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# Kinetics of leaching of a low grade matter in ferric sulphate solution

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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 $FeSO_4^{o}$ gives slightly better average and maximum errors of 8 and 15 millivolts. Including the species $FeHSO_4SO_4^{o}$ and $Fe(SO_4)_2^{-}$ 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 $FeSO_4^{o}$, 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 |
| $FeSO_4^{o}$ | 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 $FeSO_4^{o}$ 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

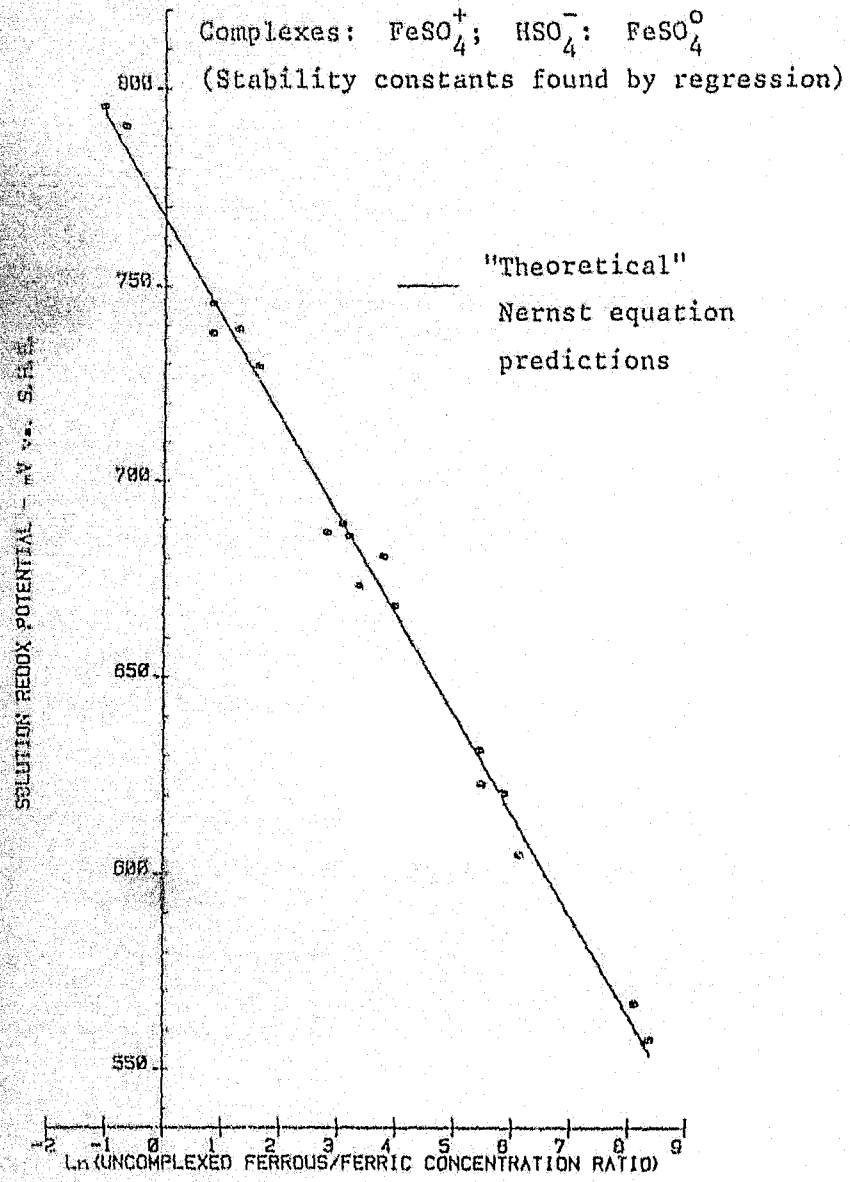

Complexes: $FeSO_4^+$; $HSO_4^-$: $FeSO_4^o$
(Stability constants found by regression)
"Theoretical" Nernst equation predictions
SOLUTION REDOX POTENTIAL - mV vs. S.H.E.
800
750
700
650
600
550
-2 -1 0 1 2 3 4 5 6 7 8 9
Ln (UNCOMPLEXED FERROUS/FERRIC CONCENTRATION RATIO)

Fig. 5.6

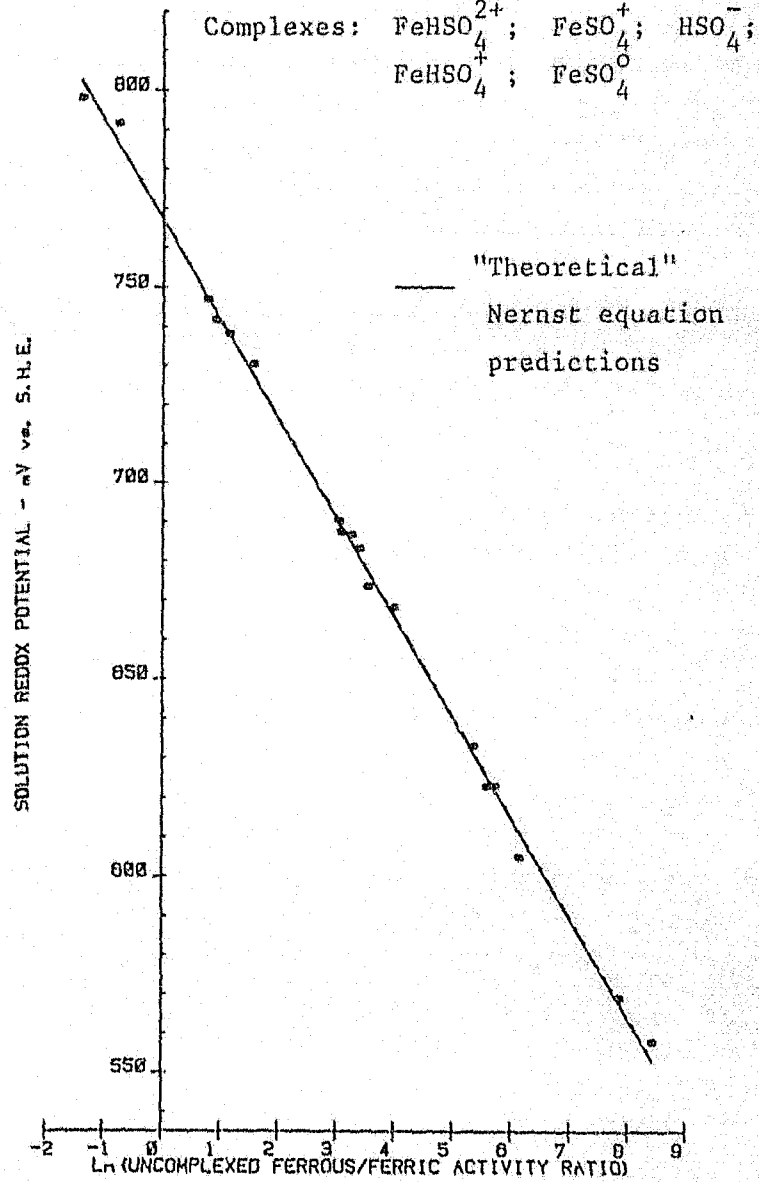

Complexes: $FeHSO_4^{2+}$; $FeSO_4^+$; $HSO_4^-$; $FeHSO_4^+$; $FeSO_4^o$
"Theoretical" Nernst equation predictions
SOLUTION REDOX POTENTIAL - mV vs. S.H.E.
800
750
700
650
600
550
-2 -1 0 1 2 3 4 5 6 7 8 9
Ln (UNCOMPLEXED FERROUS/FERRIC ACTIVITY RATIO)

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 $FeHSO_4^{2+}$, $FeSO_4^{+}$, $HSO_4^{-}$, $FeSO_4^{o}$ and $FeHSO_4^{+}$. This is in agreement with the work of Sapieszko *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 $FeSO_4^{o}$ and $FeHSO_4^{+}$. The removal of $FeHSO_4^{2+}$ and $FeHSO_4^{+}$ from the species present, or the inclusion of $FeHSO_4SO_4$ and $Fe(SO_4)_2^{-}$, both result in poorer redox potential predictions - see Appendix III.

The stability constants at zero ionic strength and 25°C for $FeHSO_4^{2+}$, $FeSO_4^{+}$, $FeSO_4^{o}$ 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 |
| $FeSO_4^{o}$ | 161 | 158 ± 18* |
| $FeHSO_4^{+}$ | 513 | 400** |

* Uncertainty in the stability constant of $FeSO_4^{o}$ 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 $FeSO_4^{o}$ 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 $\pm$ 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:

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

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

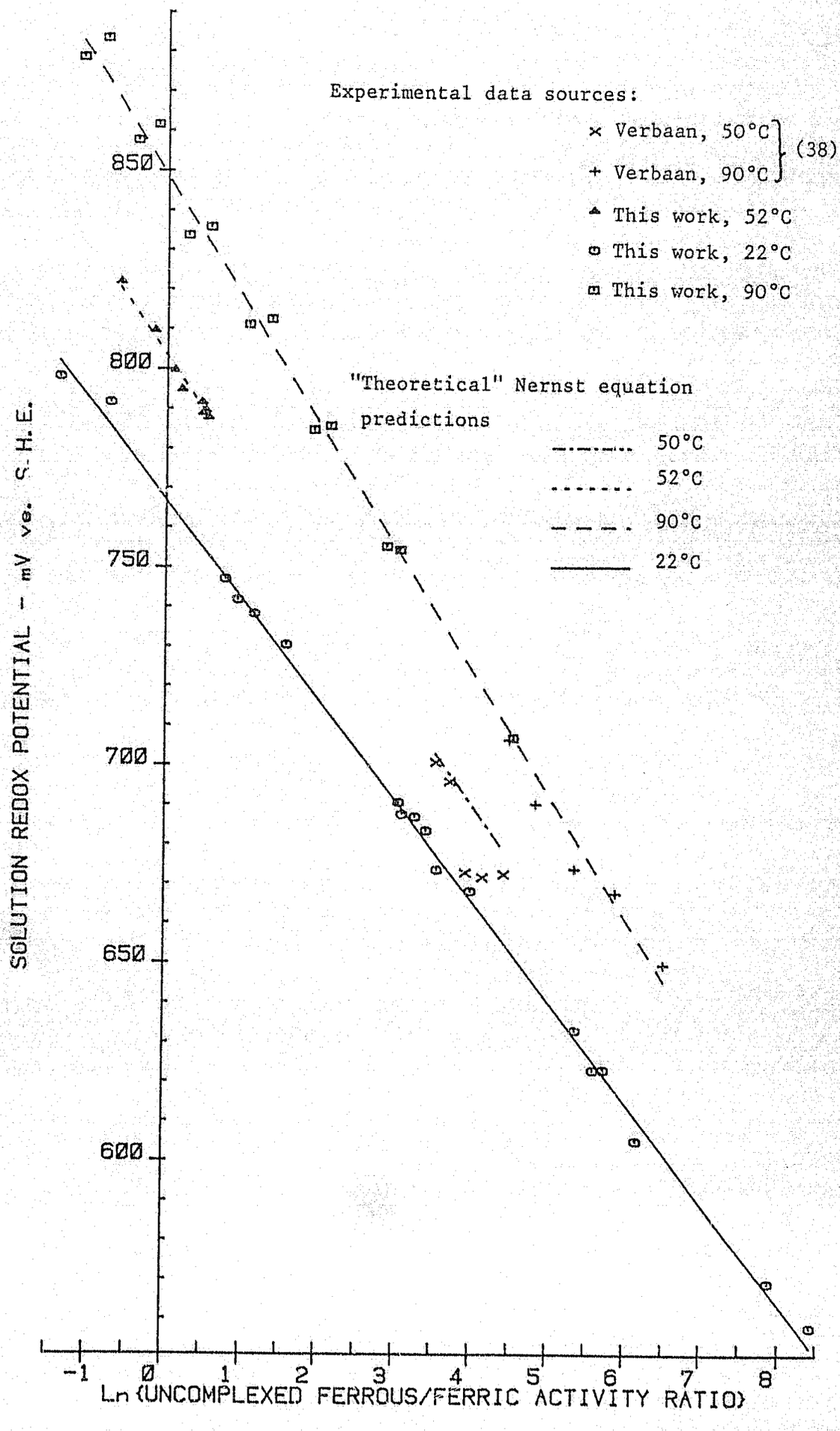

Experimental data sources:
× Verbaan, 50°C
+ Verbaan, 90°C
(38)
▲ This work, 52°C
⊙ This work, 22°C
⊡ This work, 90°C
"Theoretical" Nernst equation predictions
50°C
52°C
90°C
22°C
SOLUTION REDOX POTENTIAL - mV vs. S.H.E.
850
800
750
700
650
600
-1
0
1
2
3
4
5
6
7
8
Ln (UNCOMPLEXED FERROUS/FERRIC ACTIVITY RATIO)

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 disasterous.

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: $\Delta H$ = 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 $FeSO_4^{o}$, the assumption of constant heat of reaction ($\Delta H$) 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 |
| $FeSO_4^{o}$ | 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 $SO_4^=$ 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:

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

Where: $K^o$ = 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:

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

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 Sapieszko *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 Sapieszko *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 *et al* |
| 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:

$$Fe^{3+} + SO_4^{=} \rightleftarrows FeSO_4^{+}$$

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

$$K = \frac{\gamma_{FeSO_4^+}}{\gamma_{Fe^{3+}}\,\gamma_{SO_4^=}} \quad \frac{[FeSO_4^+]}{[Fe^{3+}][SO_4^=]}$$

or: $$\log K = \log\left\{\frac{[FeSO_4^+]}{[Fe^{3+}][SO_4^=]}\right\} + \log\left\{\frac{\gamma_{FeSO_4^+}}{\gamma_{Fe^{3+}}\gamma_{SO_4^=}}\right\}$$

Where: $[\ ]$ = species concentration

$\gamma$ = activity coefficient

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

$$\log K' = \frac{[FeSO_4^+]}{[Fe^{3+}][SO_4^=]} \quad \text{at a given ionic strength}$$

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:

$$\log K = \log K' + \log\left\{\frac{\gamma_{FeSO_4^+}}{\gamma_{Fe^{3+}}\gamma_{SO_4^=}}\right\}$$

Therefore $$\log\left\{\frac{\gamma_{FeSO_4^+}}{\gamma_{Fe^{3+}}\gamma_{SO_4^=}}\right\} = \log(K/K')$$

Figure 5.9 was constructed by the above method for the stability quotients of $FeSO_4^+$ and $FeSO_4^o$. 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 $FeSO_4^o$ 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.

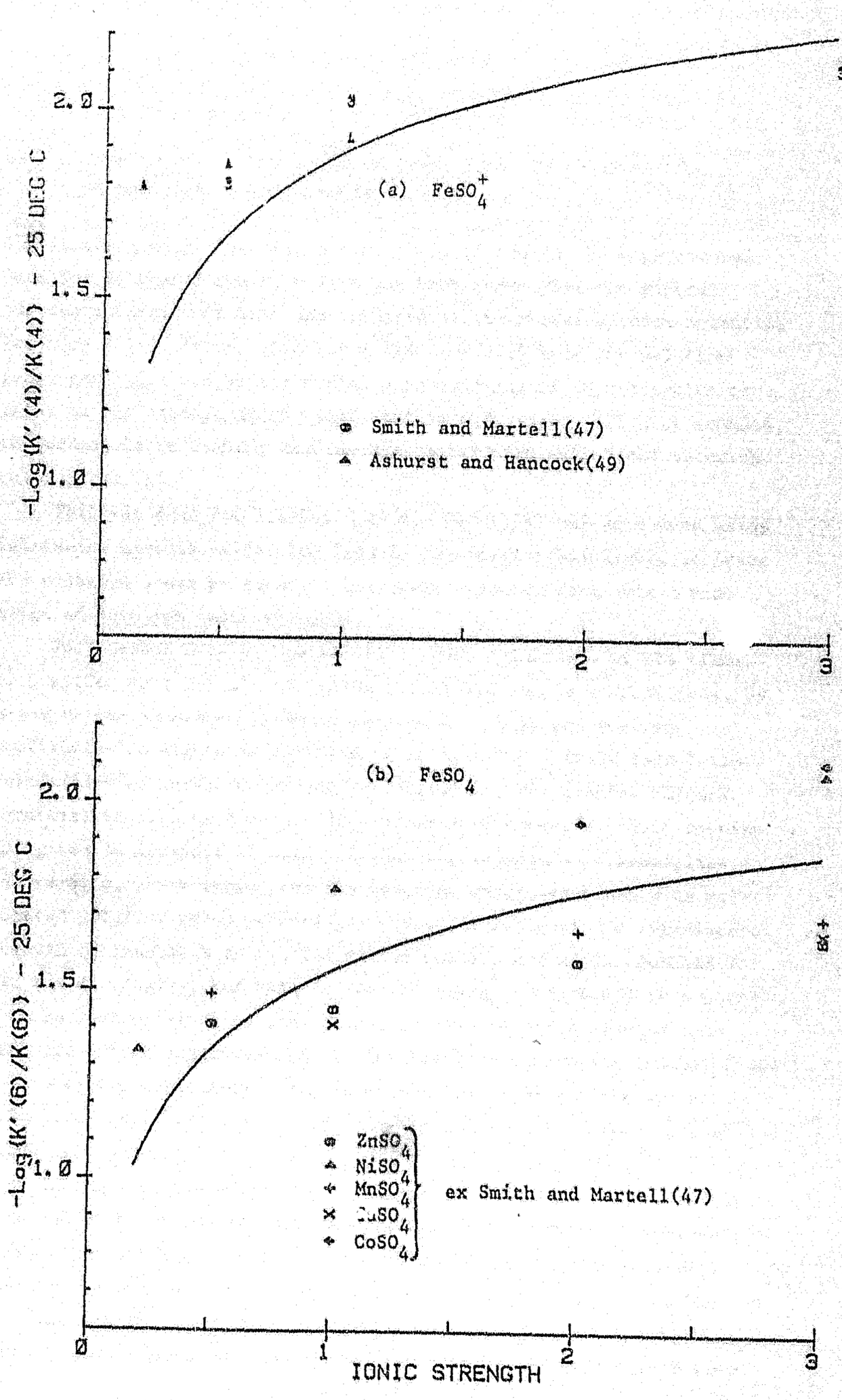



Fig. 5.9 Effect of ionic strength on equilibirum constants

## 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

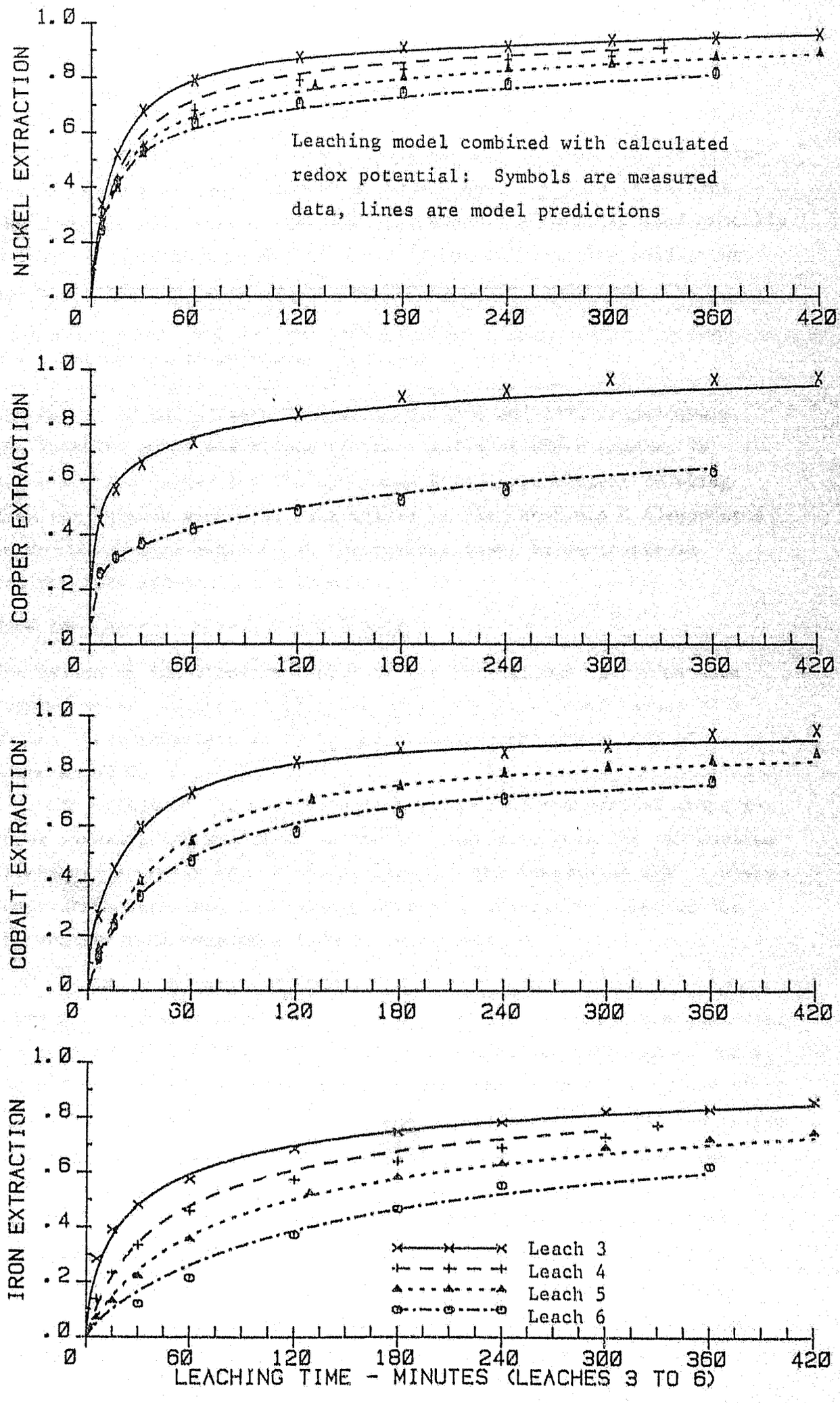

NICKEL EXTRACTION
COPPER EXTRACTION
COBALT EXTRACTION
IRON EXTRACTION
1.0
.8
.6
.4
.2
.0
0
60
120
180
240
300
360
420
Leaching model combined with calculated redox potential: Symbols are measured data, lines are model predictions
Leach 3
Leach 4
Leach 5
Leach 6
LEACHING TIME - MINUTES (LEACHES 3 TO 6)

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 $\beta_1$ 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 $\beta_1$ 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 Ahrrenius 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 ($R = 8{,}314$ g $mol^{-1}K^{-1}$), 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

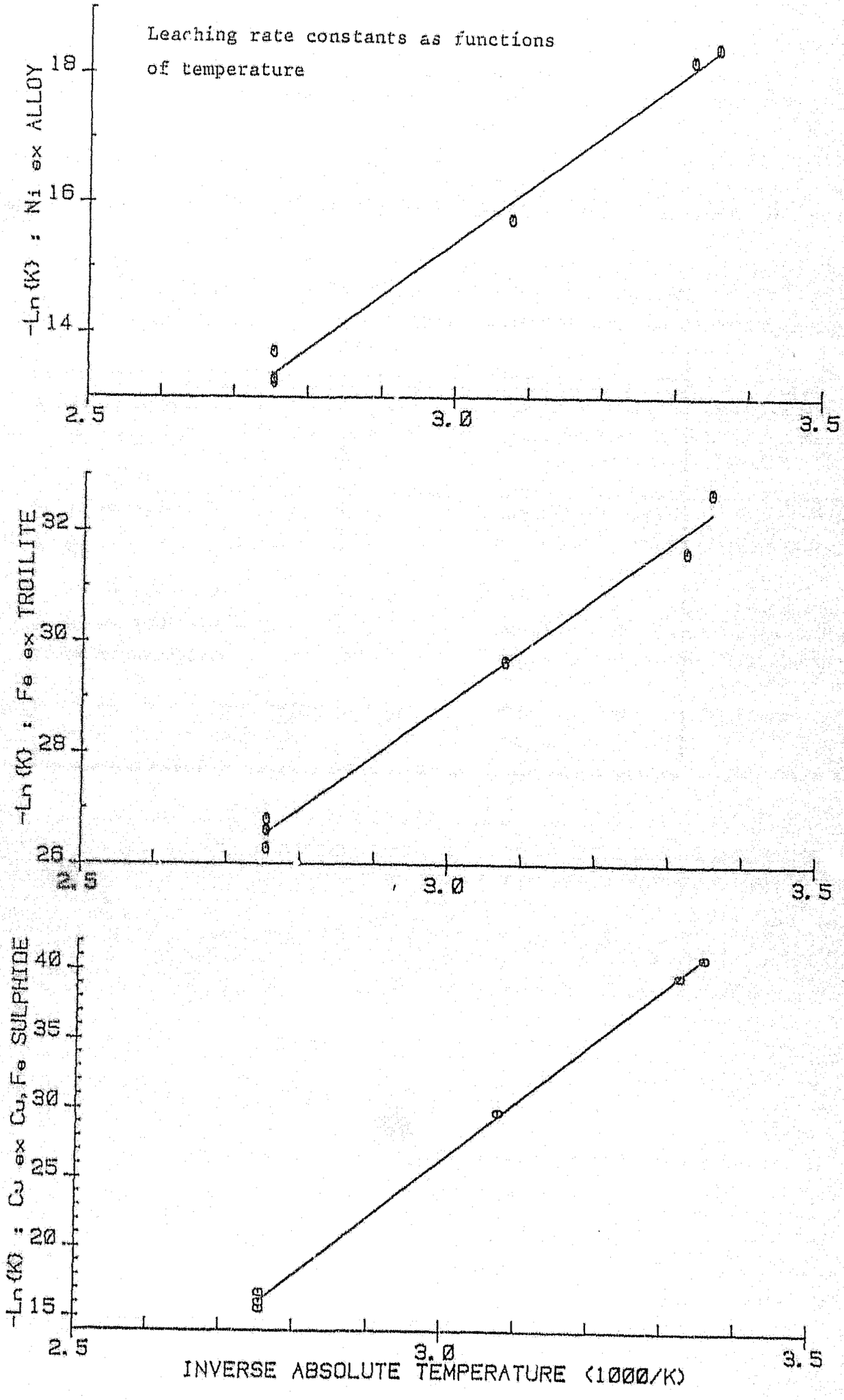

Leaching rate constants as functions of temperature
-Ln (K) : Ni ex ALLOY
18
16
14
2.5
3.0
3.5
-Ln (K) : Fe ex TROILITE
32
30
28
26
2.5
3.0
3.5
-Ln (K) : Cu ex Cu, Fe SULPHIDE
40
35
30
25
20
15
2.5
3.0
3.5
INVERSE ABSOLUTE TEMPERATURE (1000/K)

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 = zero for leaching in a cylindrical pore, and x = 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 | $5,9 \cdot 10^{-4}$ | $1,9.10^{-3}$ |
| 0,6 | $5,1.10^{-4}$ | $1,8.10^{-3}$ |
| 0,5 | $3,8 \cdot 10^{-4}$ | $1,7.10^{-3}$ |
| 0,4 | $2,9.10^{-4}$ | $1,7.10^{-3}$ |
| 0,3 | $1,9.10^{-4}$ | $1,7.10^{-3}$ |
| 0,2 | $1,2.10^{-4}$ | $1,8.10^{-3}$ |
| 0,1 | $1,3.10^{-4}$ | $2,1.10^{-3}$ |
| 0,05 | $1,5.10^{-4}$ | $2,3.10^{-3}$ |

b) Leaching of Cu ex Cu, Fe sulphide:

| x | Total squared errors | |
|---|---|---|
| | Leach 9 | Leaches 7 and 8 |
| 2/3 | $1,7.10^{-3}$ | $3,0.10^{-3}$ |
| 0,5 | $1,7.10^{-3}$ | $3,0.10^{-3}$ |
| 0,25 | $1,7.10^{-3}$ | $3,0.10^{-3}$ |
| 0,1 | $1,7.10^{-3}$ | $3,0.10^{-3}$ |

## 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 quantative 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 | 1,69 | 1 |
| 1,0499 | 1 | 1,60 | 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, % |
|---|---|
| 0,925 | 1 |
| 0,927 | 1 |
| 0,976 | 1 |
| 0,992 | 1 |
| 0,994 | 1 |
| 1,02 | 1 |
| 1,03 | 1 |
| 1,049 | 1 |
| 1,0527 | 2 |
| 1,10 | 2 |
| 1,11 | 3 |
| 1,13 | 1 |
| 1,16 | 1 |
| 1,17 | 1 |
| 1,1809 | 1 |
| 1,1853 | 1 |
| 1,19 | 1 |
| 1,22 | 1 |
| 1,26 | 1 |
| 1,28 | 1 |
| 1,31 | 2 |

| Interplanar spacing, Angstroms | Relative intensity, % |
|---|---|
| 1,325 | 5 |
| 1,33 | 5 |
| 1,34 | 1 |
| 1,42 | 1 |
| 1,44 | 2 |
| 1,46 | 2 |
| 1,48 | 2 |
| 1,51 | 1 |
| 1,63 | 3 |
| 1,72 | 30 |
| 1,74 | 3 |
| 1,78 | 1 |
| 1,93 | 4 |
| 2,09 | 100 |
| 2,146 | 4 |
| 2,47 | 2 |
| 2,52 | 5 |
| 2,65 | 40 |
| 2,984 | 30 |
| 3,33 | 3 |
| 4,71 | 2 |

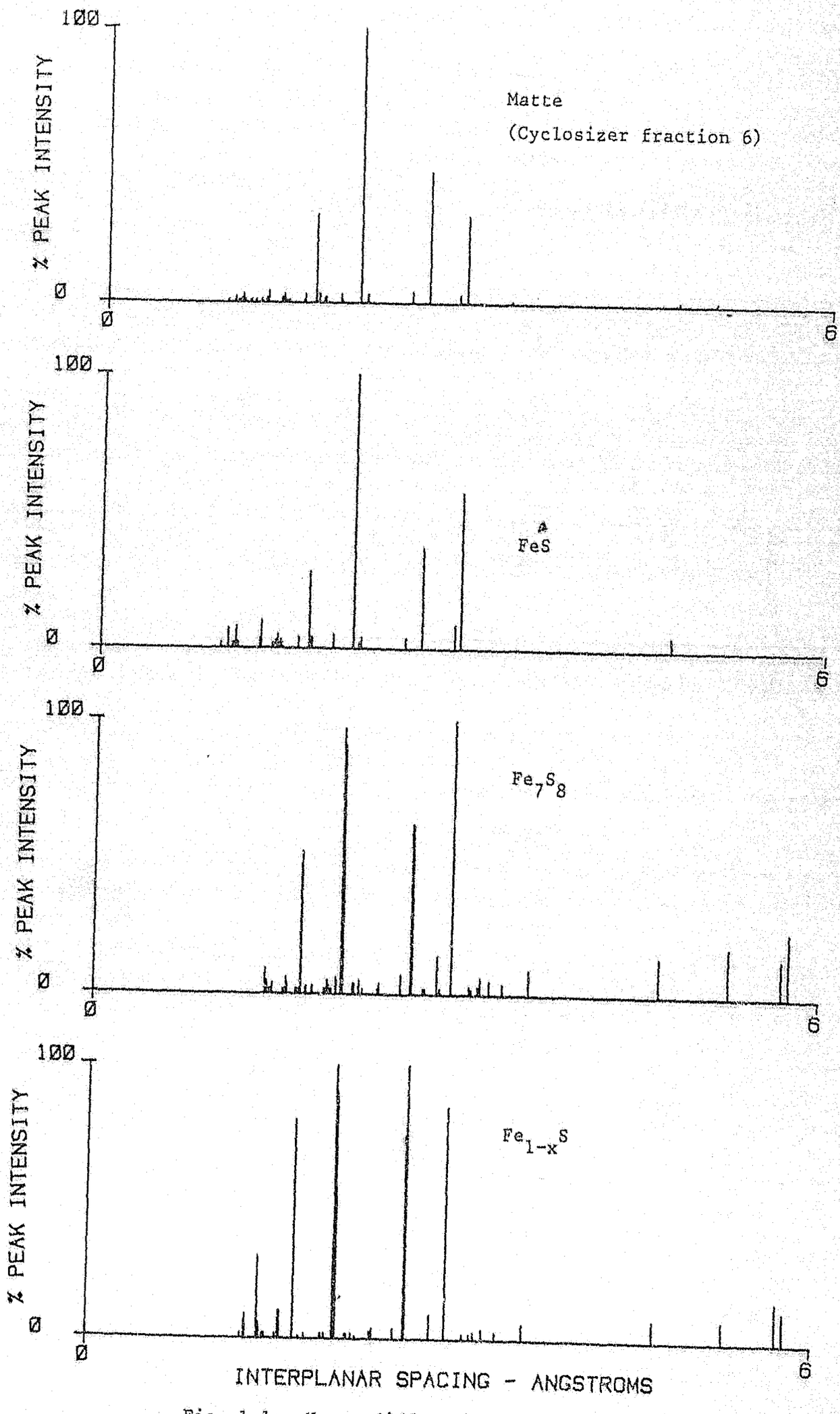



Fig. 1.1: X-ray diffraction data

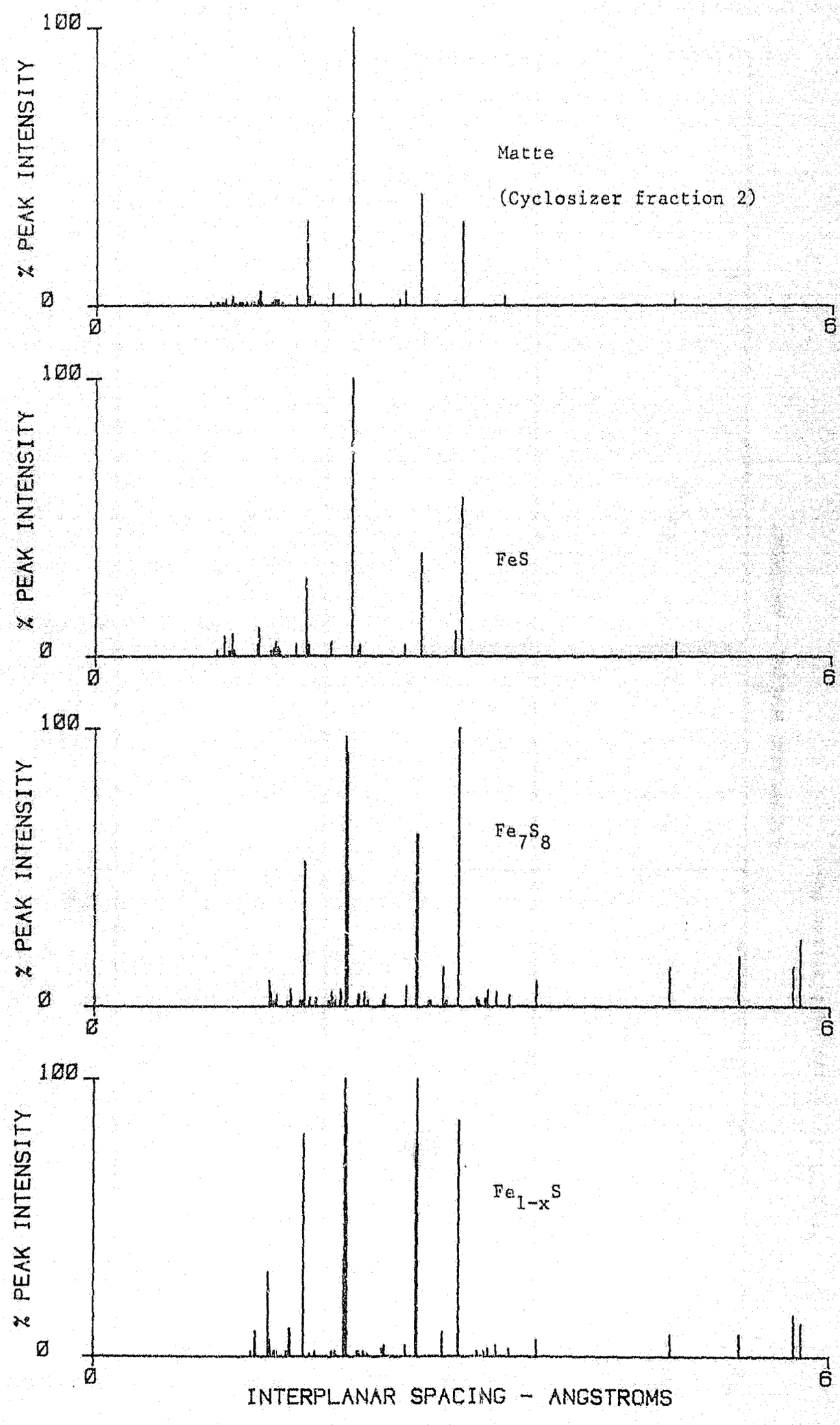



Fig. 1.2: X-ray diffraction data

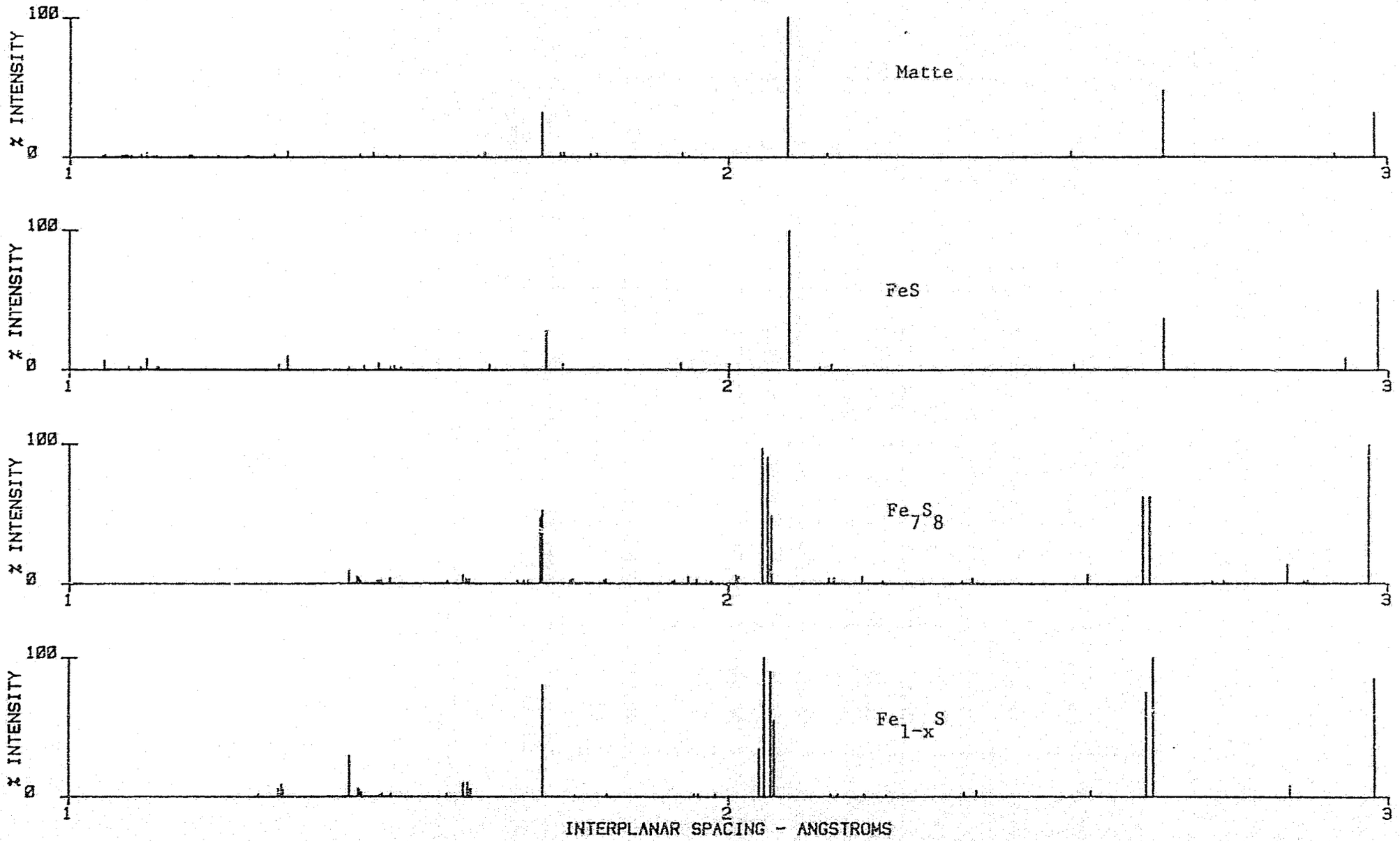



Fig. 1.3: X-ray diffraction data

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 | .40 |
| 3 | .18 | .10 |
| 4 | .66 | .03 |
| 5 | 1.47 | .77 |
| 6 | | 1.88 |

%IN PHASES.
**********

| ALLOY | TROILITE | MAGNETITE |
|---|---|---|
| 68.46 | 31.53 | .00 |
| 49.43 | 50.57 | .00 |
| 45.67 | 54.33 | .00 |
| 34[illegible].79 | 65[illegible].21 | .00 |
| 36.79 | 63.21 | .00 |
| 16.48 | 83.52 | .00 |

STOP

)

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 |
| 3 | 1.67 | 1.74 |
| 4 | 1.71 | 1.84 |
| 5 | 1.80 | 2.01 |
| 6 | 1.90 | 2.12 |
| | 2.72 | 2.73 |

%IN PHASES.
**********

| ALLOY | TROILITE | MAGNETITE |
|---|---|---|
| 6.53 | 79.84 | 13.63 |
| 3.03 | 81.96 | 15.03 |
| 3.84 | 79.86 | 17.30 |
| 4.41 | 75.86 | 19.73 |
| 4.14 | 69.43 | 26.43 |
| 4.22 | 33.22 | 62.56 |

STOP

)

Cu

PHASE COMPOSITIONS
**********

X = 2.500
Y = .400
Z = .000

ESQ = 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 |

%IN 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 |

STOP

)

Co

PHASE COMPOSITIONS
**********

X = 62.617
Y = 59.000
Z = 49.982

ESQ = 6.150E-01

CALCULATED FRN COMPOSITIONS
**********

| FRN | MASS % (C) | MASS % (M) |
|---|---|---|
| 1 | 58.96 | 59.30 |
| 2 | 59.75 | 58.60 |
| 3 | 58.64 | 58.10 |
| 4 | 58.40 | 58.00 |
| 5 | 58.19 | 58.30 |
| 6 | 55.88 | 56.00 |

STOP

)

Fe

%IN PHASES.
**********

| ALLOY | TROILITE | MAGNETITE | |
|---|---|---|---|
| 9.45 | 87.16 | 0.20 | 3.39 |
| 4.48 | 91.69 | 0.23 | 3.83 |
| 3.84 | 91.05 | 0.28 | 4.83 |
| 3.14 | 91.44 | 0.30 | 5.42 |
| 3.58 | 88.83 | 0.51 | 7.08 |
| .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

| | Mass, mg | | | Mass, g |
|---|---|---|---|---|
| | Ni | Cu | Co | Fe |
| Into leach | | | | |
| Matte in | 397 | 207 | 19 | 5,9 |
| Liquor in | 33 | 1,5 | 7,5 | 151,8 |
| Therefore: total in | 430 | 208,5 | 26,5 | 157,7 |
| Ex leach | | | | |
| Solids ex preg. liq. | 16,5 | 7,4 | <1,3 | 0,6 |
| Solids ex samples | 10,8 | 6,0 | 0,7 | 0,3 |
| Misc. solids out | 6,6 | 3,6 | 0,4 | 0,2 |
| Pregnant liquor | 327 | 162,3 | 20,7 | 128,8 |
| Wash A liquor | 9,4 | 4,3 | 0,3 | 11,8 |
| Wash B liquor | | | | |
| Samples | 55,0 | 26,4 | 3,6 | 25,8 |
| Therefore: total out | 425,3 | 210,0 | <27,0 | 167,5 |
| Mass balance, % (Out/In) | 98,9 | 100,7 | <102 | 106,2 |
| % extraction | 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, g/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

| | Mass, mg | | | Mass, g |
|---|---|---|---|---|
| | Ni | Cu | Co | Fe |
| Into leach | | | | |
| Matte in | 401 | 206 | 19 | 5,88 |
| Liquor in | 34,2 | 2,9 | 7,35 | 154,05 |
| Therefore: total in | 435,2 | 208,9 | 26,35 | 159,93 |
| Ex leach | | | | |
| Solids ex preg. liq. | 13,7 | 5,1 | <1,3 | 0,48 |
| Solids ex samples | 21,3 | 11,5 | 1,26 | 0,61 |
| Misc. solids out | | | | |
| Pregnant liquor | 332,1 | 168,5 | 21,89 | 128,66 |
| Wash A liquor | 5,1 | 2,7 | 0,34 | 1,41 |
| Wash B liquor | 6,6 | 5,8 | 0,43 | 1,24 |
| Samples | 53,0 | 26,4 | 3,48 | 22,05 |
| Therefore: total in | 431,8 | 220,0 | <28,7 | 154,45 |
| Mass balance, % (Out/In) | 99,2 | 105,3 | <109 | 96,6 |
| % extraction | 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 | 6,25 | | 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 | 93,0 | 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

| | Mass, mg | | | Mass, g |
|---|---|---|---|---|
| | Ni | Cu | Co | Fe |
| **Into leach** | | | | |
| Matte in | 398 | 202 | 19 | 5,89 |
| Liquor in | 34,2 | 2,8 | 7,49 | 151,95 |
| Therefore: total in | 432,2 | 204,8 | 26,49 | 157,84 |
| **Ex leach** | | | | |
| Solids ex preg. liq. | 19,8 | 8,5 | <1,6 | 0,74 |
| Solids ex samples | 16,8 | 9,2 | 1,10 | 0,48 |
| Misc. solids out | | | | |
| Pregnant liquor | 327,9 | 169,4 | 21,66 | 126,57 |
| Wash A liquor | 5,3 | 2,6 | 0,35 | 1,51 |
| Wash B liquor | 4,9 | 1,9 | 0,32 | 1,15 |
| Samples | 56,3 | 28,7 | 3,69 | 25,44 |
| Therefore: total out | 431,0 | 220,3 | 28,72 | 155,89 |
| Mass balance, % (Out/In) | 99,7 | 107,6 | <108,4 | 98,8 |
| % extraction | 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

| | Mass, mg | | | Mass, g |
|---|---|---|---|---|
| | Ni | Cu | Co | Fe |
| Into leach | | | | |
| Matte in | 394 | 210 | 19 | 5,81 |
| Liquor in | 46,7 | 2,2 | 9,65 | 154,28 |
| Ferrous sulphate in | | | | 10,15 |
| | 440,7 | 212,2 | 28,65 | 170,24 |
| Ex leach | | | | |
| Solids ex preg. liq. | 38,0 | 30,9 | <2,21 | 1,20 |
| Solids ex samples | 20,5 | 12,7 | 1,24 | 0,49 |
| Misc. solids out | | | | |
| Pregnant liquor | 347,9 | 180,9 | 24,29 | 139,97 |
| Wash A liquor | 4,6 | 2,2 | 0,31 | 1,51 |
| Wash B liquor | 5,7 | 3,0 | 0,43 | 1,92 |
| Samples | 41,1 | 19,7 | 2,94 | 21,13 |
| Therefore: total out | 457,8 | 249,4 | 31,42 | 166,22 |
| Mass balance, % (Out/In) | 103,9 | 117,5 | 109,7 | 97,6 |
| % extraction | 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

| | Mass, mg | | | Mass, g |
|---|---|---|---|---|
| | Ni | Cu | Co | Fe |
| Into leach | | | | |
| Matte in | 396 | 212 | 19 | 5,87 |
| Liquor in ($+FeSO_4$) | 50,6 | 5,6 | 11,42 | 172,94 |
| Therefore total in | 446,6 | 217,6 | 30,42 | 178,81 |
| Ex leach | | | | |
| Solids ex preg. liq. | 37,1 | 32,8 | 2,12 | 1,19 |
| Solids ex samples | 24,5 | 29,4 | 1,55 | 0,64 |
| Misc. solids out | | | | |
| Pregnnant liquor | 315,0 | 174,0 | 23,50 | 149,53 |
| Wash A liquor | 4,6 | 2,87 | 0,36 | 1,61 |
| Wash B liquor | 6,8 | 2,7 | 0,46 | 2,89 |
| Samples | 45,2 | 22,4 | 3,51 | 27,24 |
| Therefore: total out | 433,2 | 264,2 | 31,50 | 183,1 |
| Mass balance, % (Out/In) | 97,0 | 121,4 | 103,6 | 102,4 |
| % extraction | 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

| | Mass, mg | | | Mass, g |
|---|---|---|---|---|
| | Ni | Cu | Co | Fe |
| Into leach | | | | |
| Matte in | 400 | 218 | 20 | 5,89 |
| Liquor in (+ $FeSO_4$0 | 60,5 | 6,9 | 14,6 | 203,0 |
| Therefore: total in | 460,5 | 224,9 | 34,6 | 208,89 |
| Ex leach | | | | |
| Solids ex preg. liq. | 59,1 | 50,8 | 4,16 | 1,65 |
| Solids ex samples | 20,6 | 14,8 | 1,42 | 0,56 |
| Misc. solids out | | | | |
| Pregnant liquor | 324,2 | 153,9 | 25,94 | 178,57 |
| Wash A liquor | 4,2 | 2,4 | < 1,06 | 1,76 |
| Wash B liquor | 2,9 | 0,7 | < 1,38 | 1,36 |
| Samples | 34,4 | 12,8 | 2,85 | 24,2 |
| Therefore: total out | 445,4 | 235,4 | <36,81 | 208,10 |
| Mass balance, % (Out/In) | 96,7 | 104,7 | <106,4 | 99,6 |
| % extraction | 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

| | Mass, mg | | | Mass, g |
|---|---|---|---|---|
| | Ni | Cu | Co | Fe |
| Into leach | | | | |
| Matte in | 400 | 216 | 19,7 | 5,84 |
| Liquor in | 55,1 | 2,3 | 12,75 | 166,61 |
| Therefore: total in | 455,1 | 218,3 | 32,45 | 172,45 |
| Ex leach | | | | |
| Solids ex preg. liq. | 37,3 | 20,9 | 2,31 | 0,93 |
| Solids ex samples | 21,4 | 14,9 | 1,31 | 0,52 |
| Misc. solids out | | | | |
| Pregnant liquor | 347,0 | 164,1 | 25,02 | 140,96 |
| Wash A liquor | 2,7 | 1,5 | 0,08 | 1,11 |
| Wash B liquor | 7,0 | 2,7 | 0,35 | 1,41 |
| Samples | 47,3 | 21,6 | 3,46 | 22,14 |
| Therefore: total out | 462,7 | 225,7 | 32,53 | 167,07 |
| Mass balance, % (Out/In) | 101,7 | 103,4 | 100,2 | 96,9 |
| % extraction | 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

| | Mass, mg | | | Mass, g |
|---|---|---|---|---|
| | Ni | Cu | Co | Fe |
| Into leach | | | | |
| Matte in | 400 | 221 | 19,7 | 5,85 |
| Liquor in | 50,6 | 2,1 | 11,7 | 149,70 |
| Therefore: total in | 450,6 | 223,1 | 31,4 | 155,55 |
| Ex leach | | | | |
| Solids ex preg. liq. | 7,52 | 3,93 | 0,43 | 0,18 |
| Solids ex samples | 21,48 | 13,68 | 1,30 | 0,63 |
| Misc. solids out | | | | |
| Pregnant liquor | 342,56 | 189,54 | 26,32 | 129,89 |
| Wash A liquor | 3,30 | 1,59 | <0,6 | 1,13 |
| Wash B liquor | 4,88 | 1,12 | <0,5 | 1,11 |
| Samples | 48,93 | 25,30 | 3,88 | 22,93 |
| Therefore: total out | 428,67 | 235,16 | 31,93 | 155,87 |
| Mass balance, % (Out/In) | 95 | 105 | <105 | 100,2 |
| % extraction | 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

| | Mass, mg | | | Mass, g |
|---|---|---|---|---|
| | Ni | Cu | Co | Fe |
| Into leach: | | | | |
| Matte in | 358 | 213 | 20 | 5,93 |
| Liquor in | 17,9 | 2,0 | 4,23 | 177,0 |
| Therefore: total in | 375,9 | 215 | 24,23 | 182,9 |
| Ex leach: | | | | |
| Solids ex preg. liq. | 91,1 | 78,8 | 6,67 | 3,0 |
| Solids ex samples | 22,8 | 15,8 | 1,41 | 0,5 |
| Misc. solids out | - | - | - | - |
| Pregnant liquor | 247,0 | 80,0 | 13,44 | 154,9 |
| Wash liquor | 6,8 | 2,3 | 3,93 | 4,6 |
| Samples | 17,2 | 6,1 | 0,99 | 15,3 |
| Therefore: total out | 388,9 | 183,0 | 26,44 | 178,3 |
| Mass balance, % (Out/In) | 103,5 | 85,1 | 109,1 | 97,5 |
| Per cent extraction | 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

| | Mass, mg | | | Mass, g |
|---|---|---|---|---|
| | Ni | Cu | Co | Fe |
| Into leach: | | | | |
| Matte in | 355 | 213 | 20 | 5,91 |
| Liquor in | 18,6 | 3,36 | 4,73 | 177,0 |
| Therefore: total in | 373,6 | 216,4 | 24,73 | 182,9 |
| Ex leach: | | | | |
| Solids ex preg. liq. } Solids ex samples } | 253,0 | 144,8 | 16,09 | 5,04 |
| Pregnant liquor | 83,0 | 42,0 | 5,55 | 146,3 |
| Wash liquor | 25,0 | 2,08 | 3,25 | 3,6 |
| Samples | 6,7 | 5,36 | 0,69 | 21,3 |
| Therefore: total out | 367,7 | 194,2 | 25,58 | 176,2 |
| Mass balance, % (Out/In) | 94,4 | 89,8 | 103,4 | 96,4 |
| Per cent extraction | 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

| | Mass, mg | | | Mass, g |
|---|---|---|---|---|
| | Ni | Cu | Co | Fe |
| Into leach: | | | | |
| Matte in | 359 | 213 | 20 | 5,93 |
| Liquor in | 11,4 | 1,8 | 2,51 | 119,6 |
| Therefore: total in | 370,4 | 214,8 | 22,51 | 125,5 |
| Ex leach: | | | | |
| Solids ex preg. liq. | 236,2 | 125,0 | 13,72 | 4,20 |
| Solids ex samples | 23,8 | 13,8 | 1,42 | 0,42 |
| Pregnant liquor | 91,1 | 45,5 | 4,41 | 106,6 |
| Wash liquor | 7,5 | 2,9 | 0,49 | 2,0 |
| Samples | 6,1 | 4,8 | 0,33 | 39,7 |
| Therefore: total out | 364,7 | 192,0 | 20,37 | 126,4 |
| Mass balance, % (Out/In) | 98,5 | 89,4 | 90,5 | 100,7 |
| Per cent extraction | 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 | 24.3 | 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 $l^{-1}$ | | | |
|---|---|---|---|---|
| | $Fe^{3+}$ | $Fe^{2+}$ | $H^{+}$ | $SO_4^{=}$ |
| 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 $l^{-1}$ | | | |
|---|---|---|---|---|
| | $Fe^{3+}$ | $Fe^{2+}$ | $H^{+}$ | $SO_4^{=}$ |
| 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 REDOX POTENTIALS

| POINT | MEASURED | LIQ. JN. | CORRECTED | LN(ACT. RATIO) | BEST LINE | NERNST EQN. (EMPIRICAL) | NERNST EQN. (THEORETICAL) | IONIC STRENGTH |
|---|---|---|---|---|---|---|---|---|
| 1 | 801. | 7. | 880. | .000 | 883. | 883. | 767. | .42 |
| 2 | 755. | 6. | 739. | -2.293 | 741. | 741. | 825. | 1.09 |
| 3 | 708. | 1. | 790. | -4.595 | 800. | 799. | 884. | 7.77 |
| 4 | 816. | 6. | 824. | 2.293 | 824. | 825. | 709. | .77 |
| 5 | 869. | 5. | 875. | .000 | 883. | 883. | 767. | 1.45 |
| 6 | 727. | 1. | 729. | -2.303 | 742. | 741. | 825. | 8.13 |
| 7 | 556. | 5. | 559. | 4.595 | 565. | 566. | 650. | 4.34 |
| 8 | 805. | 2. | 808. | 2.303 | 824. | 824. | 708. | 5.01 |
| 9 | 880. | 0. | 867. | .000 | 883. | 883. | 767. | 11.69 |
| 10 | 875. | 22. | 895. | .000 | 883. | 883. | 767. | 3.18 |
| 11 | 730. | 21. | 751. | -2.293 | 741. | 741. | 825. | 3.84 |
| 12 | 705. | 16. | 801. | -4.595 | 800. | 799. | 884. | 10.53 |
| 13 | 810. | 22. | 831. | 2.293 | 824. | 825. | 709. | 5.53 |
| 14 | 871. | 21. | 842. | .000 | 883. | 883. | 767. | 4.20 |
| 15 | 729. | 16. | 745. | -2.303 | 742. | 741. | 825. | 10.88 |
| 16 | 557. | 18. | 575. | 4.595 | 565. | 566. | 650. | 7.10 |
| 17 | 811. | 18. | 824. | 2.303 | 824. | 824. | 708. | 7.76 |
| 18 | 870. | 19. | 880. | .000 | 883. | 883. | 767. | 14.45 |

EQUATIONS FITTED TO THE EXPERIMENTAL RESULTS :

| | INTERCEPT, MILLIVOLTS | SLOPE, MILLIVOLTS | AVE. ERROR MILLIVOLTS | MAX. ERROR MILLIVOLTS |
|---|---|---|---|---|
| BEST STRAIGHT LINE : | 882.7 | -25.56 | 9.7 | 18.1 |
| EMPIRICAL NERNST EQUATION : | 882.7 | -25.39 | 9.6 | 18.5 |
| THEORETICAL NERNST EQUATION : | 766.6 | -25.59 | 84.6 | 102.6 |

TOTAL CONCENTRATION RATIO USED (22 °C)

PREDICTED AND CALCULATED SOLUTION REDOX POTENTIALS

| POINT | MEASURED | LIQ. JN. | CORRECTED | CNCALC. RATIO) | BEST LINE | NERNST EQN. (EMPIRICAL) | NERNST EQN. (THEORETICAL) | IONIC STRENGTH |
|---|---|---|---|---|---|---|---|---|
| 1 | 681. | 7. | 688. | .000 | 683. | 683. | 767. | .42 |
| 2 | 733. | 6. | 739. | -2.293 | 741. | 741. | 825. | 1.09 |
| 3 | 788. | 1. | 790. | -4.595 | 800. | 799. | 884. | 7.77 |
| 4 | 618. | 6. | 624. | 2.293 | 624. | 625. | 709. | .77 |
| 5 | 669. | 5. | 675. | .000 | 683. | 683. | 767. | 1.45 |
| 6 | 727. | 1. | 729. | -2.303 | 742. | 741. | 825. | 8.13 |
| 7 | 550. | 5. | 559. | 4.595 | 565. | 566. | 650. | 4.34 |
| 8 | 605. | 2. | 606. | 2.303 | 624. | 624. | 708. | 5.01 |
| 9 | 666. | 0. | 667. | .000 | 683. | 683. | 767. | 11.69 |
| 10 | 675. | 22. | 695. | .000 | 683. | 683. | 767. | 3.18 |
| 11 | 730. | 21. | 751. | -2.293 | 741. | 741. | 825. | 3.84 |
| 12 | 785. | 16. | 801. | -4.595 | 800. | 799. | 884. | 10.53 |
| 13 | 616. | 22. | 637. | 2.293 | 624. | 625. | 709. | 4.53 |
| 14 | 671. | 21. | 692. | .000 | 683. | 683. | 767. | 4.20 |
| 15 | 729. | 16. | 745. | -2.303 | 742. | 741. | 825. | 10.88 |
| 16 | 557. | 18. | 575. | 4.595 | 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 : | 682.7 | -25.36 | 9.7 | 18.1 |
| EMPIRICAL NERNST EQUATION : | 682.7 | -25.39 | 9.6 | 18.5 |
| THEORETICAL NERNST EQUATION : | 766.6 | -25.39 | 84.6 | 102.6 |

TOTAL CONCENTRATION RATIO USED (22 °C)

CONCENTRATIONS IN SOLUTION, GMOLES/LITRE

| POINT | FE(3+) | H+ | SO4(2-) | FE(2+) | FEHSO4SO4 | FEHSO4(2+) | FESO4SO4- | FESO4+ | HSO4- | FESO4 | 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 | 2.1590 | .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 : 22.0EG 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 | LIQ. JN. | CORRECTED | LN(ACT. RATIO) | BEST LINE | NERNST EQN. (EMPIRICAL) | NERNST EQN. (THEORETICAL) | IONIC STRENGTH |
|---|---|---|---|---|---|---|---|---|
| 1 | 681. | 6. | 687. | 1.625 | 703. | 704. | 726. | .24 |
| 2 | 735. | 5. | 738. | -.320 | 752. | 753. | 775. | .39 |
| 3 | 788. | 2. | 791. | -1.481 | 781. | 783. | 804. | 1.63 |
| 4 | 618. | 4. | 623. | 4.572 | 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. | 7.734 | 550. | 549. | 570. | 2.16 |
| 8 | 603. | 1. | 604. | 5.473 | 607. | 606. | 628. | 2.25 |
| 9 | 656. | 1. | 657. | 3.393 | 659. | 659. | 681. | 3.15 |
| 10 | 673. | 17. | 689. | 2.081 | 692. | 692. | 714. | 1.24 |
| 11 | 730. | 16. | 746. | -.148 | 748. | 749. | 771. | 1.54 |
| 12 | 785. | 11. | 796. | -1.918 | 792. | 794. | 816. | 2.18 |
| 13 | 616. | 16. | 631. | 4.464 | 632. | 632. | 655. | 1.42 |
| 14 | 671. | 15. | 686. | 2.253 | 688. | 688. | 710. | 1.51 |
| 15 | 729. | 10. | 739. | .433 | 733. | 734. | 756. | 2.33 |
| 16 | 557. | 9. | 565. | 7.396 | 558. | 557. | 579. | 2.92 |
| 17 | 611. | 8. | 619. | 5.138 | 615. | 614. | 636. | 2.99 |
| 18 | 674. | 6. | 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 : | 766.8 | -25.39 | 23.6 | 38.5 |

UNCOMPLEXED CONCENTRATION RATIO USED (22°C)

COMPLEXES PRESENT : $FeSO_4^+$; $HSO_4^-$ ; $FeSO_4^o$

CONCENTRATION QUOTIENTS EX LITERATURE

CONCENTRATIONS IN SOLUTION, GMOLES/LITRE

| POINT | FE(3+) | H+ | SO4(2-) | FE(2+) | FEHSO4SO4 | FEHSO4(2+) | FESO4SO4- | FESO4+ | HSO4- | FESO4 | FEHSO4+ |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | .0010 | .1396 | .0536 | .0092 | .0000 | .0000 | .0000 | .0082 | .0644 | .0008 | .0000 |
| 2 | .0120 | .1177 | .0853 | .0087 | .0000 | .0000 | .0000 | .0870 | .0864 | .0015 | .0000 |
| 3 | .0246 | .0409 | .4624 | .0056 | .0000 | .0000 | .0000 | .9659 | .1631 | .0044 | .0000 |
| 4 | .0011 | .1104 | .0983 | .0048 | .0000 | .0000 | .0000 | .0089 | .0935 | .0142 | .0000 |
| 5 | .0081 | .0954 | .1322 | .0809 | .0000 | .0000 | .0000 | .0909 | .1086 | .0182 | .0000 |
| 6 | .0225 | .0381 | .5061 | .0532 | .0000 | .0000 | .0000 | .9675 | .1659 | .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 | .0157 | .0248 | .8393 | .4081 | .0000 | .0000 | .0000 | .9763 | .1792 | .5823 | .0000 |
| 10 | .0011 | 1.1038 | .0986 | .0086 | .0000 | .0000 | .0000 | .0089 | .9366 | .0014 | .0000 |
| 11 | .0096 | 1.0601 | .1074 | .0085 | .0000 | .0000 | .0000 | .0892 | .9800 | .0015 | .0000 |
| 12 | .0492 | .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 | .0455 | .6541 | .2461 | .0698 | .0000 | .0000 | .0000 | .9447 | 1.3860 | .0292 | .0000 |
| 16 | .0009 | .6101 | .2723 | .6768 | .0000 | .0000 | .0000 | .0096 | 1.4301 | .3132 | .0000 |
| 17 | .0059 | .5879 | .2871 | .6653 | .0000 | .0000 | .0000 | .0951 | 1.4531 | .3247 | .0000 |
| 18 | .0246 | .4088 | .4636 | .5537 | .0000 | .0000 | .0000 | .9654 | 1.6314 | .4363 | .0000 |

VALUES OF EQUILIBRIUM CONSTANTS USED

TEMPERATURE : 22.0EG C

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

UNCOMPLEXED CONCENTRATION RATIO USED (22 °C)

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

CONCENTRATION QUOTIENTS EX LITERATURE

PREDICTED AND CALCULATED SOLUTION REDOX POTENTIALS

| POINT | MEASURED | LIQ. JN. | CORRECTED | LN(ACT. RATIO) | BEST LINE | NERNST EQN. (EMPIRICAL) | NERNST EQN. (THEORETICAL) | IONIC STRENGTH |
|---|---|---|---|---|---|---|---|---|
| 1 | 681. | 6. | 687. | 1.648 | 701. | 702. | 725. | .24 |
| 2 | 753. | 5. | 758. | -.305 | 751. | 751. | 775. | .39 |
| 3 | 788. | 2. | 791. | -1.496 | 781. | 782. | 805. | 1.67 |
| 4 | 618. | 4. | 623. | 4.568 | 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. | 7.715 | 549. | 548. | 571. | 2.13 |
| 8 | 605. | 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. | -.137 | 746. | 747. | 770. | 1.36 |
| 12 | 785. | 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. | 678. | 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 : | 745.0 | -25.18 | 7.7 | 14.5 |
| EMPIRICAL NERNST EQUATION : | 745.5 | -25.39 | 7.8 | 14.7 |
| THEORETICAL NERNST 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, GMOLES/LITRE

| POINT | FE(3+) | H+ | SO4(2-) | FE(2+) | FEHSO4SO4 | FEHSO4(2+) | FESO4SO4- | FESO4+ | HSO4- | FESO4 | FEHSO4+ |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | .0017 | .1390 | .0555 | .0089 | .0000 | .0006 | .0000 | .0077 | .0640 | .0008 | .0003 |
| 2 | .0113 | .1141 | .0861 | .0084 | .0000 | .0050 | .0000 | .0827 | .0846 | .0012 | .0004 |
| 3 | .0253 | .0364 | .4762 | .0053 | .0000 | .0182 | .0000 | .9488 | .1491 | .0043 | .0005 |
| 4 | .0010 | .1083 | .0974 | .0811 | .0000 | .0005 | .0000 | .0085 | .0908 | .0154 | .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 | .0092 | .0311 | .4919 | .5167 | .0000 | .0002 | .0000 | .0096 | .1316 | .4321 | .0411 |
| 8 | .0021 | .0295 | .5236 | .5026 | .0000 | .0015 | .0000 | .0954 | .1328 | .4474 | .0403 |
| 9 | .0155 | .0192 | .8578 | .3893 | .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 | .0522 | .5442 | .2730 | .0045 | .0000 | .2134 | .0000 | .7445 | 1.2791 | .0021 | .0035 |
| 13 | .0007 | 1.0321 | .1094 | .0558 | .0000 | .0033 | .0000 | .0061 | .9721 | .0104 | .0528 |
| 14 | .0060 | .9665 | .1215 | .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 | .2108 | .3278 |
| 17 | .0050 | .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

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UNCOMPLEXED CONCENTRATION RATIO USED (22 °C)

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

CONCENTRATION QUOTIENTS EX LITERATURE

PREDICTED AND CALCULATED SOLUTION REDOX POTENTIALS

| POINT | MEASURED | LIQ. JN. | CORRECTED | LN(ACT. RATIO) | BEST LINE | NERNST EQN. (EMPIRICAL) | NERNST EQN. (THEORETICAL) | IONIC STRENGTH |
|---|---|---|---|---|---|---|---|---|
| 1 | 681. | 6. | 687. | 2.056 | 711. | 717. | 715. | .23 |
| 2 | 733. | 5. | 738. | -.024 | 757. | 769. | 767. | .32 |
| 3 | 786. | 2. | 791. | -1.787 | 795. | 814. | 812. | .95 |
| 4 | 618. | 4. | 623. | 5.056 | 646. | 640. | 638. | .46 |
| 5 | 669. | 4. | 673. | 2.833 | 694. | 697. | 695. | .52 |
| 6 | 727. | 2. | 729. | .706 | 741. | 751. | 749. | 1.09 |
| 7 | 556. | 0. | 557. | 9.509 | 549. | 527. | 525. | 2.12 |
| 8 | 603. | 0. | 604. | 7.173 | 600. | 567. | 585. | 2.14 |
| 9 | 666. | 0. | 666. | 4.458 | 659. | 656. | 654. | 2.47 |
| 10 | 673. | 17. | 689. | 3.512 | 684. | 685. | 683. | 1.23 |
| 11 | 730. | 16. | 746. | 1.028 | 734. | 743. | 741. | 1.24 |
| 12 | 785. | 13. | 797. | -1.209 | 782. | 799. | 797. | 1.44 |
| 13 | 618. | 16. | 634. | 5.718 | 632. | 624. | 622. | 1.35 |
| 14 | 671. | 15. | 686. | 3.436 | 681. | 682. | 680. | 1.37 |
| 15 | 729. | 12. | 741. | 1.192 | 730. | 739. | 737. | 1.55 |
| 16 | 557. | 8. | 565. | 9.028 | 559. | 540. | 538. | 2.47 |
| 17 | 611. | 8. | 619. | 6.737 | 609. | 598. | 596. | 2.49 |
| 18 | 674. | 6. | 680. | 4.596 | 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 | 15.4 | 24.2 |
| EMPIRICAL NERNST EQUATION : | 760.8 | -25.59 | 19.3 | 31.0 |
| THEORETICAL NERNST EQUATION : | 766.8 | -25.59 | 19.4 | 31.5 |

UNCOMPLEXED CONCENTRATION RATIO USED (22 °C)

COMPLEXES PRESENT : $FeHSO_4SO_4^0$ ; $FeHSO_4^{2+}$ ; $Fe(SO_4)_2^-$ ; $FeSO_4^+$ ; $HSO_4^-$ ; $FeSO_4^0$ ; $FeHSO_4^+$

CONCENTRATION QUOTIENTS EX LITERATURE

CONCENTRATIONS IN SOLUTION, GMOLES/LITRE

| POINT | FE(3+) | H+ | SO4(2-) | FE(2+) | FEHSO4SO4 | FEHSO4(2+) | FESO4SO4- | FESO4+ | HSO4- | FESO4 | FEHSO4+ |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | .0011 | .1402 | .0514 | .0089 | .0010 | .0004 | .0025 | .0050 | .0621 | .0008 | .0003 |
| 2 | .0049 | .1236 | .0625 | .0057 | .0104 | .0031 | .0293 | .0473 | .0665 | .0009 | .0004 |
| 3 | .0496 | .0615 | .1012 | .0083 | .0751 | .0137 | .4256 | .4254 | .0534 | .0014 | .0003 |
| 4 | .0005 | .1095 | .0942 | .0816 | .0012 | .0002 | .0039 | .0042 | .0887 | .0131 | .0044 |
| 5 | .0048 | .0999 | .1001 | .0810 | .0115 | .0021 | .0401 | .0405 | .0861 | .0138 | .0042 |
| 6 | .0395 | .0563 | .1185 | .0800 | .0755 | .0118 | .4058 | .3973 | .0575 | .0161 | .0028 |
| 7 | .0000 | .0313 | .4868 | .5194 | .0007 | .0000 | .0077 | .0016 | .1310 | .4298 | .0411 |
| 8 | .0004 | .0309 | .4718 | .5270 | .0067 | .0003 | .0754 | .0162 | .1259 | .4227 | .0401 |
| 9 | .0070 | .0280 | .3499 | .6014 | .0578 | .0031 | .7154 | .2068 | .0845 | .3577 | .0507 |
| 10 | .0002 | 1.1043 | .0975 | .0058 | .0053 | .0010 | .0017 | .0017 | .9265 | .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 | .9993 | .1101 | .0563 | .0530 | .0089 | .0184 | .0169 | .9469 | .0105 | .0322 |
| 15 | .0160 | .7071 | .1246 | .0593 | .4769 | .0708 | .2343 | .1901 | .7586 | .0126 | .0272 |
| 16 | .0001 | .5104 | .2725 | .4526 | .0050 | .0003 | .0054 | .0013 | 1.1973 | .2097 | .3273 |
| 17 | .0005 | .4961 | .2740 | .4556 | .0486 | .0033 | .0540 | .0126 | 1.1701 | .2122 | .3220 |
| 18 | .0060 | .3880 | .2760 | .4886 | .4297 | .0288 | .3847 | .1409 | .9219 | .2292 | .2720 |

VALUES OF EQUILIBRIUM CONSTANTS USED

TEMPERATURE : 22.0DEG C

REACTION 1 : 2.414E 03
REACTION 2 : 9.400E 01
REACTION 3 : 8.380E 02
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 : $FeHSO_4SO_4^0$ ; $FeHSO_4^{2+}$ ; $Fe(SO_4)_2^-$ ; $FeSO_4^+$ ; $HSO_4^-$ ; $FeSO_4^0$ ; $FeHSO_4^+$

CONCENTRATION QUOTIENTS EX LITERATURE

PREDICTED AND CALCULATED SOLUTION REDOX POTENTIALS

| POINT | MEASURED | LIQ. JN. | CORRECTED | LN(ACT. RATIO) | BEST LINE | NERNST EQN. (EMPIRICAL) | NERNST EQN. (THEORETICAL) | IONIC STRENGTH |
|---|---|---|---|---|---|---|---|---|
| 1 | 681. | 5. | 687. | 2.793 | 696. | 696. | 696. | .20 |
| 2 | 733. | 5. | 736. | .812 | 747. | 746. | 746. | .38 |
| 3 | 788. | 2. | 791. | -.664 | 785. | 784. | 784. | 1.47 |
| 4 | 618. | 4. | 623. | 5.447 | 628. | 629. | 629. | .36 |
| 5 | 669. | 4. | 673. | 3.358 | 682. | 682. | 682. | .45 |
| 6 | 721. | 2. | 729. | 1.018 | 726. | 726. | 726. | 1.54 |
| 7 | 556. | 1. | 558. | 6.372 | 554. | 554. | 554. | 1.23 |
| 8 | 605. | 1. | 605. | 6.106 | 611. | 612. | 612. | 1.28 |
| 9 | 666. | 1. | 668. | 3.967 | 666. | 666. | 666. | 2.09 |
| 10 | 675. | 16. | 689. | 3.965 | 669. | 669. | 669. | 1.15 |
| 11 | 750. | 16. | 746. | .022 | 746. | 746. | 746. | 1.21 |
| 12 | 765. | 11. | 796. | -1.056 | 794. | 794. | 794. | 1.64 |
| 13 | 616. | 16. | 651. | 5.419 | 629. | 629. | 629. | 1.28 |
| 14 | 671. | 15. | 666. | 3.175 | 686. | 686. | 686. | 1.34 |
| 15 | 729. | 10. | 759. | 1.267 | 735. | 735. | 735. | 1.94 |
| 16 | 557. | 10. | 567. | 6.105 | 560. | 561. | 561. | 2.22 |
| 17 | 611. | 10. | 621. | 5.638 | 618. | 619. | 619. | 2.25 |
| 18 | 674. | 7. | 681. | 3.753 | 672. | 672. | 672. | 2.66 |

EQUATIONS FITTED TO THE EXPERIMENTAL RESULTS :

| | INTERCEPT, MILLIVOLTS | SLOPE, MILLIVOLTS | AVG. ERROR MILLIVOLTS | MAX. ERROR MILLIVOLTS |
|---|---|---|---|---|
| BEST STRAIGHT LINE : | 767.3 | -25.55 | 5.5 | 9.2 |
| EMPIRICAL NERNST EQUATION : | 766.9 | -25.59 | 5.4 | 9.1 |
| THEORETICAL NERNST EQUATION : | 766.0 | -25.59 | 5.4 | 9.1 |

UNCOMPLEXED CONCENTRATION RATIO USED (22°C)

COMPLEXES PRESENT : $FeSO_4^+$ ; $HSO_4^-$ ; $FeSO_4^\circ$

CONCENTRATION QUOTIENTS FOUND BY REGRESSION

CONCENTRATIONS IN SOLUTION, GMOLES/LITRE
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| POINT | FE(3+) | H+ | SO4(2-) | FE(2+) | FEHSO4SO4 | FEHSO4(2+) | FESO4SO4- | FESO4+ | HSO4- | FESO4 | FEHSO4+ |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | .0005 | .1264 | .0573 | .0075 | .0000 | .0000 | .0000 | .0095 | .0777 | .0025 | .0000 |
| 2 | .0029 | .1031 | .0594 | .0066 | .0000 | .0000 | .0000 | .0961 | .1010 | .0054 | .0000 |
| 3 | .0042 | .0255 | .0242 | .0621 | .0000 | .0000 | .0000 | .9858 | .1786 | .0079 | .0000 |
| 4 | .0003 | .0990 | .0644 | .0652 | .0000 | .0000 | .0000 | .0097 | .1051 | .0058 | .0000 |
| 5 | .0020 | .0830 | .0884 | .0551 | .0000 | .0000 | .0000 | .0970 | .1210 | .0033 | .0000 |
| 6 | .0090 | .0247 | .0413 | .0203 | .0000 | .0000 | .0000 | .9860 | .1794 | .0088 | .0000 |
| 7 | .0001 | .0396 | .2513 | .5082 | .0000 | .0000 | .0000 | .0099 | .1645 | .0015 | .0000 |
| 8 | .0006 | .0369 | .2745 | .2899 | .0000 | .0000 | .0000 | .0984 | .1672 | .7004 | .0000 |
| 9 | .0031 | .0194 | .5779 | .1627 | .0000 | .0000 | .0000 | .9869 | .1846 | .8275 | .0000 |
| 10 | .0003 | 1.0639 | .0557 | .0067 | .0000 | .0000 | .0000 | .0097 | .9764 | .0033 | .0000 |
| 11 | .0029 | 1.0221 | .0604 | .0065 | .0000 | .0000 | .0000 | .0961 | 1.0181 | .0035 | .0000 |
| 12 | .0153 | .6393 | .1329 | .0046 | .0000 | .0000 | .0000 | .9767 | 1.4007 | .0054 | .0000 |
| 13 | .0003 | 1.0122 | .0616 | .0642 | .0000 | .0000 | .0000 | .0097 | 1.0279 | .0348 | .0000 |
| 14 | .0020 | .9716 | .0667 | .0024 | .0000 | .0000 | .0000 | .0964 | 1.0684 | .0366 | .0000 |
| 15 | .0124 | .6096 | .1423 | .0440 | .0000 | .0000 | .0000 | .9776 | 1.4306 | .0550 | .0000 |
| 16 | .0001 | .5676 | .1247 | .4719 | .0000 | .0000 | .0000 | .0099 | 1.3726 | .5178 | .0000 |
| 17 | .0013 | .6425 | .1520 | .4577 | .0000 | .0000 | .0000 | .0977 | 1.3985 | .5518 | .0000 |
| 18 | .0070 | .4226 | .2522 | .5251 | .0000 | .0000 | .0000 | .9824 | 1.6184 | .6645 | .0000 |

VALUES OF EQUILIBRIUM CONSTANTS USED
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TEMPERATURE : 22.0E6 C

REACTION 1 : 0.000E-01
REACTION 2 : 0.000E-01
REACTION 3 : 0.000E-01
REACTION 4 : 5.547E 02
REACTION 5 : 1.049E 01
REACTION 6 : 6.801E 00
REACTION 7 : 0.000E-01



UNCOMPLEXED CONCENTRATION RATIO USED (22°C)

COMPLEXES PRESENT : $FeSO_4^+$ ; $HSO_4^-$ ; $FeSO_4^\circ$

CONCENTRATION QUOTIENTS FOUND BY REGRESSION

PREDICTED AND CALCULATED SOLUTION REDOX POTENTIALS

| POINT | MEASURED | LIQ. JN. | CORRECTED | LN(ACT. RATIO) | BEST LINE | NERNST EQN. (EMPIRICAL) | NERNST EQN. (THEORETICAL) | IONIC STRENGTH |
|---|---|---|---|---|---|---|---|---|
| 1 | 661. | 5. | 687. | 5.251 | 685. | 685. | 664. | .19 |
| 2 | 755. | 5. | 750. | 1.144 | 738. | 738. | 738. | .32 |
| 3 | 786. | 3. | 792. | -.741 | 786. | 786. | 766. | 1.78 |
| 4 | 618. | 5. | 623. | 5.720 | 622. | 622. | 622. | .36 |
| 5 | 669. | 4. | 674. | 3.541 | 677. | 677. | 677. | .49 |
| 6 | 727. | 3. | 730. | 1.565 | 728. | 728. | 727. | 1.91 |
| 7 | 556. | 2. | 556. | 8.420 | 554. | 554. | 553. | 1.76 |
| 8 | 603. | 2. | 605. | 6.148 | 611. | 611. | 611. | 1.67 |
| 9 | 666. | 2. | 668. | 3.972 | 667. | 666. | 666. | 3.07 |
| 10 | 673. | 18. | 690. | 3.332 | 690. | 690. | 690. | 1.55 |
| 11 | 730. | 17. | 747. | .765 | 748. | 748. | 747. | 1.71 |
| 12 | 785. | 13. | 798. | -1.[illegible]7 | 802. | 803. | 802. | 3.42 |
| 13 | 636. | 17. | 653. | 5.548 | 632. | 632. | 631. | 1.63 |
| 14 | 671. | 17. | 687. | 3.078 | 689. | 689. | 689. | 1.79 |
| 15 | 729. | 13. | 742. | .925 | 744. | 744. | 743. | 3.49 |
| 16 | 557. | 12. | 569. | 7.865 | 568. | 568. | 567. | 2.49 |
| 17 | 611. | 12. | 623. | 5.586 | 626. | 626. | 625. | 2.65 |
| 18 | 674. | 10. | 683. | 3.596 | 681. | 681. | 681. | 4.23 |

EQUATIONS FITTED TO THE EXPERIMENTAL RESULTS :

| | INTERCEPT, MILLIVOLTS | SLOPE, MILLIVOLTS | AVE. ERROR MILLIVOLTS | MAX. ERROR MILLIVOLTS |
|---|---|---|---|---|
| BEST STRAIGHT LINE : | 787.2 | -25.54 | 3.0 | 6.4 |
| EMPIRICAL NERNST EQUATION : | 767.9 | -25.59 | 3.0 | 6.3 |
| THEORETICAL NERNST EQUATION : | 786.6 | -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, GMOLES/LITRE

| POINT | FE(3+) | H+ | SO4(2-) | FE(2+) | FEHSO4SO4 | FEHSO4(2+) | FESO4SO4- | FESO4+ | HSO4- | FESO4 | FEHSO4+ |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | .0000 | .1259 | .0366 | .0059 | .0000 | .0003 | .0000 | .0091 | .0767 | .0051 | .0011 |
| 2 | .0044 | .1104 | .0710 | .0052 | .0000 | .0032 | .0000 | .0915 | .0894 | .0057 | .0011 |
| 3 | .0212 | .0837 | .5309 | .0053 | .0000 | .0292 | .0000 | .9400 | .0898 | .0055 | .0014 |
| 4 | .0005 | .1085 | .0745 | .0524 | .0000 | .0003 | .0000 | .0092 | .0843 | .0557 | .0109 |
| 5 | .0038 | .0994 | .1133 | .0479 | .0000 | .0030 | .0000 | .0922 | .0903 | .0498 | .0114 |
| 6 | .0298 | .0793 | .5657 | .0327 | .0000 | .0279 | .0000 | .9417 | .0836 | .0551 | .0133 |
| 7 | .0005 | .8561 | .4594 | .5650 | .0000 | .0002 | .0000 | .0095 | .0524 | .5117 | .0934 |
| 8 | .0029 | .0568 | .4775 | .3755 | .0000 | .0020 | .0000 | .0946 | .0517 | .5211 | .0935 |
| 9 | .0102 | .0483 | .0800 | .5105 | .0000 | .0178 | .0000 | .9543 | .0453 | .5872 | .0927 |
| 10 | .0005 | 1.2598 | .2561 | .0019 | .0000 | .0031 | .0000 | .0066 | .7714 | .0016 | .0064 |
| 11 | .0026 | 1.2291 | .2975 | .0018 | .0000 | .0302 | .0000 | .0663 | .7757 | .0017 | .0065 |
| 12 | .0109 | 1.0103 | .7817 | .0013 | .0000 | .2755 | .0000 | .6990 | .7492 | .0020 | .0067 |
| 13 | .0005 | 1.2105 | .2808 | .0188 | .0000 | .0030 | .0000 | .0067 | .7638 | .0166 | .0635 |
| 14 | .0025 | 1.1017 | .5254 | .0178 | .0000 | .0294 | .0000 | .0671 | .7664 | .0172 | .0640 |
| 15 | .0157 | .9743 | .6102 | .0127 | .0000 | .2667 | .0000 | .7060 | .7332 | .0205 | .0658 |
| 16 | .0992 | .8165 | .5653 | .1653 | .0000 | .0023 | .0000 | .0075 | .6248 | .2275 | .5978 |
| 17 | .0019 | .8017 | .6128 | .1607 | .0000 | .0228 | .0000 | .0743 | .6186 | .2306 | .5986 |
| 18 | .0142 | .6715 | 1.0895 | .1348 | .0000 | .2049 | .0000 | .7713 | .5740 | .2641 | .5916 |

VALUES OF EQUILIBRIUM CONSTANTS USED

TEMPERATURE : 22.00 C

REACTION 1 : 0.000E-01
REACTION 2 : 1.701E 03
REACTION 3 : 0.000E-01
REACTION 4 : 9.389E 03
REACTION 5 : 3.705E 01
REACTION 6 : 1.363E 02
REACTION 7 : 5.035E 02



ACTIVITY COEFFICIENTS USED (22°C)

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

CONCENTRATIONS IN SOLUTION, GMOLES/LITRE
**********

| POINT | FE(3+) | H+ | SO4(2-) | FE(2+) | FEHSO4SO4 | FEHSO4(2+) | FESO4SO4- | FESO4+ | HSO4- | FESO4 | FEHSO4+ |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | .0006 | .1259 | .0366 | .0059 | .0000 | .0003 | .0000 | .0091 | .0767 | .0051 | .0011 |
| 2 | .0044 | .1104 | .0710 | .0052 | .0000 | .0032 | .0000 | .0915 | .0894 | .0057 | .0011 |
| 3 | .0212 | .0857 | .3309 | .0033 | .0000 | .0292 | .0000 | .9400 | .0898 | .0055 | .0014 |
| 4 | .0005 | .1085 | .0745 | .0524 | .0000 | .0003 | .0000 | .0092 | .0843 | .0057 | .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 | .0005 | .0561 | .4394 | .5850 | .0000 | .0002 | .0000 | .0095 | .0524 | .5117 | .0934 |
| 8 | .0024 | .0566 | .4775 | .5755 | .0000 | .0020 | .0000 | .0946 | .0517 | .5211 | .0935 |
| 9 | .0102 | .0483 | .4800 | .5105 | .0000 | .0178 | .0000 | .9543 | .0453 | .5072 | .0927 |
| 10 | .0005 | 1.2598 | .2561 | .0019 | .0000 | .0031 | .0000 | .0066 | .7714 | .0016 | .0064 |
| 11 | .0026 | 1.2291 | .2975 | .0018 | .0000 | .0302 | .0000 | .0663 | .7757 | .0017 | .0065 |
| 12 | .0100 | 1.0103 | .7817 | .0013 | .0000 | .2755 | .0000 | .6990 | .7492 | .0020 | .0067 |
| 13 | .0005 | 1.2105 | .2808 | .0188 | .0000 | .0030 | .0000 | .0067 | .7638 | .0166 | .0635 |
| 14 | .0025 | 1.1817 | .3234 | .0178 | .0000 | .0294 | .0000 | .0671 | .7664 | .0172 | .0640 |
| 15 | .0157 | .9745 | .0102 | .0127 | .0000 | .2607 | .0000 | .7060 | .7352 | .9205 | .0658 |
| 16 | .0002 | .8165 | .5653 | .1653 | .0000 | .0023 | .0000 | .0075 | .6244 | .2275 | .5978 |
| 17 | .0019 | .8017 | .6128 | .1607 | .0000 | .0228 | .0000 | .0743 | .6186 | .2508 | .5986 |
| 18 | .0142 | .6715 | 1.0895 | .1348 | .0000 | .2049 | .0000 | .7713 | .5740 | .2641 | .5916 |

VALUES OF EQUILIBRIUM CONSTANTS USED
**********

TEMPERATURE : 22.0EG C

REACTION 1 : 0.000E-01
REACTION 2 : 1.701E 03
REACTION 3 : 0.000E-01
REACTION 4 : 9.389E 03
REACTION 5 : 3.707E 01
REACTION 6 : 1.305E 02
REACTION 7 : 5.655E 02

ACTIVITY COEFFICIENTS USED (22°C)

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

PREDICTED AND CALCULATED SOLUTION REDOX POTENTIALS

| POINT | MEASURED | LIQ. JN. | CORRECTED | LN(ACT. RATIO) | BEST LINE | NERNST EQN. (EMPIRICAL) | NERNST EQN. (THEORETICAL) | IONIC STRENGTH |
|---|---|---|---|---|---|---|---|---|
| 1 | 681. | 5. | 667. | 3.528 | 694. | 694. | 682. | .20 |
| 2 | 755. | 5. | 738. | 1.228 | 748. | 747. | 736. | .32 |
| 3 | 786. | 4. | 792. | -.626 | 796. | 794. | 783. | 1.75 |
| 4 | 618. | 5. | 623. | 5.604 | 650. | 631. | 619. | .38 |
| 5 | 669. | 4. | 674. | 3.628 | 686. | 686. | 675. | .50 |
| 6 | 727. | 3. | 731. | 1.076 | 736. | 736. | 724. | 1.86 |
| 7 | 556. | 3. | 554. | 8.491 | 581. | 563. | 551. | 1.66 |
| 8 | 603. | 3. | 606. | 6.218 | 620. | 620. | 609. | 1.96 |
| 9 | 666. | 3. | 669. | 4.045 | 675. | 676. | 664. | 3.10 |
| 10 | 673. | 18. | 690. | 3.693 | 685. | 685. | 675. | 1.55 |
| 11 | 730. | 17. | 747. | 1.437 | 743. | 742. | 730. | 1.67 |
| 12 | 785. | 16. | 800. | -.033 | 796. | 794. | 783. | 2.96 |
| 13 | 616. | 17. | 633. | 6.025 | 625. | 625. | 614. | 1.72 |
| 14 | 671. | 17. | 688. | 3.765 | 684. | 683. | 671. | 1.64 |
| 15 | 729. | 15. | 744. | 1.671 | 737. | 736. | 724. | 3.10 |
| 16 | 557. | 15. | 572. | 8.525 | 560. | 562. | 550. | 3.14 |
| 17 | 611. | 15. | 626. | 6.248 | 619. | 620. | 608. | 3.24 |
| 18 | 674. | 14. | 688. | 4.045 | 676. | 676. | 664. | 4.31 |

EQUATIONS FITTED TO THE EXPERIMENTAL RESULTS :

| | INTERCEPT, MILLIVOLTS | SLOPE, MILLIVOLTS | AVE. ERROR MILLIVOLTS | MAX. ERROR MILLIVOLTS |
|---|---|---|---|---|
| BEST STRAIGHT LINE : | 779.5 | -25.12 | 8.2 | 13.6 |
| EMPIRICAL NERNST EQUATION : | 778.3 | -25.59 | 8.1 | 14.4 |
| THEORETICAL NERNST EQUATION : | 766.6 | -25.59 | 14.0 | 23.5 |

ACTIVITY COEFFICIENTS USED (22 °C)

COMPLEXES PRESENT : $FeSO_4^+$ ; $HSO_4^-$ ; $FeSO_4^\circ$

CONCENTRATIONS IN SOLUTION, GMOLES/LITRE
**********

| POINT | FE(3+) | H+ | SO4(2-) | FE(2+) | FEHSO4SO4 | FEHSO4(2+) | FESO4SO4- | FESO4+ | HSO4- | FESO4 | FEHSO4+ |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | .0006 | .1268 | .0369 | .0066 | .0000 | .0000 | .0000 | .0094 | .0772 | .0054 | .0000 |
| 2 | .0043 | .1130 | .0702 | .0059 | .0000 | .0000 | .0000 | .0945 | .0911 | .0041 | .0000 |
| 3 | .0220 | .0980 | .5160 | .0039 | .0000 | .0000 | .0000 | .9684 | .1061 | .0061 | .0000 |
| 4 | .0003 | .1153 | .0767 | .0590 | .0000 | .0000 | .0000 | .0095 | .0887 | .0400 | .0000 |
| 5 | .0040 | .1078 | .1140 | .0548 | .0000 | .0000 | .0000 | .0950 | .0963 | .0447 | .0000 |
| 6 | .0217 | .0993 | .5511 | .0360 | .0000 | .0000 | .0000 | .9687 | .1048 | .0610 | .0000 |
| 7 | .0003 | .1102 | .4441 | .4314 | .0000 | .0000 | .0000 | .0097 | .0959 | .5569 | .0000 |
| 8 | .0026 | .1095 | .4802 | .4210 | .0000 | .0000 | .0000 | .0964 | .0945 | .5694 | .0000 |
| 9 | .0109 | .1067 | .8654 | .3475 | .0000 | .0000 | .0000 | .9716 | .0973 | .6426 | .0000 |
| 10 | .0004 | 1.2665 | .2569 | .0054 | .0000 | .0000 | .0000 | .0096 | .7744 | .0046 | .0000 |
| 11 | .0038 | 1.2533 | .2893 | .0053 | .0000 | .0000 | .0000 | .0952 | .7883 | .0047 | .0000 |
| 12 | .0237 | 1.1713 | .6706 | .0040 | .0000 | .0000 | .0000 | .9667 | .8706 | .0060 | .0000 |
| 13 | .0004 | 1.2581 | .2957 | .0519 | .0000 | .0000 | .0000 | .0096 | .7822 | .0470 | .0000 |
| 14 | .0036 | 1.2469 | .3287 | .0504 | .0000 | .0000 | .0000 | .0954 | .7947 | .0486 | .0000 |
| 15 | .0231 | 1.1706 | .7064 | .0395 | .0000 | .0000 | .0000 | .9673 | .8709 | .0596 | .0000 |
| 16 | .0003 | 1.2292 | .6360 | .4214 | .0000 | .0000 | .0000 | .0097 | .8117 | .5685 | .0000 |
| 17 | .0025 | 1.2227 | .6673 | .4145 | .0000 | .0000 | .0000 | .0965 | .8185 | .5758 | .0000 |
| 18 | .0196 | 1.1510 | .9996 | .3562 | .0000 | .0000 | .0000 | .9705 | .8906 | .6559 | .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 : 9.389E 03
REACTION 5 : 6.767E 01
REACTION 6 : 1.563E 02
REACTION 7 : 0.000E-01



ACTIVITY COEFFICIENTS USED (22 °C)

COMPLEXES PRESENT : $FeSO_4^+$ ; $HSO_4^-$ ; $FeSO_4^\circ$

PREDICTED AND CALCULATED SOLUTION REDOX POTENTIALS

| POINT | MEASURED | LIQ. JN. | CORRECTED | LN(ACT. RATIO) | BEST LINE | NERNST EQN. (EMPIRICAL) | NERNST EQN. (THEORETICAL) | IONIC STRENGTH |
|---|---|---|---|---|---|---|---|---|
| 1 | 681. | 5. | 687. | 5.836 | 708. | 709. | 669. | .19 |
| 2 | 733. | 5. | 738. | 1.647 | 760. | 765. | 725. | .24 |
| 3 | 788. | 2. | 790. | -.395 | 808. | 817. | 777. | .87 |
| 4 | 618. | 4. | 623. | 6.469 | 645. | 643. | 603. | .55 |
| 5 | 669. | 4. | 673. | 4.211 | 699. | 700. | 660. | .40 |
| 6 | 727. | 2. | 729. | 1.969 | 752. | 757. | 717. | 1.01 |
| 7 | 556. | 2. | 556. | 9.601 | 570. | 563. | 523. | 1.75 |
| 8 | 605. | 1. | 605. | 7.263 | 626. | 622. | 582. | 1.79 |
| 9 | 666. | 0. | 667. | 4.720 | 687. | 687. | 647. | 2.31 |
| 10 | 673. | 18. | 690. | 5.528 | 667. | 666. | 626. | 1.52 |
| 11 | 730. | 17. | 747. | 3.206 | 723. | 725. | 685. | 1.48 |
| 12 | 765. | 13. | 778. | .625 | 784. | 791. | 751. | 1.14 |
| 13 | 616. | 17. | 633. | 7.684 | 611. | 607. | 567. | 1.61 |
| 14 | 671. | 17. | 688. | 5.564 | 666. | 666. | 626. | 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 | 611. | 12. | 623. | 8.316 | 601. | 598. | 556. | 2.44 |
| 18 | 674. | 6. | 682. | 5.788 | 661. | 660. | 620. | 2.24 |

EQUATIONS FITTED TO THE EXPERIMENTAL RESULTS :

| | INTERCEPT, MILLIVOLTS | SLOPE, MILLIVOLTS | AVE. ERROR MILLIVOLTS | MAX. ERROR MILLIVOLTS |
|---|---|---|---|---|
| BEST STRAIGHT LINE : | 798.9 | -23.81 | 20.8 | 25.5 |
| EMPIRICAL NERNST EQUATION : | 806.8 | -25.39 | 22.6 | 32.2 |
| THEORETICAL NERNST EQUATION : | 766.8 | -25.39 | 45.9 | 72.2 |

ACTIVITY COEFFICIENTS USED (22°C)

COMPLEXES PRESENT : $FeHSO_4SO_4^+$ ; $FeHSO_4^{2+}$ ; $FeSO_4^+$ ; $Fe(SO_4)_2^-$ ;

$HSO_4^-$ ; $FeSO_4^0$ ; $FeHSO_4^+$

CONCENTRATIONS IN SOLUTION, GMOLES/LITRE

| POINT | FE(3+) | H+ | SO4(2-) | FE(2+) | FEHSO4SO4 | FEHSO4(2+) | FESO4SO4- | FESO4+ | HSO4- | FESO4 | FEHSO4+ |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | .0003 | .1253 | .0346 | .0059 | .0033 | .0002 | .0012 | .0050 | .0741 | .0050 | .0010 |
| 2 | .0026 | .1023 | .0460 | .0058 | .0311 | .0015 | .0145 | .0490 | .0681 | .0055 | .0009 |
| 3 | .0255 | .0275 | .1585 | .0055 | .1513 | .0049 | .2971 | .5126 | .0199 | .0042 | .0005 |
| 4 | .0002 | .1074 | .0718 | .0529 | .0036 | .0001 | .0017 | .0043 | .0821 | .0554 | .0107 |
| 5 | .0021 | .0886 | .0854 | .0523 | .0331 | .0012 | .0188 | .0437 | .0713 | .0575 | .0094 |
| 6 | .0216 | .0261 | .1863 | .0527 | .1510 | .0046 | .3163 | .4960 | .0189 | .0429 | .0034 |
| 7 | .0001 | .0572 | .4351 | .3875 | .0035 | .0001 | .0035 | .0029 | .0514 | .5112 | .0919 |
| 8 | .0008 | .0492 | .4366 | .3947 | .0310 | .0006 | .0360 | .0306 | .0432 | .5155 | .0799 |
| 9 | .0121 | .0184 | .4602 | .4416 | .1397 | .0028 | .4408 | .3941 | .0125 | .5173 | .0505 |
| 10 | .0000 | 1.2573 | .2506 | .0020 | .0088 | .0003 | .0004 | .0005 | .7674 | .0016 | .0064 |
| 11 | .0062 | 1.2062 | .2426 | .0020 | .0865 | .0025 | .0040 | .0057 | .7388 | .0017 | .0065 |
| 12 | .0845 | .7359 | .1894 | .0029 | .8015 | .0257 | .0602 | .0977 | .4729 | .0022 | .0049 |
| 13 | .0000 | 1.2083 | .2752 | .0190 | .0068 | .0002 | .0004 | .0005 | .7601 | .0166 | .0033 |
| 14 | .0002 | 1.1571 | .2676 | .0197 | .0866 | .0024 | .0042 | .0056 | .7319 | .0172 | .0021 |
| 15 | .0041 | .6985 | .2157 | .0270 | .0854 | .0237 | .0840 | .0944 | .4663 | .0227 | .0487 |
| 16 | .0000 | .8130 | .5605 | .1662 | .0087 | .0001 | .0006 | .0005 | .6223 | .2277 | .5960 |
| 17 | .0001 | .7736 | .5549 | .1715 | .0860 | .0014 | .0065 | .0049 | .5954 | .2545 | .5655 |
| 18 | .0022 | .4447 | .5131 | .2344 | .7694 | .0137 | .1030 | .0816 | .3494 | .3117 | .4434 |

VALUES OF EQUILIBRIUM CONSTANTS USED

TEMPERATURE : 22.0E6 C

REACTION 1 : 8.100E 06
REACTION 2 : 1.701E 05
REACTION 3 : 2.40ME 05
REACTION 4 : 9.589E 05
REACTION 5 : 8.767E 01
REACTION 6 : 1.565E 02
REACTION 7 : 5.035E 02

ACTIVITY COEFFICIENTS USED (22°C)

COMPLEXES PRESENT : $FeHSO_4SO_4^+$ ; $FeHSO_4^{2+}$ ; $FeSO_4^+$ ; $Fe(SO_4)_2^-$ ;

$HSO_4^-$ ; $FeSO_4^0$ ; $FeHSO_4^+$

PREDICTED AND CALCULATED SOLUTION REDOX POTENTIALS

| POINT | MEASURED | LIQ. JN. | CORRECTED | LN(ACT. RATIO) | BEST LINE | NERNST EQN. (EMPIRICAL) | NERNST EQN. (THEORETICAL) | IONIC STRENGTH |
|---|---|---|---|---|---|---|---|---|
| 1 | 699. | 7. | 706. | 4.465 | 707. | 709. | 709. | .14 |
| 2 | 684. | 6. | 690. | 4.428 | 696. | 697. | 698. | .19 |
| 3 | 669. | 4. | 674. | 5.328 | 680. | 682. | 682. | .30 |
| 4 | 664. | 3. | 668. | 5.856 | 665. | 665. | 665. | .57 |
| 5 | 647. | 2. | 650. | 6.485 | 645. | 645. | 645. | 1.39 |
| 6 | 874. | 5. | 879. | -1.098 | 885. | 883. | 883. | 3.86 |
| 7 | 853. | 5. | 858. | -.398 | 862. | 861. | 861. | 3.85 |
| 8 | 829. | 5. | 834. | .267 | 841. | 840. | 840. | 3.86 |
| 9 | 807. | 4. | 811. | 1.049 | 816. | 815. | 816. | 3.81 |
| 10 | 781. | 4. | 785. | 1.915 | 789. | 788. | 788. | 3.75 |
| 11 | 752. | 3. | 755. | 2.860 | 758. | 759. | 759. | 3.70 |
| 12 | 869. | 4. | 865. | -.799 | 875. | 873. | 873. | 3.81 |
| 13 | 858. | 4. | 862. | -.132 | 854. | 852. | 852. | 3.84 |
| 14 | 852. | 4. | 856. | .545 | 852. | 851. | 851. | 3.83 |
| 15 | 809. | 4. | 813. | 1.546 | 807. | 806. | 806. | 3.79 |
| 16 | 782. | 4. | 786. | 2.125 | 782. | 782. | 782. | 3.76 |
| 17 | 751. | 4. | 754. | 3.037 | 753. | 753. | 753. | 3.68 |
| 18 | 704. | 3. | 707. | 4.518 | 705. | 707. | 707. | 3.53 |

EQUATIONS FITTED TO THE EXPERIMENTAL RESULTS :

| | INTERCEPT, MILLIVOLTS | SLOPE, MILLIVOLTS | AVE. ERROR MILLIVOLTS | MAX. ERROR MILLIVOLTS |
|---|---|---|---|---|
| BEST STRAIGHT LINE : | 849.6 | -31.94 | 5.3 | 8.1 |
| EMPIRICAL NERNST EQUATION : | 848.3 | -31.29 | 5.4 | 10.2 |
| THEORETICAL NERNST EQUATION : | 848.3 | -31.29 | 5.4 | 10.1 |

ACTIVITY COEFFICIENTS USED (90°C)

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

CONCENTRATIONS IN SOLUTION, GMOLES/LITRE

| POINT | FE(3+) | H+ | SO4(2-) | FE(2+) | FEHSO4SO4 | FEHSO4(2+) | FESO4SO4- | FESO4+ | HSO4- | FESO4 | FEHSO4+ |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | .0001 | .0659 | .0119 | .0036 | .0000 | .0017 | .0000 | .0161 | .1029 | .0009 | .0134 |
| 2 | .0002 | .0576 | .0230 | .0004 | .0000 | .0030 | .0000 | .0416 | .1100 | .0032 | .0332 |
| 3 | .0002 | .0319 | .0572 | .0161 | .0000 | .0056 | .0000 | .0857 | .1057 | .0107 | .0628 |
| 4 | .0003 | .0158 | .1508 | .0348 | .0000 | .0059 | .0000 | .1749 | .0751 | .0357 | .1091 |
| 5 | .0000 | .0051 | .4155 | .1159 | .0000 | .0035 | .0000 | .4437 | .0240 | .1625 | .1713 |
| 6 | .0016 | .2705 | .7932 | .0002 | .0000 | .5378 | .0000 | 1.1640 | .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 | .0008 | .0466 |
| 9 | .0010 | .2298 | .8307 | .0015 | .0000 | .4763 | .0000 | 1.2145 | .8355 | .0019 | .0959 |
| 10 | .0016 | .1787 | .8847 | .0030 | .0000 | .3952 | .0000 | 1.2978 | .6943 | .0047 | .1893 |
| 11 | .0015 | .1284 | .9515 | .0075 | .0000 | .2943 | .0000 | 1.3865 | .5387 | .0127 | .3630 |
| 12 | .0018 | .1722 | .8986 | .0002 | .0000 | .4234 | .0000 | 1.4414 | .6773 | .0005 | .0134 |
| 13 | .0017 | .1925 | .8800 | .0004 | .0000 | .4520 | .0000 | 1.3751 | .7402 | .0006 | .0279 |
| 14 | .0017 | .1974 | .8731 | .0008 | .0000 | .4518 | .0000 | 1.3411 | .7533 | .0012 | .0550 |
| 15 | .0017 | .1804 | .8866 | .0018 | .0000 | .4148 | .0000 | 1.3483 | .7009 | .0028 | .1124 |
| 16 | .0016 | .1722 | .8953 | .0037 | .0000 | .5817 | .0000 | 1.3003 | .6771 | .0059 | .2295 |
| 17 | .0015 | .1387 | .9341 | .0084 | .0000 | .2962 | .0000 | 1.2547 | .5721 | .0141 | .4557 |
| 18 | .0011 | .0726 | 1.0118 | .0290 | .0000 | .1340 | .0000 | 1.0881 | .3293 | .0538 | .8683 |

VALUES OF EQUILIBRIUM CONSTANTS USED

TEMPERATURE : 90.DEG C

REACTION 1 : 0.000E-01
REACTION 2 : 2.250E 05
REACTION 3 : 0.000E-01
REACTION 4 : 5.155E 05
REACTION 5 : 4.993E 02
REACTION 6 : 2.570E 02
REACTION 7 : 4.060E 04

ACTIVITY COEFFICIENTS USED (90°C)

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

PREDICTED AND CALCULATED SOLUTION REDOX POTENTIALS

| POINT | MEASURED | LIQ. JN. | CORRECTED | LN(ACT. RATIO) | BEST LINE | NERNST EQN. (EMPIRICAL) | NERNST EQN. (THEORETICAL) | IONIC STRENGTH |
|---|---|---|---|---|---|---|---|---|
| 1 | 694. | 6. | 701. | 3.520 | 702. | 694. | 703. | .18 |
| 2 | 690. | 5. | 696. | 3.702 | 694. | 689. | 698. | .25 |
| 3 | 688. | 4. | 693. | 3.908 | 684. | 685. | 692. | .38 |
| 4 | 688. | 3. | 692. | 4.129 | 675. | 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 : | 869.7 | -47.58 | 7.5 | 12.2 |
| EMPIRICAL NERNST EQUATION : | 792.1 | -27.84 | 6.9 | 10.6 |
| THEORETICAL NERNST EQUATION : | 800.7 | -27.84 | 11.1 | 19.2 |



ACTIVITY COEFFICIENTS USED (50 °C)

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

CONCENTRATIONS IN SOLUTION, MOLES/LITRE

| POINT | FE(3+) | H+ | SO4(2-) | FE(2+) | FEHSO4SO4 | FEHSO4(2+) | FESO4SO4- | FESO4+ | HSO4- | FESO4 | FEHSO4+ |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | .0000 | .1907 | .0240 | .0081 | .0000 | .0018 | .0000 | .0155 | .0949 | .0056 | .0065 |
| 2 | .0012 | .0818 | .0419 | .0185 | .0000 | .0039 | .0000 | .0397 | .1021 | .0181 | .0162 |
| 3 | .0019 | .0625 | .0760 | .0334 | .0000 | .0064 | .0000 | .0613 | .1039 | .0250 | .0312 |
| 4 | .0029 | .0444 | .1616 | .0599 | .0000 | .0099 | .0000 | .1664 | .0924 | .0619 | .0573 |
| 5 | .0055 | .0247 | .4122 | .1363 | .0000 | .0152 | .0000 | .4274 | .0542 | .2017 | .1098 |

VALUES OF EQUILIBRIUM CONSTANTS USED

TEMPERATURE : 50.0EG C

REACTION 1 : 0.000E-01
REACTION 2 : 1.676E 04
REACTI 3 : 0.000E-01
REACTI 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 : $FeHSO_4^{2+}$ ; $FeSO_4^+$ ; $HSO_4^-$ ; $FeSO_4^\circ$ ; $FeHSO_4^+$

PREDICTED AND CALCULATED SOLUTION REDOX POTENTIALS

| POINT | MEASURED | LIQ. JN. | CORRECTED | LN(ACT. RATIO) | BEST LINE | NERNST EQN. (EMPIRICAL) | NERNST EQN. (THEORETICAL) | IONIC STRENGTH |
|---|---|---|---|---|---|---|---|---|
| 1 | 819. | 5. | 822. | -.619 | 822. | 820. | 820. | 4.28 |
| 2 | 807. | 3. | 810. | -.170 | 809. | 806. | 806. | 4.26 |
| 3 | 797. | 3. | 800. | .101 | 800. | 800. | 800. | 4.22 |
| 4 | 792. | 3. | 795. | .194 | 798. | 796. | 798. | 4.43 |
| 5 | 789. | 3. | 792. | .450 | 79[illegible] | 790. | 791. | 4.19 |
| 6 | 787. | 3. | 790. | .493 | 78[illegible]. | 789. | 789. | 4.23 |
| 7 | 786. | 3. | 789. | .496 | 789. | 790. | 790. | 4.36 |
| 8 | 785. | 3. | 788. | .529 | 787. | 788. | 788. | 4.30 |

EQUATIONS FITTED TO THE EXPERIMENTAL RESULTS :

| | INTERCEPT, MILLIVOLTS | SLOPE, MILLIVOLTS | AVE. ERROR MILLIVOLTS | MAX. ERROR MILLIVOLTS |
|---|---|---|---|---|
| BEST STRAIGHT LINE : | 803.5 | -30.37 | 1.3 | 2.8 |
| EMPIRICAL NERNST EQUATION : | 803.1 | -28.02 | 1.5 | 2.8 |
| THEORETICAL NERNST EQUATION : | 803.1 | -28.02 | 1.5 | 2.9 |



ACTIVITY COEFFICIENTS USED (52 °C)

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

CONCENTRATIONS IN SOLUTION, GMOLES/LITRE
**********

| POINT | FE(3+) | H+ | SO4(2-) | FE(2+) | FEHSO4SO4 | FEHSO4(2+) | FESO4SO4+ | FESO4+ | HSO4- | FESO4 | FEHSO4+ |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | .0129 | .1769 | 1.1224 | .0021 | .0000 | .4580 | .0000 | 1.5091 | .4131 | .0043 | .0206 |
| 2 | .0137 | .1396 | 1.1653 | .0035 | .0000 | .3983 | .0000 | 1.6630 | .3365 | .0075 | .0281 |
| 3 | .0137 | .1249 | 1.1595 | .0046 | .0000 | .3736 | .0000 | 1.6777 | .3143 | .0099 | .0345 |
| 4 | .0132 | .1666 | 1.1731 | .0048 | .0000 | .4540 | .0000 | 1.5855 | .4056 | .0102 | .0460 |
| 5 | .0136 | .1214 | 1.1634 | .0065 | .0000 | .3533 | .0000 | 1.6979 | .2951 | .0141 | .0463 |
| 6 | .0137 | .1290 | 1.1655 | .0068 | .0000 | .3704 | .0000 | 1.6750 | .3134 | .0146 | .0507 |
| 7 | .0132 | .1571 | 1.1672 | .0064 | .0000 | .4500 | .0000 | 1.5935 | .3808 | .0135 | .0572 |
| 8 | .0133 | .1466 | 1.1630 | .0068 | .0000 | .4063 | .0000 | 1.6151 | .3546 | .0146 | .0576 |

VALUES OF EQUILIBRIUM CONSTANTS USED
**********

TEMPERATURE : 52.DEG C

REACTION 1 : 9.000E-01
REACTION 2 : 1.951E 04
REACTION 3 : 8.660E-01
REACTION 4 : 2.551E 04
REACTION 5 : 2.082E 02
REACTION 6 : 2.082E 02
REACTION 7 : 5.900E 03



ACTIVITY COEFFICIENTS USED (52°C)

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

# 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 $cm^2$

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 $cm^2$

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 | .5 | .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 IO = 1.895E-02

CONSTANT K = 1.319E-02

CURRENT = IO*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 $FeHSO_4SO_4$.

a) Activities of uncomplexed ferric and ferrous ions in solution

By stoichiometry, the total amounts of $Fe^{3+}$, $Fe^{2}+$, $H^{+}$ and $SO_4^{=}$ in solution can be defined in terms of the concentrations of uncomplexed $Fe^{3+}$, $Fe^{2+}$, $H^{+}$ and $SO_4^{=}$, and the concentrations of the various complexes, i.e.:

$$[Fe^{3+}]_T = [Fe^{3+}] + [FeHSO_4SO_4] + [FeHSO_4^{2+}] + [Fe(SO_4)_2^{-}] + [FeSO_4^{+}]$$

$$[Fe^{2+}]_T = [Fe^{2+}] + [FeSO_4] + [FeHSO_4^{+}]$$

$$[H^{+}]_T = [H^{+}] + [HSO_4^{-}] + [FeHSO_4SO_4] + [FeHSO_4^{2+}] + [FeHSO_4^{+}]$$

$$[SO_4^{=}]_T = [SO_4^{=}] + [HSO_4^{-}] + 2[FeHSO_4SO_4] + 2[Fe(SO_4)_2^{-}] + [FeHSO_4^{2+}] + [FeSO_4^{+}] + [FeSO_4] + [FeHSO_4^{+}]$$

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 $SO_4^{=}$ in solution, as follows:

$$\{FeHSO_4SO_4\} = K(i)\{Fe^{3+}\}\{H^{+}\}\{SO_4^{=}\}^2$$

$$\{FeHSO_4^{2+}\} = K(ii)\{Fe^{3+}\}\{H^{+}\}\{SO_4^{=}\}$$

$$\{Fe(SO^4)_2^{-}\} = K(iii)\{Fe^{3+}\}\{SO_4\}^2$$

$$\{FeSO_4^{+}\} = K(iv)\{Fe^{3+}\}\{SO_4^{=}\}$$

$$\{HSO_4^{-}\} = K(v)\{H^{+}\}\{SO_4^{=}\}$$

$$\{FeSO_4\} = K(vi)\{Fe^{2+}\}\{SO_4^{=}\}$$

$$\{FeHSO_4^{+}\} = K(vii)\{Fe^{2+}\}\{H^{+}\}\{SO_4^{=}\}$$

Where: { } denotes aotivity

K(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:

$$[FeHSO_4SO_4] = \frac{K(i)\gamma(Fe^{3+})[Fe^{3+}]\gamma(H^+)[H^+]\gamma^2(SO_4^{=})[SO_4^{=}]^2}{\gamma(FeHSO_4SO_4)}$$

i.e.: $$[FeHSO_4SO_4] = K'(i)[Fe^{3+}][H^+][SO_4^{=}]^2$$

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

Similarly:

$$[FeHSO_4^{2+}] = K'(ii)[Fe^{3+}][H^+][SO_4^{=}]$$
$$[Fe(SO_4)_2^{-}] = K'(iii)[Fe^{3+}][SO_4^{=}]^2$$
$$[FeSO_4^{+}] = K'(iv)[Fe^{3+}][SO_4^{=}]$$
$$[HSO_4^{-}] = K'(v)[H^+][SO_4^{=}]$$
$$[FeSO_4] = K'(vi)[Fe^{2+}][SO_4^{=}]$$
$$[FeHSO_4^{+}] = K'(vii)[Fe^{2+}][H^+][SO_4^{=}]$$

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

$$[Fe^{3+}]_T = [Fe^{3+}] + K'(i)[Fe^{3+}][H^+][SO_4^{=}]^2 + K'(ii)[Fe^{3+}][H^+][SO_4^{=}] + K'(iii)[Fe^{3+}][SO_4^{=}]^2 + K'(iv)[Fe^{3+}][SO_4^{=}]$$

$$[Fe^{2+}]_T = [Fe^{2+}] + K'(vi)[Fe^{2+}][SO_4^{=}] + K'(vii)[Fe^{2+}][H^+][SO_4^{=}]$$

$$[H^+]_T = [H^+] + K'(i)[Fe^{3+}][H^+][SO_4^{=}]^2 + K(ii)'[Fe^{3+}][H^+][SO_4^{=}] + K'(v)[H^+][SO_4^{=}] + K(vii)'[Fe^{2+}][H^+][SO_4^{=}]$$

$$[SO_4^{=}]_T = [SO_4^{=}] + 2K'(i)[Fe^{3+}][H^+][SO_4^{=}]^2 + K'(ii)[Fe^{3+}][H^+][SO_4^{=}] + 2K'(iii)[Fe^{3+}][SO_4^{=}]^2 + K'(iv)[Fe^{3+}][SO_4^{=}] + K'(v)[H^+][SO_4^{=}] + K'(vi)[Fe^{2+}][SO_4^{=}] + K'(vii)[Fe^{2+}][H^+][SO_4^{=}]$$

Rearranging these equations gives:

$$[Fe^{3+}]_T = [Fe^{3+}]\{1 + X(Fe^{3+})\}$$
$$[Fe^{2+}]_T = [Fe^{2+}]\{1 + X(Fe^{2+})\}$$
$$[H^+]_T = [H^+]\{1 + X(H^+)\}$$
$$[SO_4^=]_T = [SO_4^=]\{1 + X(SO_4^=)\}$$

Where:

$$X(Fe^{3+}) = K'(i)[H^+][SO_4^=]^2 + K'(ii)[H^+][SO_4^=] + K'(iii)[SO_4^=]^2 + K'(iv)[SO_4^=]$$

$$X(Fe^{2+}) = K'(vi)[SO_4^=] + K'(vii)[H^+][SO_4^=]$$

$$X(H^+) = K'(i)[Fe^{3+}][SO_4^=]^2 + K'(ii)[Fe^{3+}][SO_4^=] + K'(v)[SO_4^=] + K'(vii)[Fe^{2+}][SO_4^=]$$

$$X(SO_4^=) = 2K'(i)[Fe^{3+}][H^+][SO_4^=] + K'(ii)[Fe^{3+}][H^+] + 2K'(iii)[Fe^{3+}][SO_4^=] + K'(iv)[Fe^{3+}] + K'(v)[H^+] + K'(vi)[Fe^{2+}] + K'(vii)[Fe^{2+}][H^+]$$

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 $X(Fe^{3+})$, $X(Fe^{2+})$, $X(H^+)$ and $X(SO_4^=)$ can be made by assuming total dissociation, i.e., the values of the concentrations of $Fe^{3+}$, $Fe^{2+}$, $H^+$ and $SO_4^=$ 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 $X(Fe^{3+})$, $X(Fe^{2+})$, $X(H^+)$ and $X(SO_4^=)$ are then calculated. An improved guess is then made of the uncomplexed concentrations, as follows:

$$[Fe^{3+}] = [Fe^{3+}]_T/\{1 + X(Fe^{3+})\}$$
$$[Fe^{2+}] = [Fe^{2+}]_T/\{1 + X(Fe^{2+})\}$$
$$[H^+] = [H^+]_T/\{1 + X(H^+)\}$$
$$[SO_4^=] = [SO_4^=]_T/\{1 + X(SO_4^=)\}$$

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:

$$[Fe^{3+}]_T = [Fe^{3+}]\{1 + X(Fe^{3+})\}$$
$$[Fe^{2+}]_T = [Fe^{2+}]\{1 + X(Fe^{2+})\}$$
$$[H^+]_T = [H^+]\{1 + X(H^+)\}$$
$$[SO_4^{=}]_T = [SO_4^{=}]\{1 + X(SO_4^{=})\}$$

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 $FeHSO_4SO_4$

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 |
| $Fe2^{+}$ | 0,3556 | 0,1956 | 0,1618 | 0,1539 |
| $SO_4^{=}$ | 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 |
| $FeHSO_4SO_4$ | 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:

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

Therefore $K^o = 223$

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

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

Therefore $K^o = 42 \pm 7$

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

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

Therefore $K^o = 33 \pm 8$

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:

$$Fe^{3+} + HSO_4^- \rightleftarrows FeHSO_4^{2+}$$

The equilibrium for bisulphate formation:

$$H^+ + SO_4^= \rightleftarrows HSO_4^-$$

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:

$$Fe^{3+} + H^+ + SO_4^= \rightleftarrows FeHSO_4^{2+}$$

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) $FeHSO_4SO_4$

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

$$Fe^{3+} + HSO_4^- + SO_4^= \rightleftarrows FeHSO_4SO_4$$

results in zero-ionic strength values of:

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

Therefore $K^o = 82200 \pm 10800$

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

$$Fe^{3+} + H+ + 2SO_4^= \rightleftarrows FeHSO_4SO_4$$

beomes: $K^o = (8,1 \pm 1,2) \cdot 10^6$

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 $FeHSO_4SO_4$, 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 $SO_4^=$ 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:

$$Fe^{2+} + HSO_4^- \rightleftharpoons FeHSO_4^+$$

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

Therefore $K^o \doteqdot 4$

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

$$Fe^{2+} + H^+ + SO_4^= \rightleftharpoons FeHSO_4^+$$

as: $K^o \doteqdot 400$

APPENDIX VI

Values of A, B and $\mathring{a}$ 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 $\mathring{a}$, in angstroms:

| Species | $\mathring{a}$ |
|---|---|
| $Fe^{3+}$ | 9 |
| $H^{+}$ | 9 |
| $SO_4^{=}$ | 4 |
| $Fe^{2+}$ | 6 |
| $OH^{-}$ | 3 |
| $FeHSO_4SO_4$ | - |
| $FeHSO_4^{2+}$ | 8 |
| $Fe(SO_4)_2^{-}$ | 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 | $\mathring{\lambda}$, mho - $cm^2$/equivalent |
|---|---|
| $Fe^{3+}$ | 70 |
| $H^+$ | 350 |
| $SO_4^=$ | 80 |
| $Fe^{2+}$ | 53,6 |
| $OH^-$ | 197 |
| $FeHSO_4 \cdot SO_4$ | - |
| $FeHSO_4^{2+}$ | 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

```
C*************************************************************
C                                                             *
C     COMPUTER PROGRAM OF THE MATHEMATICAL MODEL USED TO EXPLAIN    *
C     THE EXPERIMENTAL RESULTS OF LEACHING THE LOW GRADE MATTE      *
C     IN CONCENTRATED FERRIC-FERROUS SULPHATE SOLUTION.             *
C                                                             *
C*************************************************************
C
C
C
C
      PARAMETER NXM=6, NVM=4, NDM=15, NSM=13, NTM=3
      INTEGER NXP(NXM),TITLE(30),NTT(NVM)
      REAL T(NXM,NDM),P(NXM,NDM),X(NXM,NVM,NDM),XI(NXM,NVM,NDM),MWT(NVM),A(NSM),L(NSM),
     1     C(NVM,NSM),R(NVM,NSM,NTM),TT(NVM,NTM),
     2     C1(NTM,NVM),CS1(NTM,NVM,2),SC1(NTM,NVM,2),CL(NTM),FRN(NVM,NTM),
     3     M0(NVM),M(NVM),MAS0(NVM,NSM,NTM),MAS1(NVM,NSM,NTM),
     4     MASS(NVM,NSM,NTM),KRXN(NVM,NSM,NTM),NK(2),EOLO(NVM),
     5     D1E(NTM),D2E(NTM),XMX(NVM),
     6     ESU(NVM,3,NTM),CONST(NTM,NVM),
     7     SH(NDM),DENS(NDM),B(NSM,NTM),M1(NVM,NTM),M10(NVM,NTM),
     8     CONC0(NXM,4),CONCT(4),CONC(12),ACTV(12),KEQ(17),
     9     KOC,ER,RATE(NSM),AREA(NSM),LO,MECH(NVM,NTM),FE(NXM,NDM)
      OPEN 2,"LDATA"
      READ  (2,73) TITLE
      READ FREE (2) NV,NS,(NTT(I),I=1,NV),NX,(NXP(N),N=1,NX)
      EPS=0.001
      DO 1 N=1,NX
      NO=NXP(N)
      READ FREE (2) (T(N,J),P(N,J),(X(N,I,J),I=1,NV),FE(N,J),J=1,NO)
    1 CONTINUE
      READ FREE (2) FEED,VOL,(MWT(I),I=1,NV)
      READ FREE (2) (L(J),SH(J),DENS(J),A(J),(B(J,K),K=1,NTM),J=1,NS)
      DO 2 I=1,NV
      NT=NTT(I)
      READ FREE (2) (C(I,J),(R(I,J,K),K=1,NT),J=1,NS)
    2 CONTINUE
      S1=0.
      S2=0.
      DO 3 J=1,NS
      IF (NV.LT.NVM) GO TO 3
      S1=S1+A(J)/DENS(J)
      S2=S2+A(J)*M(NV,J,2)*C(NV,J)
    3 L(J)=L(J)/10000
      IF (NV.EQ.NVM) RHO=S2/S1/MWT(NV)
      JM=1
      DO 4 I=1,NV
      NT=NTT(I)
      READ FREE (2) (MECH(I,K),TT(I,K),C1(K,I),K=1,NT)
      IF (MECH(I,K).GT.0.0) JM=JM+2
    4 CONTINUE
      IF (JM.GT.0) READ FREE (2) FRT,B1,B2
      IF (NV.LT.NVM) GO TO 49
      READ FREE (2) (CL(K),(FRN(I,K),I=1,NV),K=1,NTM)
      DO 48 I=1,NV
      NT=NTT(I)
      DO 48 K=1,NT
      IF (CL(K).LT.0.) GO TO 48
      TT(I,K)=CL(K)*FRN(I,K)
   48 CONTINUE
   49 DO 5 I=1,NV
      NT=NTT(I)
```

```
      DO 5 K=1,NT
      CS1(K,I,2)=TT(I,K)/2
      IF (TT(I,K).GE.0.) GO TO 5
      TT(I,K)=-TT(I,K)
      CS1(K,I,2)=0.
    5 CONTINUE
      READ FREE (2) DT0,DTMAX,EPS
      NPOTL=0
      IF (NV.EQ.NVM) ACCEPT "NPOTL ",NPOTL
      IF (NPOTL.EQ.0) GO TO 6
      OPEN 4,"POUT"
      TYPE "FILE POUT CREATED"
      READ FREE (2) ((CONC0(N,I),I=1,4),N=1,NX)
      READ FREE (2) TEMP,DFE3,DFE2,SRF,DL0
      CALL KEQLM (TEMP,KEQ)
    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=NIT(I)
      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,I=1,NV)
      IF (MODE.NE.0) WRITE (10,70) (MMM,I=1,NV)
      IF (NPRINT.EQ.0) GO TO 8
      OPEN 12,"@LPT",ATT="P"
      WRITE (12,75) TITLE
      WRITE (12,76)
      WRITE (12,77) (MMM,I,I=1,NV)
      WRITE (12,78) (MMM,I=1,NV)
      WRITE (12,73) MMM
      WRITE (10,73) MMM
    8 KOUNT=0
      DO 10 I=1,NV
      NT=NIT(I)
      EOLD(I)=100.
      XMX(I)=0.
      M0(I)=0.
      DO 9 J=1,NS
      M0(I)=M0(I)+A(J)*C(I,J)
      DO 9 K=1,NT
      MAS0(I,J,K)=FEED/VOL*A(J)*C(I,J)*R(I,J,K)/MWT(I)
      M10(I,K)=M10(I,K)+MAS0(I,J,K)
    9 XMX(I)=XMX(I)+MAS0(I,J,K)
      M0(I)=M0(I)+FEED/VOL/MWT(I)
      XMX(I)=XMX(I)/M0(I)
      DO 10 K=1,NT
   10 M1(I,K)=M1(I,K)/M0(I)
      IJK=1
      NK(1)=0
      NK(2)=0
      KK=1
   11 DO 12 I=1,NV
      ES0(I,1,1)=0.
      DO 12 K=1,NT
```

```
      ESO(I,K,2)=0.
   12 ESN(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)=CONC0(N,I)
   13 CONC(I) =CONC0(N,I)
      DO 14 I=5,12
   14 CONC(I)=0.
   15 ND=NX(N)
      DPOTL=0.
      II=0
      DT=DT0
      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)
     1           /3/MASO(I,J,K)**(2./3.)
   16 MASS(I,J,K)=MASO(I,J,K)
      TIME=0.
      DL=DL0/10000.
      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)
      PTLE=PTL
      IF (NPOTL.NE.0) CALL REDOX (CONC,ACTV,TEMP,ELJ,PTL)
      IF (NPOTL.GT.0) POTL=PTL
      IF (NPOTL.EQ.0) PTL=POTL
      NV1=2
      IF (MODE.EQ.2) WRITE (3,61) NV1
      NTME=2
   18 IF ((TIME+DT).GT.T(N,NTME)) II=-2
      IF (II.LT.0.) DT=T(N,NTME)-TIME
      CALL IRON2 (TIME,FE2,DFE2,I,FE,N,ND)
      IF (NPOTL.GE.0) GO TO 25
      RATO=0.
      SPTL=100.
      KOUNT2=0
      FE3=CONCT(1)
      FE2=CONCT(4)
      SO4=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,I)*PTLE)
      IF (MECH(I,K).GT.0) CHI=EXP((2-B1-B2)*FRT*PTLE)/
     1                        (FE2*EXP(-B1*FRT*PTLE)+C1(K,I)*EXP((1-B2)*FRT*PTLE))
      DO 20 J=1,NS
   20 RATO=RATO+A(J)*B(J,K)*TT(I,K)*CHI
      RATMAX=DFE3*FE3/3/SRF/DL*0.99
      IF (RATO.GT.RATMAX) RATO=RATMAX
      CONCT(1)=FE3-3*DL/DFE3*RATO*SRF
      CONCT(4)=FE2+2*DL/DFE2*RATO*SRF
      CONCT(3)=1.5*CONCT(1)+0.5*CONCT(2)+CONCT(4)
      CALL CONCTN (TEMP,CONCT,ACTV,KEQ,CONC,EPS)
      CALL REDOX (CONC,ACTV,TEMP,ELJ,PTL1)
      IF (ABS(PTL1-PTLE).LT.0.01) GO TO 21
      DPTL=PTLE-PTL1
      IF ((DPTL*SPTL).LT.0.) SPTL=-SPTL/2
```

```
      IF ((DPTL/SPTL).GT.1.) DPTL= SPTL
      PTLE=PTLE-DPTL
      SPTL=DPTL
      KOUNT2=KOUNT2+1
      IF (KOUNT2.LT.100) GO TO 19
   21 RATO=RATO*3216000.
      DO 24 J=1,NS
      RATE(J)=0.
      AREA(J)=0.
      DO 23 K=1,NIH
      RTE=0.
      ARA=0.
      DO 22 I=1,NV
      IF (K.GT.NTT(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*PTLE)/
     1                        (FE2*EXP(-B1*FRT*PTLE)+C1(K,I)*EXP((1-B2)*FRT*PTLE))
      RTE=RTE+3*KRXN(I,J,K)*CHI*MASS(I,J,K)**(2./3.)
      ARA=ARA+I1(I,K)*CHI
   22 CONTINUE
      ARA=RTE/ARA
      RATE(J)=RATE(J)+RATE
   23 AREA(J)=AREA(J)+ARA
   24 RATE(J)=RATE(J)/AREA(J)*3216000.
      DL1=L(1)/2*(1.-(MASS(NV,1,2)/MASO(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 CONCIN (TEMP,CONCT,ACTV,KEQ,CONC,EPS)
      CALL REDOX (CONC,ACTV,TEMP,ELJ,PTL1)
      DL2=L(NS)/2*(1.-(MASS(NV,NS,2)/MASO(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 CONCIN (TEMP,CONCT,ACTV,KEQ,CONC,EPS)
      CALL REDOX (CONC,ACTV,TEMP,ELJ,PTL2)
      CONCT(1)=FE3
      CONCT(4)=FE2
      CONCT(3)=SO4
      LO=DL*10000.
      IF (ABS(NPOTL).LE.1) WRITE (4,62) TIME,POTL,PTL,PTLE,PTL1,PTL2,LO
      IF (ABS(NPOTL).GT.1) WRITE (4,62) TIME,POTL,PTL,PTLE,PTL1,PTL2,
     1                  LO,EXCH,RATO,(RATE(J),J=1,NS)
      DL=DL+DT*SRF*TT(NV,2)/RHO*EXP(C1(2,NV)*PTLE)
   25 CONTINUE
      DO 26 I=1,NV
      NI=NTT(I)
      DO 26 K=1,NI
      IF (MECH(I,K).GT.0) GO TO 26
      CHI=EXP(C1(K,I)*POTL)
      DCHI=CHI*C1(K,I)*DPOTL
      GO TO 27
   26 CHI=EXP((2-B1-B2)*FRT*POTL)/(FE2*EXP(-B1*FRT*POTL)+C1(K,I)*EXP((1-B2)*FRT*POTL))
      DCHI=CHI*((2-B1-B2)*FRT*DPOTL-((DFE2-B1*FRT*DPOTL*FE2)*EXP(-B1*FRT*POTL)
     1         +(1-B2)*FRT*DPOTL*C1(K,I)*EXP((1-B2)*FRT*POTL))
     2         /(FE2*EXP(-B1*FRT*POTL)+C1(K,I)*EXP((1-B2)*FRT*POTL)))
   27 DO 28 J=1,NS
      IF (II.EQ.0) MAS1(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))
      AKRX=DT*KRXN(I,J,K)
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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 (II.EQ.0.AND.NTEST.EQ.0) DT=DT*2
      IF (DT.GT.DTMAX) DT=DTMAX
      IF (II.GE.0) DTIME=DT
      IF (II.GE.0.AND.TIME.LT.T(N,NTME)) GO TO 18
      DO 38 I=1,NV
      IF (IJK.EQ.1) XI(N,I,NTME)=XMX(I)-M(I)/MO(I)
      EI=XMX(I)-M(I)/MO(I)-X(N,I,NTME)
      ESQ(I,1,1)=ESQ(I,1,1)+EI**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=ES/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*EI*EKJ
      ESQ(I,K,3)=ESQ(I,K,3)+2*EKJ**2
   38 CONTINUE
      IF (MODE.EQ.0) GO TO 39
      FE3=CONC1(1)*55.847
      FE2=CONC1(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
      II=0
      IF (NTME.LE.NO) GO TO 18
   40 CONTINUE
      IF (MODE.NE.0) GO TO 56
      IF (NV.LT.NVM) GO TO 47
      DO 41 K=1,NTM
      D1E(K)=0.
      D2E(K)=0.
      DO 41 I=1,NV
      D1E(K)=D1E(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,NTM
      SC1(K,1,1)=-D1E(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,NTM
      IF (ABS(SC1(K,1,2)).GE.EPS) GO TO 44
   43 CONTINUE
      GO TO 57
   44 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)
      GO TO 57
```

```
      MASS(I,J,K)=AMAS*AKRX*(CHI+DT*DCHI/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 (II.NE.0) GO TO 28
      MAS1(I,J,K)=AMAS*2*AKRX*(CHI+DT*DCHI)
      IF (MAS1(I,J,K).LT.0.) MAS1(I,J,K)=0.
      IF (MAS1(I,J,K).GT.0..AND.MECH(I,K).GE.0) MAS1(I,J,K)=MAS1(I,J,K)**3
      IF (MAS1(I,J,K).GT.0..AND.MECH(I,K).LT.0) MAS1(I,J,K)=MAS1(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,2)
      DO 29 I=1,NV
      NT=NTT(I)
      DO 29 K=1,NT
      DO 29 J=1,NS
      CONCT(1)=CONCT(1)-2*(MASS(I,J,K)-MASS(I,J,K))
   29 CONCT(4)=CONCT(4)+2*(MASS(I,J,K)-MASS(I,J,K))
      NT=NTT(NV)
      DO 30 K=1,NT
      DO 30 J=1,NS
   30 CONCT(4)=CONCT(4)+MASS(NV,J,K)-MASS(NV,J,K)
   31 II=II+1
      IF (II.LT.2) GO TO 33
      IF (DT.EQ.DTMAX) GO TO 33
      NTEST=0
      DO 32 I=1,NV
      NT=NTT(I)
      DO 32 J=1,NS
      DO 32 K=1,NT
      IF (MASS(I,J,K).EQ.0.) GO TO 32
      TEST=(MASS(I,J,K)-MAS1(I,J,K))/MASS(I,J,K)
      IF (ABS(TEST).GE.EPS) NTEST=NTEST+1
   32 CONTINUE
      II=0
   33 DO 34 I=1,NV
      NT=NTT(I)
      M(I)=0.
      DO 34 K=1,NT
      M1(I,K)=0.
      DO 34 J=1,NS
      M1(I,K)=M1(I,K)+MASS(I,J,K)
   34 M(I)=M(I)+MASS(I,J,K)
      TIME=TIME+DT
      IF (NPOTL.LE.0) CALL PE3FE2 (TIME,POTL,DPOTL,T,P,N,ND)
      IF (NPOTL.NE.0) CALL CONCTN (TEMP,CONCT,ACTV,KEQ,CONC,EPS)
      IF (NPOTL.NE.0) CALL REDOX (CONC,ACTV,TEMP,ELJ,PTL)
      IF (NPOTL.GT.0) POTL=PTL
      IF (NPOTL.EQ.0) PTL=POTL
      IF (MODE.LT.2) GO TO 37
      DO 35 I=1,NV
      NT=NTT(I)
      XI(N,I,NTIME)=XMX(I)-M(I)/MO(I)
      DO 35 K=1,NT
   35 M1(I,K)=M1(I,K)/M10(I,K)
      WRITE (3,63) TIME,POTL,(XI(N,I,NTMP),I=1,NV)
      IF (MODE.LT.3) GO TO 37
      DO 36 I=1,NV
      NT=NTT(I)
      WRITE (3,64) (M1(I,K),K=1,NT)
      DO 36 K=1,NT
      IF (MODE.LT.4) GO TO 36
```

```
      NTEST=0
      DO 54 I=1,NV
      DO 54 K=1,NT
      IF (CSI(K,I,2).EQ.0.) GO TO 54
      SCI(K,I,2)=-ESO(I,K,2)/ESO(I,K,3)
      SCI(K,I,1)=SCI(K,I,2)/TT(I,K)
      IF ((SCI(K,I,2)*CSI(K,I,2)).LT.0.) CSI(K,I,2)=-CSI(K,I,2)/2
      IF ((SCI(K,I,2)/CSI(K,I,2)).GT.1.) SCI(K,I,2)= CSI(K,I,2)
      IF (ABS(SCI(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) (ESO(I,1,1),I=1,NV)
      IF (NPRINT.NE.0) WRITE (12,80) (ESO(I,1,1),I=1,NV)
      IF (MODE.NE.0) GO TO 59
      DO 5  I=1,NV
      NT=N.   ")
      DO 56   1,NT
      IF (CSI(K,I,2).EQ.0.) GO TO 56
      IF ((TT(I,K)+SCI(K,I,2)).LE.0.) SCI(K,I,2)=-0.9*TT(I,K)
      TT(I,K)=TT(I,K)+SCI(K,I,2)
   56 CONTINUE
      DO 53 I=1,NV
      WRITE (10,66) KOUNT,ESO(I,1,1),(TT(I,K),K=1,NTM),(SCI(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) (MMM,I,I=1,NV)
      WRITE (10,70) (MMM,I=1,NV)
      DO 58 N=1,NX
      ND=NXP(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
      NT=NIT(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 (I4,4H 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 (I5,F10.5,1P3E10.2,2X,0P3F8.5)
   67 FORMAT (//,23HSUM OF SQUARED ERRORS =,1P4E12.2)
   68 FORMAT (23HMAX ITERATIONS EXCEEDED)
   69 FORMAT (///,34HPREDICTED VS. MEASURED EXTRACTIONS,/,34(1H*),//)
   70 FORMAT (/,4HTIME,3X,4HPOTL,4(A2,1X,4HMEAS,3X,4HCALC),/)
   71 FORMAT (F4.0,4F7.4)
   72 FORMAT (//,9HCOMPONENT,I2,1H,,8H MINERAL,I2,3H  ,5X,4HC1 =,
     1          1PE12.5,5X,4HC2 =,1PE12.5)
   73 FORMAT (30A2)
   74 FORMAT (11X,4(A2,1X,9HCOMPONENT,I2))
   75 FORMAT (1H1,30A2)
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 76  FORMAT (1H0,34HPREDICTED VS. MEASURED EXTRACTIONS,/,1X,34(1H*),/)
 77  FORMAT (1H0,11X,4(A2,1X,9HCOMPONENT,I2))
 78  FORMAT (1H0,4HTIME,3X,4HPOIL,4(A2,1X,4HMEAS,3X,4HCALC),/)
 79  FORMAT (1H ,F4.0,F7.0,8F7.4,2F6.1)
 80  FORMAT (1H0,23HSUM OF SQUARED ERRORS =,1P4E10.1)
 81  FORMAT (1H0,"RATE CONSTANT VALUES :",/,1X,22("*"),///,
     1          10X,"1'ST CONSTANT",5X,"2'ND CONSTANT",//,
     2          A1,"ALLOY     :",1PE10.3,10X,0PF7.5,/,
     3          A1,"IROILITE  :",1PE10.3,10X,0PF7.5,/,
     4          A1,"CU,FE-S   :",1PE10.3,10X,0PF7.5)
      END
```

```
      SUBROUTINE KEQLM (T,KK,N)
      REAL KK(17)
C
C     SET ALL EQUILIBRIUM CONSTANTS TO ZERO.
C
C     IF N IS SPECIFIED AS TWO OR GREATER, THE
C     EQUILIBRIUM CONSTANT VALUES ARE LEFT
C     AT ZERO.
C
      DO 1 I=1,17
    1 KK(I)=0.
      IF (N.GT.0) GO TO 2
C
C     SET THE EQUILIBRIUM CONSTANT VALUES TO THE
C     VALUES GIVEN IN THE LITERATURE FOR ZERO
C     IONIC STRENGTH.
C
C     IF N IS SPECIFIED AS ZERO, THIS OPTION IS
C     SELECTED.
C
      KK(2)=EXP(33.334-7629.9/T)
C     IF (T.LE.325.15) KK(4)=EXP(19.804-3140.0/T)
C     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
C
C     SET THE EQUILIBRIUM CONSTANTS TO THE VALUES
C     GIVEN IN THE LITERATURE FOR NON-ZERO IONIC
C     STRENGTHS.
C
C     IF N IS SPECIFIED AS ONE, THIS OPTION IS
C     SELECTED.
C
      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,DPOTL,X,Y,NN,ND)
      REAL X(NXM,NDM),Y(NXM,NDM)
      DO 1 I=2,ND
      N=I
      IF (X(NN,I).GT.XX) GO TO 2
    1 CONTINUE
    2 TAU=0.018
      PTF=Y(NN,ND)-(Y(NN,1)-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-B*X1
      POTL=PTF+EXP(A+B*ALOG(XX+TAU))
      DPOTL=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=I
      IF (X(NN,I).GT.XX) GO TO 2
    1 CONTINUE
    2 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))
    1 CONTINUE
      ELJ=0.08617*T*PL1/PL2*ALOG(PL3/PL4)
      E0=530+1.19*(T-298.15)
      POTL=E0-0.08617*T*ALOG(C(4)*A(4)/C(1)/A(1))
      POTL=POTL-ELJ
      RETURN
      END
```

```
      SUBROUTINE CONCTN (T,C,Y,KK,X,EPS)
C
C
C     COMPONENTS AND COMPLEXES ARE ASSIGNED THE FOLLOWING SUBSCRIPTS
C
C
C     (1) = FE(3+)
C     (2) = H(+)
C     (3) = SO4(2-)
C     (4) = FE(2+)
C     (5) = NOT USED
C     (6) = FE.H.SO4.SO4
C     (7) = FE.H.SO4(2+)
C     (8) = FE.SO4.SO4(-)
C     (9) = FE.SO4(+)
C    (10) = H.SO4(-)
C    (11) = FE.SO4
C    (12) = FE.H.SO4(+)
C
C
      REAL C(4),E(4),XO(4),XE(4),XF(4),DXO(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 A0/9,9,4,6,3,0,8,8,6,4,0,4/
      CALL DEBUG (1,AA,BB)
      KOUNT=0
      TAUMAX=0.
      DO 1 I=1,4
      XF(I)=C(I)
      DXO(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 (T,TAU,KK(5))
      TAU=SQRT(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)
      XO(1)=1.+K(1)*X(2)*X(3)**2+K(2)*X(2)*X(3)+K(3)*X(3)**2+K(4)*X(3)
      XO(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)
      XO(3)=1.+2*K(1)*X(1)*X(2)*X(3)+K(2)*X(1)*X(2)+2*K(3)*X(1)*X(3)
     1        +K(4)*X(1)+K(5)*X(2)+K(6)*X(4)+K(7)*X(2)*X(4)
      DXO(3)=2*(K(1)*X(1)*X(2)+K(3)*X(1))
      XO(4)=1.+K(6)*X(3)+K(7)*X(2)*X(3)
      NER=0
      DO 3 I=1,4
      E(I)=X(I)*XO(I)-C(I)
      IF (ABS(E(I)).LT.(EPS*C(I))) GO TO 3
      NER=NER+1
      XF(I)=-E(I)/(XO(I)+X(I)*DXO(I))
```

```
      SUBROUTINE CONCTN (T,C,Y,KK,X,EPS)
C
C
C     COMPONENTS AND COMPLEXES ARE ASSIGNED THE FOLLOWING SUBSCRIPTS
C
C     (1) = FE(3+)
C     (2) = H(+)
C     (3) = SO4(2-)
C     (4) = FE(2+)
C     (5) = NOT USED
C     (6) = FE.H.SO4.SO4
C     (7) = FE.H.SO4(2+)
C     (8) = FE.SO4.SO4(-)
C     (9) = FE.SO4(+)
C    (10) = H.SO4(-)
C    (11) = FE.SO4
C    (12) = FE.H.SO4(+)
C
C
      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 (T,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 (T,TAU,KK(5))
      TAU=SQRT(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(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)
     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)
      NER=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
      NER=NER+1
      XF(I)=-E(I)/(XD(I)+X(I)*DXD(I))
```

```
      IF ((XE(I)*XF(I)).LT.0.) XF(I)=-XF(I)/2
      IF ((XE(I)/XF(I)).GT.1.) XE(I)= XF(I)
      IF ((X(I)+XE(I)).LT.0.)  XE(I)=-X(I)
      IF ((X(I)+XE(I)).GT.C(I)) XE(I)*C(I)-X(I)
      X(I)=X(I)+XE(I)
    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(5)**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 (NEN.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(I),AA(I),BB(I),I=1,18)/
     1   0,.3466,.2294,  5,.3466,.2299, 10,.3492,.2305,
     2  15,.3514,.2311, 18,.3538,.2315, 20,.3549,.2318,
     3  25,.3562,.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
```

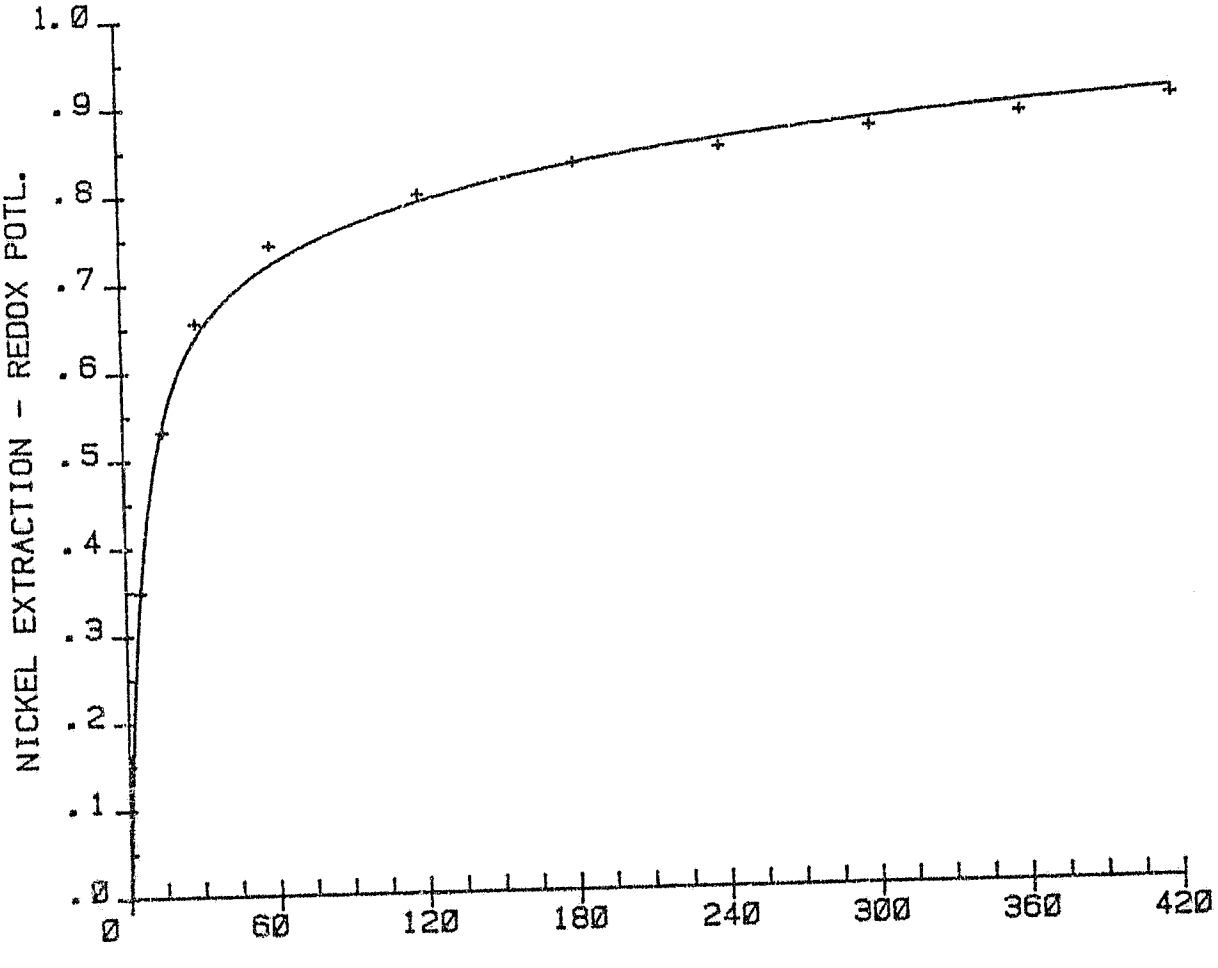
```
      SUBROUTINE KHSO4 (T,TAU,K)
      REAL K,K2,M,MH,M1,M2,I,II
      K2=EXP(14.03231-2825.2/T)
      BH10= 0.05584+ 46.040/T
      BH11=-0.65758+336.514/T
      BH20=-0.32806+ 98.607/T
      CH2U= 0.25533- 63.124/T
      AD=0.3770+4.684E-4*(T-273.15)+3.741E-6*(T-273.15)**2
      I=SQRT(TAU/2)
      F=-AD*(I/(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=CH2U/2.0**1.5
      M=TAU/2
      MH=M
      M1=M
      M2=0.
      DM=M/2
      N=1
    1 ACTV=EXP(4*F+2*(M1-MH)*BH1+2*(M2+MH)*BH20
     1           +2*MH*(2*M2+MH)*CH2+4*M1*MH*BH2)
      K=K2*ACTV
      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.0) GO TO 1
      E=M*2*M2-TAU/2
      IF (ABS(E).LT.0.001) GO TO 3
      DE=(3.*K*M)/SQRT((1.-K*M)**2+8*K*M)
      DM=-E/DE
      IF ((DM*DM).LT.0.) DM=-DM/2
      IF ((DM/DM).GT.1.) DM= DM
      M=M+DM
      J=1
      N=N+1
      IF (N.LE.1000) GO TO 2
      WRITE (10,1000)
    3 RETURN
 1000 FORMAT ("WARNING : SUBROUTINE KHSO4 HAS NOT CONVERGED")
      END
```

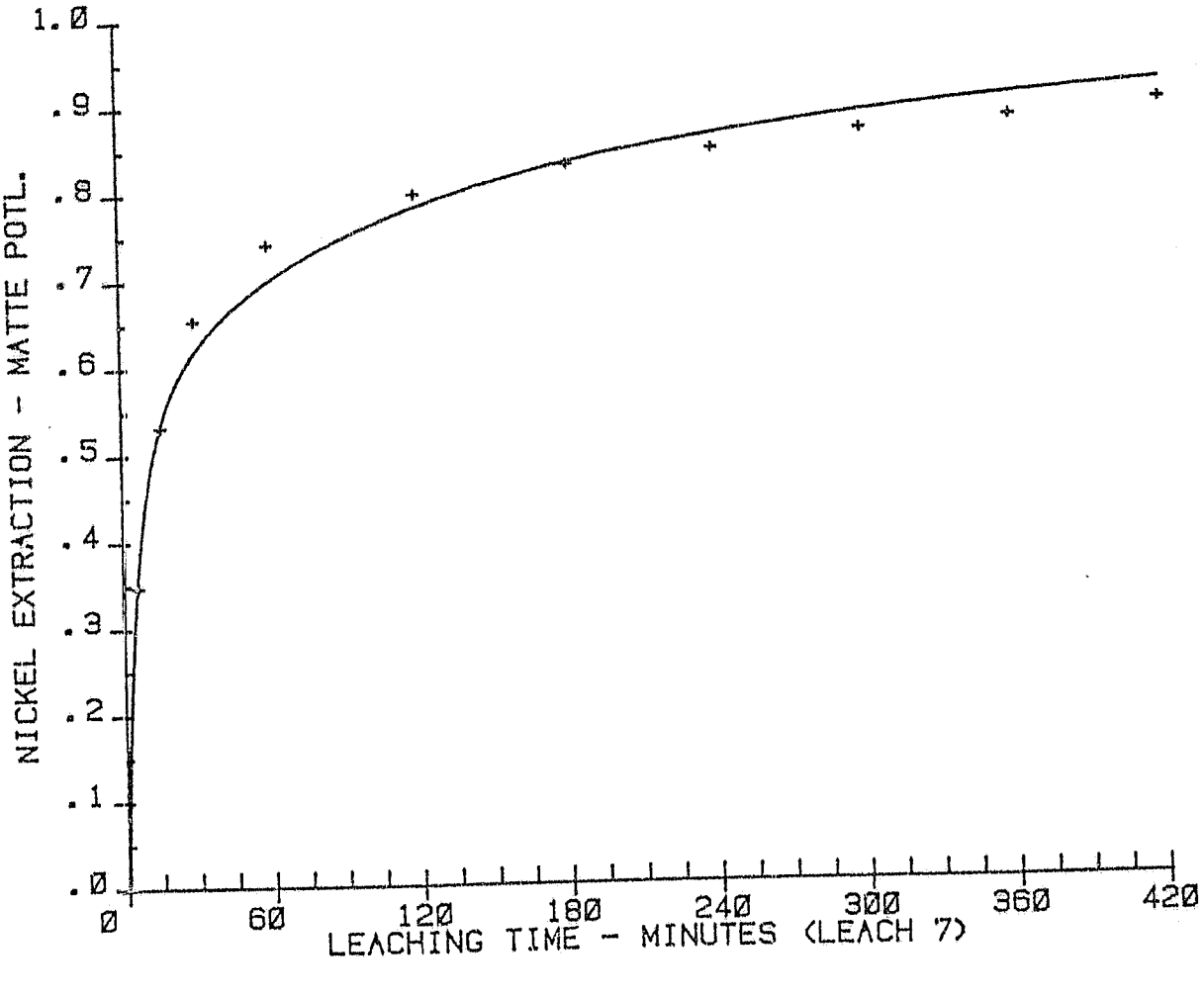
# APPENDIX IX

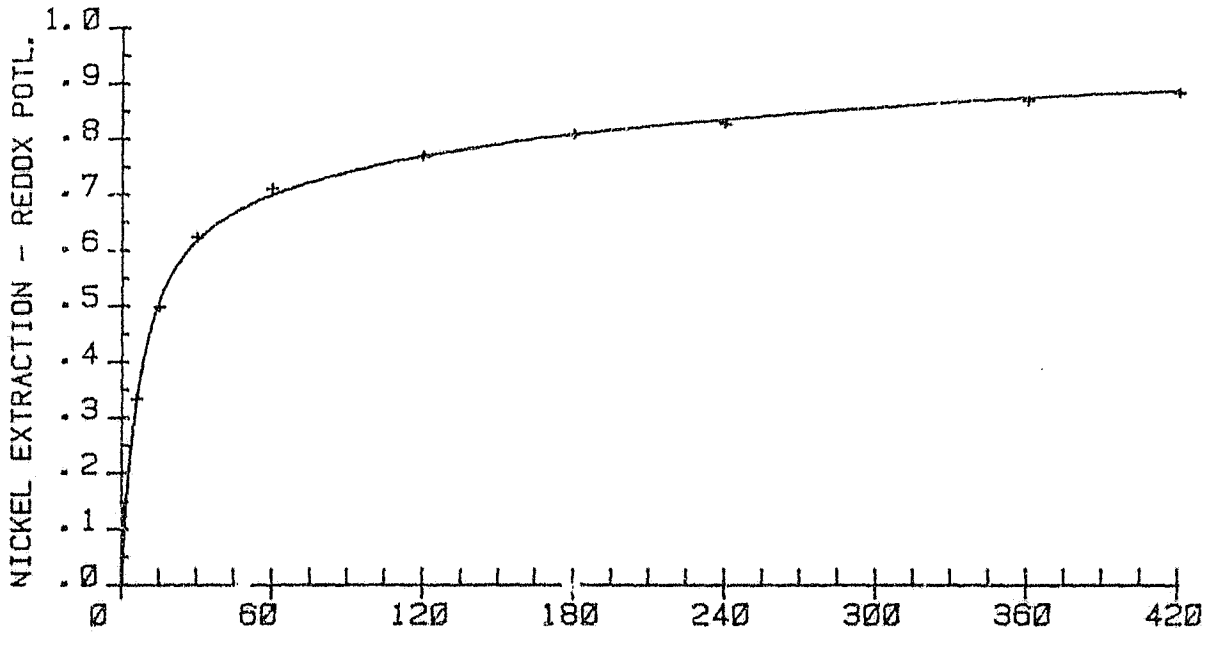
Results of fitting the leaching model -

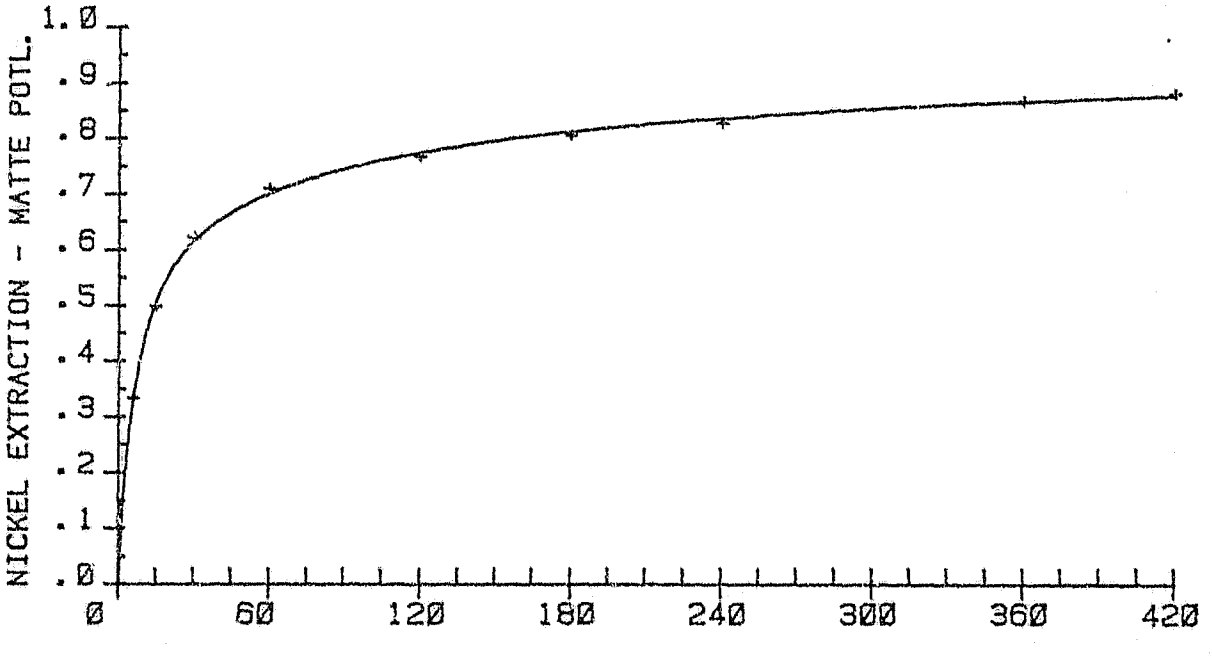
Graphs of predicted and measured extraction $\bar{vs}$ time curves for nickel, copper, cobalt and iron, for leaches 7 and 8, using redox, matte and residue potentials to approximate the particle surface potential during leaching.

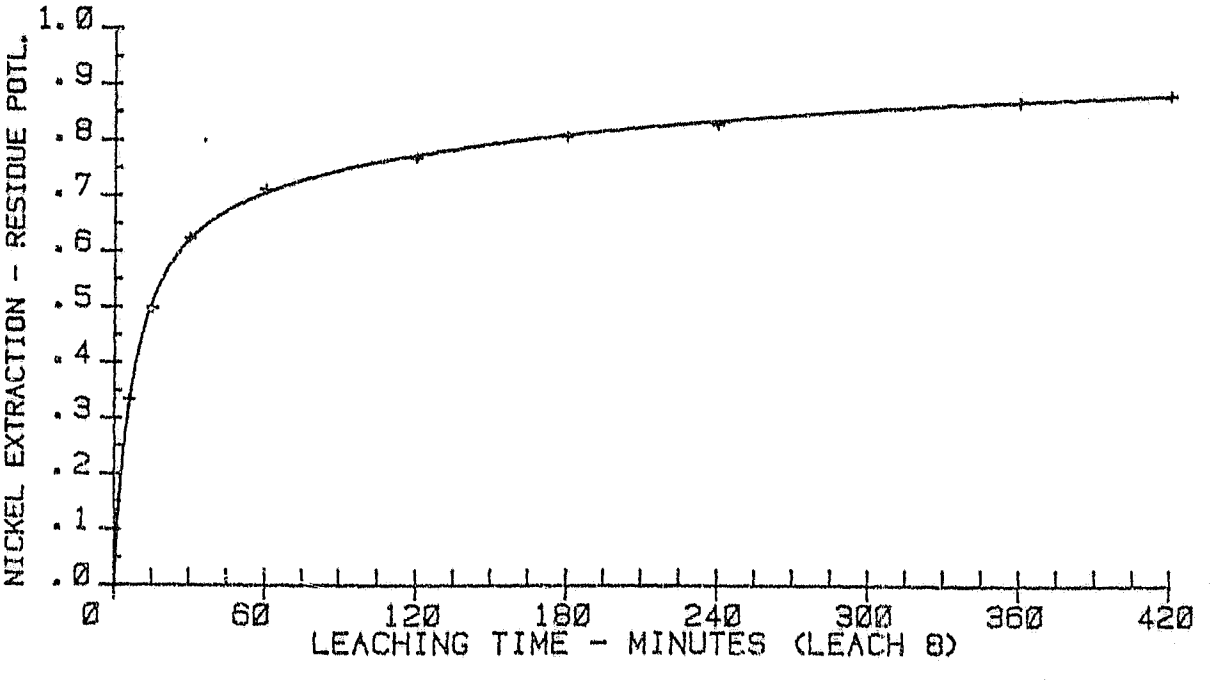
Leaching model computer printouts.

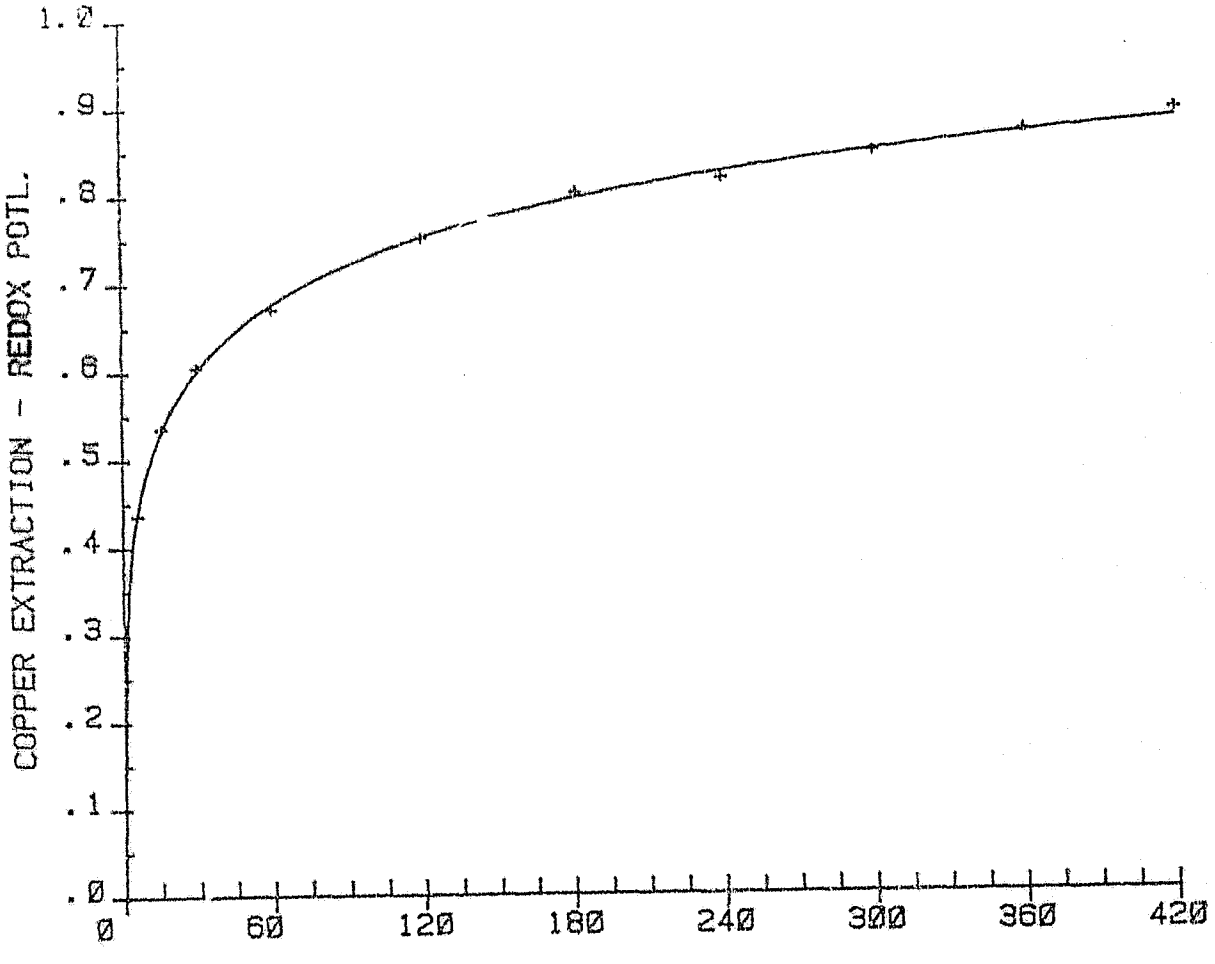

NICKEL EXTRACTION - REDOX POTL.
1.0
.9
.8
.7
.6
.5
.4
.3
.2
.1
.0
0
60
120
180
240
300
360
420

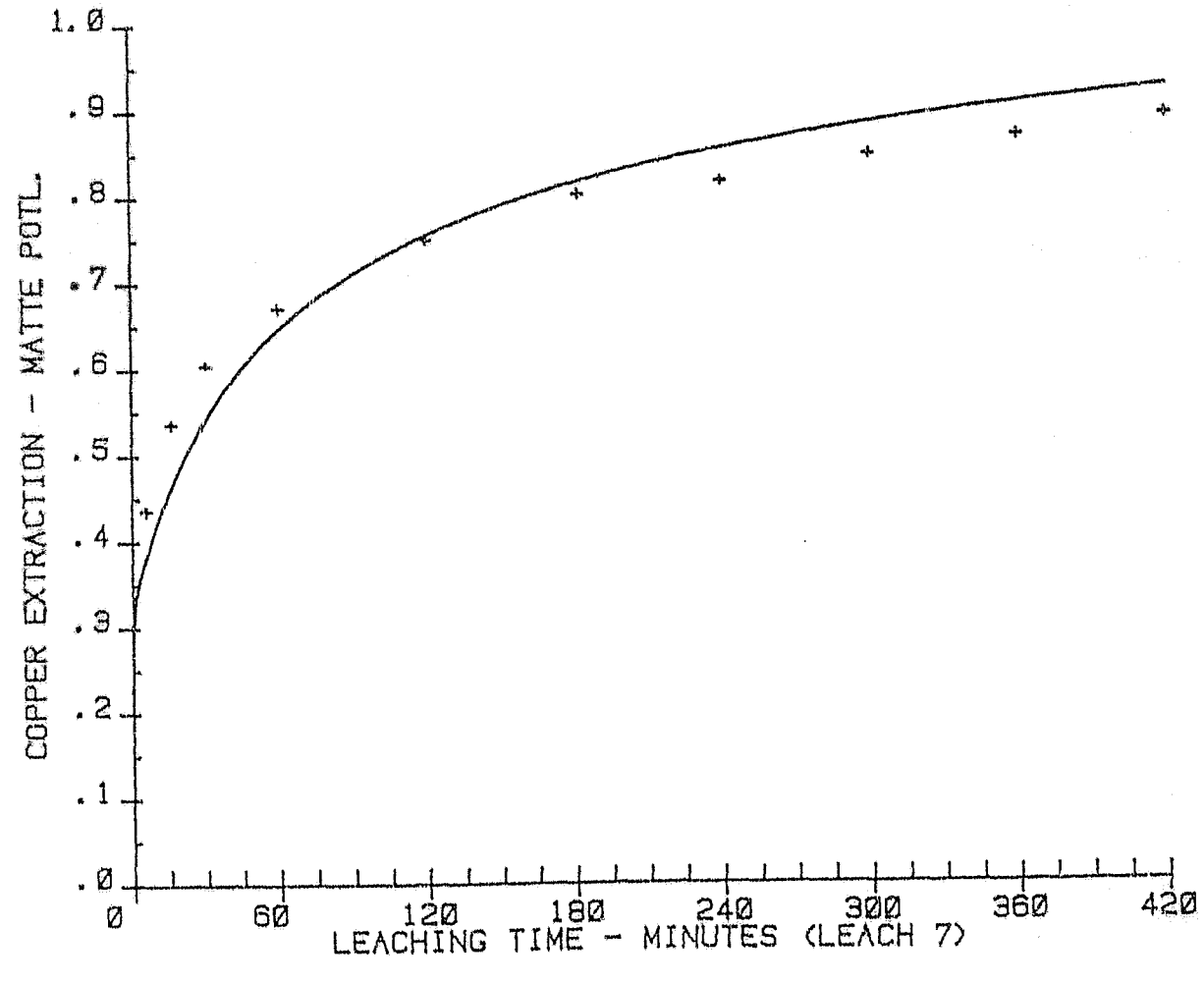

NICKEL EXTRACTION - MATTE POTL.
1.0
.9
.8
.7
.6
.5
.4
.3
.2
.1
.0
0
60
120
180
240
300
360
420
LEACHING TIME - MINUTES (LEACH 7)

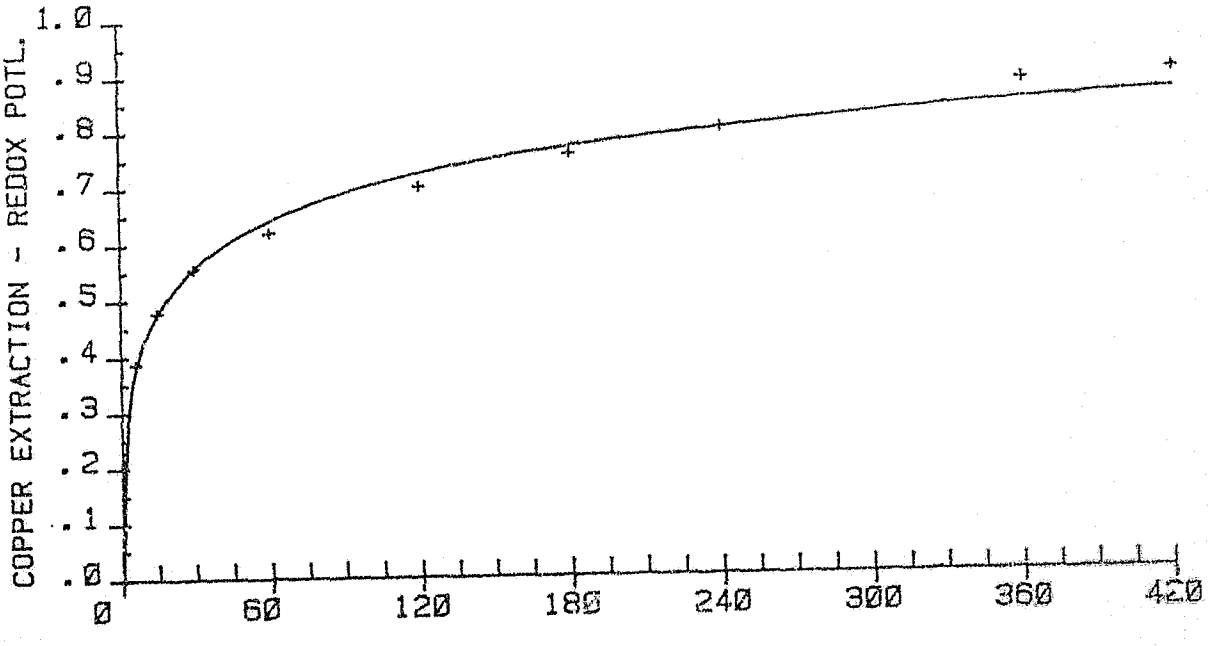

NICKEL EXTRACTION - REDOX POTL.
1.0
.9
.8
.7
.6
.5
.4
.3
.2
.1
.0
0
60
120
180
240
300
360
420

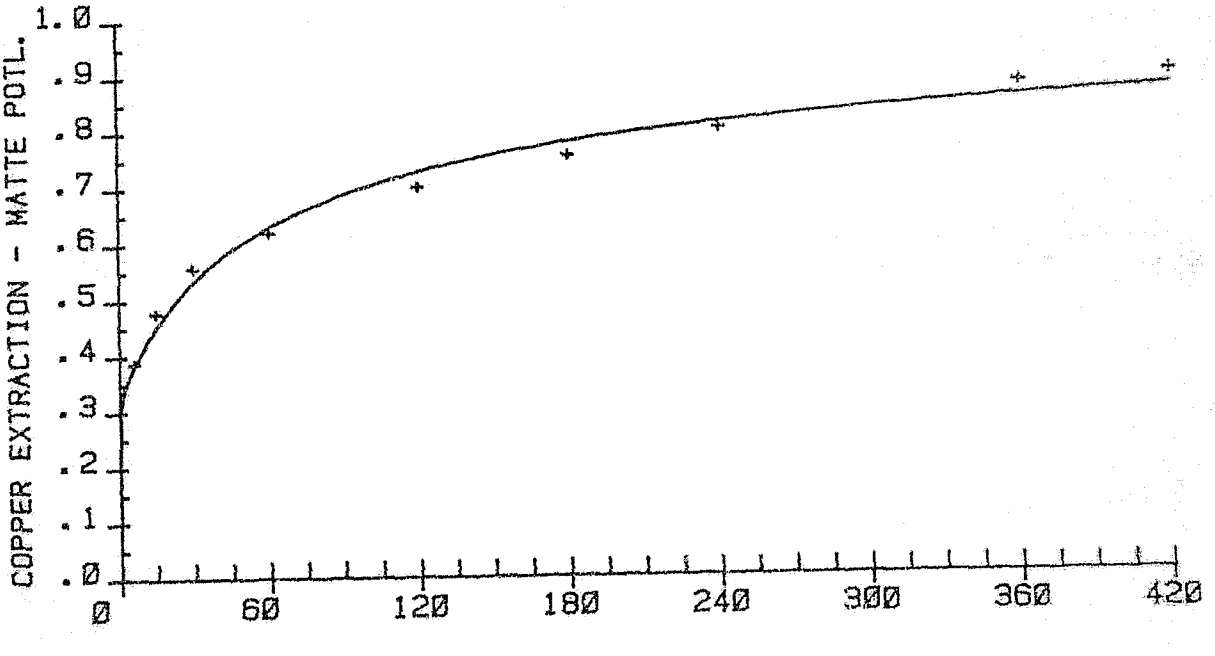

NICKEL EXTRACTION - MATTE POTL.
1.0
.9
.8
.7
.6
.5
.4
.3
.2
.1
.0
0
60
120
180
240
300
360
420

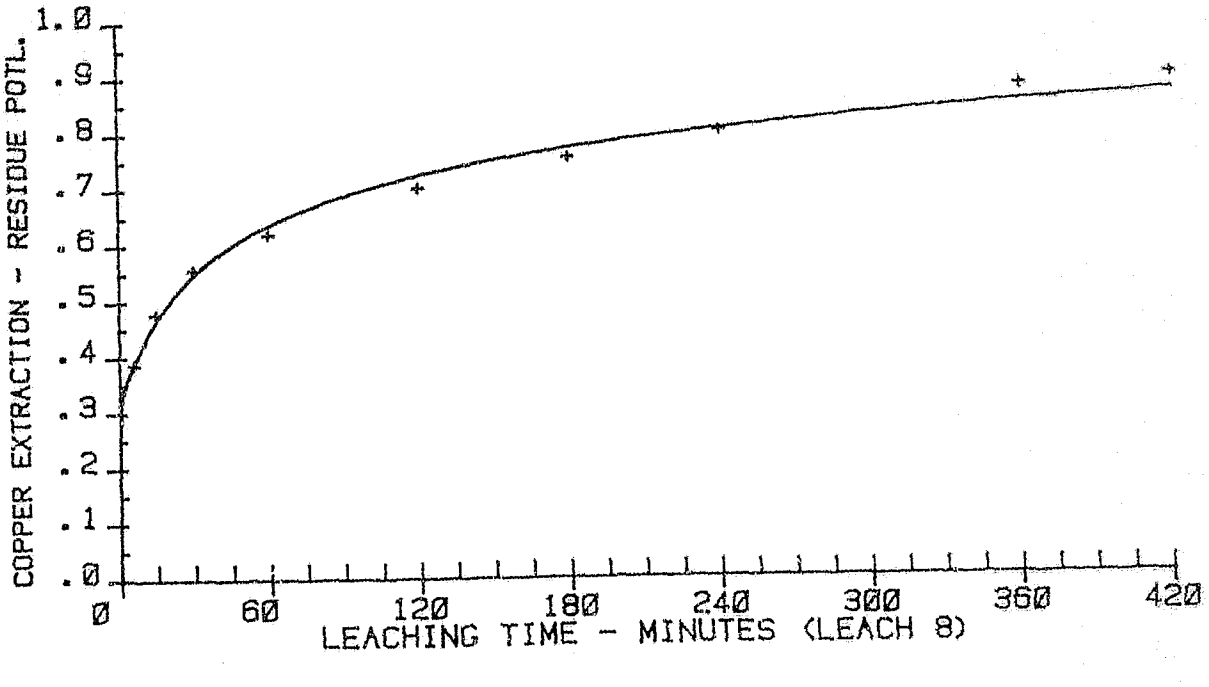

NICKEL EXTRACTION - RESIDUE POTL.
1.0
.9
.8
.7
.6
.5
.4
.3
.2
.1
.0
0
60
120
180
240
300
360
420
LEACHING TIME - MINUTES (LEACH 8)

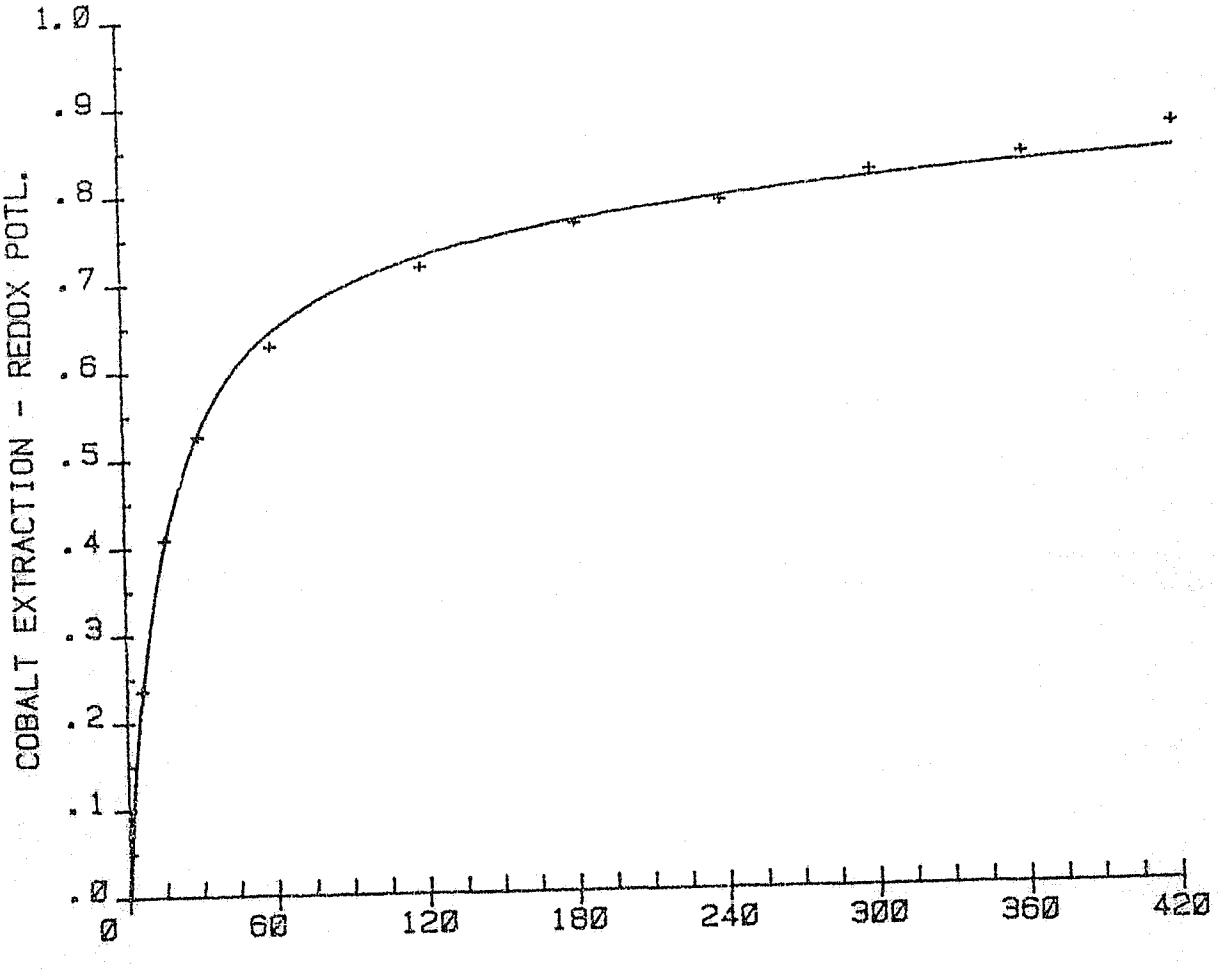

COPPER EXTRACTION - REDOX POTL.
1.0
.9
.8
.7
.6
.5
.4
.3
.2
.1
.0
0
60
120
180
240
300
360
420

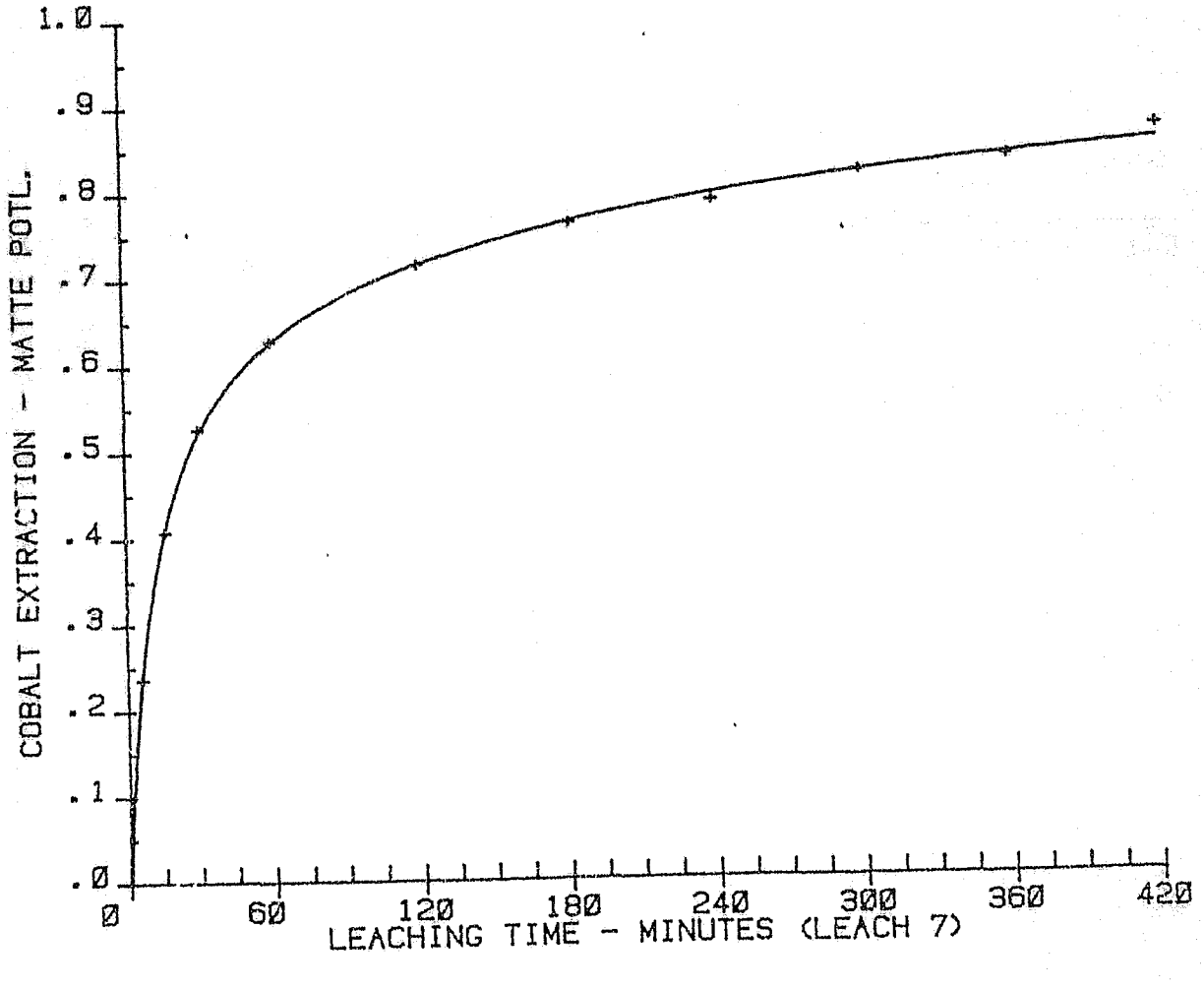

COPPER EXTRACTION - MATTE POTL.
1.0
.9
.8
.7
.6
.5
.4
.3
.2
.1
.0
0
60
120
180
240
300
360
420
LEACHING TIME - MINUTES (LEACH 7)

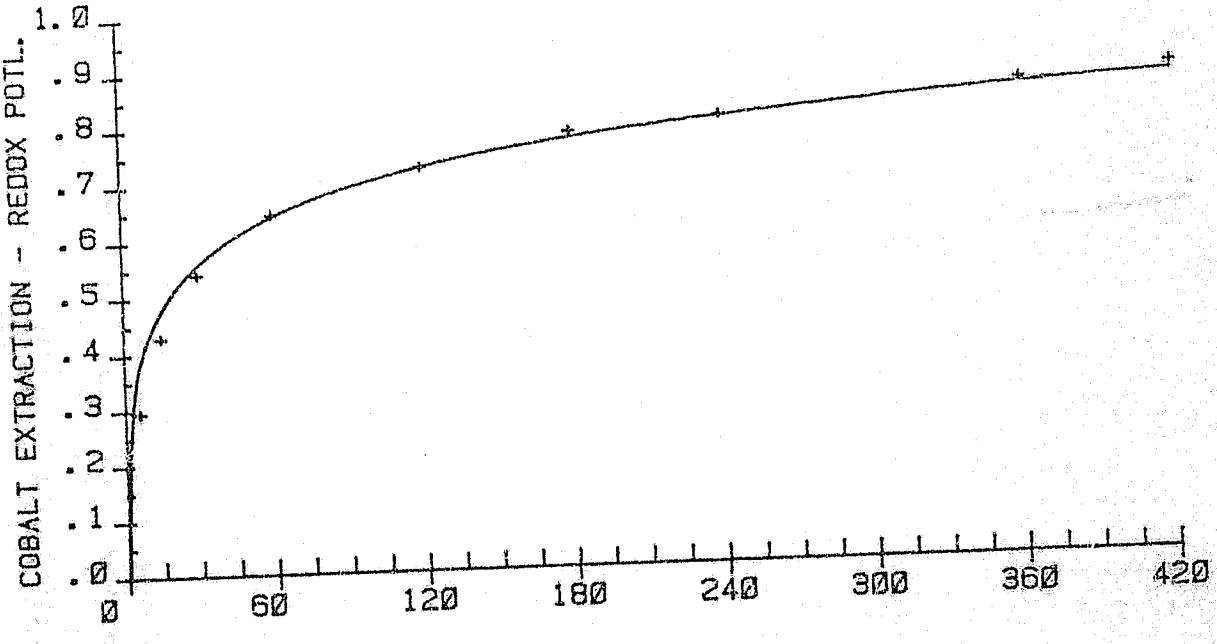

COPPER EXTRACTION - REDOX POTL.
1.0
.9
.8
.7
.6
.5
.4
.3
.2
.1
.0
0
60
120
180
240
300
360
420

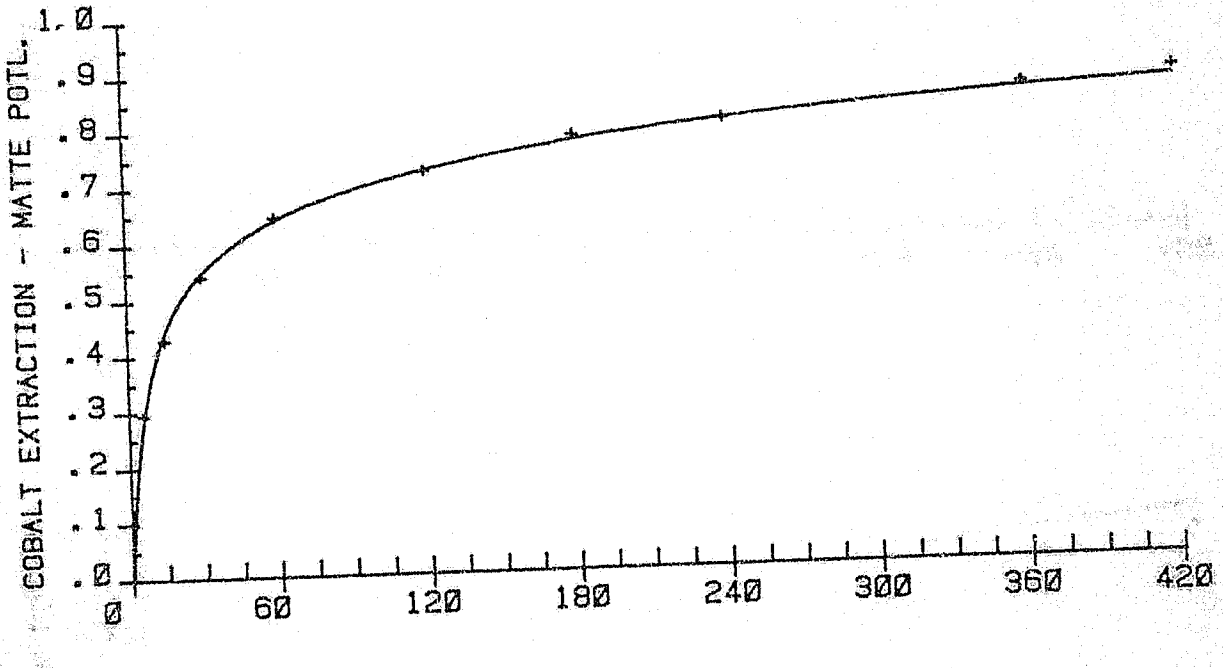

COPPER EXTRACTION - MATTE POTL.
1.0
.9
.8
.7
.6
.5
.4
.3
.2
.1
.0
0
60
120
180
240
300
360
420

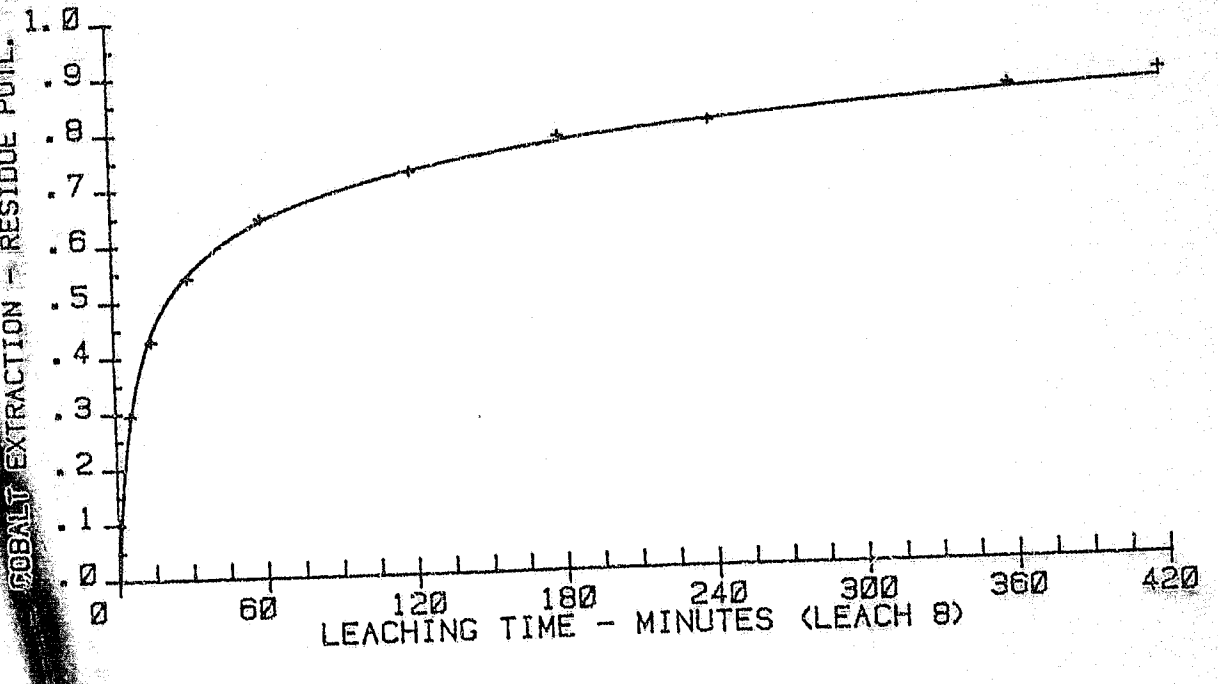

COPPER EXTRACTION - RESIDUE POTL.
1.0
.9
.8
.7
.6
.5
.4
.3
.2
.1
.0
0
60
120
180
240
300
360
420
LEACHING TIME - MINUTES (LEACH 8)

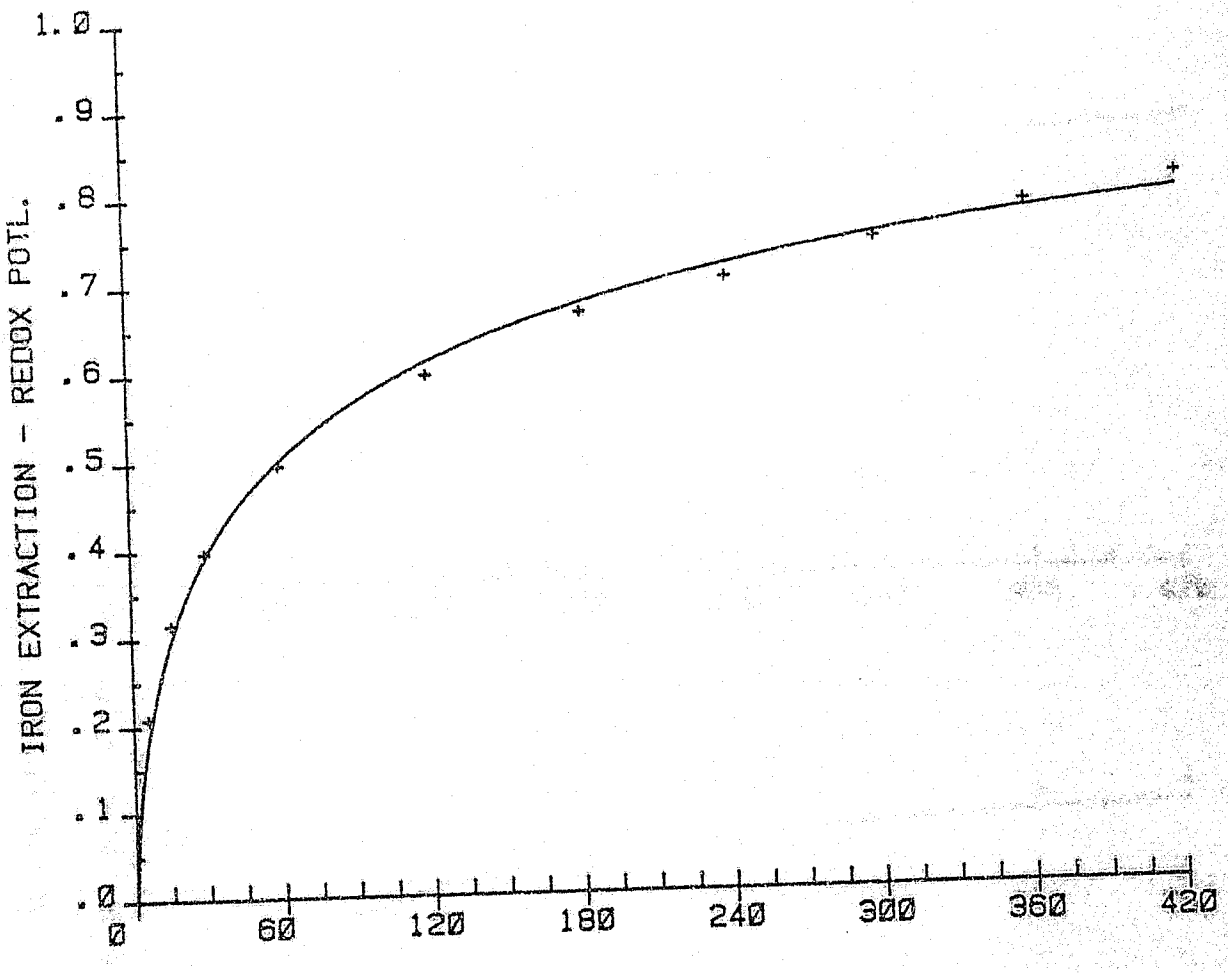

COBALT EXTRACTION - REDOX POTL.
1.0
.9
.8
.7
.6
.5
.4
.3
.2
.1
.0
0
60
120
180
240
300
360
420

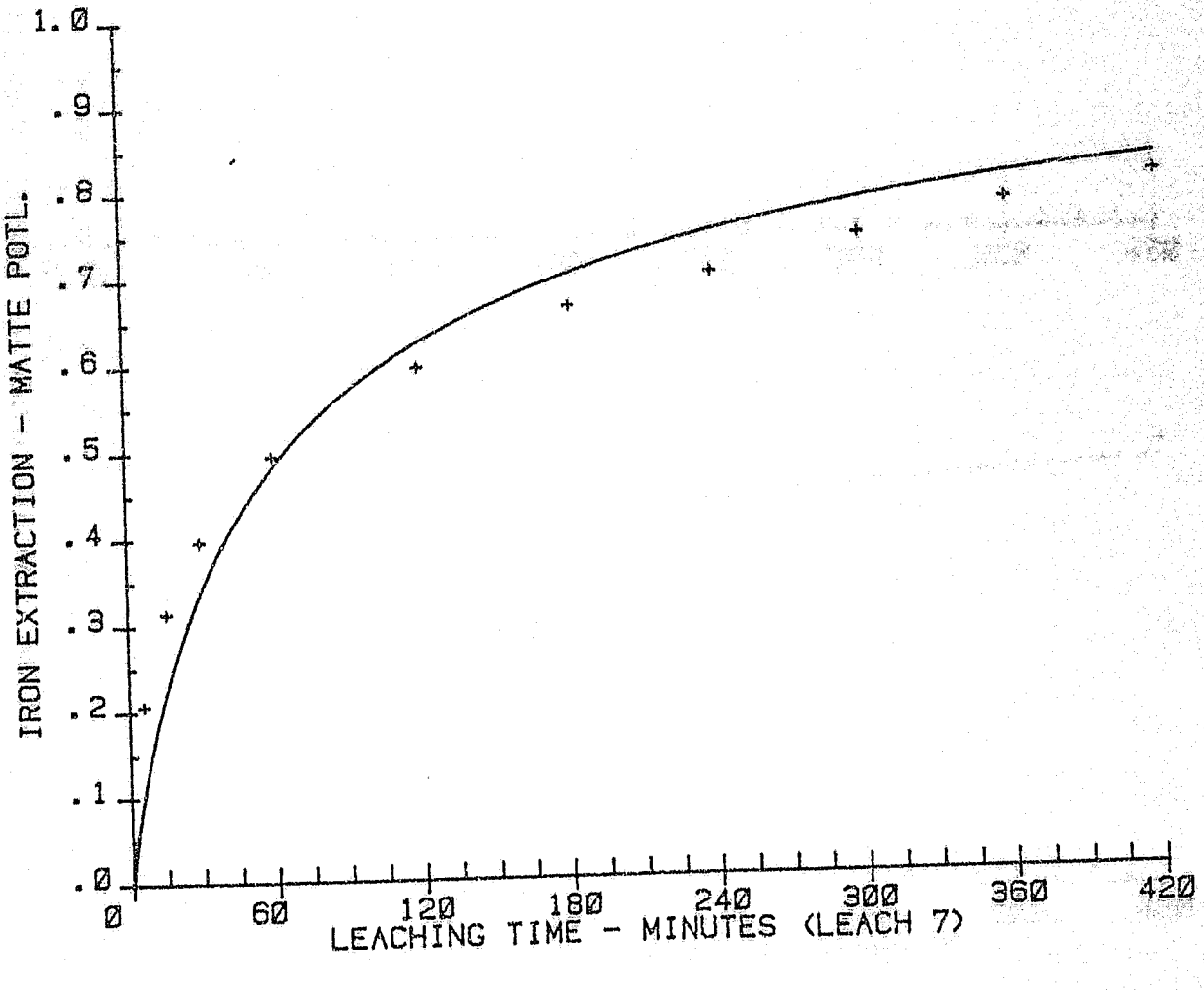

COBALT EXTRACTION - MATTE POTL.
1.0
.9
.8
.7
.6
.5
.4
.3
.2
.1
.0
0
60
120
180
240
300
360
420
LEACHING TIME - MINUTES (LEACH 7)

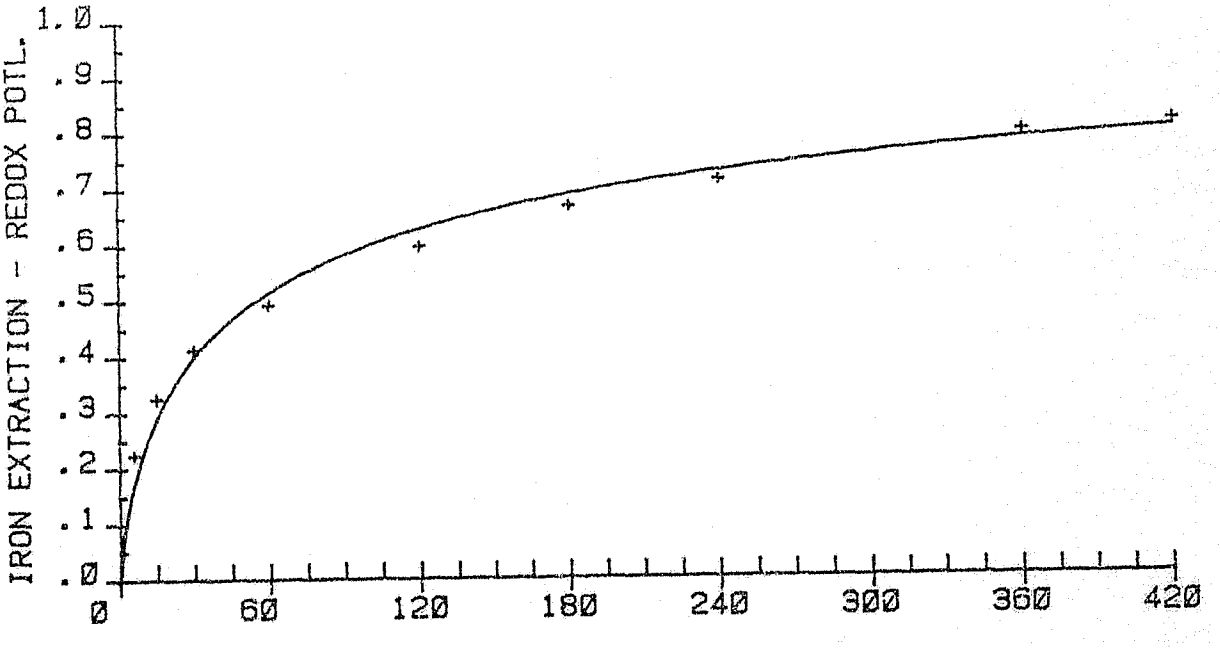

COBALT EXTRACTION - REDOX POTL.
1.0
.9
.8
.7
.6
.5
.4
.3
.2
.1
.0
0
60
120
180
240
300
360
420

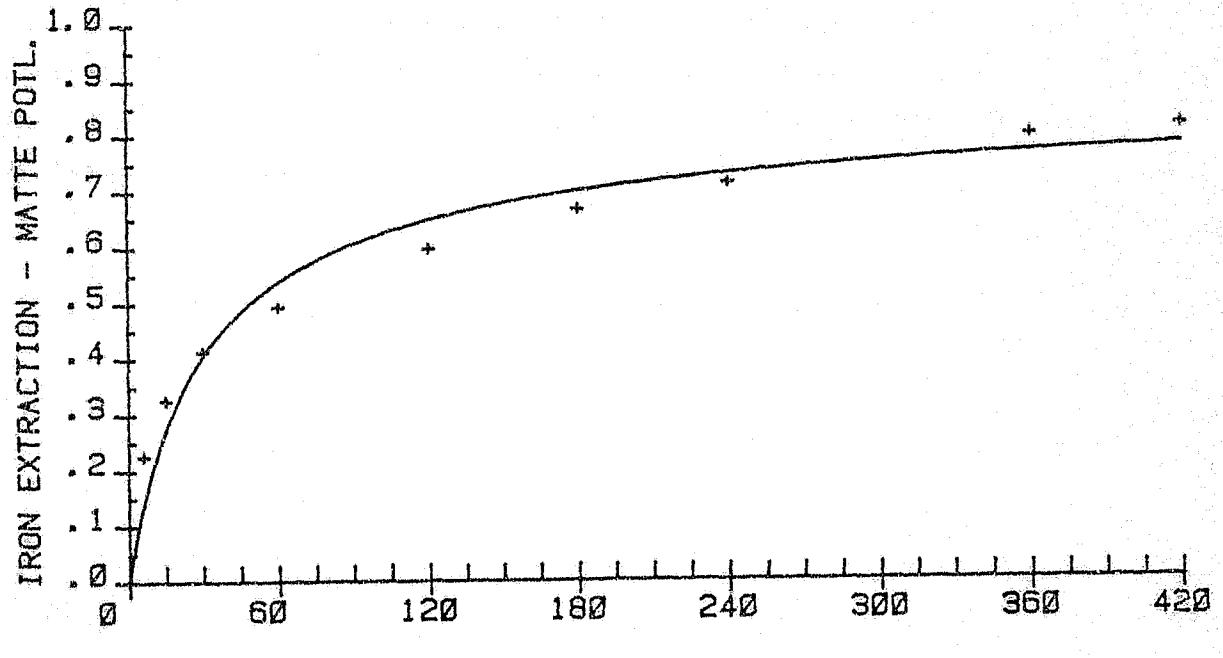

COBALT EXTRACTION - MATTE POTL.
1.0
.9
.8
.7
.6
.5
.4
.3
.2
.1
.0
0
60
120
180
240
300
360
420

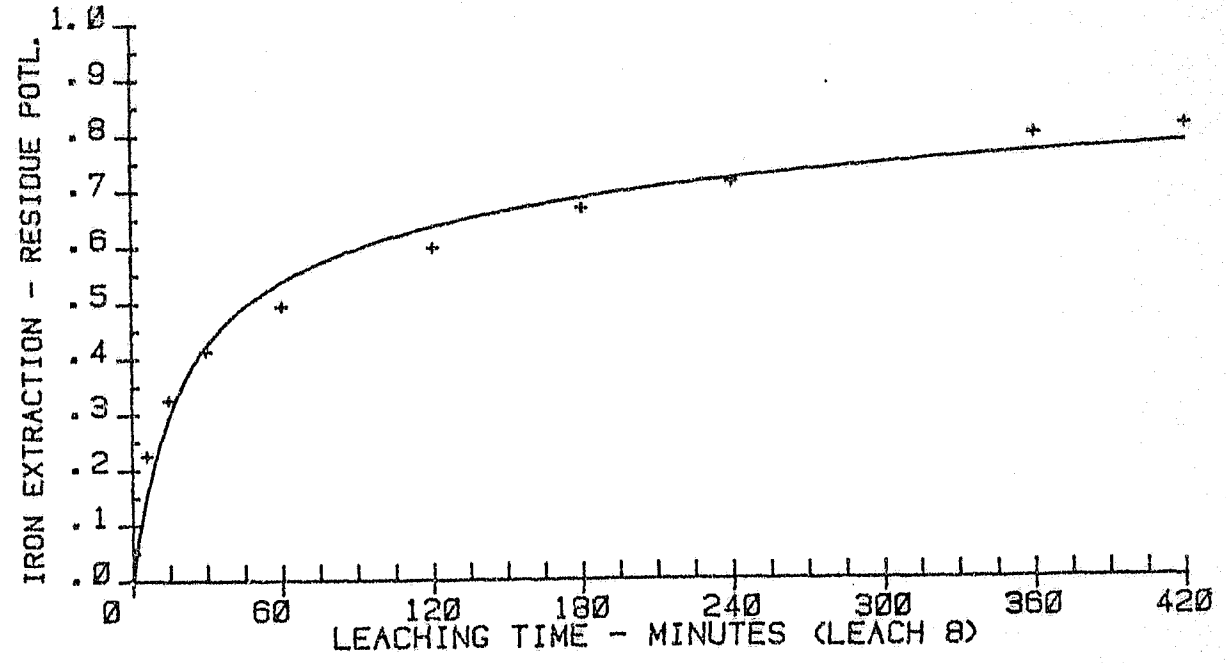

COBALT EXTRACTION - RESIDUE POTL.
1.0
.9
.8
.7
.6
.5
.4
.3
.2
.1
.0
0
60
120
180
240
300
360
420
LEACHING TIME - MINUTES (LEACH 8)


IRON EXTRACTION - REDOX POTL.
1.0
.9
.8
.7
.6
.5
.4
.3
.2
.1
.0
0
60
120
180
240
300
360
420


IRON EXTRACTION - MATTE POTL.
1.0
.9
.8
.7
.6
.5
.4
.3
.2
.1
.0
0
60
120
180
240
300
360
420
LEACHING TIME - MINUTES (LEACH 7)


IRON EXTRACTION - REDOX POTL.
1.0
.9
.8
.7
.6
.5
.4
.3
.2
.1
.0
0
60
120
180
240
300
360
420


IRON EXTRACTION - MATTE POTL.
1.0
.9
.8
.7
.6
.5
.4
.3
.2
.1
.0
0
60
120
180
240
300
360
420


IRON EXTRACTION - RESIDUE POTL.
1.0
.9
.8
.7
.6
.5
.4
.3
.2
.1
.0
0
60
120
180
240
300
360
420
LEACHING TIME - MINUTES (LEACH 8)

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 :
**********

| | 1'ST CONSTANT | 2'ND 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 | .00000 |
| TROILITE | : 1.755E-09 | .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 | .00000 |
| TROILITE | : 3.647E-14 | .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 :
**********

| | 1'ST CONSTANT | 2'ND 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 :
**********

| | 1'ST CONSTANT | 2'ND CONSTANT |
|---|---|---|
| ALLOY | : 1.456E-07 | .00000 |
| TROILITE | : 2.102E-15 | .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 | .00000 |
| TROILITE | : 2.102E-15 | .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 | .00000 |
| TROILITE | : 1.950E-16 | .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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