

EQUATIONS FITTED TO THE EXPERIMENTAL RESULTS :

	INTERCEPT, MILLIVOLTS	SLOPE, MILLIVOLTS	AVE. ERROR MILLIVOLTS	MAX. ERROR MILLIVOLTS
BEST STRAIGHT LINE :	744.2	-25.13	8.7	16.4
EMPIRICAL NERNST EQUATION :	744.9	-25.39	8.8	16.6
THEORETICAL NERNST EQUATION :	706.8	-25.39	23.6	38.5

UNCOMPLEXED CONCENTRATION RATIO USED (22°C)

COMPLEXES PRESENT : FeSO_4^+ ; HSO_4^- ; FeSO_4^0

CONCENTRATION QUOTIENTS EX LITERATURE

CONCENTRATIONS IN SOLUTION, GMOL/LITRE

POINT	FE(3+)	H+	SO4(2-)	FE(2+)	FEH2O4SO4	FEHSO4(2+)	FE2O4SO4=	FE2O4+	H2SO4-	FE2O4	FEHSO4+
1	.0010	.1346	.0536	.0042	.0000	.0000	.0000	.0082	.0644	.0008	.0000
2	.0120	.1177	.0853	.0087	.0000	.0000	.0000	.0870	.0864	.0013	.0000
3	.0246	.0409	.4624	.0056	.0000	.0000	.0000	.9659	.1631	.0044	.0000
4	.0011	.1104	.0983	.0848	.0000	.0000	.0000	.0089	.0935	.0142	.0000
5	.0081	.0954	.1322	.0809	.0000	.0000	.0000	.0409	.1086	.0182	.0000
6	.0225	.0381	.5061	.0532	.0000	.0000	.0000	.9675	.1654	.0458	.0000
7	.0002	.0394	.4848	.5428	.0000	.0000	.0000	.0098	.1646	.4474	.0000
8	.0022	.0375	.5152	.5280	.0000	.0000	.0000	.0968	.1665	.4624	.0000
9	.0137	.0248	.8343	.4081	.0000	.0000	.0000	.9763	.1792	.5823	.0000
10	.0011	1.1038	.0986	.0086	.0000	.0000	.0000	.0089	.9366	.0014	.0000
11	.0098	1.0601	.1074	.0085	.0000	.0000	.0000	.0892	.9800	.0015	.0000
12	.0442	.6937	.2255	.0072	.0000	.0000	.0000	.9408	1.3465	.0028	.0000
13	.0010	1.0424	.1112	.0832	.0000	.0000	.0000	.0090	.9980	.0157	.0000
14	.0088	1.0002	.1208	.0821	.0000	.0000	.0000	.0901	1.0402	.0169	.0000
15	.0453	.6541	.2461	.0698	.0000	.0000	.0000	.9447	1.3860	.0292	.0000
16	.0004	.6101	.2723	.6768	.0000	.0000	.0000	.0096	1.4301	.5132	.0000
17	.0034	.5879	.2871	.6653	.0000	.0000	.0000	.0951	1.4531	.3247	.0000
18	.0246	.4088	.4630	.5537	.0000	.0000	.0000	.9654	1.6314	.4363	.0000

VALUES OF EQUILIBRIUM CONSTANTS USED

TEMPERATURE : 22.DEG C

REACTION 1 : 0.000E-01
 REACTION 2 : 0.000E-01
 REACTION 3 : 0.000E-01
 REACTION 4 : 8.479E 01
 REACTION 5 : 8.009E 00
 REACTION 6 : 1.700E 00
 REACTION 7 : 0.000E-01

UNCOMPLEXED CONCENTRATION RATIO USED (22°C)

COMPLEXES PRESENT : $FeSO_4^+$; $H2SO_4^-$; $FeSO_4^0$

CONCENTRATION QUOTIENTS EX LITERATURE

PREDICTED AND CALCULATED SOLUTION REDOX POTENTIALS

POINT	MEASURED	LIQ. JN.	CORRECTED	LN(ACT. RATIO)	BEST LINE	NEERNST EQN. (EMPIRICAL)	NEERNST EQN. (THEORETICAL)	IONIC STRENGTH
1	681.	6.	687.	1.648	701.	702.	725.	.24
2	733.	5.	730.	-1.505	751.	751.	775.	.39
3	788.	2.	791.	-1.496	781.	782.	805.	1.67
4	618.	4.	623.	4.368	633.	633.	656.	.47
5	669.	4.	673.	2.295	685.	685.	709.	.61
6	727.	2.	729.	.841	722.	722.	745.	1.84
7	556.	0.	557.	7.115	549.	548.	571.	2.13
8	603.	1.	604.	5.455	606.	605.	628.	2.21
9	660.	1.	667.	3.377	658.	658.	681.	3.15
10	673.	17.	689.	2.104	690.	690.	713.	1.24
11	730.	16.	745.	-1.137	746.	747.	770.	1.36
12	765.	9.	794.	-1.474	793.	794.	817.	2.41
13	616.	16.	631.	4.449	631.	631.	654.	1.36
14	671.	15.	686.	2.208	687.	687.	711.	1.48
15	729.	8.	737.	.360	734.	734.	758.	2.52
16	557.	8.	565.	7.228	561.	560.	583.	2.48
17	611.	8.	618.	4.976	618.	617.	640.	2.58
18	674.	4.	676.	2.992	668.	668.	691.	3.54

EQUATIONS FITTED TO THE EXPERIMENTAL RESULTS :

	INTERCEPT, MILLIVOLTS	SLOPE, MILLIVOLTS	AVE. ERROR MILLIVOLTS	MAX. ERROR MILLIVOLTS
BEST STRAIGHT LINE :	743.0	-25.18	7.7	14.5
EMPIRICAL NEERNST EQUATION :	743.5	-25.39	7.8	14.7
THEORETICAL NEERNST EQUATION :	766.6	-25.39	24.6	38.0

UNCOMPLEXED CONCENTRATION RATIO USED (22°C)

COMPLEXES PRESENT : FeHSO_4^{2+} ; FeSO_4^+ ; HSO_4^- ; FeSO_4^0 ; FeHSO_4^+

CONCENTRATION QUOTIENTS EX LITERATURE

CONCENTRATIONS IN SOLUTION, GMOL/LITRE

POINT	FE(3+)	H+	SO4(2-)	FE(2+)	FEHSO4SO4	FEHSO4(2+)	FESO4SO4-	FESO4+	HSO4-	FESO4	FEHSO4+
1	.0017	.1390	.0535	.0089	.0000	.0006	.0000	.0077	.0640	.0008	.0003
2	.0113	.1141	.0861	.0084	.0000	.0050	.0000	.0827	.0846	.0012	.0004
3	.0255	.0364	.4762	.0055	.0000	.0182	.0000	.9488	.1491	.0043	.0005
4	.0010	.1083	.0974	.0811	.0000	.0005	.0000	.0085	.0908	.0134	.0044
5	.0077	.0911	.1326	.0769	.0000	.0042	.0000	.0871	.1040	.0175	.0048
6	.0216	.0334	.5190	.0502	.0000	.0168	.0000	.9521	.1494	.0443	.0045
7	.0002	.0311	.4919	.5167	.0000	.0002	.0000	.0096	.1316	.4321	.0411
8	.0021	.0295	.5236	.5026	.0000	.0015	.0000	.0454	.1328	.4474	.0403
9	.0133	.0192	.8578	.3693	.0000	.0098	.0000	.9669	.1417	.5677	.0333
10	.0007	1.1009	.0985	.0058	.0000	.0034	.0000	.0059	.9335	.0010	.0033
11	.0065	1.0328	.1094	.0056	.0000	.0326	.0000	.0599	.9723	.0010	.0033
12	.0322	.5442	.2730	.0045	.0000	.2134	.0000	.7445	1.2791	.0021	.0035
13	.0007	1.0321	.1094	.0558	.0000	.0033	.0000	.0061	.9721	.0104	.0328
14	.0000	.9665	.1213	.0545	.0000	.0314	.0000	.0616	1.0093	.0112	.0332
15	.0503	.5103	.2947	.0434	.0000	.2033	.0000	.7564	1.2944	.0217	.0339
16	.0003	.5083	.2749	.4512	.0000	.0020	.0000	.0076	1.2028	.2106	.3278
17	.0030	.4771	.2967	.4419	.0000	.0193	.0000	.0767	1.2184	.2228	.3252
18	.0181	.2824	.5518	.3602	.0000	.1259	.0000	.8461	1.3416	.3379	.2919

VALUES OF EQUILIBRIUM CONSTANTS USED

TEMPERATURE : 22.DEG C

REACTION 1 :	0.000E-01
REACTION 2 :	4.466E 01
REACTION 3 :	0.000E-01
REACTION 4 :	8.479E 01
REACTION 5 :	8.609E 00
REACTION 6 :	1.700E 00
REACTION 7 :	5.200E 00

UNCOMPLEXED CONCENTRATION RATIO USED (22°C)

COMPLEXES PRESENT : FeHSO_4^{2+} ; FeSO_4^+ ; HSO_4^- ; FeSO_4^0 ; FeHSO_4^+

CONCENTRATION QUOTIENTS EX LITERATURE

PREDICTED AND CALCULATED SOLUTION REDOX POTENTIALS

POINT	MEASURED	LID. JN.	CORRECTED	LN(ACT. RATIO)	BEST LINE	NEHRNST EQN. (EMPIRICAL)	NEHRNST EQN. (THEORETICAL)	IONIC STRENGTH
1	681.	6.	687.	2.056	711.	717.	715.	.23
2	733.	5.	738.	-0.024	757.	769.	767.	.32
3	788.	2.	791.	-1.787	745.	814.	812.	.95
4	818.	4.	823.	5.056	646.	640.	638.	.46
5	869.	4.	873.	2.833	694.	697.	695.	.52
6	727.	2.	729.	.706	741.	751.	749.	1.09
7	556.	0.	557.	4.504	549.	527.	525.	2.12
8	603.	0.	604.	1.173	600.	507.	585.	2.14
9	666.	0.	668.	4.458	659.	656.	654.	2.47
10	673.	17.	689.	3.312	684.	685.	683.	1.23
11	730.	16.	746.	1.028	734.	743.	741.	1.24
12	785.	13.	797.	-1.204	782.	749.	797.	1.44
13	818.	16.	831.	5.718	632.	624.	622.	1.35
14	671.	15.	686.	3.430	681.	682.	680.	1.37
15	729.	12.	741.	1.142	730.	739.	737.	1.55
16	557.	8.	565.	4.628	554.	540.	538.	2.47
17	611.	8.	619.	0.737	609.	598.	596.	2.49
18	674.	6.	680.	4.546	660.	657.	655.	2.67

EQUATIONS FITTED TO THE EXPERIMENTAL RESULTS :

	INTERCEPT, MILLIVOLTS	SLOPE, MILLIVOLTS	AVE. ERROR MILLIVOLTS	MAX. ERROR MILLIVOLTS
BEST STRAIGHT LINE :	756.0	-21.77	13.4	24.2
EMPIRICAL NEHRNST EQUATION :	768.8	-25.54	19.3	31.0
THEORETICAL NEHRNST EQUATION :	766.8	-25.54	19.4	31.5

UNCOMPLEXED CONCENTRATION RATIO USED (22°C)

COMPLEXES PRESENT : FeHSO_4^0 ; FeHSO_4^{2+} ; $\text{Fe}(\text{SO}_4)_2^-$; FeSO_4^+ ;
 HSO_4^- ; FeSO_4^0 ; FeHSO_4^+

CONCENTRATION QUOTIENTS EX LITERATURE

CONCENTRATIONS IN SOLUTION, GMOL/LITRE

POINT	FE(3+)	H+	SO4(2+)	FE(2+)	FEHSO4SO4	FEHSO4(2+)	FEHSO4SO4-	FEHSO4+	H2SO4-	FEHSO4	FEHSO4+
1	.0011	.1402	.0514	.0089	.0010	.0004	.0025	.0050	.0621	.0008	.0003
2	.0009	.1236	.0625	.0037	.0104	.0031	.0293	.0473	.0665	.0009	.0004
3	.0046	.0613	.1012	.0083	.0751	.0137	.4256	.4254	.0534	.0014	.0003
4	.0005	.1095	.0942	.0816	.0012	.0002	.0034	.0042	.0887	.0131	.0044
5	.0048	.0999	.1001	.0810	.0115	.0021	.0401	.0405	.0861	.0138	.0042
6	.0395	.0563	.1185	.0800	.0755	.0118	.4658	.3973	.0575	.0161	.0028
7	.0000	.0313	.4868	.5194	.0007	.0000	.0077	.0016	.1310	.4298	.0411
8	.0004	.03.0	.4718	.5270	.0007	.0003	.0754	.0162	.1259	.4227	.0401
9	.0070	.0280	.3499	.6014	.0578	.0031	.7154	.2068	.0845	.3577	.0307
10	.0002	1.1043	.0975	.0058	.0053	.0010	.0017	.0017	.4265	.0010	.0032
11	.0021	1.0661	.0990	.0058	.0525	.0098	.0171	.0175	.9085	.0010	.0032
12	.0204	.7511	.1135	.0061	.4757	.0776	.2200	.1961	.7337	.0012	.0027
13	.0002	1.0357	.1083	.0560	.0054	.0009	.0018	.0017	.9657	.0103	.0327
14	.0018	.9943	.1101	.0563	.0530	.0089	.0144	.0169	.9469	.0105	.0322
15	.0160	.7071	.1246	.0543	.4769	.0708	.2343	.1901	.7586	.0126	.0272
16	.0001	.5104	.2725	.4526	.0050	.0003	.0034	.0013	1.1973	.2097	.3273
17	.0005	.4961	.2740	.4556	.0486	.0033	.0340	.0126	1.1701	.2122	.3220
18	.0000	.3880	.2760	.4886	.4297	.0288	.3847	.1409	.9219	.2292	.2720

VALUES OF EQUILIBRIUM CONSTANTS USED

TEMPERATURE : 22.0 DEG C

REACTION 1 : 2.414E 03
 REACTION 2 : 4.466E 01
 REACTION 3 : 8.386E 02
 REACTION 4 : 8.479E 01
 REACTION 5 : 6.609E 00
 REACTION 6 : 1.700E 00
 REACTION 7 : 5.200E 00

UNCOMPLEXED CONCENTRATION RATIO USED (22°C)

COMPLEXES PRESENT : $\text{FeHSO}_4\text{SO}_4^0$; FeHSO_4^{2+} ; $\text{Fe}(\text{SO}_4)_2^-$; FeSO_4^+ ;
 HSO_4^- ; FeSO_4^0 ; FeHSO_4^+

CONCENTRATION QUOTIENTS EX LITERATURE

PREDICTED AND CALCULATED SUBSTITUTED MEDIA POTENTIALS

POINT	MEASURED	LIO. JR.	CORRECTED EMF ACT. RATIO	BEST LINE	WERNST EOR. (EMPIRICAL)	WERNST EOR. (THEORETICAL)	IONIC STRENGTH
1	681.	5.	687.	696.	696.	696.	.20
2	733.	5.	738.	747.	746.	746.	.50
3	758.	2.	791.	785.	784.	784.	1.47
4	818.	4.	823.	828.	829.	829.	.56
5	809.	4.	873.	882.	882.	882.	.45
6	727.	2.	729.	726.	726.	726.	1.54
7	530.	1.	558.	554.	554.	554.	1.23
8	883.	1.	885.	811.	812.	812.	1.28
9	808.	1.	888.	886.	886.	886.	2.09
10	873.	16.	889.	889.	889.	889.	1.15
11	730.	16.	740.	746.	746.	746.	1.21
12	765.	11.	790.	794.	794.	794.	1.84
13	816.	16.	831.	829.	829.	829.	1.28
14	871.	15.	888.	886.	886.	886.	1.34
15	724.	10.	759.	735.	735.	735.	1.44
16	537.	10.	567.	560.	561.	561.	2.22
17	811.	10.	821.	818.	819.	819.	2.25
18	874.	7.	881.	872.	872.	872.	2.86

EQUATIONS FITTED TO THE EXPERIMENTAL RESULTS :

	INTERCEPT, MILLIVOLTS	SLOPE, MILLIVOLTS	APL. ERROR MILLIVOLTS	MAX. ERROR MILLIVOLTS
BEST STRAIGHT LINE :	767.3	-25.53	5.5	4.2
EMPIRICAL WERNST EQUATION :	700.9	-25.59	5.4	4.1
THEORETICAL WERNST EQUATION :	700.0	-25.59	5.4	4.1

UNCOMPLEXED CONCENTRATION RATIO USED (22°C)

COMPLEXES PRESENT : FeSO_4^+ ; H_2SO_4^- ; FeSO_4

CONCENTRATION QUOTIENTS FOUND BY REGRESSION

CONCENTRATIONS IN SOLUTION, GRAMS/LITER

POINT	FE(5+)	H+	SU4(2-)	FE(2+)	FEHSO4SU4	FEHSO4(2+)	FEHSO4SU4-	FEHSO4+	H5O4-	FE5O4	FEHSO4+
1	.0005	.1264	.0575	.0075	.0000	.0000	.0000	.0695	.0777	.0025	.0000
2	.0024	.1051	.0594	.0000	.0000	.0000	.0000	.0961	.1010	.0034	.0000
3	.0042	.0255	.0242	.0000	.0000	.0000	.0000	.0858	.1786	.0079	.0000
4	.0003	.0990	.0649	.0000	.0000	.0000	.0000	.0097	.1051	.0358	.0000
5	.0020	.0830	.0884	.0000	.0000	.0000	.0000	.0970	.1210	.0433	.0000
6	.0040	.0247	.0413	.0000	.0000	.0000	.0000	.0860	.1794	.0788	.0000
7	.0001	.0396	.2513	.0000	.0000	.0000	.0000	.0099	.1643	.0815	.0000
8	.0000	.0369	.2745	.0000	.0000	.0000	.0000	.0984	.1672	.0000	.0000
9	.0031	.0194	.5779	.0000	.0000	.0000	.0000	.0869	.1846	.0275	.0000
10	.0003	1.0639	.0557	.0000	.0000	.0000	.0000	.0097	.9764	.0033	.0000
11	.0024	1.0221	.0604	.0000	.0000	.0000	.0000	.0961	1.0181	.0035	.0000
12	.0153	.6393	.1329	.0000	.0000	.0000	.0000	.9767	1.4007	.0034	.0000
13	.0003	1.0122	.0616	.0000	.0000	.0000	.0000	.0097	1.0279	.0348	.0000
14	.0020	.9710	.0667	.0000	.0000	.0000	.0000	.0964	1.0684	.0360	.0000
15	.0124	.6090	.1423	.0000	.0000	.0000	.0000	.9776	1.4306	.0550	.0000
16	.0001	.5676	.1247	.0000	.0000	.0000	.0000	.0099	1.3726	.5178	.0000
17	.0613	.6425	.1520	.0000	.0000	.0000	.0000	.0977	1.3985	.5318	.0000
18	.0070	.4226	.2522	.0000	.0000	.0000	.0000	.9824	1.6184	.6645	.0000

VALUES OF EQUILIBRIUM CONSTANTS USED

TEMPERATURE : 22.066 C

REACTION 1 : 0.000E-01
REACTION 2 : 0.000E-01
REACTION 3 : 0.000E-01
REACTION 4 : 5.547E 02
REACTION 5 : 1.044E 01
REACTION 6 : 6.001E 00
REACTION 7 : 0.000E-01

UNCOMPLEXED CONCENTRATION RATIO USED (22°C)

COMPLEXES PRESENT : FeSO_4^+ ; H5O_4^+ ; FeSO_4^0

CONCENTRATION QUOTIENTS FOUND BY REGRESSION

PREDICTED AND CALCULATED SOLUTION MEDIA POTENTIALS

POINT	MEASURED	LID. JN.	CORRECTED EMF ACT. NATIOJ	BEST LINE	MEANSI EMF. (EMPIRICAL)	NEKMSI EMF. (THEORETICAL)	IONIC STRENGTH
1	681.	5.	5.251	685.	685.	684.	.19
2	733.	5.	1.144	738.	738.	738.	.32
3	786.	3.	792.	786.	786.	786.	1.78
4	618.	5.	623.	622.	622.	622.	.36
5	609.	4.	674.	677.	677.	677.	.49
6	727.	3.	738.	728.	728.	727.	1.91
7	750.	2.	755.	754.	754.	753.	1.76
8	683.	2.	685.	687.	687.	686.	1.67
9	686.	2.	688.	690.	690.	690.	3.07
10	673.	18.	675.	677.	677.	677.	1.55
11	730.	17.	732.	738.	738.	738.	1.71
12	705.	13.	707.	708.	708.	707.	3.42
13	615.	17.	617.	619.	619.	619.	1.63
14	671.	17.	673.	675.	675.	675.	1.79
15	724.	13.	726.	728.	728.	728.	3.49
16	557.	12.	559.	561.	561.	561.	2.49
17	611.	12.	613.	615.	615.	615.	2.65
18	674.	19.	676.	678.	678.	678.	4.23

EQUATIONS FILLED IN THE EXPERIMENTAL RESULTS

BEST STRAIGHT LINE	INTERCEPT, MILLIVOLTS	SLOPE, MILLIVOLTS	AVE. ERROR MILLIVOLTS	MAX. ERROR MILLIVOLTS
EMPIRICAL MEANSI EQUATION	707.2	-25.54	3.0	6.4
THEORETICAL MEANSI EQUATION	707.9	-25.54	3.0	6.3
	706.6	-25.59	3.0	5.9

ACTIVITY COEFFICIENTS USED (22°C)

COMPLEXES PRESENT : FeHSO_4^{2+} ; FeSO_4^+ ; HSO_4^- ; FeSO_4^0 ; FeHSO_4^+

CONCENTRATIONS IN SOLUTION, GMOL/LITRE

POINT	FE(3+)	H+	SO4(2-)	FE(2+)	FEHSO4SO4	FEHSO4(2+)	FEHSO4SO4-	FEHSO4+	HSO4-	FEHSO4	FEHSO4+
1	.0000	.1254	.0360	.0054	.0000	.0003	.0000	.0091	.0767	.0051	.0011
2	.0044	.1104	.0710	.0052	.0000	.0032	.0000	.0915	.0894	.0057	.0011
3	.0212	.0837	.0309	.0033	.0000	.0292	.0000	.9400	.0896	.0053	.0014
4	.1085	.1085	.0745	.0524	.0000	.0003	.0000	.0092	.0843	.0357	.0109
5	.0030	.0994	.1133	.0479	.0000	.0030	.0000	.0922	.0903	.0348	.0114
6	.0208	.0793	.0657	.0327	.0000	.0279	.0000	.9417	.0836	.0531	.0133
7	.0003	.0501	.4344	.0350	.0000	.0002	.0000	.0095	.0524	.5117	.0434
8	.0024	.0508	.4775	.0355	.0000	.0176	.0000	.0946	.0517	.5211	.0935
9	.0102	.0483	.0800	.0105	.0000	.0031	.0000	.9543	.0453	.5072	.0927
10	.0003	1.2588	.2561	.0019	.0000	.0302	.0000	.0060	.7714	.0016	.0064
11	.0020	1.2291	.2975	.0018	.0000	.2755	.0000	.0663	.7757	.0017	.0065
12	.0100	1.0103	.7817	.0013	.0000	.0030	.0000	.6990	.7492	.0020	.0067
13	.0003	1.2105	.2808	.0188	.0000	.0000	.0000	.0067	.7638	.0166	.0635
14	.0025	1.1017	.5234	.0170	.0000	.0294	.0000	.0671	.7664	.0172	.0635
15	.0157	.9743	.0102	.0127	.0000	.2607	.0000	.7060	.7332	.0205	.0658
16	.0042	.8165	.0653	.0127	.0000	.0023	.0000	.0075	.6244	.2273	.5978
17	.0014	.8017	.6128	.1607	.0000	.0226	.0000	.0743	.6186	.2308	.5486
18	.0142	.6715	1.0895	.1340	.0000	.2049	.0000	.7713	.5740	.2641	.5916

VALUES OF EQUILIBRIUM CONSTANTS USED

TEMPERATURE : 22.000 C

REACTION 1 : 0.000E-01
REACTION 2 : 1.701E-03
REACTION 3 : 0.000E-01
REACTION 4 : 9.309E-03
REACTION 5 : 3.707E-01
REACTION 6 : 1.203E-02
REACTION 7 : 5.035E-02

ACTIVITY COEFFICIENTS USED (22°C)
COMPLEXES PRESENT : FeHSO_4^{1+} ; FeSO_4^{2+} ; HSO_4^- ; FeSO_4^0 ; FeHSO_4^+

CONCENTRATIONS IN SOLUTION, MOLES/LITRE

POINT	FE (3+)	H+	SO4 (2-)	FE (2+)	FEHSO4SO4	FEHSO4 (2+)	FEHSO4SO4-	FE3O4+	HSO4-	FE3O4	FEHSO4+
1	.0000	.1259	.0360	.0059	.0000	.0003	.0000	.0091	.0767	.0051	.0011
2	.0044	.1104	.0710	.0052	.0000	.0032	.0000	.0915	.0894	.0057	.0011
3	.0212	.0837	.2309	.0053	.0000	.0292	.0000	.9400	.0896	.0053	.0014
4	.0005	.1085	.0745	.0524	.0000	.0003	.0000	.0092	.0843	.0357	.0109
5	.0038	.0994	.1133	.0479	.0000	.0030	.0000	.0922	.0903	.0348	.0114
6	.0208	.0793	.5657	.0327	.0000	.0279	.0000	.9417	.0836	.0531	.0133
7	.0003	.0501	.4394	.5050	.0000	.0002	.0000	.0095	.0524	.5117	.0434
8	.0024	.0560	.4775	.3755	.0000	.0020	.0000	.0946	.0517	.5211	.0435
9	.0102	.0403	.0800	.3105	.0000	.0178	.0000	.9543	.0453	.5072	.0427
10	.0005	1.2598	.2561	.0019	.0000	.0031	.0000	.0060	.0453	.0016	.0064
11	.0020	1.2291	.2975	.0018	.0000	.0302	.0000	.0663	.0774	.0017	.0065
12	.0100	1.0103	.7817	.0013	.0000	.2755	.0000	.6990	.0757	.0020	.0067
13	.0005	1.2105	.2808	.0188	.0000	.0030	.0000	.0067	.07638	.0166	.0035
14	.0025	1.1817	.5234	.0178	.0000	.0294	.0000	.0671	.0764	.0172	.0040
15	.0157	.9743	.0102	.0127	.0000	.2607	.0000	.7060	.0732	.0205	.0658
16	.0002	.8165	.5653	.1653	.0000	.0023	.0000	.0075	.6244	.2215	.5978
17	.0019	.8017	.6128	.1607	.0000	.0228	.0000	.0743	.6186	.2500	.5486
18	.0142	.6715	1.0895	.1348	.0000	.2049	.0000	.7713	.5740	.2641	.5916

VALUES OF EQUILIBRIUM CONSTANTS USED

TEMPERATURE : 22.0 DEG C

REACTION 1 :	0.000E-01
REACTION 2 :	1.701E-03
REACTION 3 :	0.000E-01
REACTION 4 :	9.589E-03
REACTION 5 :	3.707E-01
REACTION 6 :	1.203E-02
REACTION 7 :	3.035E-02

ACTIVITY COEFFICIENTS USED (22°C)

COMPLEXES PRESENT : FeHSO_4^{2+} ; FeSO_4^+ ; HSO_4^- ; FeSO_4^0 ; FeHSO_4^+

PREDICTED AND CALCULATED SOLUTION REDOX POTENTIALS

POINT	MEASURED	LIO. JN.	CORRECTED	LN(ACT. RATIO)	BEST LINE	HEMST EDN. (EMPIRICAL)	HEMST EDN. (THEORETICAL)	IONIC STRENGTH
1	601.	5.	607.	5.528	694.	694.	682.	.20
2	733.	5.	734.	1.228	748.	747.	736.	.32
3	766.	4.	792.	-.626	792.	794.	783.	1.75
4	618.	5.	623.	5.804	650.	631.	619.	.36
5	604.	4.	674.	3.628	686.	686.	675.	.50
6	727.	3.	731.	1.076	736.	736.	724.	1.86
7	550.	3.	554.	8.441	501.	505.	551.	1.86
8	605.	3.	606.	0.218	620.	620.	609.	1.86
9	660.	3.	664.	9.045	675.	676.	664.	1.96
10	675.	18.	690.	3.693	685.	685.	675.	3.10
11	730.	17.	747.	1.437	743.	742.	730.	1.55
12	785.	10.	800.	-.053	796.	794.	783.	1.67
13	610.	17.	653.	6.025	625.	625.	614.	2.96
14	671.	17.	680.	3.785	681.	683.	671.	1.72
15	729.	15.	744.	1.671	737.	736.	724.	1.84
16	557.	15.	572.	8.525	560.	560.	550.	3.10
17	611.	15.	626.	0.246	619.	620.	608.	3.14
18	674.	14.	686.	4.043	676.	676.	664.	3.24
								4.51

EQUATIONS FITTED TO THE EXPERIMENTAL RESULTS :

BEST STRAIGHT LINE	INTERCEPT, MILLIVOLTS	SLOPE, MILLIVOLTS	AVE. ERROR MILLIVOLTS	MAX. ERROR MILLIVOLTS
	179.5	-25.12	8.2	13.6
EMPIRICAL NERNST EQUATION :	778.3	-25.59	8.1	14.4
THEORETICAL NERNST EQUATION :	760.0	-25.59	14.0	23.5

ACTIVITY COEFFICIENTS USED (22 °C)

COMPLEXES PRESENT : FeSO_4^+ ; HSO_4^- ; FeSO_4^0

CONCENTRATIONS IN SOLUTION, GMULES/LITRE

POINT	FE(3+)	H+	SO4(2-)	FE(2+)	FEHSO4SO4	FEHSO4(2+)	FEHSO4SO4	FEHSO4+	HSO4-	FEHSO4	FEHSO4+
1	.0000	.1268	.0369	.0000	.0000	.0000	.0000	.0094	.0772	.0034	.0000
2	.0042	.1130	.0702	.0059	.0000	.0000	.0000	.0945	.0911	.0041	.0000
3	.0220	.0980	.5160	.0039	.0000	.0000	.0000	.9684	.1061	.0061	.0000
4	.0002	.1153	.0767	.0590	.0000	.0000	.0000	.0095	.0887	.0400	.0000
5	.0040	.1078	.1140	.0544	.0000	.0000	.0000	.0950	.0963	.0447	.0000
6	.0217	.0993	.5511	.0300	.0000	.0000	.0000	.9687	.1048	.0610	.0000
7	.0003	.1102	.4441	.4314	.0000	.0000	.0000	.0097	.0959	.5509	.0000
8	.0000	.1095	.4802	.4210	.0000	.0000	.0000	.0964	.0945	.5094	.0000
9	.0104	.1067	.8654	.3475	.0000	.0000	.0000	.9716	.0973	.6426	.0000
10	.0604	1.2665	.2509	.0054	.0000	.0000	.0000	.0096	.7744	.0046	.0000
11	.0058	1.2533	.2893	.0053	.0000	.0000	.0000	.0952	.7883	.0047	.0000
12	.0237	1.1713	.0700	.0040	.0000	.0000	.0000	.9667	.8706	.0060	.0000
13	.0004	1.2541	.2957	.0519	.0000	.0000	.0000	.0096	.7822	.0470	.0000
14	.0050	1.2469	.5287	.0504	.0000	.0000	.0000	.0954	.7947	.0466	.0000
15	.0231	1.1708	.7064	.0395	.0000	.0000	.0000	.9673	.8709	.0540	.0000
16	.0003	1.2292	.6500	.4214	.0000	.0000	.0000	.0097	.8117	.5683	.0000
17	.0025	1.2227	.0673	.4145	.0000	.0000	.0000	.0965	.8185	.5758	.0000
18	.0190	1.1510	.9996	.3562	.0000	.0000	.0000	.9705	.8906	.6359	.0000

VALUES OF EQUILIBRIUM CONSTANTS USED

TEMPERATURE : 22.000 C

REACTION 1 : 0.000E-01
REACTION 2 : 0.000E-01
REACTION 3 : 0.000E-01
REACTION 4 : 9.589E 03
REACTION 5 : 0.767E 01
REACTION 6 : 1.563E 02
REACTION 7 : 0.000E-01

ACTIVITY COEFFICIENTS USED (22 °C)
COMPLEXES PRESENT : FeSO_4^+ ; HSO_4^- ; FeSO_4^0

PREDICTED AND CALCULATED SOLUTION MEDIA POTENTIALS

POINT	MEASURED	LIV. JN.	CONNECTED	LN(ACI. RAIIJO)	BEST LINE	NEHRST EGN. (EMPIRICAL)	NEHRST EGN. (THEORETICAL)	IONIC STRENGTH
1	601.	5.	587.	5.856	708.	709.	669.	.19
2	733.	5.	738.	1.647	760.	765.	725.	.24
3	786.	2.	790.	-5.595	808.	817.	777.	.87
4	816.	4.	823.	6.469	645.	643.	603.	.35
5	869.	4.	873.	4.211	699.	700.	660.	.40
6	727.	2.	729.	1.969	752.	751.	711.	1.01
7	558.	2.	556.	9.601	570.	563.	523.	1.75
8	803.	1.	805.	7.263	626.	622.	582.	1.74
9	608.	0.	607.	4.720	687.	687.	647.	2.31
10	873.	18.	890.	5.528	667.	666.	626.	1.52
11	730.	17.	747.	3.206	723.	725.	685.	1.48
12	705.	13.	746.	.825	784.	791.	751.	1.14
13	616.	17.	633.	7.084	611.	607.	567.	1.61
14	871.	17.	888.	5.584	866.	866.	826.	1.56
15	729.	13.	741.	2.999	728.	731.	691.	1.24
16	557.	12.	569.	10.628	546.	557.	497.	2.47
17	811.	12.	823.	8.316	601.	596.	556.	2.44
18	674.	0.	682.	5.788	661.	660.	620.	2.24

EQUATIONS FITTED TO THE EXPERIMENTAL RESULTS :

BEST STRAIGHT LINE	:	INTERCEPT, MILLIVOLTS	SLOPE, MILLIVOLTS	AVE. ERROR MILLIVOLTS	MAX. ERROR MILLIVOLTS
	:	798.9	-23.81	20.8	25.3
EMPIRICAL NEHRST EQUATION	:	806.8	-25.39	22.6	32.2
THEORETICAL NEHRST EQUATION	:	706.8	-25.39	45.9	72.2

ACTIVITY COEFFICIENTS USED (22°C)

COMPLEXES PRESENT : $\text{FeH}_2\text{SO}_4\text{SO}_4^0$; $\text{FeH}_2\text{SO}_4^{2+}$; FeSO_4^+ ; $\text{Fe}(\text{SO}_4)_2^-$;
 HSO_4^- ; FeSO_4^0 ; $\text{FeH}_2\text{SO}_4^+$

CONCENTRATIONS IN SOLUTION, GMULES/LITRE

POINT	FE(3+)	H+	SO4(2-)	FE(2+)	FEHSO4SO4	FEHSO4(2+)	FEHSO4SO4*	FEHSO4+	HSO4-	FEHSO4	FEHSO4+
1	.0003	.1253	.0344	.0054	.0033	.0002	.0012	.0050	.0741	.0050	.0010
2	.0026	.1023	.0400	.0058	.0311	.0015	.0145	.0490	.0681	.0053	.0004
3	.0025	.0275	.1585	.0055	.1513	.0049	.2971	.5126	.0199	.0042	.0003
4	.0002	.1074	.0718	.0529	.0036	.0001	.0017	.0043	.0821	.0554	.0107
5	.0021	.0889	.0834	.0523	.0331	.0012	.0188	.0437	.0713	.0375	.0094
6	.0216	.0261	.1863	.0527	.1510	.0046	.3163	.4960	.0189	.0429	.0034
7	.0001	.0572	.4351	.3473	.0035	.0001	.0055	.0029	.0514	.5112	.0019
8	.0008	.0492	.4360	.3947	.0310	.0006	.0360	.0306	.0432	.5155	.0799
9	.0121	.0184	.4802	.4414	.1347	.0028	.4408	.3941	.0125	.5173	.0305
10	.0000	1.2573	.2506	.0020	.0088	.0003	.0004	.0005	.7674	.0016	.0064
11	.0024	1.2062	.2426	.0020	.0865	.0025	.0040	.0057	.7388	.0017	.0063
12	.0045	.7359	.1894	.0029	.8015	.0257	.0602	.0977	.4729	.0022	.0049
13	.0000	1.2083	.2752	.0140	.0088	.0002	.0004	.0005	.7601	.0108	.0053
14	.0002	1.1571	.2676	.0197	.0800	.0024	.0042	.0056	.7319	.0172	.0021
15	.0041	.6985	.2157	.0270	.8034	.0237	.0840	.0944	.4663	.0227	.0087
16	.0000	.8130	.5605	.1662	.0087	.0001	.0006	.0005	.6223	.2277	.5960
17	.0001	.7736	.5549	.1715	.0860	.0014	.0065	.0049	.5954	.2345	.5635
18	.0022	.4447	.5131	.2344	.7044	.0137	.1030	.0816	.3494	.3117	.4434

VALUES OF EQUILIBRIUM CONSTANTS USED

TEMPERATURE : 22.0 DEG C

REACTION 1 :	0.100E 06
REACTION 2 :	1.701E 03
REACTION 3 :	2.444E 05
REACTION 4 :	9.389E 03
REACTION 5 :	0.767E 01
REACTION 6 :	1.563E 02
REACTION 7 :	3.835E 02

ACTIVITY COEFFICIENTS USED (22°C)

COMPLEXES PRESENT : $\text{FeHSO}_4\text{SO}_4^0$; FeHSO_4^{1+} ; FeSO_4^+ ; $\text{Fe(SO}_4)_2^-$;

HSO_4^- ; FeSO_4^0 ; FeHSO_4^+

PREDICTED AND CALCULATED SOLUTION REDOX POTENTIALS

POINT	MEASURED	LIO. JN.	CORRECTED EMF(ACI. RATIO)	BEST LINE	HEMNST EUN. (EMPIRICAL)	HEMNST EUN. (THEORETICAL)	IONIC STRENGTH
1	699.	7.	700.	707.	709.	709.	.14
2	694.	6.	690.	696.	697.	698.	.19
3	694.	4.	674.	680.	682.	682.	.30
4	698.	3.	668.	683.	685.	685.	.57
5	647.	2.	650.	643.	645.	645.	1.39
6	674.	5.	679.	685.	683.	683.	3.86
7	653.	5.	656.	662.	661.	661.	3.85
8	629.	5.	634.	641.	640.	640.	3.86
9	607.	4.	611.	616.	615.	616.	3.81
10	761.	4.	765.	789.	788.	788.	3.75
11	752.	3.	755.	758.	759.	759.	3.70
12	680.	4.	683.	675.	673.	673.	3.81
13	678.	4.	662.	654.	652.	652.	3.84
14	632.	4.	630.	632.	631.	631.	3.83
15	604.	4.	613.	607.	606.	606.	3.79
16	702.	4.	706.	702.	702.	702.	3.76
17	751.	4.	754.	753.	753.	753.	3.68
18	704.	3.	707.	705.	707.	707.	3.53

EQUATIONS FITTED TO THE EXPERIMENTAL RESULTS :

	INTERCEPT, MILLIVOLTS	SLOPE, MILLIVOLTS	AVE. ERROR MILLIVOLTS	MAX. ERROR MILLIVOLTS
BEST SIGNIFICANT LINE :	644.0	-51.94	5.3	6.1
EMPIRICAL HEMNST EQUATION :	648.3	-51.29	5.4	10.2
THEORETICAL HEMNST EQUATION :	648.3	-51.29	5.4	10.1

ACTIVITY COEFFICIENTS USED (90°C)

COMPLEXES PRESENT : FeHSO_4^{2+} ; FeSO_4^+ ; HSO_4^- ; FeSO_4^0 ; FeHSO_4^+

CONCENTRATIONS IN SOLUTION, MOLES/LITRE

POINT	FE(3+)	H+	SO4(2-)	FE(2+)	FEHSO4S04	FEHSO4(2+)	FEHSO4S04-	FE8O4+	H3O4-	FE5O4	FEHSO4+
1	.0001	.0659	.0119	.0030	.0000	.0017	.0000	.0161	.1029	.0009	.0134
2	.0002	.0570	.0230	.0004	.0000	.0030	.0000	.0416	.1100	.0032	.0332
3	.0002	.0319	.0572	.0101	.0000	.0036	.0000	.0857	.1057	.0107	.0628
4	.0003	.0158	.1508	.0342	.0000	.0059	.0000	.1749	.0751	.0557	.1091
5	.0000	.0051	.4155	.1159	.0000	.0035	.0000	.4437	.0240	.1625	.1713
6	.0016	.2705	.7932	.0002	.0000	.5378	.0000	1.1840	.9366	.0002	.0126
7	.0010	.2702	.7928	.0003	.0000	.5338	.0000	1.1570	.9353	.0004	.0253
8	.0010	.2691	.7948	.0006	.0000	.5280	.0000	1.1490	.9338	.0006	.0466
9	.0010	.2292	.8307	.0013	.0000	.4703	.0000	1.2145	.8355	.0019	.0959
10	.0016	.1767	.8847	.0030	.0000	.3952	.0000	1.2976	.6943	.0047	.1893
11	.0015	.1289	.9515	.0075	.0000	.2943	.0000	1.3465	.5387	.0127	.3630
12	.0010	.1122	.8986	.0002	.0000	.4234	.0000	1.4414	.6773	.0003	.0134
13	.0017	.1925	.8800	.0009	.0000	.4520	.0000	1.3751	.7402	.0006	.0279
14	.0017	.1974	.8731	.0008	.0000	.4516	.0000	1.3411	.7533	.0012	.0550
15	.0017	.1804	.8800	.0014	.0000	.4146	.0000	1.3483	.7009	.0026	.1124
16	.0010	.1722	.8953	.0037	.0000	.5817	.0000	1.3003	.6771	.0059	.2295
17	.0015	.1387	.9341	.0004	.0000	.2962	.0000	1.2547	.5721	.0141	.4357
18	.0011	.0726	1.0118	.0290	.0000	.1340	.0000	1.0881	.3293	.0536	.8683

VALUES OF EQUILIBRIUM CONSTANTS USED

TEMPERATURE : 90.000 C

REACTION 1 :	0.000E-01
REACTION 2 :	2.250E-05
REACTION 3 :	0.000E-01
REACTION 4 :	5.153E-05
REACTION 5 :	4.993E-02
REACTION 6 :	2.570E-02
REACTION 7 :	4.000E-04

ACTIVITY COEFFICIENTS USED (90°C)

COMPLEXES PRESENT : FeHSO_4^{2+} ; FeSO_4^+ ; HSO_4^- ; FeSO_4 ; FeHSO_4^+

PREDICTED AND CALCULATED SOLUTION REDOX POTENTIALS

POINT	MEASURED	LIO. JR.	CORRECTED	LN(ACI. RATIO)	BEST LINE	NEHRNST ERM. (EMPIRICAL)	NEHRNST ERM. (THEORETICAL)	IONIC STRENGTH
1	094.	6.	701.	3.520	702.	694.	703.	.18
2	090.	5.	696.	3.702	694.	684.	698.	.25
3	668.	4.	673.	3.908	684.	683.	692.	.38
4	008.	3.	672.	4.129	673.	677.	686.	.66
5	670.	2.	672.	4.403	660.	669.	678.	1.46

EQUATIONS FITTED TO THE EXPERIMENTAL RESULTS :

	INTERCEPT, MILLIVOLTS	SLOPE, MILLIVOLTS	AVE. ERROR MILLIVOLTS	MAX. ERROR MILLIVOLTS
BEST STRAIGHT LINE :	009.7	-47.50	7.5	12.2
EMPIRICAL NEHRNST EQUATION :	792.1	-27.84	6.9	10.6
THEORETICAL NEHRNST EQUATION :	000.7	-27.04	11.1	19.2

ACTIVITY COEFFICIENTS USED (50°C)

COMPLEXES PRESENT : $\text{FeH}_2\text{SO}_4^{2+}$; FeSO_4^+ ; HSO_4^- ; FeSO_4^0 ; FeHSO_4^+

CONCENTRATIONS IN SOLUTION, MOLES/LITER

POINT	FE (3+)	HT	SO4 (2-)	FE (2+)	FE ²⁺ HSO4 ⁻	FE ²⁺ SO4 ²⁻	FE ²⁺	HSO4 ⁻	FE ²⁺	FE ²⁺ SO4 ²⁻
1	.0090	.1007	.0240	.0081	.0000	.0018	.0155	.0949	.0030	.0000
2	.0012	.0818	.0419	.0185	.0000	.0034	.0397	.1021	.0030	.0000
3	.0019	.0625	.0700	.0334	.0000	.0064	.0013	.1039	.0030	.0000
4	.0029	.0444	.1616	.0599	.0000	.0099	.1664	.0924	.0019	.0000
5	.0055	.0247	.4122	.1363	.0000	.0152	.4274	.0542	.0017	.0000

VALUES OF EQUILIBRIUM CONSTANTS USED

TEMPERATURE : 50.0 DEG C

REACTION 1 : 0.000E+01
REACTION 2 : 1.676E-04
REACTION 3 : 0.000E-01
REACTION 4 : 2.405E-04
REACTION 5 : 1.977E-02
REACTION 6 : 1.972E-02
REACTION 7 : 5.400E-03

ACTIVITY COEFFICIENTS USED (50°C)
COMPLEXES PRESENT : FeHSO_4^{2+} ; FeSO_4^+ ; HSO_4^- ; FeSO_4^0 ; FeHSO_4^+

PREDICTED AND CALCULATED SOLUTION MEDIA POTENTIALS

POINT	MEASURED	LIO, JM.	CORRECTED (NACT. NATIO)	BEST LINE	NERNST EQN. (EMPIRICAL)	NERNST EQN. (THEORETICAL)	IONIC STRENGTH
1	814.	5.	822.	822.	820.	820.	4.28
2	807.	3.	810.	809.	808.	808.	4.26
3	797.	3.	800.	800.	800.	800.	4.22
4	792.	3.	795.	798.	796.	798.	4.43
5	789.	3.	792.	797.	790.	791.	4.19
6	787.	3.	790.	787.	789.	789.	4.23
7	780.	3.	789.	789.	790.	790.	4.36
8	785.	3.	786.	787.	788.	788.	4.30

EQUATIONS FITTED TO THE EXPERIMENTAL RESULTS :

	INTERCEPT, MILLIVOLTS	SLOPE, MILLIVOLTS	AVE. ERROR MILLIVOLTS	% ERROR MILLIVOLTS
BEST STRAIGHT LINE :	803.5	-30.57	1.3	2.6
EMPIRICAL NERNST EQUATION :	803.1	-28.02	1.5	2.6
THEORETICAL NERNST EQUATION :	803.1	-28.02	1.5	2.9

ACTIVITY COEFFICIENTS USED (52°C)

COMPLEXES PRESENT : $\text{FeH}_2\text{SO}_4^{2+}$; FeSO_4^+ ; HSO_4^- ; FeSO_4^0 ; $\text{FeH}_2\text{SO}_4^+$

CONCENTRATIONS IN SOLUTION, MOLES/LITRE

POINT	FE(3+)	HY	SO4(2-)	FE(2+)	FESO4SO4	FESO4(2+)	FESO4SO4	FESO4	FESO4+
1	.0129	.1764	1.1224	.0021	.0000	.4580	.0000	.0043	.0206
2	.0137	.1396	1.1653	.0035	.0000	.3983	.0000	.0075	.0261
3	.0137	.1299	1.1595	.0046	.0000	.3736	.0000	.0099	.0365
4	.0132	.1666	1.1731	.0046	.0000	.4540	.0000	.0102	.0460
5	.0136	.1214	1.1634	.0065	.0000	.3533	.0000	.0141	.0463
6	.0137	.1290	1.1655	.0068	.0000	.3704	.0000	.0146	.0507
7	.0132	.1571	1.1672	.0064	.0000	.4500	.0000	.0135	.0572
8	.0133	.1466	1.1630	.0068	.0000	.4063	.0000	.0140	.0576

VALUES OF EQUILIBRIUM CONSTANTS USED

TEMPERATURE : 52.066 C

REACTION 1 :	0.000E+01
REACTION 2 :	1.931E+04
REACTION 3 :	0.000E+01
REACTION 4 :	2.551E+04
REACTION 5 :	2.022E+02
REACTION 6 :	2.002E+02
REACTION 7 :	5.006E+03

ACTIVITY COEFFICIENTS USED (52°C)
COMPLEXES PRESENT : FeHSO_4^{2+} ; FeSO_4^+ ; HSO_4^- ; FeSO_4^0 ; FeHSO_4^+

APPENDIX IV

Results of electrochemical current-potential curve measurement

- a) Raw data
- b) Computer printout of measured vs predicted results

a) Raw data

Applied electrode potential, mV	Measured electrode current, mA
250	1,0
300	1,2
350	1,6
400	2,4
450	4,4
500	10,4
550	17,2
600	32,3
650	60,2

Measured electrode resistance 0,15 ohms

Electrode superficial cross-section: $1,33 \text{ cm}^2$

a) Raw data

Applied electrode potential, mV	Measured electrode current, mA
250	1,0
300	1,2
350	1,6
400	2,4
450	4,4
500	10,4
550	17,2
600	32,3
650	60,2

Measured electrode resistance 0,15 ohms

Electrode superficial cross-section: $1,33 \text{ cm}^2$

PREDICTED VS MEASURED RESULTS

POTENTIAL, MILLIVOLTS	CURRENT, MILLIAMPS/SQ.CM	MEASURED	CALCULATED	MODELLED
220.		1.0	.3	.3
270.		1.2	.7	.5
320.		1.6	1.3	1.0
370.		2.4	2.5	2.0
419.		4.4	4.8	4.0
468.		10.4	9.2	8.0
517.		17.2	17.5	15.9
565.		32.3	32.8	31.4
611.		60.2	60.0	61.4

AREA = 25.1 SQUARE CENTIMETERS

CONSTANT I0 = 1.895E-02

CONSTANT K = 1.319E-02

CURRENT = I0*EXP(K*POTENTIAL)

PREDICTED VS MEASURED RESULTS

POTENTIAL,
MILLIVOLTS

CURRENT, MILLIAMPS/SQ.CM

	MEASURED	CALCULATED	MODELLED
220.	1.0	.3	.3
270.	1.2	.7	.5
320.	1.6	1.3	1.0
370.	2.4	2.5	2.0
419.	4.4	4.8	4.0
468.	10.4	9.2	8.0
517.	17.2	17.5	15.9
565.	32.3	32.8	31.4
611.	60.2	60.0	61.4

AREA = 25.1 SQUARE CENTIMETERS

CONSTANT I0 = 1.895E-02

CONSTANT K = 1.319E-02

CURRENT = I0*EXP(K*POTENTIAL)

APPENDIX V

- a) Derivation of the activities of the uncomplexed ferrous and ferric ions in the concentrated sulphate solution.

- b) Calculation of zero-ionic strength stability constants for FeHSO_4^{2+} , FeHSO_4^+ and $\text{FeHSO}_4\text{SO}_4$.

a) Activities of uncomplexed ferric and ferrous ions in solution

By stoichiometry, the total amounts of Fe^{3+} , Fe^{2+} , H^+ and $\text{SO}_4^{=}$ in solution can be defined in terms of the concentrations of uncomplexed Fe^{3+} , Fe^{2+} , H^+ and $\text{SO}_4^{=}$, and the concentrations of the various complexes, i.e.:

$$\begin{aligned} [\text{Fe}^{3+}]_T &= [\text{Fe}^{3+}] + [\text{FeHSO}_4\text{SO}_4] + [\text{FeHSO}_4^{2+}] \\ &\quad + [\text{Fe}(\text{SO}_4)_2^-] + [\text{FeSO}_4^+] \\ [\text{Fe}^{2+}]_T &= [\text{Fe}^{2+}] + [\text{FeSO}_4] + [\text{FeHSO}_4^+] \\ [\text{H}^+]_T &= [\text{H}^+] + [\text{HSO}_4^-] + [\text{FeHSO}_4\text{SO}_4] \\ &\quad + [\text{FeHSO}_4^{2+}] + [\text{FeHSO}_4^+] \\ [\text{SO}_4^{=}]_T &= [\text{SO}_4^{=}] + [\text{HSO}_4^-] + 2[\text{FeHSO}_4\text{SO}_4] \\ &\quad + 2[\text{Fe}(\text{SO}_4)_2^-] + [\text{FeHSO}_4^{2+}] + [\text{FeSO}_4^+] \\ &\quad + [\text{FeSO}_4] + [\text{FeHSO}_4^+] \end{aligned}$$

Where: $[\]_T$ denotes total concentration
 $[\]$ denotes concentration in the solution

The activity of each complex present can be defined in terms of its equilibrium reaction and the uncomplexed Fe^{3+} , Fe^{2+} , H^+ and $\text{SO}_4^{=}$ in solution, as follows:

$$\begin{aligned} \{\text{FeHSO}_4\text{SO}_4\} &= K(\text{i})\{\text{Fe}^{3+}\}\{\text{H}^+\}\{\text{SO}_4^{=}\}^2 \\ \{\text{FeHSO}_4^{2+}\} &= K(\text{ii})\{\text{Fe}^{3+}\}\{\text{H}^+\}\{\text{SO}_4^{=}\} \\ \{\text{Fe}(\text{SO}_4)_2^-\} &= K(\text{iii})\{\text{Fe}^{3+}\}\{\text{SO}_4^{=}\}^2 \\ \{\text{FeSO}_4^+\} &= K(\text{iv})\{\text{Fe}^{3+}\}\{\text{SO}_4^{=}\} \\ \{\text{HSO}_4^-\} &= K(\text{v})\{\text{H}^+\}\{\text{SO}_4^{=}\} \\ \{\text{FeSO}_4\} &= K(\text{vi})\{\text{Fe}^{2+}\}\{\text{SO}_4^{=}\} \\ \{\text{FeHSO}_4^+\} &= K(\text{vii})\{\text{Fe}^{2+}\}\{\text{H}^+\}\{\text{SO}_4^{=}\} \end{aligned}$$

Where: $\{ \}$ denotes activity
 $K(\text{j})$ = equilibrium constant j

Activity is the product of concentration and the activity coefficient, thus the above equations can be re-written in terms of concentration, as follows:

$$[\text{FeHSO}_4\text{SO}_4] = \frac{K(i)\gamma(\text{Fe}^{3+})[\text{Fe}^{3+}]\gamma(\text{H}^+)[\text{H}^+]\gamma^2(\text{SO}_4^{=})[\text{SO}_4^{=}]^2}{\gamma(\text{FeHSO}_4\text{SO}_4)}$$

$$\text{i.e.: } [\text{FeHSO}_4\text{SO}_4] = K'(i)[\text{Fe}^{3+}][\text{H}^+][\text{SO}_4^{=}]^2$$

$$K'(i) = \frac{K(i)(\text{activity coefficients of uncomplexed components})}{(\text{activity coefficient of complex})}$$

Similarly:

$$[\text{FeHSO}_4^{2+}] = K'(ii)[\text{Fe}^{3+}][\text{H}^+][\text{SO}_4^{=}]$$

$$[\text{Fe}(\text{SO}_4)_2^{=}] = K'(iii)[\text{Fe}^{3+}][\text{SO}_4^{=}]^2$$

$$[\text{FeSO}_4^+] = K'(iv)[\text{Fe}^{3+}][\text{SO}_4^{=}]$$

$$[\text{HSO}_4^-] = K'(v)[\text{H}^+][\text{SO}_4^{=}]$$

$$[\text{FeSO}_4] = K'(vi)[\text{Fe}^{2+}][\text{SO}_4^{=}]$$

$$[\text{FeHSO}_4^+] = K'(vii)[\text{Fe}^{2+}][\text{H}^+][\text{SO}_4^{=}]$$

Substituting for the complex species in the equations for total concentrations gives:

$$[\text{Fe}^{3+}]_T = [\text{Fe}^{3+}] + K'(i)[\text{Fe}^{3+}][\text{H}^+][\text{SO}_4^{=}]^2 + K'(ii)[\text{Fe}^{3+}][\text{H}^+][\text{SO}_4^{=}] + K'(iii)[\text{Fe}^{3+}][\text{SO}_4^{=}]^2 + K'(iv)[\text{Fe}^{3+}][\text{SO}_4^{=}]$$

$$[\text{Fe}^{2+}]_T = [\text{Fe}^{2+}] + K'(vi)[\text{Fe}^{2+}][\text{SO}_4^{=}] + K'(vii)[\text{Fe}^{2+}][\text{H}^+][\text{SO}_4^{=}]$$

$$[\text{H}^+]_T = [\text{H}^+] + K'(i)[\text{Fe}^{3+}][\text{H}^+][\text{SO}_4^{=}]^2 + K'(ii)[\text{Fe}^{3+}][\text{H}^+][\text{SO}_4^{=}] + K'(v)[\text{H}^+][\text{SO}_4^{=}] + K'(vii)[\text{Fe}^{2+}][\text{H}^+][\text{SO}_4^{=}]$$

$$[\text{SO}_4^{=}]_T = [\text{SO}_4^{=}] + 2K'(i)[\text{Fe}^{3+}][\text{H}^+][\text{SO}_4^{=}]^2 + K'(ii)[\text{Fe}^{3+}][\text{H}^+][\text{SO}_4^{=}] + 2K'(iii)[\text{Fe}^{3+}][\text{SO}_4^{=}]^2 + K'(iv)[\text{Fe}^{3+}][\text{SO}_4^{=}] + K'(v)[\text{H}^+][\text{SO}_4^{=}] + K'(vi)[\text{Fe}^{2+}][\text{SO}_4^{=}] + K'(vii)[\text{Fe}^{2+}][\text{H}^+][\text{SO}_4^{=}]$$

Rearranging these equations gives:

$$[\text{Fe}^{3+}]_T = [\text{Fe}^{3+}] \{1 + X(\text{Fe}^{3+})\}$$

$$[\text{Fe}^{2+}]_T = [\text{Fe}^{2+}] \{1 + X(\text{Fe}^{2+})\}$$

$$[\text{H}^+]_T = [\text{H}^+] \{1 + X(\text{H}^+)\}$$

$$[\text{SO}_4^{=}]_T = [\text{SO}_4^{=}] \{1 + X(\text{SO}_4^{=})\}$$

Where:

$$X(\text{Fe}^{3+}) = K'(1)[\text{H}^+][\text{SO}_4^{=}]^2 + K'(11)[\text{H}^+][\text{SO}_4^{=}] \\ + K'(111)[\text{SO}_4^{=}]^2 + K'(1v)[\text{SO}_4^{=}]$$

$$X(\text{Fe}^{2+}) = K'(vi)[\text{SO}_4^{=}] + K'(v11)[\text{H}^+][\text{SO}_4^{=}]$$

$$X(\text{H}^+) = K'(1)[\text{Fe}^{3+}][\text{SO}_4^{=}]^2 + K'(11)[\text{Fe}^{3+}][\text{SO}_4^{=}] \\ + K'(v)[\text{SO}_4^{=}] + K'(v11)[\text{Fe}^{2+}][\text{SO}_4^{=}]$$

$$X(\text{SO}_4^{=}) = 2K'(1)[\text{Fe}^{3+}][\text{H}^+][\text{SO}_4^{=}] + K'(11)[\text{Fe}^{3+}][\text{H}^+] \\ + 2K'(111)[\text{Fe}^{3+}][\text{SO}_4^{=}] + K'(1v)[\text{Fe}^{3+}] \\ + K'(v)[\text{H}^+] + K'(vi)[\text{Fe}^{2+}] \\ + K'(v11)[\text{Fe}^{2+}][\text{H}^+]$$

and: $[]_T$ denotes total concentration

$[]$ denotes uncomplexed concentration

K' denotes equilibrium constants, converted by the activity coefficients to concentration equilibrium constants

The total concentrations are known from solution analyses. A first guess of the values of the terms $X(\text{Fe}^{3+})$, $X(\text{Fe}^{2+})$, $X(\text{H}^+)$ and $X(\text{SO}_4^{=})$ can be made by assuming total dissociation, i.e., the values of the concentrations of Fe^{3+} , Fe^{2+} , H^+ and $\text{SO}_4^{=}$ are first set equal to the total in solution values. The ionic strength and activity coefficient for each species are calculated, and the equilibrium constants are converted from activity to concentration constants. The terms $X(\text{Fe}^{3+})$, $X(\text{Fe}^{2+})$, $X(\text{H}^+)$ and $X(\text{SO}_4^{=})$ are then calculated. An improved guess is then made of the uncomplexed concentrations, as follows:

$$[\text{Fe}^{3+}] = [\text{Fe}^{3+}]_T / \{1 + X(\text{Fe}^{3+})\}$$

$$[\text{Fe}^{2+}] = [\text{Fe}^{2+}]_T / \{1 + X(\text{Fe}^{2+})\}$$

$$[\text{H}^+] = [\text{H}^+]_T / \{1 + X(\text{H}^+)\}$$

$$[\text{SO}_4^{=}] = [\text{SO}_4^{=}]_T / \{1 + X(\text{SO}_4^{=})\}$$

Using the new uncomplexed concentration values (or a weighted average of some kind to facilitate convergence), the calculation is repeated. Convergence is reached when the relations:

$$[\text{Fe}^{3+}]_T = [\text{Fe}^{3+}]\{1 + X(\text{Fe}^{3+})\}$$

$$[\text{Fe}^{2+}]_T = [\text{Fe}^{2+}]\{1 + X(\text{Fe}^{2+})\}$$

$$[\text{H}^+]_T = [\text{H}^+]\{1 + X(\text{H}^+)\}$$

$$[\text{SO}_4^{=}]_T = [\text{SO}_4^{=}]\{1 + X(\text{SO}_4^{=})\}$$

are satisfied to within a given tolerance.

The resulting uncomplexed ferric and ferrous ion concentrations and activity coefficients can then be used in the Nernst equation to calculate the solution redox potential.

b) Calculation of zero-ionic strength stability constants for FeHSO_4^{2+} , FeHSO_4^+ and $\text{FeHSO}_4\text{SO}_4$

The Debye-Hückel activity coefficients of the various individual species are as follows (6, 7, 8):

Species	Individual activity coefficient			
	I = 0,15	I = 1,2	I = 2,67	I = 3,4
Fe^{3+}	0,1478	0,0649	0,0515	0,0486
Fe^{2+}	0,3556	0,1956	0,1618	0,1539
$\text{SO}_4^{=}$	0,2986	0,1208	0,0869	0,0793
HSO_4^-	0,7392	0,5896	0,5429	0,5307
FeHSO_4^{2+}	0,4052	0,2648	0,2341	0,2268
FeHSO_4^+	0,7392	0,5896	0,5429	0,5307
$\text{FeHSO}_4\text{SO}_4$	1	1	1	1

(I = Ionic strength)

i) FeHSO_4^{2+}

Using Sykes' stability constant at ionic strength = 0,15 and 19°C(89) results in:

$$K^0 = 60 (0,4052/0,1478/0,7392)$$

$$\text{Therefore } K^0 = 223$$

Lister and Rivington's value(91) at ionic strength = 1,2 gives:

$$K^0 = (6 \pm 1) (0,2648/0,0649/0,5896)$$

$$\text{Therefore } K^0 = 42 \pm 7$$

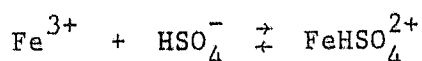
The value from Sapiaszko *et al*(48) at ionic strength 2,67 gives:

$$K^0 = (4 \pm 1) (0,2341/0,0515/0,5429)$$

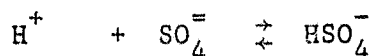
$$\text{Therefore } K^0 = 33 \pm 8$$

The stability constant of FeHSO_4^{2+} thus seems to lie between about 200 and 20. This is the stability constant for the association

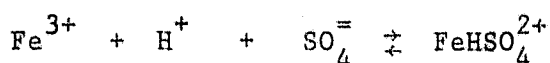
equilibrium:



The equilibrium for bisulphate formation:



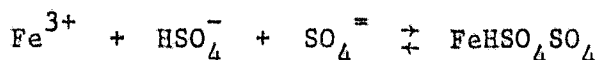
has a stability constant at zero ionic strength and 25°C of between 95,5 and 100(47). Combining the two equilibria gives the overall stability constant for the equilibrium:



as between 1900 and 20 000. The data of Lister and Rivington and Sapieszko *et al* are in reasonable agreement, while that of Sykes gives a stability constant about 10 times greater than the other two. If the value from Sykes' data is ignored, the overall stability constant ranges reduces to between 1900 and 4900. This seems more likely to contain the correct value.

ii) $\text{FeHSO}_4\text{SO}_4$

Lister and Rivington's value(91) of 380 ± 50 at 25°C and ionic strength 1,2 for the equilibrium constant for the reaction

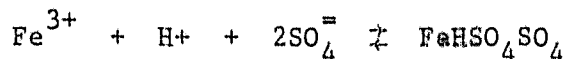


results in zero-ionic strength values of:

$$K^0 = (380 \pm 50)(1/0,0649/0,5896/0,1208)$$

$$\text{Therefore } K^0 = 82200 \pm 10800$$

Combining this with the stability constant of HSO_4^- , the constant for the equilibrium:

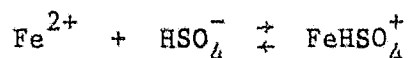


$$\text{beomes: } K^0 = (8,1 \pm 1,2) \cdot 10^6$$

As was pointed out in section 4.2.2(a), however, this value is based only on one report, and no other authors have reported the existence of $\text{FeHSO}_4\text{SO}_4$, thus it is not impossible that its stability constant is zero - i.e. this complex may not exist.

iii) FeHSO_4^+

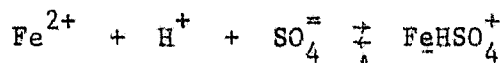
Beukenkamp and Herrington(21) studied the formation of FeSO_4 and FeHSO_4^+ in sulphuric acid solutions of 2,2 molar and lower concentrations. Using their data for the concentrations of H^+ , HSO_4^- and $\text{SO}_4^{=}$ in 2,2 molar sulphuric acid results in a maximum ionic strength for their measurements of about 3,4. Using this ionic strength and their value of 1,7 for the stability constant of FeSO_4 results in a zero ionic strength value of about 140 for the stability constant of FeSO_4 . This is close to the value of 158 given by Smith and Martell (47), thus the ionic strength of 3,4 can be used to calculate the zero-ionic strength equilibrium constant of the reaction:



to be: $K^0 \doteq 0,61$ (05307/0,5307/0,1539)

Therefore $K^0 \doteq 4$

Combining this with the bisulphate stability constant gives the equilibrium constant (47) for the reaction:



as: $K^0 \doteq 400$

APPENDIX VI

Values of A, B and $\overset{\circ}{a}$ in the Debye-Hückel equation

a) Values of the constants A and B at 90°C:

$$A = 0,5940$$

$$B = 0,3468$$

b) Values of the parameter $\overset{\circ}{a}$, in angstroms:

Species	$\overset{\circ}{a}$
Fe^{3+}	9
H^+	9
$\text{SO}_4^{=}$	4
Fe^{2+}	6
OH^-	3
$\text{FeHSO}_4\text{SO}_4$	-
FeHSO_4^{2+}	8
$\text{Fe}(\text{SO}_4)_2^-$	8
FeSO_4^+	8
HSO_4^+	4
FeSO_4	-
FeHSO_4^+	4

APPENDIX VII

Values of limiting ionic conductivity used for calculation of liquid junction potential

Species	λ° , mho - cm ² /equivalent
Fe ³⁺	70
H ⁺	350
SO ₄ ⁼	80
Fe ²⁺	53,6
OH ⁻	197
FeHSO ₄ ·SO ₄	-
FeHSO ₄ ²⁺	36,2
Fe(SO ₄) ₂ ⁻	50
FeSO ₄ ⁺	60
HSO ₄ ⁻	50
FeSO ₄	-
FeHSO ₄ ⁺	50

APPENDIX VIII

Fortran V Computer programme of the leaching model

 COMPUTER PROGRAM OF THE MATHEMATICAL MODEL USED TO EXPLAIN
 THE EXPERIMENTAL RESULTS OF LEACHING THE LOW GRADE MATTE
 IN CONCENTRATED FERRIC-FERROUS SULPHATE SOLUTION.

```

PARAMETER NXH=6, NVH=4, NDH=15, NSH=13, NTH=3
INTEGER NXP(NXH), TITLE(30), NTI(NVH)
REAL 1 (NXH,NDH), P(NXH,NDH), X(NXH,NVH,NDH), XI(NXH,NVH,NDH), MHT(NVH), A(NSH), L(NSH),
1 C(NVH,NSH), R(NVH,NSH,NTH), TI(NVH,NTH),
2 C1(NTH,NVH), CS1(NTH,NVH,2), SC1(NTH,NVH,2), CL(NTH), FRN(NVH,NTH),
3 MU(NVH), H(NVH), HASO(NVH,NSH,NTH), HAS1(NVH,NSH,NTH),
4 MASS(NVH,NSH,NTH), KRXN(NVH,NSH,NTH), NK(2), EOLO(NVH),
5 DIE(NTH), DZE(NTH), XHX(NVH),
6 ESU(NVH,3,NTH), CONST(NTH,NVH),
7 SH(NDH), DENS(NDH), B(NSH,NTH), M1(NVH,NTH), M10(NVH,NTH),
8 CONCO(NXH,4), CONCT(4), CONC(12), ACTV(12), KEO(17),
9 KOC, IR, RATE(NSH), AREA(NSH), LO, MECH(NVH,NTH), FE(NXH,NDH)
OPEN 2, 'LU1A'
READ (2,73) TITLE
READ FREE (2) NV, NS, (NTI(I), I=1, NV), HX, (NXP(N), N=1, NX)
EPS=0.001
DO 1 N=1, NX
  NUNXP(N)
  READ FREE (2) (T(N,J), P(N,J), (X(H,I,J), I=1, NV), FE(N,J), J=1, NO)
1 CONTINUE
  READ FREE (2) FFED, VOL, (MHT(I), I=1, NV)
  READ FREE (2) (L(J), SH(J), DENS(J), A(J), (B(J,K), K=1, NTH), J=1, NS)
  DO 2 I=1, NV
    NT=NTI(I)
    READ FREE (2) (C(I,J), (R(I,J,K), K=1, NTH), J=1, NS)
2 CONTINUE
  S1=0,
  S2=0,
  DO 3 J=1, NS
    IF (NV.LI.NVH) GO TO 3
    S1=S1+A(J)/DENS(J)
    S2=S2+A(J)*H(NV,J,2)*C(NV,J)
3 L(J)=L(J)/10000
  IF (NV.EQ.NVH) RHQ=S2/S1/MHT(NV)
  JM=1
  DO 4 I=1, NV
    NT=NTI(I)
    READ FREE (2) (MECH(I,K), TI(I,K), C1(K,I), K=1, NTH)
    IF (MECH(I,K).GT.0.0) JM=JM+2
4 CONTINUE
  IF (JM.GI.0) READ FREE (2) FRI, B1, B2
  IF (NV.LI.NVH) GO TO 49
  READ FREE (2) (CL(K), (FRN(I,K), I=1, NV), K=1, NTH)
  DO 4B I=1, NV
    NT=NTI(I)
    DO 4B K=1, NTH
      IF (CL(K).LI.0.) GO TO 4B
      TI(I,K)=CL(K)*FRN(I,K)
4B CONTINUE
49 DO 5 I=1, NV
  NT=NTI(I)

```

```

DO 5 K=1,NT
  CSI(K,1,2)=IT(1,K)/2
  IF (IT(1,K).GE.0.) GO TO 5
  IT(1,K)=-IT(1,K)
  CSI(K,1,2)=0.
5 CONTINUE
  READ FREE (2) OT0,OTMAX,EP8
  NPOTL=0
  IF (NV,EW,NVM) ACCEPT "NPOTL ",NPOTL
  IF (NPOTL,EW,0) GO TO 6
  OPEN 4,"PUOT"
  TYPE "FILE POUT CREATED"
  READ FREE (2) ((CONCO(N,1),I=1,4),N=1,NX)
  READ FREE (2) TEMP,OFE3,OFE2,SFP,OLD
  CALL KEDLM (TEMP,KEP)
6 CLOSE 2
  ACCEPT "MODE ",MODE
  NPRINT=0
  IF (MODE,LT,0) NPRINT=1
  MODE=ABS(MODE)
  IF (MODE,GE,2) OPEN 3,"OUTP"
  IF (MODE,GE,2) TYPE "FILE OUTP CREATED"
  JJ=2
  DO 7 I=1,NV
    NT=NT+1
    DO 7 K=1,NT
7    M1(I,K)=0.
    IF (MODE,NE,0) WRITE (10,73) TITLE
    IF (MODE,NE,0) WRITE (10,69)
    MMM=" "
    IF (MODE,NE,0) WRITE (10,74) (MMM,I=1,NV)
    IF (MODE,NE,0) WRITE (10,70) (MMM,I=1,NV)
    IF (NPRINT,EQ,0) GO TO 8
    OPEN 12,"OLPT",ATT="P"
    WRITE (12,75) TITLE
    WRITE (12,76)
    WRITE (12,77) (MMM,I=1,NV)
    WRITE (12,78) (MMM,I=1,NV)
    WRITE (12,73) MMM
    WRITE (10,73) MMM
8    COUNT=0
    DO 10 I=1,NV
      NT=NT+1
      EOLD(1)=100.
      XMX(1)=0.
      MO(1)=0.
      DO 9 J=1,NS
        MO(1)=MO(1)+A(J)*C(I,J)
      DO 9 K=1,NT
        MASO(1,J,K)=FEED/VOL*A(J)*C(I,J)*R(I,J,K)/MWT(1)
        M10(1,K)=M10(1,K)+MASO(1,J,K)
9      XMX(1)=XMX(1)+MASO(1,J,K)
      MO(1)=MO(1)+FEED/VOL/MWT(1)
      XMX(1)=XMX(1)/MO(1)
      DO 10 K=1,NT
10     M1(I,K)=M1(1,K)/MO(1)
        IJK=1
        NK(1)=0
        NK(2)=0
        KK=1
11     DO 12 I=1,NV
          ESH(I,1,1)=0.
          DO 12 K=1,NT

```

```

      ESQ(I,K,2)=0.
12  ESQ(I,K,3)=0.
      DO 40 N=1,NX
      IF (NPOTL.EQ.0) GO TO 15
      JJ=21
      WRITE (4,61) JJ
      DO 13 I=1,4
      CONCT(I)=CONCO(N,1)
13  CONCT(I)=CONCO(N,1)
      DO 14 I=5,12
14  CONCT(I)=0.
15  ND=NX(N)
      DPOTL=0.
      II=0
      OT=OTO
      DO 16 I=1,NV
      NT=NTT(I)
      DO 16 K=1,NT
      DO 16 J=1,NS
      KRXN(I,J,K)=TT(I,K)*SH(J)*FEED*A(J)*B(J,K)/VOL/DENS(J)/L(J)
      /3/MASO(I,J,K)**(2./3.)
16  MASS(I,J,K)=MASO(I,J,K)
      TIME=0.
      OL=OL0/10000.
      IF (NPOTL.LE.0) CALL FE3FE2 (TIME,POTL,DPOTL,I,P,N,ND)
      IF (NPOTL.NE.0) CALL CONCTN (TEMP,CONCT,ACTV,KEQ,CONC,EPS)
      PTL=P(N,1)
      PILE=PIL
      IF (NPOTL.NE.0) CALL REDJ. (CONC,ACTV,TEMP,ELJ,PTL)
      IF (NPOTL.GI.0) POTL=PTL
      IF (NPOTL.EQ.0) PTL=POTL
      NV1=2
      IF (MODE.FQ,2) WRITE (3,61) NV1
      NTME=2
18  IF ((TIME+DT).GT.1(N,NTME)) II=-2
      IF (II.LT.0.) DT=1(N,NTME)-TIME
      CALL IRUN2 (TIME,FE2,DFE2,I,FE,N,ND)
      IF (NPOTL.GE.0) GO TO 25
      RATO=0.
      SPIL=100.
      KOUNT2=0
      FE3=CONCT(1)
      FE2=CONCT(4)
      SU4=CONCT(3)
19  RATO=0.
      DO 20 I=1,NV
      NT=NTT(I)
      DO 20 K=1,NT
      IF (MECH(I,K).LE.0) CHI=EXP(C1(K,1)*PTLE)
      IF (MECH(I,K).GT.0) CHI=EXP((2-B1-B2)*FRT*PTLE)/
      (FE2*EXP(-B1*FRT*PTLE)+C1(K,1)*EXP((1-B2)*FRT*PTLE))
      DO 20 J=1,NS
      RATO=RATO+A(J)*R(J,K)*TT(I,K)*CHI
      RATMAX=DFE3*FE3/3/SRF/OL*0.99
      IF (RATO.GT.RATMAX) RATO=RATMAX
      CONCT(1)=FE3-3*OL/DFE3*RATO*SRF
      CONCT(4)=FE2+2*OL/DFE2*RATO*SRF
      CONCT(3)=1.5*CONCT(1)+0.5*CONCT(2)+CONCT(4)
      CALL CONCTN (TEMP,CONCT,ACTV,KEQ,CONC,EPS)
      CALL REDUX (CONC,ACTV,TEMP,ELJ,PIL1)
      IF (ABS(PIL1-PTLE).LT.0.01) GO TO 21
      DPIL=PILE-PIL1
      IF (DPIL.GT.0) PTL=PTL+DPIL/2

```

```

IF ((DPTL/SPIL).GT.1.) DPTL= SPIL
PTLE=PILE-DPTL
SPIL=DPTL
KUUNT2=KUUNT2+1
IF (KUUNT2.LT.100) GO TO 19
21 RATIO=RATIO+3216000.
DO 24 J=1,NS
RATE(J)=0.
AREA(J)=0.
DO 23 K=1,NIM
RTE=0.
ARA=0.
DO 22 I=1,NV
IF (K.GT.NT(I)) GO TO 22
IF (MECH(I,K).EQ.0) CHI=EXP(C1(K,I)*POTL)
IF (MECH(I,K).NE.0) CHI=EXP((2-B1-B2)*FRT*POTL)/
(FE2*EXP(-B1*FRT*POTL)+C1(K,I)*EXP((1-B2)*FRT*POTL))
1 RTE=RTE+3*AKXN(I,J,K)*CHI*MASS(I,J,K)**(2./3.)
ARA=ARA+11(I,K)*CHI
22 CONTINUE
ARA=RIE/ARA
RATE(J)=RATE(J)+RTE
23 AREA(J)=AREA(J)+ARA
24 RATE(J)=RATE(J)/AREA(J)*3216000.
DL1=L(1)/2*(1.-(MASS(NV,1,2)/MASQ(NV,1,2))**(1./3.))
CONCT(1)=FE3-3*DL1/DFE3*RATE(1)/3216000.*(L(1)/2-DL1)/(L(1)/2+DL0/10000.)
CONCT(4)=FE2+2*DL1/DFE2*RATE(1)/3216000.*(L(1)/2-DL1)/(L(1)/2+DL0/10000.)
CONCT(3)=1.5*CONCT(1)+0.5*CONCT(2)+CONCT(4)
CALL CUNCI (TEMP,CONCT,ACTV,KEQ,CONC,EP5)
CALL REDUX (CONC,ACTV,TEMP,ELJ,PTL1)
DL2=L(NS)/2*(1.-(MASS(NV,NS,2)/MASQ(NV,NS,2))**(1./3.))
CONCT(1)=FE3-3*DL2/DFE3*RATE(NS)/3216000.*(L(NS)/2-DL2)/(L(NS)/2+DL0/10000.)
CONCT(4)=FE2+2*DL2/DFE2*RATE(NS)/3216000.*(L(NS)/2-DL2)/(L(NS)/2+DL0/10000.)
CONCT(3)=1.5*CONCT(1)+0.5*CONCT(2)+CONCT(4)
CALL CUNCI (TEMP,CONCT,ACTV,KEQ,CONC,EP5)
CALL REDUX (CONC,ACTV,TEMP,ELJ,PTL2)
CONCT(1)=FE3
CONCT(4)=FE2
CONCT(3)=SQ4
LD=DL*10000.
IF (ABS(NPOTL).LE.1) WRITE (4,62) TIME,POTL,PIL,PTLE,PIL1,PTL2,LD
IF (ABS(NPOTL).GT.1) WRITE (4,62) TIME,POTL,PTL,PTLE,PTL1,PTL2.
1 LD=DL+DT*BNF*TI(NV,2)/NHO*EXP(C1(2,NV)*PTLE)
25 CONTINUE
DO 26 I=1,NV
NT=NT(I)
DO 28 K=1,N1
IF (MECH(I,K).GT.0) GO TO 26
CHI=EXP(C1(K,I)*POTL)
QC(I)=CHI*C1(K,I)*NPOTL
GO TO 27
26 CHI=EXP((2-B1-B2)*FRT*POTL)/(FE2*EXP(-B1*FRT*POTL)+C1(K,I)*EXP((1-B2)*FRT*POTL))
UCHI=CHI*(12-B1-B2)*FRT*NPOTL+((DFE2-B1*FRT*NPOTL*FE2)*EXP(-B1*FRT*POTL)
+((1-B2)*FRT*NPOTL*C1(K,I)*EXP((1-B2)*FRT*POTL))
/((FE2*EXP(-B1*FRT*POTL)+C1(K,I)*EXP((1-B2)*FRT*POTL)))
27 DO 28 J=1,NS
IF (I.EQ.0) MASS(I,J,K)=0.
IF (MASS(I,J,K).EQ.0.) GO TO 28
IF (MECH(I,K).GE.0) AMAS=MASS(I,J,K)**(1./3.)
IF (MECH(I,K).LT.0) AMAS=MASS(I,J,K)**(1.+MECH(I,K))
AKX=DT*AKXN(I,J,K)
IF (MECH(I,K).LT.0) AKX=AKX*AMAS

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```

DO 51 J=1,NS
51 RATE(J)=MASS(I,J,K)/MASO(I,J,K)
WRITE (3,64) (RATE(J),J=1,NS)
36 CONTINUE
37 IF (I1.EQ.0.AND.NTEST.EQ.0) DT=DT*2
IF (D1.GT.D1MAX) DT=DTMAX
IF (I1.GE.0) DTIME=DT
IF (I1.GE.0.AND.TIME.LT.I(N,NTME)) GO TO 18
DO 38 I=1,NV
IF (IJR.EQ.1) XI(N,I,NTME)=XMX(I)-M(I)/MO(I)
E1=XMX(I)-M(I)/MO(I)-X(N,I,NTME)
ESQ(I,1,1)=ESQ(I,1,1)+E1**2
NT=NTT(I)
DO 38 K=1,NT
DO 38 J=1,NS
IF (MASS(I,J,K).EQ.0.) GO TO 38
EKJ=S/MO(I)/TT(I,K)*(MASS(I,J,K)-MASO(I,J,K)**(1./3.)*MASS(I,J,K)**(2./3.))
ESQ(I,K,2)=ESQ(I,K,2)-2*E1*EKJ
ESQ(I,K,3)=ESQ(I,K,3)+2*EKJ**2
38 CONTINUE
IF (MODE.EQ.0) GO TO 39
FE3=CONCI(1)*55.847
FE2=CONCI(4)*55.847
WRITE (10,65) TIME,PTL,(X(N,I,NTME),XI(N,I,NTME),I=1,NV),FE3,FE2
IF (NPRINT.EQ.0) GO TO 39
WRITE (12,79) TIME,PTL,(X(N,I,NTME),XI(N,I,NTME),I=1,NV)
39 CONTINUE
NTME=NTME+1
DT=DTIME
I1=0
IF (NTME.LE.NO) GO TO 18
40 CONTINUE
IF (MODE.NE.0) GO TO 55
IF (N9.LT.NVM) GO TO 47
DO 41 K=1,NIM
DIE(K)=0.
D2E(K)=0.
DO 41 I=1,NV
DIE(K)=DIE(K)+ESQ(I,K,2)*FRN(I,K)
41 D2E(K)=D2E(K)+ESQ(I,K,3)*FRN(I,K)**2
DO 42 K=1,NIM
SC1(K,1,1)=-DIE(K)/D2E(K)
SC1(K,1,2)=SC1(K,1,1)/CL(K)
IF ((SC1(K,1,1)+C81(K,1,1)).LT.0.) C81(K,1,1)=-C81(K,1,1)/2
IF ((SC1(K,1,1)/C81(K,1,1)).GT.1.) SC1(K,1,1)=C81(K,1,1)
42 CONTINUE
WRITE (10,1000) KOUNT,(E80(1,1,1),I=1,NV),(SC1(K,1,2),K=1,NTM)
1000 FORMAT (15,F10.5)
DO 43 K=1,NIM
IF (ABS(SC1(K,1,2)).GE.EPS) GO TO 44
43 CONTINUE
GO TO 57
DO 45 K=1,NTM
IF ((CL(K)+SC1(K,1,1)).LE.0.) SC1(K,1,1)=0.9*CL(K)
45 CL(K)=CL(K)+SC1(K,1,1)
DO 46 I=1,NV
NT=NTT(I)
DO 46 K=1,NT
46 TT(I,K)=CL(K)*FRN(I,K)
KOUNT=KOUNT+1
IF (KOUNT.LT.100) GO TO 11
WRITE (10,68)
END

```

```

MASS(I,J,K)=AMAS-AXRX*(CHI+DT*DCHT/2)
IF (MASS(I,J,K).LT.0.) MASS(I,J,K)=0.
IF (MASS(I,J,K).GT.0. AND MECH(I,K).GE.0) MASS(I,J,K)=MASS(I,J,K)**3
IF (MASS(I,J,K).GT.0. AND MECH(I,K).LT.0) MASS(I,J,K)=MASS(I,J,K)**(1./(1.+MECH(I,K)))
IF (I1.NE.0) GO TO 28
MASI(I,J,K)=AMAS-2*AXRX*(CHI+DT*DCHI)
IF (MASI(I,J,K).LT.0.) MASI(I,J,K)=0.
IF (MASI(I,J,K).GT.0. AND MECH(I,K).GE.0) MASI(I,J,K)=MASI(I,J,K)**3
IF (MASI(I,J,K).GT.0. AND MECH(I,K).LT.0) MASI(I,J,K)=MASI(I,J,K)**(1./(1.+MECH(I,K)))
28 CONTINUE
IF (NPOTL.EQ.0) GO TO 31
CONCT(1)=CONC0(N,1)
CONCT(4)=CONC0(N,4)
DO 29 I=1,NV
MT=NTI(I)
DO 29 K=1,MT
DO 29 J=1,NS
CONCT(1)=CONCT(1)-2*(MASO(I,J,K)-MASS(I,J,K))
29 CONCT(4)=CONCT(4)+2*(MASO(I,J,K)-MASS(I,J,K))
MT=NTI(NV)
DO 30 K=1,MT
DO 30 J=1,NS
30 CONCT(4)=CONCT(4)+MASO(NV,J,K)-MASS(NV,J,K)
31 I1=I1+1
IF (I1.LI.2) GO TO 33
IF (DT.EQ.DIMAX) GO TO 33
NTEST=0
DO 32 I=1,NV
MT=NTI(I)
DO 32 J=1,NS
DO 32 K=1,MT
IF (MASO(I,J,K).EQ.0.) GO TO 32
TEST=(MASO(I,J,K)-MASI(I,J,K))/MASO(I,J,K)
IF (ABS(TEST).GE.EPS) NTEST=NTEST+1
32 CONTINUE
I1=0
33 DO 34 I=1,NV
MT=NTI(I)
MCI=0.
DO 34 K=1,MT
MCI(I,K)=0.
DO 34 J=1,NS
MCI(I,K)=MCI(I,K)+MASS(I,J,K)
34 MCI=4(I)*MASS(I,J,K)
TIME=TIME+DT
IF (NPOTL.NE.0) CALL PEZFER (TIME,POTL,DROT,1,P,N,ND)
IF (NPOTL.NE.0) CALL CONCTN (TEMP,CONCT,ACTV,XEO,CONC,EPS)
IF (NPOTL.NE.0) CALL REDOX (CONC,ACTV,TEMP,ELJ,PIL)
IF (NPOTL.NE.0) POTL=PIL
IF (NPOTL.EQ.0) PIL=POTL
IF (MODE.LI.2) GO TO 37
DO 35 I=1,NV
MT=NTI(I)
XI(N,1,TIME)=XMX(I)*M(I)/M0(I)
DO 35 K=1,MT
35 M1(I,K)=M1(I,K)/M10(I,K)
WRITE (3,43) TIME,POTL,(XI(N,1,NTHP),I=1,NV)
IF (MODE.LI.3) GO TO 37
DO 36 I=1,NV
MT=NTI(I)
WRITE (3,64) (M1(I,K),K=1,MT)
DO 36 K=1,MT
IF (MODE.LI.3) GO TO 36

```

```

44 NTEST=0
DO 54 I=1,NV
DO 54 K=1,NT
IF (CS1(K,I,2).EQ.0.) GO TO 54
SC1(K,I,2)=-ESQ(I,K,2)/ESQ(I,K,3)
SC1(K,I,1)=SC1(K,I,2)/TT(I,K)
IF ((SC1(K,I,2)*CS1(K,I,2)).LT.0.) CS1(K,I,2)=-CS1(K,I,2)/2
IF ((SC1(K,I,2)/CS1(K,I,2)).GT.1.) SC1(K,I,2)=CS1(K,I,2)
IF (ABS(SC1(K,I,1)).LT.EPS) GO TO 54
NTEST=NTEST+1
54 CONTINUE
IF (NTEST.EQ.0) GO TO 57
55 IJK=1
IF (MODE.EQ.2) CLOSE 3
KK=1
IF (MODE.NE.0) WRITE (10,67) (ESQ(I,1,1),I=1,NV)
IF (NPRINT.NE.0) WRITE (12,80) (ESQ(I,1,1),I=1,NV)
IF (MODE.NE.0) GO TO 59
DO 55 I=1,NV
NT=N.
DO 55 I,NT
IF (CS1(K,I,2).EQ.0.) GO TO 56
IF ((TT(I,K)+SC1(K,I,2)).LE.0.) SC1(K,I,2)=-0.9*TT(I,K)
TT(I,K)=TT(I,K)+SC1(K,I,2)
56 CONTINUE
DO 53 I=1,NV
WRITE (10,66) KOUNT,ESQ(I,1,1),(TT(I,K),K=1,NTM),(SC1(K,I,1),K=1,NT)
53 CONTINUE
KOUNT=KOUNT+1
IF (KOUNT.LT.100) GO TO 11
WRITE (10,68)
57 WRITE (10,69)
WRITE (10,70)
WRITE (10,74) (MM,1,I=1,NV)
WRITE (10,70) (MM,1,I=1,NV)
DO 58 N=1,NX
ND=NX*(N)
DO 58 J=1,ND
WRITE (10,71) T(N,J),(X(N,I,J),XI(N,I,J),I=1,NV)
58 CONTINUE
59 DO 60 I=1,NV
N1=NT(I)
NCH=" "
WRITE (10,72) (I,K,TT(I,K),CI(K,I),K=1,NT)
IF (NPRINT.NE.0) WRITE (12,81) (NCH,TT(I,K),CI(K,I),K=1,NT)
60 CONTINUE
STOP
61 FORMAT (14,4H 0 0)
62 FORMAT (F8.2,4X,5(F7.1,2X),F10.1,5X,1P2E12.3,/,1P13E10.2,/)
63 FORMAT (F7.3,F6.0,4F7.4)
64 FORMAT (13X,13F7.4)
65 FORMAT (F4.0,F7.0,8F7.4,2F6.1)
66 FORMAT (15,F10.5,1P3E10.2,2X,0P3F8.5)
67 FORMAT (//,2HSUM OF SQUARED ERRORS =,1P4E12.2)
68 FORMAT (2SHMAX ITERATIONS EXCEEDED)
69 FORMAT (///,34HPREDICTED VS. MEASURED EXTRACTIORS,/,30(1H*),/)
70 FORMAT (/,4HTIME,3X,4HPDCL,4(A2,1X,4HMEAS,3X,4HCALC),/)
71 FORMAT (F4.0,4F7.4)
72 FORMAT (//,9HCOMPONENT,12,1H,,8H MINERAL,12,3H 1,5X,4HCl =,
1 1PE12.5,5X,4HC2 =,1PE12.5)
73 FORMAT (30A2)
74 FORMAT (11X,4(A2,1X,9HCOMPONENT,12))
75 FORMAT (1H1,50A2)

```

```

76 FORMAT (1H0,34HPREDICTED VS. MEASURED EXTRACTIONS,/,1X,34(1H*),/)
77 FORMAT (1H0,11X,4(A2,1X,9HCOMPONENT,I2))
78 FORMAT (1H0,4HTIME,3X,4HP01L,4(A2,1X,4HMEAS,3X,4HCALC1,/)
79 FORMAT (1H ,F4.0,F7.0,8F7.4,2F6.1)
80 FORMAT (1H0,23HSUM OF SQUARED ERRORS =,1P4E10.1)
81 FORMAT (1H4,"RATE CONSTANT VALUES :",/,1X,22("**"),/,/,
1      10X,"1'ST CONSTANT",5X,"2'ND CONSTANT",/,/,
2      A1,"ALLOY :",1PE10.3,10X,0PF7.5,/,
3      A1,"TROILITE :",1PE10.3,10X,0PF7.5,/,
4      A1,"CU,FE-S :",1PE10.3,10X,0PF7.5)
END

```

SUBROUTINE KEQLM (T, KK, N)
REAL KK(17)

SET ALL EQUILIBRIUM CONSTANTS TO ZERO.

IF N IS SPECIFIED AS TWO OR GREATER, THE
EQUILIBRIUM CONSTANT VALUES ARE LEFT
AT ZERO.

DO 1 I=1,17

1 KK(I)=0.

IF (N.GT.0) GO TO 2

SET THE EQUILIBRIUM CONSTANT VALUES TO THE
VALUES GIVEN IN THE LITERATURE FOR ZERO
IONIC STRENGTH.

IF N IS SPECIFIED AS ZERO, THIS OPTION IS
SELECTED.

KK(2)=EXP(33.334-7629.9/T)

IF (T.LE.325.15) KK(4)=EXP(19.804-3140.0/T)

IF (T.GT.325.15) KK(4)=EXP(34.182-7815.2/T)

KK(4)=EXP(-900.421+39110.926/T+136.626*ALOG(T))

KK(5)=EXP(13.696-2717.4/T)

KK(6)=10.**(-3.339-337.37/T)

KK(7)=EXP(30.692-7290.4/T)

GO TO 3

2 IF (N.GT.1) GO TO 3

SET THE EQUILIBRIUM CONSTANTS TO THE VALUES
GIVEN IN THE LITERATURE FOR NON-ZERO IONIC
STRENGTHS.

IF N IS SPECIFIED AS ONE, THIS OPTION IS
SELECTED.

KK(1)=10.**(-22.742-5704.2/T)

KK(2)=10.**(-14.980-3927.7/T)

KK(3)=10.**(-9.752-2012.0/T)

KK(4)=10.**(-10.936-2654.1/T)

KK(5)=10.**(-8.526-2236.7/T)

KK(6)=10.**(-0.725-122.36/T)

KK(7)=10.**(-0.700-122.36/T)

3 RETURN

END

```

PARAMETER NXM=6,NDM=15
SUBROUTINE FE3FE2 (XX,POTL,OPOTL,X,Y,NN,ND)
REAL X(NXM,NDM),Y(NXM,NDM)
DO 1 I=2,ND
N=1
IF (X(NN,I).GT.XX) GO TO 2
CONTINUE
TAU=0.018
PTF=Y(NN,ND)-(Y(NN,I)-Y(NN,ND))*1.05
X1=ALOG(X(NN,N-1)+TAU)
Y1=ALOG(Y(NN,N-1)-PTF)
X2=ALOG(X(NN,N)+TAU)
Y2=ALOG(Y(NN,N)-PTF)
B=(Y2-Y1)/(X2-X1)
A=Y1-H*X1
POTL=PTF+EXP(A+B*ALOG(XX+TAU))
OPOTL=EXP(A+B*ALOG(XX+TAU))*B/(XX+TAU)
RETURN
END

```

```

PARAMETER NXM=6,NDM=15
SUBROUTINE IRON2 (XX,FE2,DFE2,X,Y,NN,ND)
REAL X(NXM,NDM),Y(NXM,NDM)
DO 1 I=2,ND
N=1
IF (X(NN,I).GT.XX) GO TO 2
CONTINUE
B=(Y(NN,N)-Y(NN,N-1))/(X(NN,N)-X(NN,N-1))
A=Y(NN,N)-B*X(NN,N)
FE2=A+B*XX
DFE2=B
RETURN
END

```

```

SUBROUTINE REDOX (C,A,T,ELJ,POTL)
REAL C(12),A(12),U(12),DU(12)
INTEGER N(12)
DATA N/3,1,-2,2,-1,0,2,-1,1,-1,0,1/
DATA U/70.,350.,80.,53.6,197.,0.,36.2,50.,50.,50.,0.,50./
DATA DU/.02,.0139,.022,.02,.0139,.00,.02,.02,.02,.02,.00,.02/
PL1=-4.2*(73.52+76.35)
PL2=-4.2*(73.52+76.35)
PL3= 0.
PL4= 4.2*(73.52+76.35)
DO 1 I=1,12
IF (N(I).EQ.0) GO TO 1
PL1=PL1+U(I)/N(I)*C(I)*ABS(N(I))
PL2=PL2+U(I)*C(I)*ABS(N(I))
PL3=PL3+U(I)*C(I)*ABS(N(I))
CONTINUE
ELJ=0.08617*T*PL1/PL2*ALOG(PL3/PL4)
EO=530+1.19*(T-298.15)
POTL=EO-0.08617*T*ALOG(C(4)*A(4)/C(1)/A(1))
POTL=POTL-ELJ
RETURN
END

```

SUBROUTINE CONCTN (T,C,Y,KK,X,EPS)

COMPONENTS AND COMPLEXES ARE ASSIGNED THE FOLLOWING SUBSCRIPTS

(1) = FE(3+)
 (2) = H(+)
 (3) = SO4(2-)
 (4) = FE(2+)
 (5) = NOT USED
 (6) = FE,H,SO4,SO4
 (7) = FE,H,SO4(2+)
 (8) = FE,SO4,SO4(-)
 (9) = FE,SO4(+)
 (10) = H,SO4(-)
 (11) = FE,SO4
 (12) = FE,H,SO4(+)

```

REAL C(4),E(4),XD(4),XE(4),XF(4),DXD(4),
1   K(7),KK(17),
2   X(12),Y(12),N(12),AO(12)
DATA N/3,1,-2,2,-1,0,2,-1,1,-1,0,1/
DATA AO/9,9,4,6,3,0,8,8,8,4,0,4/
CALL DEHUC (1,AA,BB)
KOUNT=0
TAUMAX=0.
DO 1 I=1,4
  XF(I)=C(I)
  DXD(I)=0.
  IF (C(I).GE.0.) GO TO 1
  TYPE "SUBROUTINE CONCTN : NEGATIVE TOTAL COMPOSITION INPUT"
  WRITE (10,1000)
  RETURN 0
1  TAUMAX=TAUMAX+C(I)*N(I)**2
2  TAU=0.
  DO 11 I=1,12
11 TAU=TAU+X(I)*N(I)**2
    IF (TAU.GT.TAUMAX) TAU=TAUMAX
    CALL KHSO4 (1,TAU,KK(5))
    TAI=SQRT(TAU)
    DO 12 I=1,12
12 Y(I)=10**(-AA*N(I)*N(I)*TAU/(1.+AO(I)*BB*TAU))
    K( 1)=KK( 1)/Y(6)*Y(1)*Y(2)*Y(3)**2
    K( 2)=KK( 2)/Y(7)*Y(1)*Y(2)*Y(3)
    K( 3)=KK( 3)/Y(8)*Y(1)*Y(3)**2
    K( 4)=KK( 4)/Y(9)*Y(1)*Y(3)
    K( 5)=KK( 5)
    K( 6)=KK( 6)/Y(11)*Y(3)*Y(4)
    K( 7)=KK( 7)/Y(12)*Y(2)*Y(3)*Y(4)
    XD(1)=1.+K(1)*X(2)*X(3)**2+K(2)*X(2)*X(3)+K(3)*X(3)**2+K(4)*X(3)
    XD(2)=1.+K(1)*X(1)*X(3)**2+K(2)*X(1)*X(3)+K(5)*X(3)+K(7)*X(3)*X(4)
    XD(3)=1.+2*K(1)*X(1)*X(2)*X(3)+K(2)*X(1)*X(2)+2*K(3)*X(1)*X(3)
    XD(4)=1.+K(4)*X(1)+K(5)*X(2)+K(6)*X(4)+K(7)*X(2)*X(4)
    DXD(3)=2*(K(1)*X(1)*X(2)+K(3)*X(1))
    XD(4)=1.+K(6)*X(3)+K(7)*X(2)*X(3)
    NEH=0
    DO 3 I=1,4
    E(I)=X(I)*XD(I)-C(I)
    IF (ABS(E(I)).LT.(EPS*C(I))) GO TO 3
    NEH=NEH+1
    XF(I)=-E(I)/(XD(1)+X(1)+DXD(1))
  
```

SUBROUTINE CONCTN (T,C,Y,KK,X,EP9)

COMPONENTS AND COMPLEXES ARE ASSIGNED THE FOLLOWING SUBSCRIPTS

(1) = FE(3+)
 (2) = H(+)
 (3) = SO4(2-)
 (4) = FE(2+)
 (5) = NOT USED
 (6) = FE.H.SO4.SO4
 (7) = FE.H.SO4(2+)
 (8) = FE.SO4.SO4(-)
 (9) = FE.SO4(+)
 (10) = H.SU4(-)
 (11) = FE.SO4
 (12) = FE.H.SO4(+)

```

REAL C(4),E(4),XD(4),XE(4),XF(4),DXD(4),
1   K(7),KK(17),
2   X(12),Y(12),N(12),A0(12)
DATA N/3,1,-2,2,-1,0,2,-1,1,-1,0,1/
DATA A0/9,9,4,6,3,0,8,8,8,4,0,4/
CALL DEHUC (1,AA,BB)
KOUNT=0
TAUMAX=0.
DO 1 I=1,4
  XF(I)=C(I)
  DXD(I)=0.
  IF (C(I).GE.0.) GO TO 1
  TYPE "SUBROUTINE CONCTN : NEGATIVE TOTAL COMPOSITION INPUT"
  WRITE (10,1000)
  RETURN 0
1  TAUMAX=TAUMAX+C(I)*N(I)**2
2  TAU=0.
  DO 11 I=1,12
11 TAU=TAU+X(I)*N(I)**2
    IF (TAU.GT.TAUMAX) TAU=TAUMAX
    CALL KHSO4 (1,TAU,KK(5))
    TAU=SDRT(TAU)
    DO 12 I=1,12
      Y(I)=10**(-AA*N(I)*N(I)*TAU/(1.+A0(I)*BB*TAU))
12 CONTINUE
    K( 1)=KK( 1)/Y(6)*Y(1)*Y(2)*Y(3)**2
    K( 2)=KK( 2)/Y(7)*Y(1)*Y(2)*Y(3)
    K( 3)=KK( 3)/Y(8)*Y(1)*Y(3)**2
    K( 4)=KK( 4)/Y(9)*Y(1)*Y(3)
    K( 5)=KK( 5)
    K( 6)=KK( 6)/Y(11)*Y(3)*Y(4)
    K( 7)=KK( 7)/Y(12)*Y(2)*Y(3)*Y(4)
    XD(1)=1.+K(1)*X(2)*X(3)**2+K(2)*X(3)+K(3)*X(3)**2+K(4)*X(3)
    XD(2)=1.+K(1)*X(1)*X(3)**2+K(2)*X(1)+K(5)*X(3)+K(7)*X(3)*X(4)
    XD(3)=1.+2*K(1)*X(1)*X(2)*X(3)+K(2)*X(1)*X(2)+2*K(3)*X(1)*X(3)
      +K(4)*X(1)+K(5)*X(2)+K(6)*X(4)+K(7)*X(2)*X(4)
1  DXU(3)=2*(K(1)*X(1)*X(2)+K(3)*X(1))
    XD(4)=1.+K(6)*X(3)+K(7)*X(2)*X(3)
    NER=0
    DO 3 I=1,4
      E(I)=X(I)*XD(I)=C(I)
      IF (ABS(E(I)).LT.(EP9*C(I))) GO TO 3
      NER=NER+1
    XF(I)=-E(I)/(XD(1)+X(1)+DXD(1))

```

```

IF ((XE(1)*XF(1)),LT.0.) XF(1)=-XF(1)/2
IF ((XE(1)/XF(1)),GT.1.) XE(1)=XF(1)
IF ((X(1)+XE(1)),LT.0.) XE(1)=-X(1)
IF ((X(1)+XE(1)),GT.C(1)) XE(1)=C(1)-X(1)
X(1)=X(1)+XE(1)
3 CONTINUE
X( 6)= K( 1)*X(1)*X(2)*X(3)**2
X( 7)= K( 2)*X(1)*X(2)*X(3)
X( 8)= K( 3)*X(1)*X(3)**2
X( 9)= K( 4)*X(1)*X(3)
X(10)= K( 5)*X(2)*X(3)
X(11)= K( 6)*X(4)*X(3)
X(12)= K( 7)*X(4)*X(2)*X(3)
IF (NEH.EQ.0) GO TO 4
KOUNT=KOUNT+1
IF (KOUNT.LE.10000) GO TO 2
WRITE (10,1000)
RETURN 0
4 RETURN
1000 FORMAT (24HSUBROUTINE CONCTN FAILED)
END

```

```

SUBROUTINE DEHUC (T,A,B)
REAL TT(18),AA(18),BB(18)
DATA TT(1),AA(1),BB(1),I=1,18)/
1 0.,.3466,.2294, 5.,.3466,.2294, 10.,.3492,.2305,
2 15.,.3510,.2311, 18.,.3538,.2315, 20.,.3549,.2318,
3 25.,.3582,.2325, 30.,.3616,.2332, 35.,.3653,.2340,
4 40.,.3692,.2348, 45.,.3733,.2357, 50.,.3777,.2366,
5 55.,.3823,.2376, 60.,.3871,.2386, 70.,.3973,.2407,
6 80.,.4083,.2429, 90.,.4200,.2452,100.,.4325,.2476/
DO 1 I=2,18
IF (T.LE.TT(I)) GO TO 2
1 CONTINUE
2 A=AA(I-1)+(T-TT(I-1))*(AA(I)-AA(I-1))/(TT(I)-TT(I-1))
B=BB(I-1)+(T-TT(I-1))*(BB(I)-BB(I-1))/(TT(I)-TT(I-1))
RETURN
END

```

```

SUBROUTINE KHS04 (T,TAU,K)
REAL K,K2,M,MH,M1,M2,I,J
K2=EXP(14.03231-2825.2/T)
BH10= 0.05584+ 46.040/T
BH11=-0.05758+336.514/T
BH20=-0.52806+ 98.607/T
CH20= 0.25333- 63.124/T
AD=0.3770+4.684E-4*(T-273.15)+3.74E-6*(T-273.15)**2
I=SQRT(1/TAU/2)
S=-AU*(1/(1.+1./2**I)+(2/1.2)*ALOG(1.+1./2**I))
BH1=BH10+BH11/TAU*(1.-1./2**I)*EXP(-2**I)
BH2=BH11/(TAU**2/2)*(-1.+(1.+2*I*TAU)*EXP(-2**I))
CH2=CH20/2.0**1.5
M=TAU/2
MH=M
M1=M
M2=0.
DM=M/2
N=1
1 ACTIV=EXP(4*F+2*(M1-MH)*BH1+2*(M2+MH)*BH2
+2*MH*(2*M2+MH)*CH2+4*M1*MH*BH2)
K=K2*ACTIV
J=-1
2 MH=(K*M-1.+SQRT((1.-K*M)**2+8*K*M))/(2*K)
M1=2*M-MH
M2=M-M1
IF (J.GT.01 GO TO 1
E=M+2*M2-TAU/2
IF (ABS(E).LT.0.001) GO TO 3
DE=(1.+K*M)/SQRT((1.-K*M)**2+8*K*M)
SM=E/DE
IF ((SM*DM).LT.0.) DM=-DM/2
IF ((SM/DM).GT.1.) SM=DM
M=M+SM
J=1
N=N+1
IF (N.LE.1000) GO TO 2
WRITE (10,1000)
3 RETURN
1000 FORMAT ('*****') SUBROUTINE KHS04 HAS NOT CONVERGED"
END

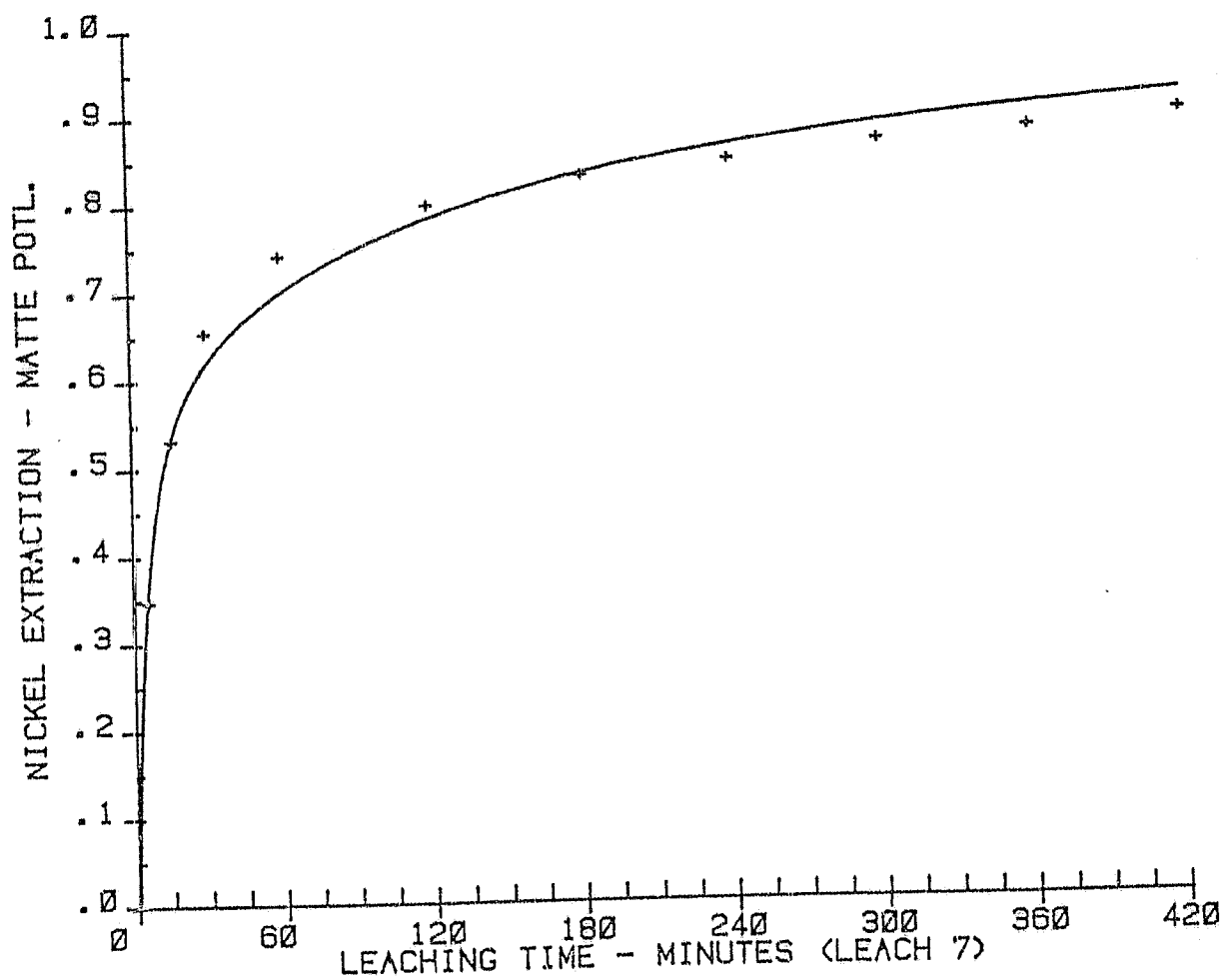
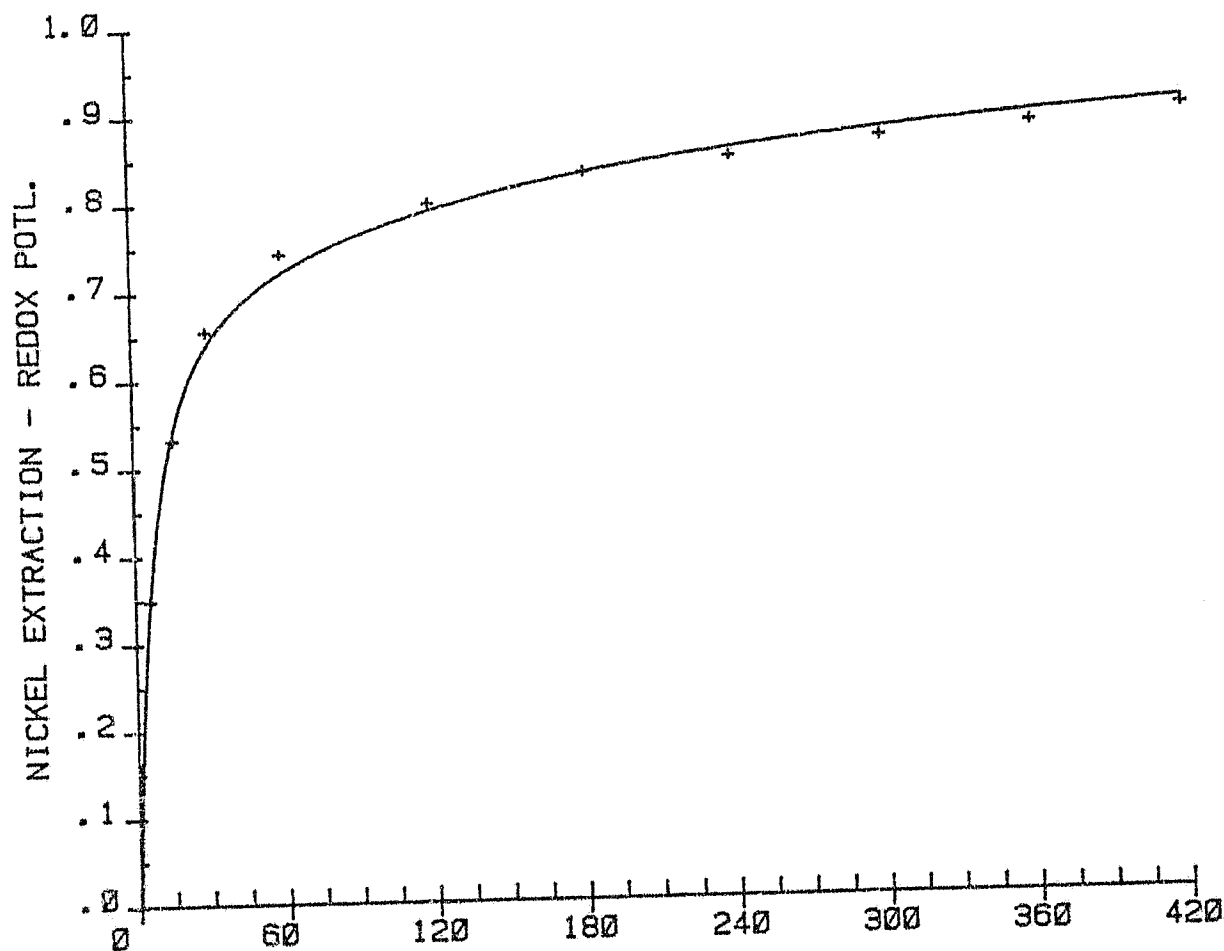
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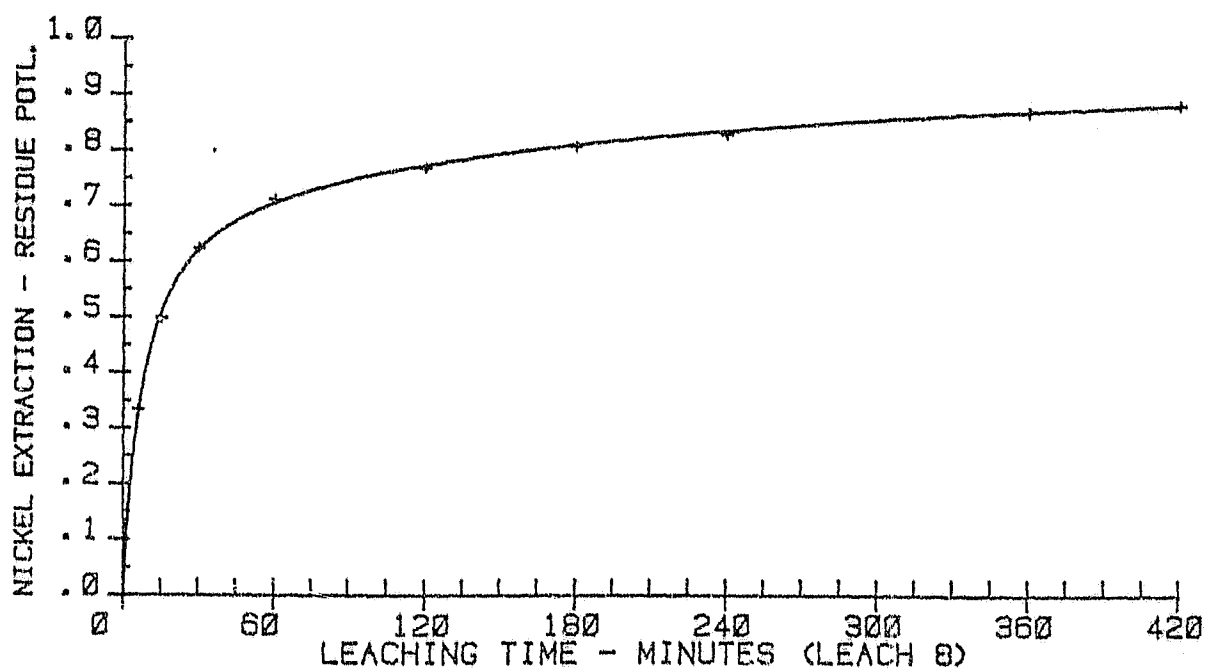
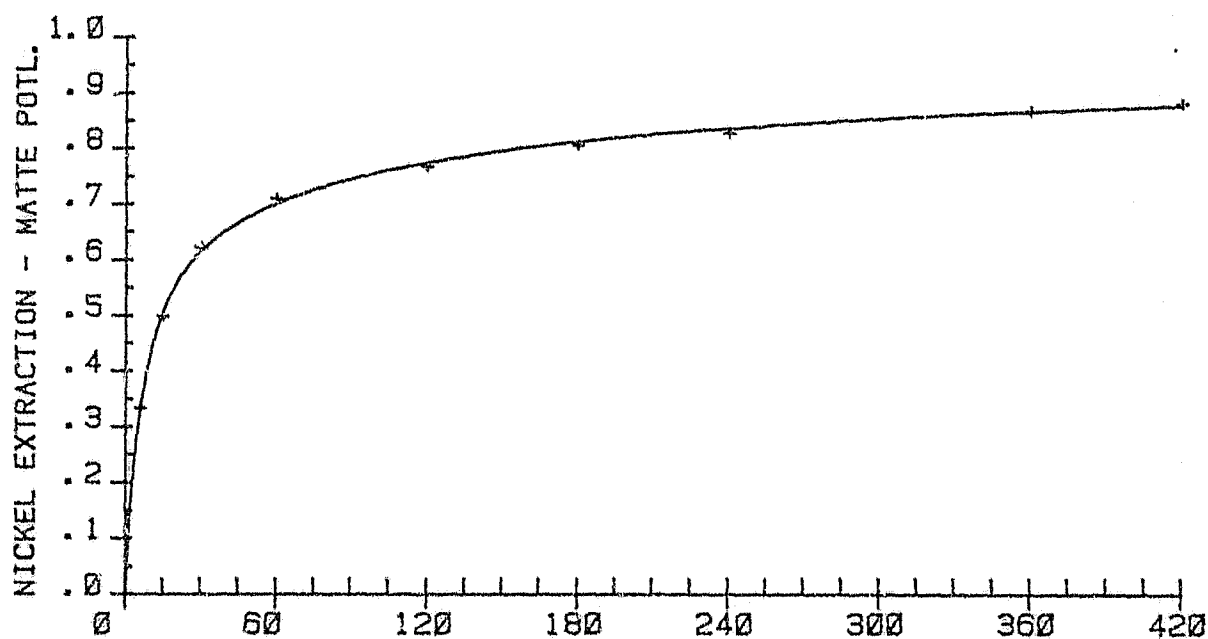
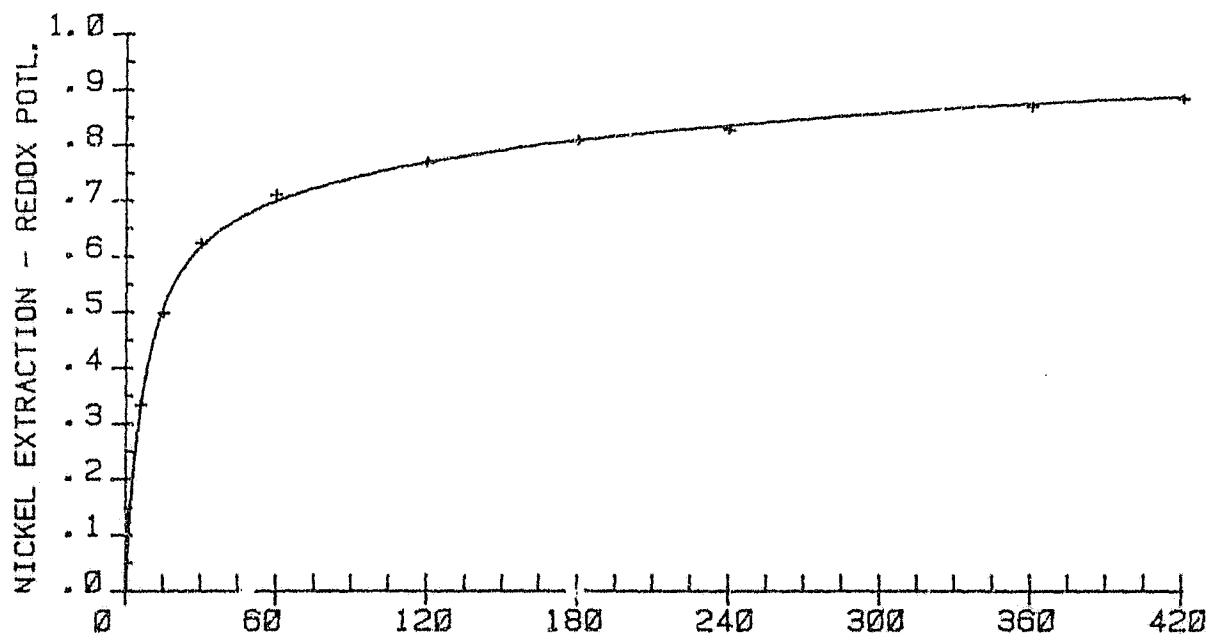
APPENDIX IX

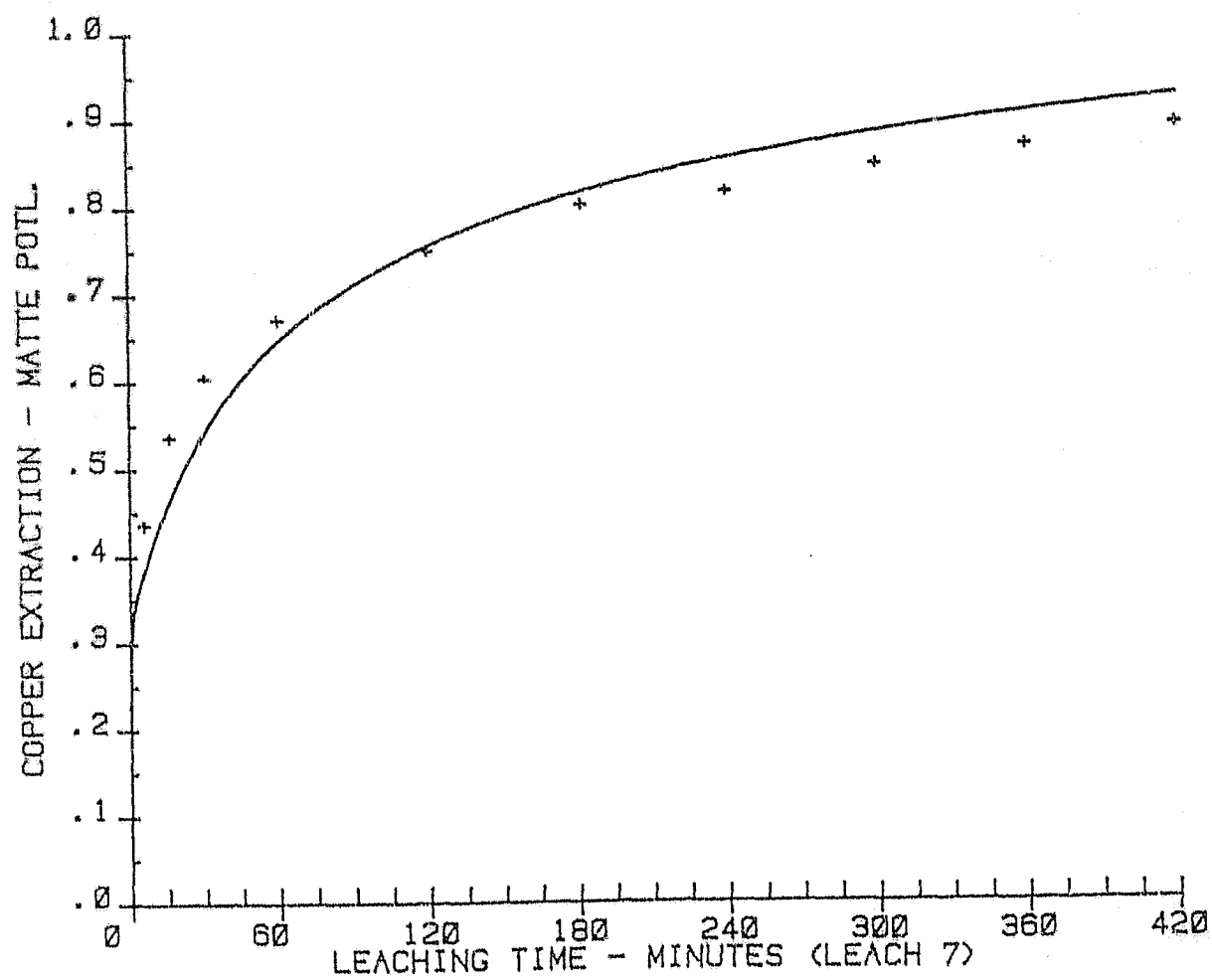
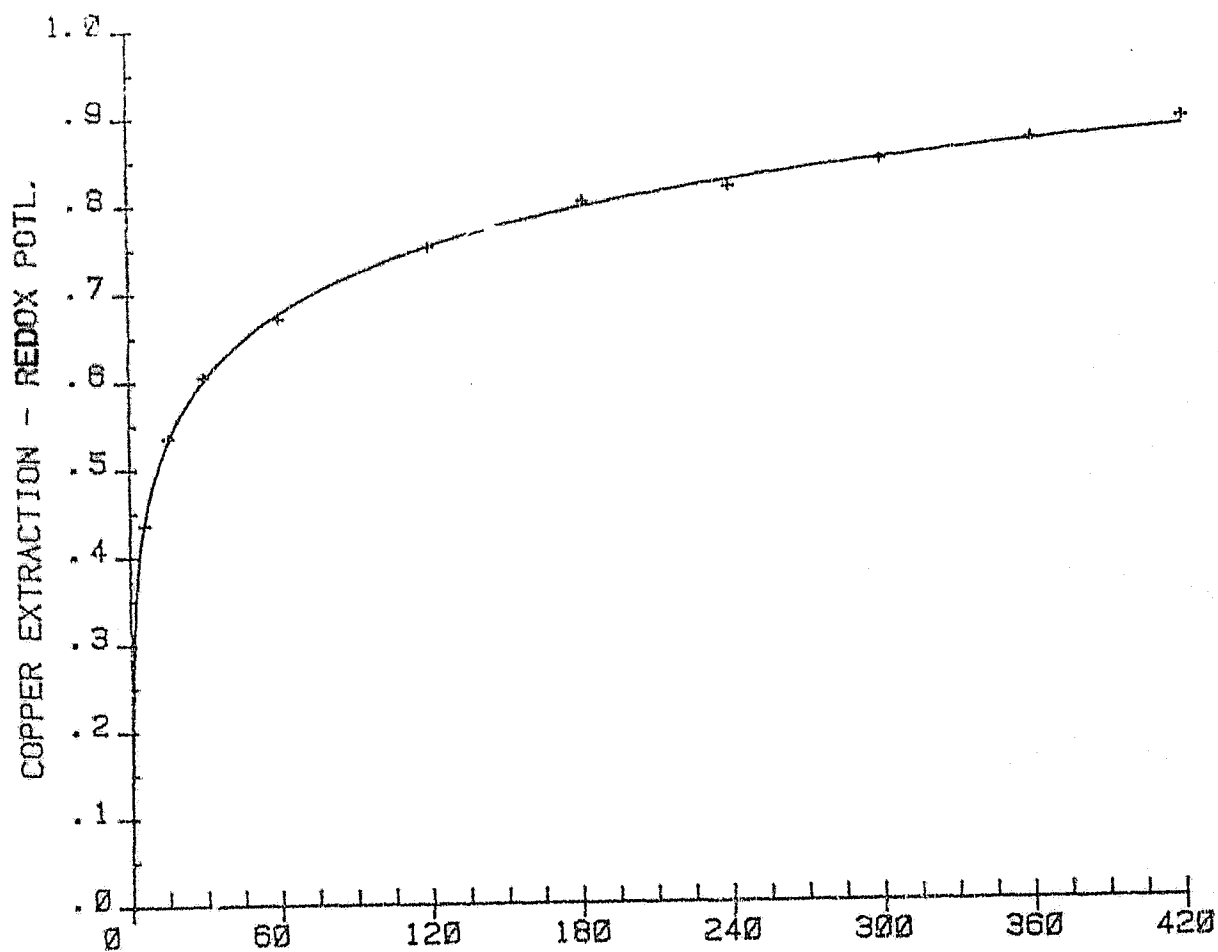
Results of fitting the leaching model -

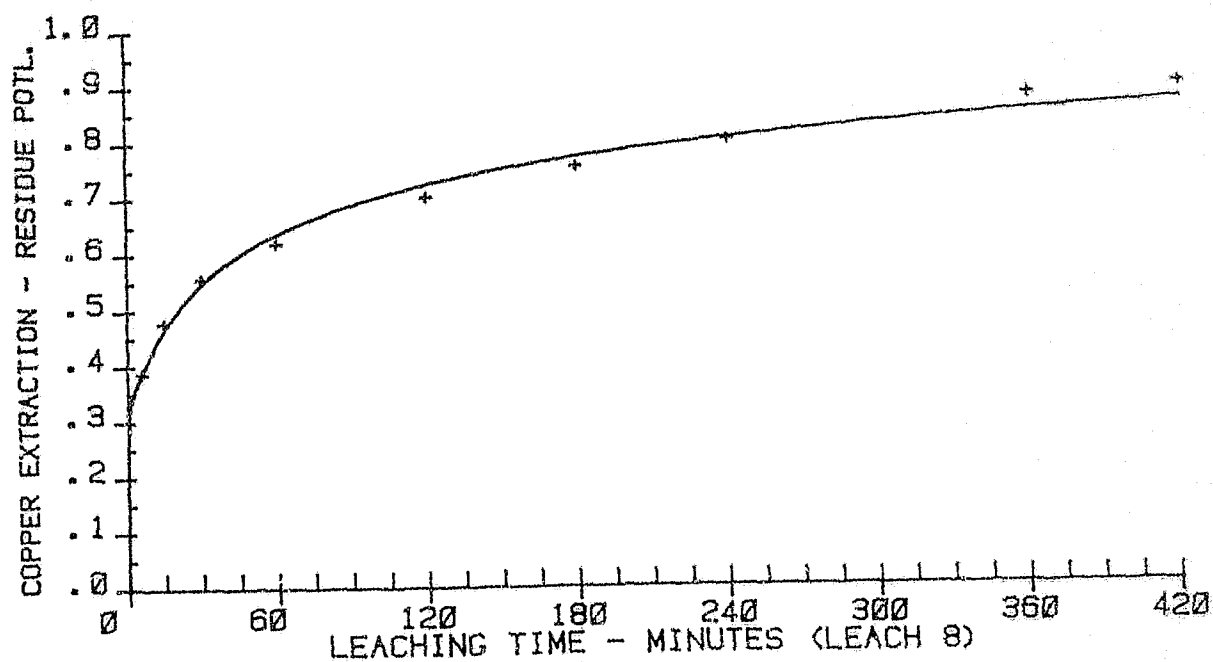
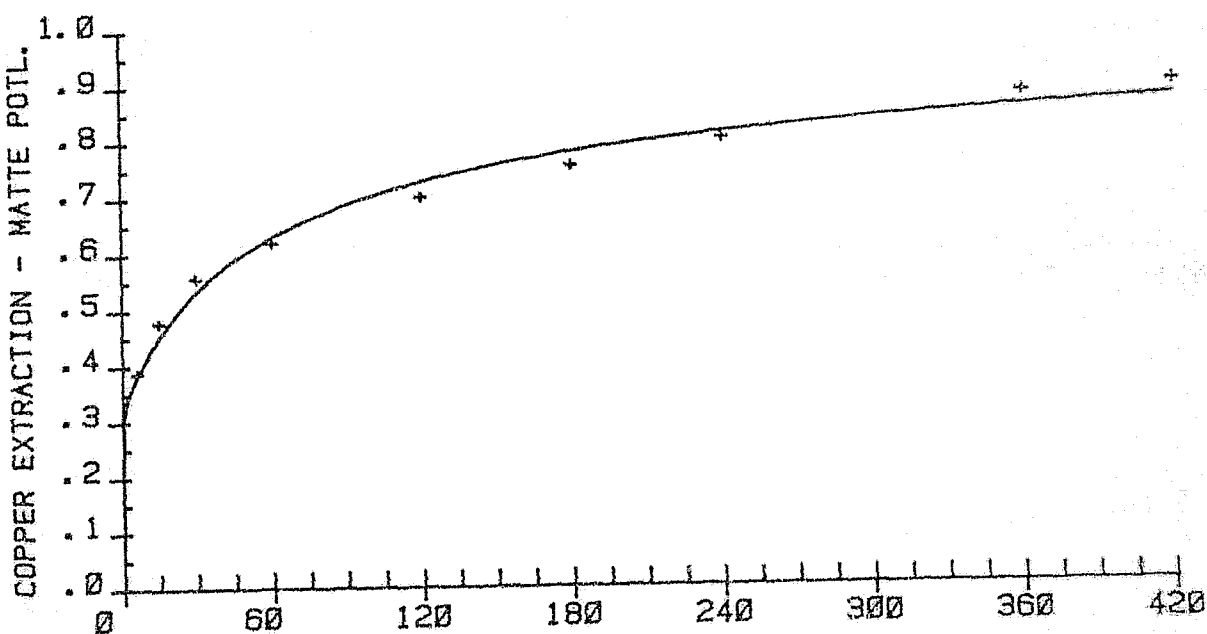
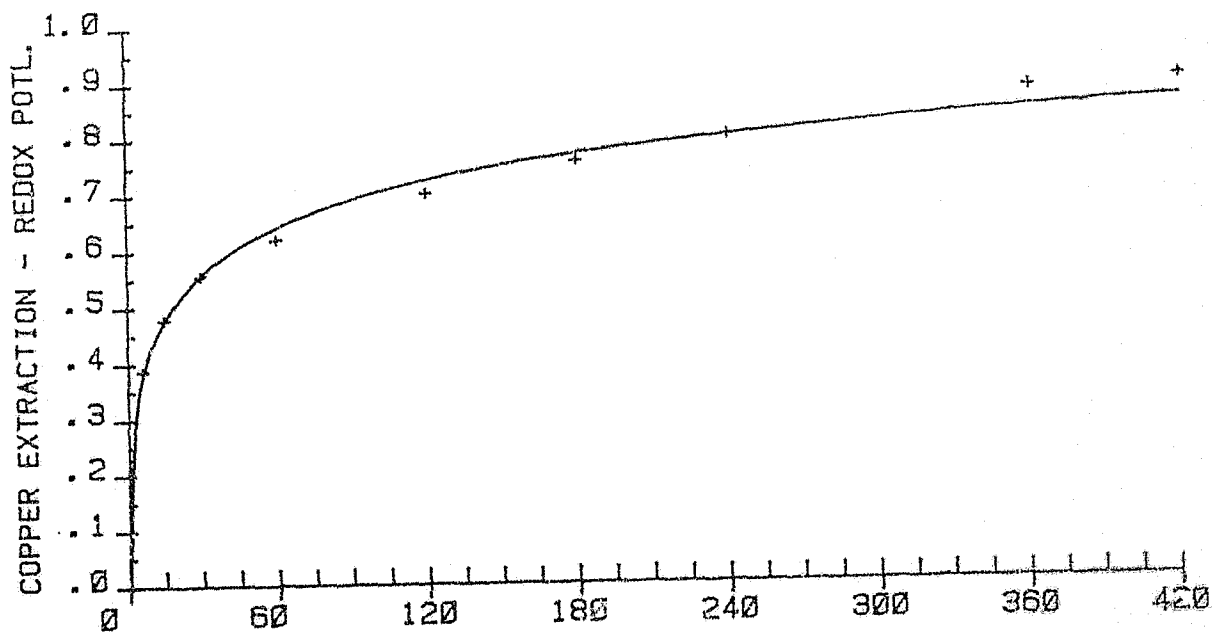
Graphs of predicted and measured extraction vs time curves for nickel, copper, cobalt and iron, for leaches 7 and 8, using redox, matte and residue potentials to approximate the particle surface potential during leaching.

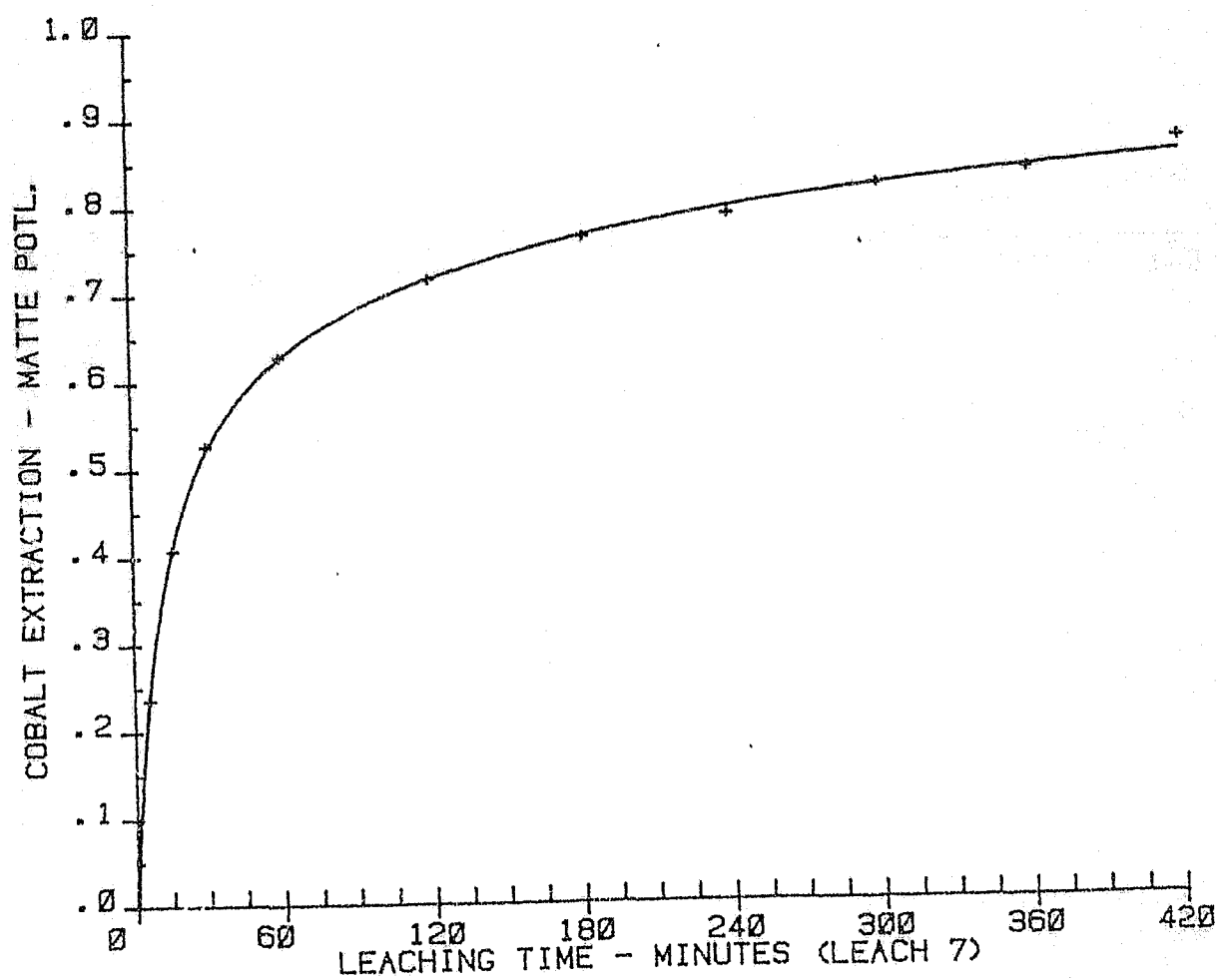
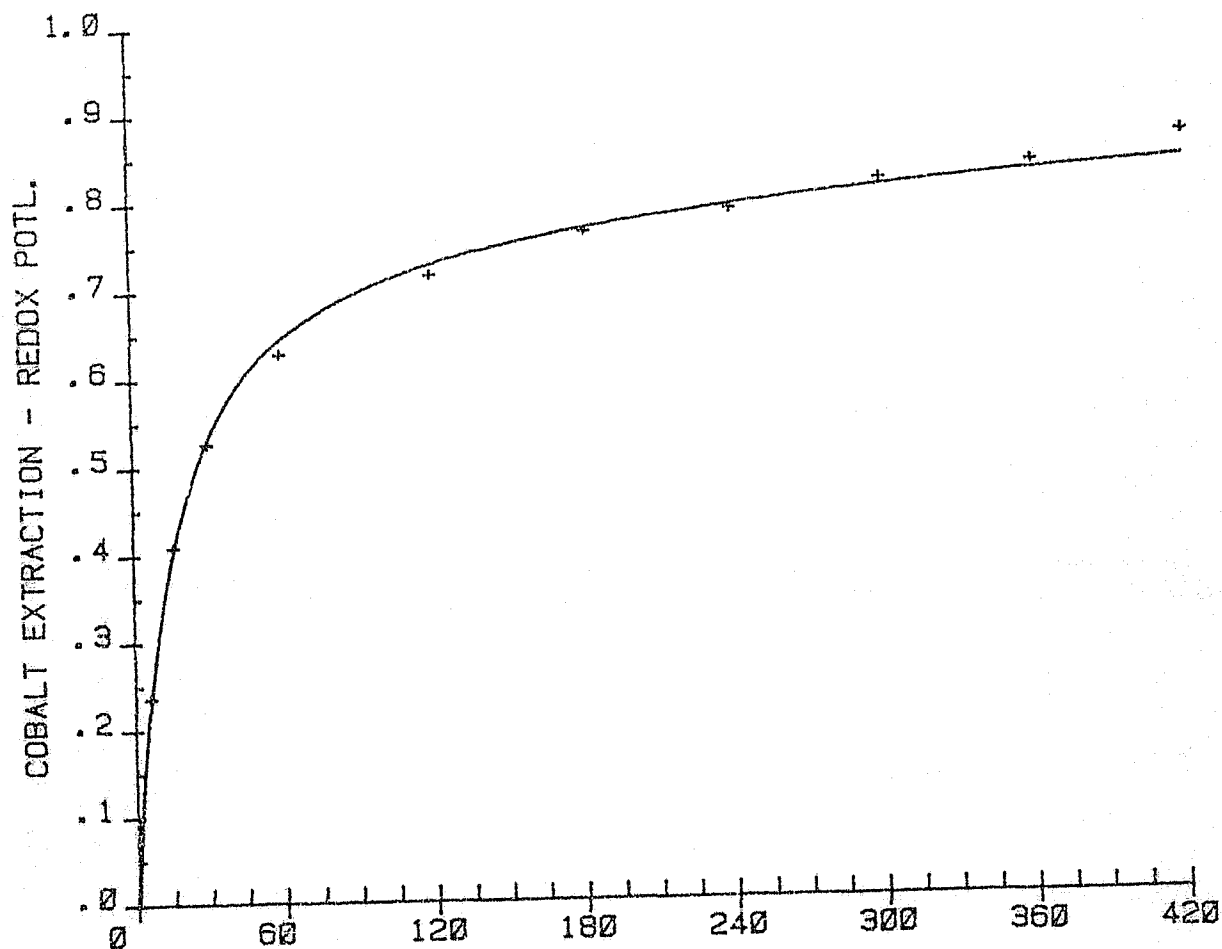
Leaching model computer printouts.

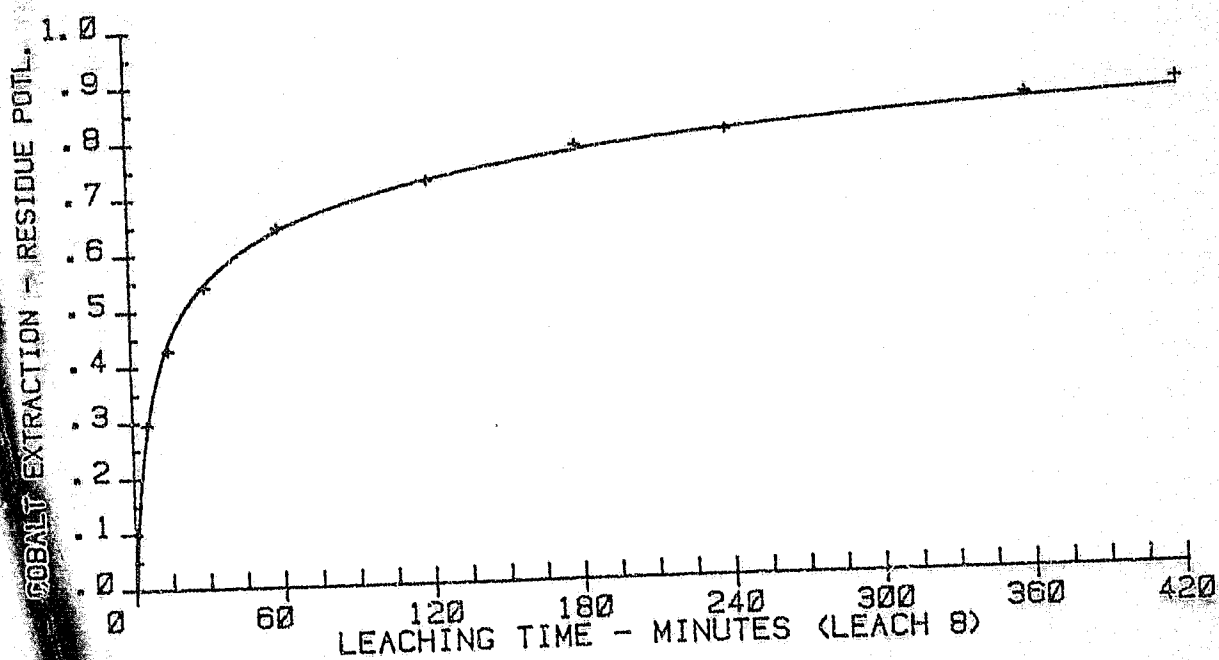
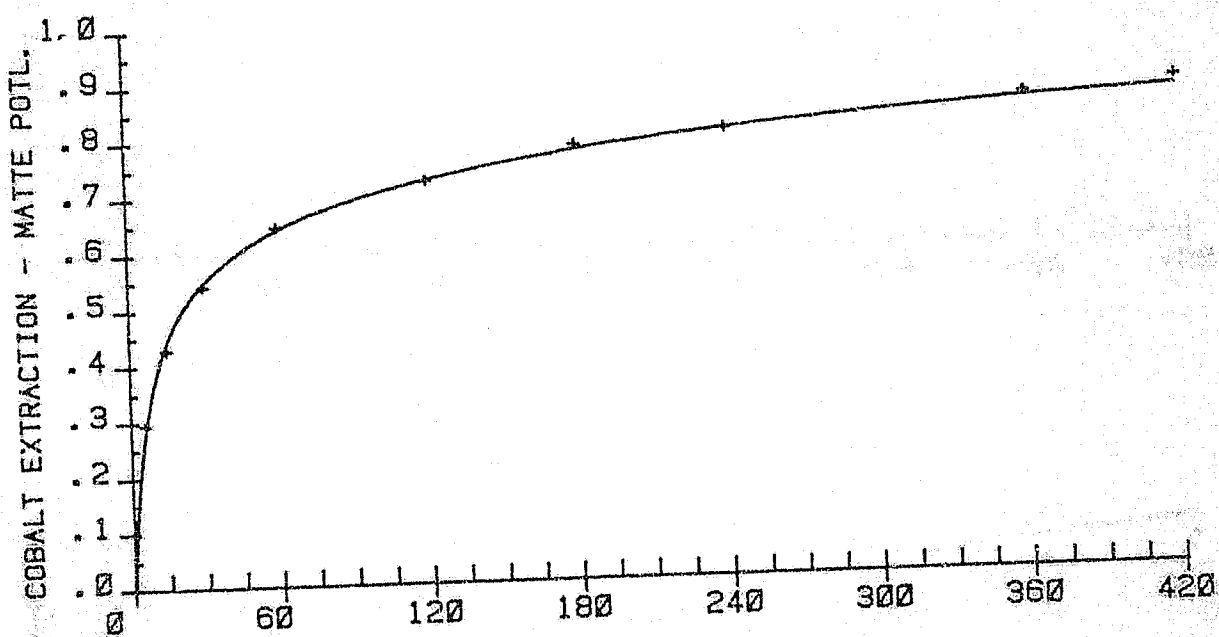
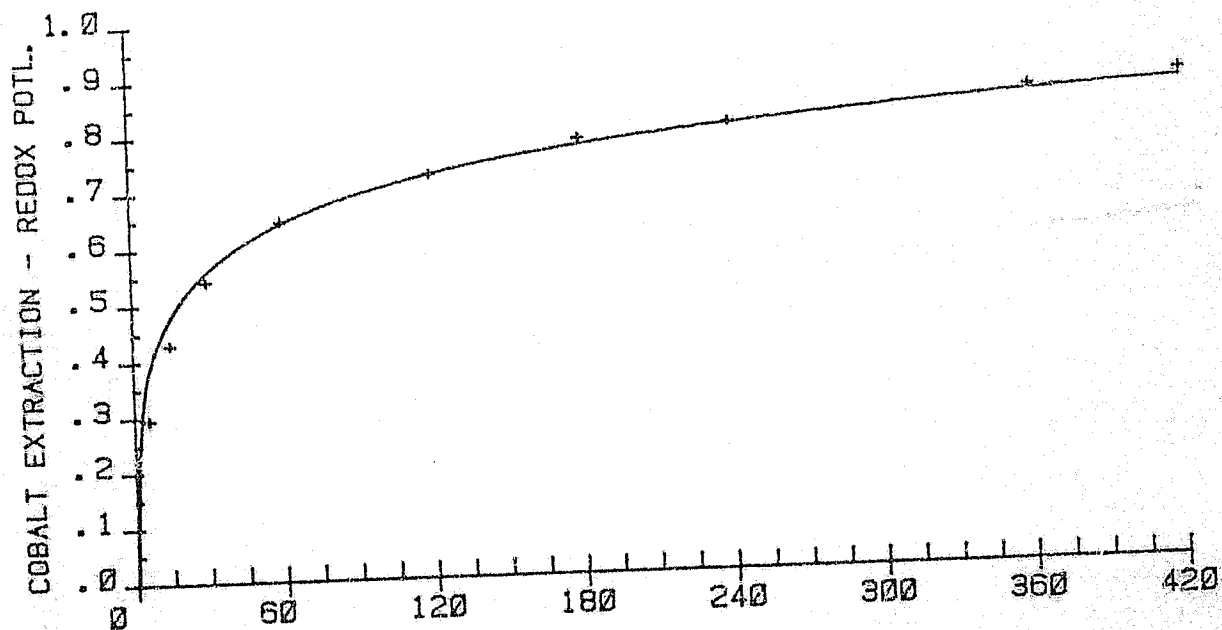


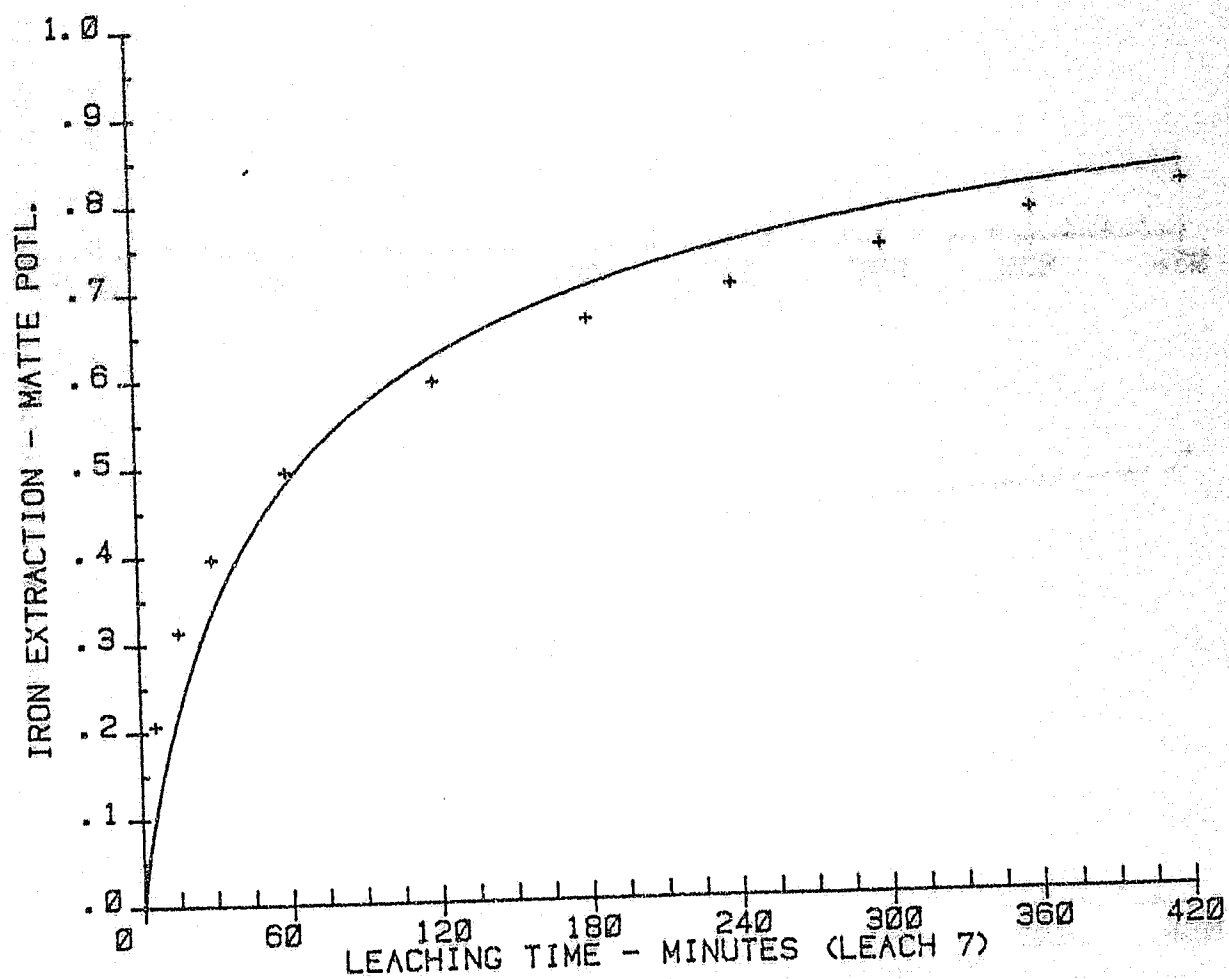
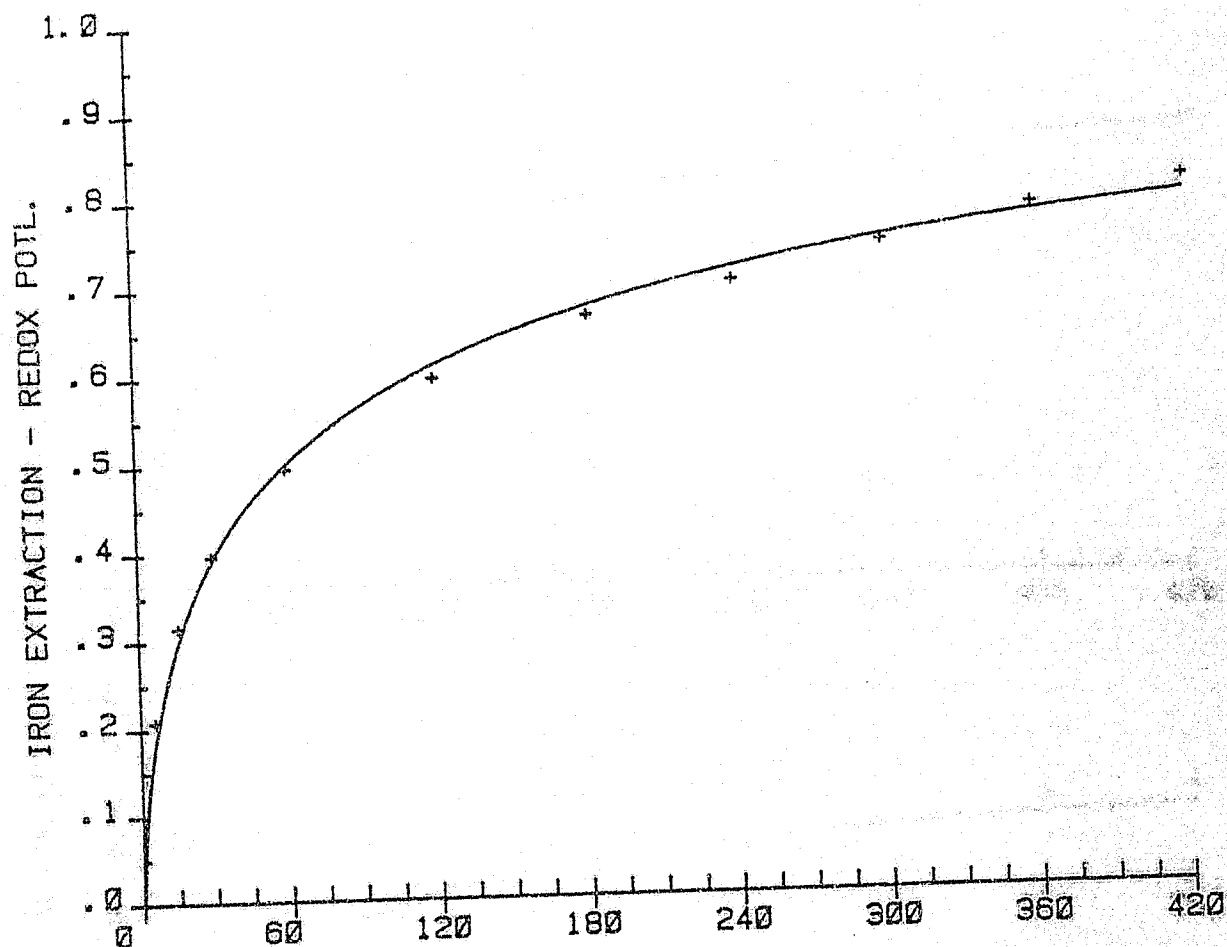


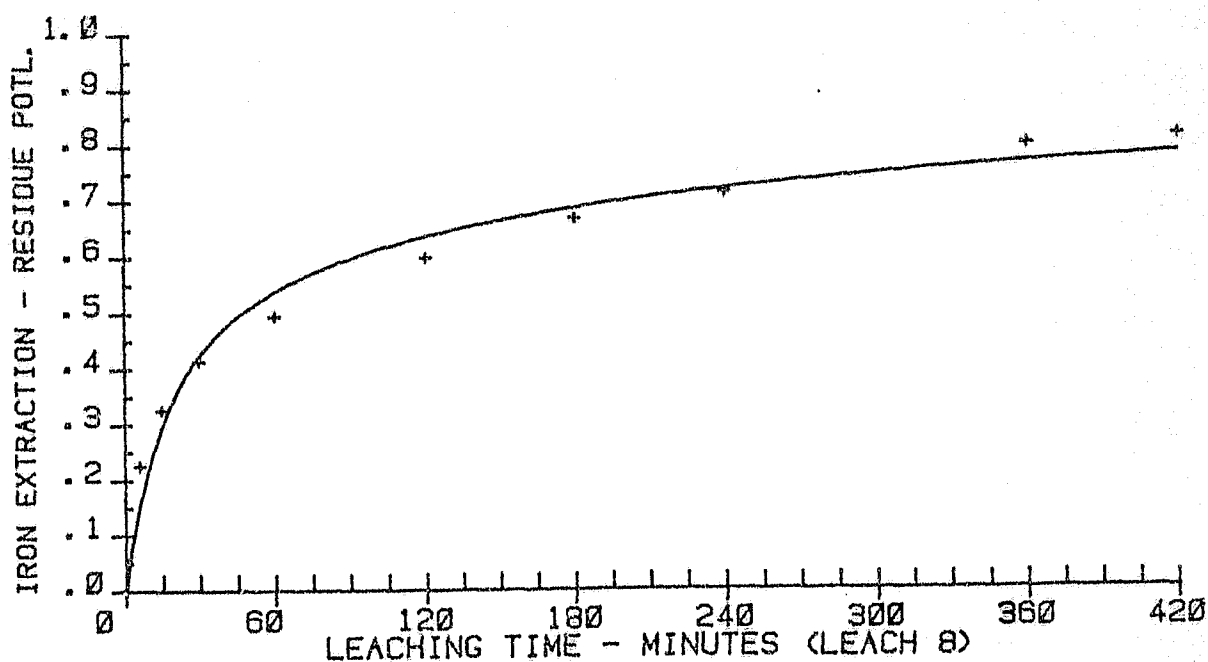
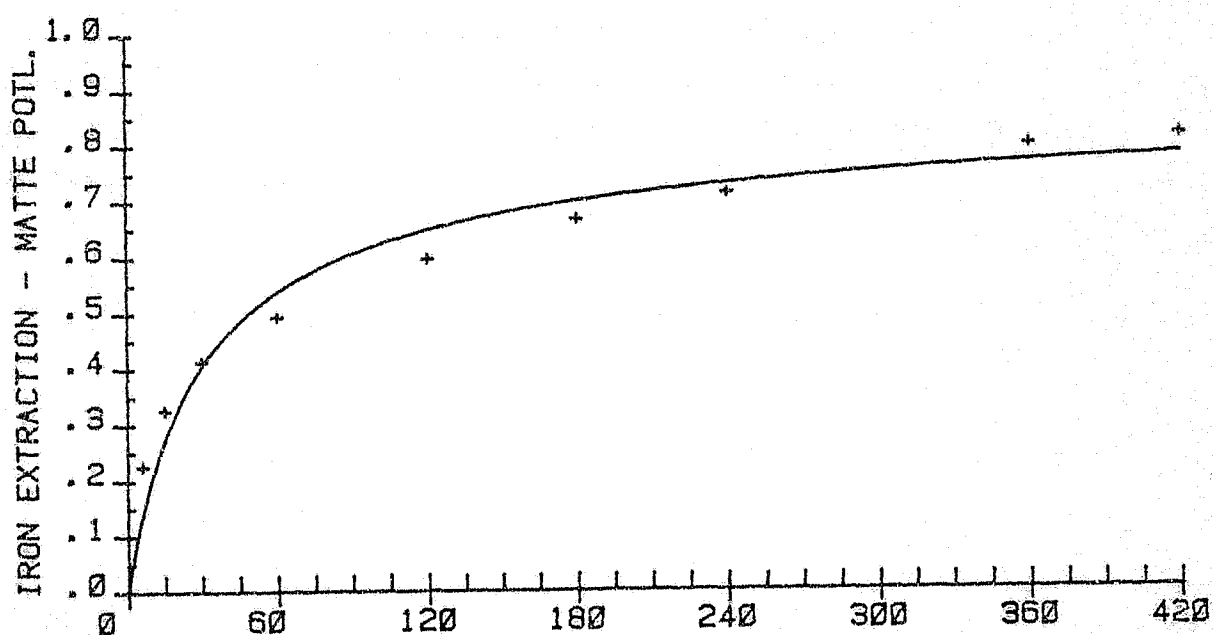
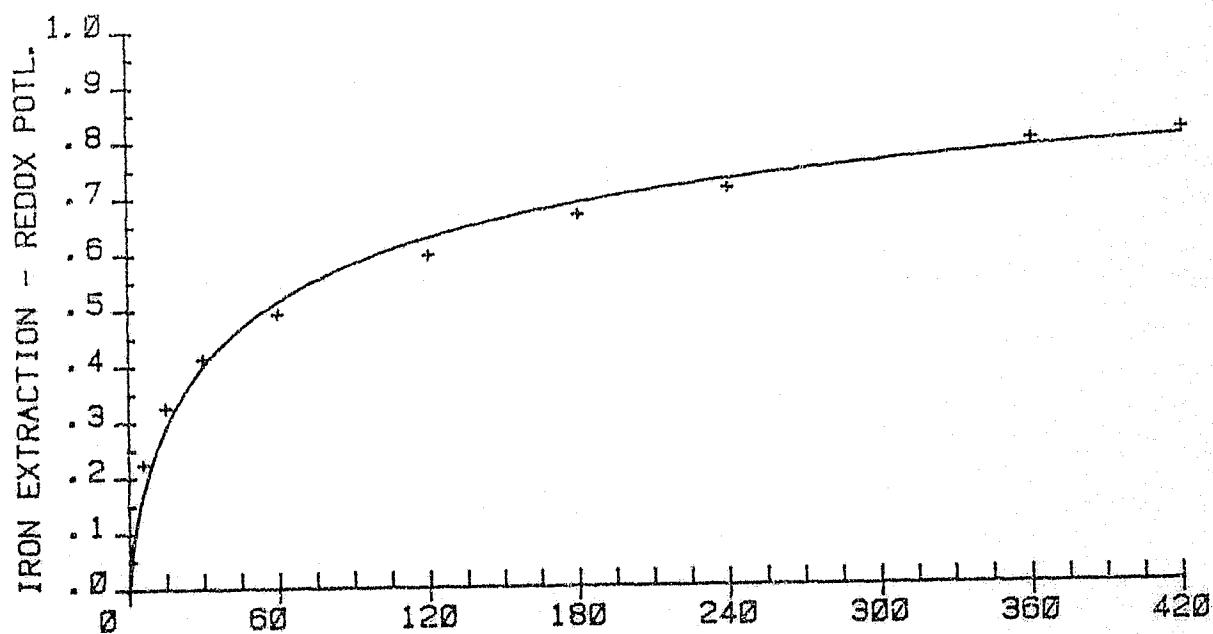












Computer printouts of leaching results

NOTE:

The "1st CONSTANT" in the following printouts refers to the constant K in equation 14 (page 58) of section 4.1.1.1.

The "2nd CONSTANT" is the value for the constant k in equation 22 (page 61) of section 4.1.1.2.

LEACHING OF NICKEL FROM MATTE - LEACHES 3 TO 6

PREDICTED VS. MEASURED EXTRACTIONS

COMPONENT 1

TIME	POTL	MEAS	CALC
6.	486.	.2460	.2382
15.	486.	.4180	.4031
30.	484.	.5350	.5228
60.	483.	.6320	.6110
120.	479.	.7010	.6820
180.	478.	.7410	.7242
240.	476.	.7720	.7564
360.	473.	.8090	.8017
6.	517.	.2550	.2448
15.	516.	.3940	.4185
30.	514.	.5200	.5505
60.	511.	.6530	.6560
129.	506.	.7620	.7516
180.	505.	.7960	.7893
240.	504.	.8290	.8212
300.	503.	.8460	.8447
360.	503.	.8670	.8629
420.	502.	.8830	.8774
6.	551.	.2920	.2581
15.	545.	.4250	.4463
30.	541.	.5440	.5937
60.	537.	.6770	.7146
120.	533.	.7840	.8071
180.	530.	.8250	.8494
240.	528.	.8620	.8758
300.	527.	.8730	.8947
330.	524.	.9030	.9020
6.	582.	.3390	.3156
15.	573.	.5220	.5169
30.	564.	.6820	.6705
60.	558.	.7880	.7859
120.	550.	.8720	.8621
180.	547.	.9100	.8936
240.	546.	.9140	.9136
300.	544.	.9360	.9283
360.	544.	.9440	.9396
420.	543.	.9550	.9485

SUM OF SQUARED ERRORS = 1.2E-02

RATE CONSTANT VALUES :

1'ST CONSTANT

2'ND CONSTANT

ALLOY : 1.123E-06

.00000

TROILITE : 7.784E-14

.01900

LEACHING OF NICKEL FROM MATTE - LEACH 7 - REDOX POTENTIAL

PREDICTED VS. MEASURED EXTRACTIONS

COMPONENT 1

TIME	POTL	MEAS	CALC
6.	587.	.3480	.3487
16.	576.	.5320	.5409
30.	568.	.6540	.6393
60.	560.	.7410	.7200
120.	556.	.7960	.7882
182.	552.	.8280	.8284
240.	552.	.8440	.8541
300.	548.	.8630	.8733
360.	547.	.8750	.8879
420.	546.	.8910	.8996

SUM OF SQUARED ERRORS = 1.2E-03

RATE CONSTANT VALUES :

1ST CONSTANT

2ND CONSTANT

ALLOY	:	1.777E-06	.00000
TROILITE	:	3.843E-14	.01900

LEACHING OF NICKEL FROM MATTE - LEACH 7 - MATTE POTENTIAL

PREDICTED VS. MEASURED EXTRACTIONS

COMPONENT 1

TIME	POTL	MEAS	CALC
6.	447.	.3480	.3585
16.	450.	.5320	.5340
30.	454.	.6540	.6184
60.	457.	.7410	.6987
120.	471.	.7960	.7818
182.	466.	.8280	.8317
240.	455.	.8440	.8621
300.	446.	.8630	.8845
360.	436.	.8750	.9012
420.	434.	.8910	.9144

SUM OF SQUARED ERRORS = 5.4E-03

RATE CONSTANT VALUES :

1'ST CONSTANT

2'ND CONSTANT

ALLOY : 2.187E-06
 TROILITE : 1.755E-09

.00000
 .00000

LEACHING OF NICKEL FROM MATTE - LEACH 8 - REDOX POTENTIAL

PREDICTED VS. MEASURED EXTRACTIONS

COMPONENT 1

TIME	POT.	MEAS	CALC
6.	579.	.3340	.3296
15.	571.	.4980	.5074
30.	563.	.6230	.6176
60.	556.	.7100	.6986
120.	550.	.7670	.7676
180.	546.	.8060	.8075
240.	544.	.8270	.8350
300.	543.	.8630	.8554
360.	540.	.8660	.8711
420.	538.	.8790	.8835

SUM OF SQUARED ERRORS = 4.4E+04

RATE CONSTANT VALUES :

1'ST CONSTANT

2'ND CONSTANT

ALLOY : 1.694E-06
TROILITE : 3.647E-14

.00000
.01900

LEACHING OF NICKEL FROM MATTE - LEACH 8 - MATTE POTENTIAL

PREDICTED VS. MEASURED EXTRACTIONS

COMPONENT 1

TIME	POTL	MEAS	CALC
6.	497.	.3340	.3308
15.	496.	.4980	.5064
30.	493.	.6230	.6155
60.	487.	.7100	.7014
120.	475.	.7670	.7744
180.	467.	.8060	.8123
240.	454.	.8270	.8360
300.	450.	.8630	.8530
360.	441.	.8660	.8655
420.	438.	.8790	.8753

SUM OF SQUARED ERRORS = 5.0E-04

RATE CONSTANT VALUES :

1'ST CONSTANT

2'ND CONSTANT

ALLOY	:	1.832E-06	.00000
TROILITE	:	4.210E-13	.01700

LEACHING OF NICKEL FROM MATTE - LEACH 8 - RESIDUE POTENTIAL

PREDICTED VS. MEASURED EXTRACTIONS

COMPONENT 1

TIME	POTL	MEAS	CALC
6.	498.	.3340	.3274
15.	493.	.4980	.5077
30.	478.	.6230	.6210
60.	455.	.7100	.7041
120.	436.	.7670	.7710
180.	424.	.8060	.8083
240.	417.	.8270	.8336
300.	413.	.8630	.8524
360.	409.	.8660	.8670
420.	407.	.8790	.8789

SUM OF SQUARED ERRORS = 3.6E-04

RATE CONSTANT VALUES :

1ST CONSTANT

2ND CONSTANT

ALLOY	: 1.761E-06	.00000
TROILITE	: 1.569E-11	.01000

LEACHING OF NICKEL FROM MATTE - LEACH 9

PREDICTED VS. MEASURED EXTRACTIONS

COMPONENT 1

TIME	POTL	MEAS	CALC
12.	593.	.1170	.1004
30.	581.	.2160	.2057
63.	571.	.3360	.3377
122.	566.	.4660	.4793
180.	563.	.5600	.5634
240.	561.	.6230	.6211
307.	560.	.6660	.6662
368.	559.	.7010	.6966

SUM OF SQUARED ERRORS = 5.9E-04

RATE CONSTANT VALUES :

1ST CONSTANT

2ND CONSTANT

ALLOY : 1.456E-07
 TROILITE : 2.102E-15

.00000
 .02120

LEACHING OF NICKEL FROM MATTE - LEACH 9

PREDICTED VS. MEASURED EXTRACTIONS

COMPONENT 1

TIME	POTL	MEAS	CALC
12.	593.	.1170	.1004
30.	581.	.2160	.2057
63.	571.	.3360	.3377
122.	566.	.4660	.4793
180.	563.	.5600	.5634
240.	561.	.6230	.6211
307.	560.	.6660	.6662
368.	559.	.7010	.6966

SUM OF SQUARED ERRORS = 5.9E-04

RATE CONSTANT VALUES :

1'ST CONSTANT

2'ND CONSTANT

ALLOY : 1.456E-07
 TROILITE : 2.102E-15

.00000
 .02120

LEACHING OF NICKEL FROM MATTE - LEACH 10

PREDICTED VS. MEASURED EXTRACTIONS

COMPONENT 1

TIME	POTL	MEAS	CALC
6.	640.	.0040	.0088
15.	620.	.0130	.0179
31.	600.	.0270	.0309
61.	580.	.0560	.0514
119.	571.	.0920	.0864
173.	566.	.1200	.1160
242.	565.	.1600	.1509
305.	563.	.1730	.1803
380.	562.	.2070	.2126

SUM OF SQUARED ERRORS = 3.0E-04

RATE CONSTANT VALUES :

1'ST CONSTANT

2'ND CONSTANT

ALLOY	: 1.053E-08	.00000
TROILITE	: 1.410E-16	.02310

LEACHING OF NICKEL FROM MATTE - LEACH 11

PREDICTED VS. MEASURED EXTRACTIONS

COMPONENT 1

TIME	POTL	MEAS	CALC
15.	598.	.0050	.0159
30.	576.	.0160	.0284
60.	555.	.0430	.0503
120.	540.	.0870	.0887
180.	535.	.1240	.1231
240.	532.	.1550	.1544
300.	531.	.1860	.1830
362.	530.	.2100	.2102
440.	529.	.2430	.2416

SUM OF SQUARED ERRORS = 3.4E-04

RATE CONSTANT VALUES :

1'ST CONSTANT

2'ND CONSTANT

ALLOY : 1.274E-08
TROILITE : 1.950E-16

.00000
.02290

Author Dry M J

Name of thesis Kinetics of leaching of a low grade matte in ferric sulphate solution 1984

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