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MODELLING AND OPTIMISATION OF A MANGANESE ELECTROWINNING PLANT

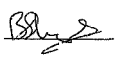
Brett Stephen Cronje

A dissertation submitted to the Faculty of Engineering, University of the Witwatersrand, Johannesburg, in fulfilment of the requirements for the degree of Master of Science in Engineering

Johannesburg, 1985

DECLARATION

I declare that this Dissertation is my own, unaided work. It is being submitt for the Degree of Master of Science in Engineering in the University of the Witwatersrand, Johannesburg. It has not been submitted before for any degree or examination in any other University.



12 day of August 1985

ABSTRACT

A steady-state model of an existing manganese electrowinning plant is presented. The model concerns the flow circuit of the electrolyte, includes the leaching of ore, the purification of the electrolyte, and the process of electroplating in the cells. The model uses simple costs of the operation to provide a financial basis for comparison of performance. In this respect it is possible to examine optimisation of the complete production procedure. The model is implemented on a computer and is formatted to permit ease of use and understanding by those involved with actual production.

ACKNOWLEDGEMENTS

I would like to thank Delta Manganese (Pty) Ltd for their assistance, both financial and practical, in this dissertation. I would also like to thank the Council for Scientific and Industrial Research and the University of the Witwatersrand for their financial assistance.

To Professor Bryson and Mr Williams, my supervisors, go a special thanks for the advice and help that they have extended to me.

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1 INTRODUCTION

South Africa is one of the foremost producers of manganese metal in the free world. Vast deposits of manganese ore are found in the Republic, especially in the Western Cape. There are various ways of refining the ore to extract the metal, but the one method which gives perhaps the purest product is electrolytic winning. In this method, an electrolyte solution containing the metal is fed to an electrochemical cell through which a current is passing. The product at the cathode is very pure manganese metal. Harris, Meyer and Auerswald (1977) give a discussion of the process at the Delta Manganese plant in Nelspruit, South Africa. It is this selfsame plant that is modelled in this dissertation.

To obtain the electrolyte it is necessary to leach the manganese ore with the relevant acid. The electrolyte is normally a sulphate solution, although Lewis, Scaife and Swinbels (1976) report manganese electrowinning using a chloride solution. In the electrochemical cell the reaction at the anode results in oxygen evolution, leaving behind hydrogen ions to associate with the anions in solution. The acid that is used in the leach is therefore regenerated in the cells. The electrolyte solution thus flows in a closed circuit from the leach tanks to the cell house and back again, with some steps in between for the purification of the solution. A simplified flow diagram of the solution circuit is presented in Figure 1 on page 3 showing the areas of major interest. Ideally then, there should be no need for fresh acid, although in practice acid gets lost in the purifying steps. Ammonium sulphate is also added to the electrolyte solution. It does not become directly involved with any of the reactions but has some important functions: it buffers the electrolyte solution in the pH range 6-8, it increases the conductivity of the solution in the cells, it aids in the leaching of the manganese in the leach tanks, and it helps reduce the precipitation of manganese

hydroxide in the cells. There is no net process consumption or production of ammonium sulphate although there are losses throughout the circuit.

The manganese ore is first calcined to reduce the manganese from its MnO_2 form to MnO so that it can be leached. After the reduction the manganese is mostly present as MnO with some additional Mn_2O_3. The reduced ore contains approximately 54% w/w of manganese, a fair amount of iron (ferrous), and trace amounts of elements such as cobalt, nickel etc. The remainder of the ore is a gangue of silicates. The metal impurities are also leached into the solution and have a large deleterious effect on the performance in the cells and the quality of the metal product. These impurities must therefore be removed from the solution. The leach is kept at a pH in the range 6-7. At lower pHs very much more iron is leached. The ferrous ions in solution are oxidised to the ferric form by sparging air through the tanks. Aluminium sulphate is added to remove silica which co-precipitates with hydrated ferric oxide. A settling tank is then used to separate the precipitate and the residue gangue from the solution. The underflow is sent to a belt filter to recover the electrolyte it contains. Inefficient washing and the ensuing entrapment of solution in the filter cake is the cause of the major losses of acid, ammonium sulphate and manganese sulphate in the system.

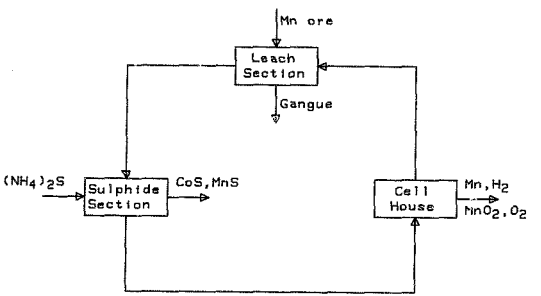


Figure 1. Solution Circuit Diagram.

The impurities still present are cobalt, nickel, zinc and other similar species. Their concentrations are small, the total being less than 50 ppm, but they have a strong influence on the cells. Cobalt in particular has the most harmful effect and in the analysis of this dissertation will be considered as representative of all such species. The solution is pumped from the belt filter to the cobalt purification step. Ammonium sulphide is introduced into the solution. It reacts with the metal ions to form insoluble metal sulphides which are then separated in large settling tanks. Most of the metal sulphides consist of MnS, so this is another area where manganese is lost. From the sulphide precipitation settling tanks the overflow is sent to the cells.

Previous workers who studied the process have concentrated on separate areas. Bijsterveld (1983) examined the kinetics of the sulphide precipitation reactions, and identified the major species and complexes in the solution. He found that the precipitation reactions were autocatalysed, and proceeded rapidly within minutes.

Jones (1983) studied the leach reactions with respect to their kinetics. He too found that the reactions were completed within minutes.

Rodrigues (1983) attempted to model the performance of the cells. He developed a kinetic model of the cathode performance, and experimentally determined the solution equilibria of the more important species in the cell house. He also extended the work done by Bryson and Lawrence (1980) on the mass transfer in the membrane of a chlor-alkali cell to the particular case in question. This information was then fitted together into the framework formulated by Bryson (1981) to form a model of the electrowinning cells. Unfortunately he did not complete the various mass balances in the cell successfully, and therefore did not have a workable model.

The scope of this work is to establish the important mass balances in the plant, and to implement them together with the applicable kinetics and the solution equilibria into a model of the entire plant. This allows one to obtain a better idea of the interrelationships of the process, and to optimise overall performance instead of the performance of each section.

The model is designed to follow the steady-state behaviour of the plant. As the actual plant, like most other flow processes in the world, has surge and storage tanks that enable the process to be controlled, the plant may never actually be operating at a steady state. However the tanks are of a finite size so that over a period of time the average plant operating conditions will constitute a steady state. It is also expected that the deviation at any point in time from steady state will not be significant.

Many approximations and assumptions have been made to achieve this model. The plant will therefore not be exactly described. However the model is sufficiently accurate to give insight into the various processes, and to be useful in the operation of the plant. Specific approximations are discussed in the relevant chapters, while a few more general approaches are presented below.

The three main process functions of leach, sulphide precipitation, and cell house are each examined in separate chapters. There is also a chapter on the way they interrelate via the overall mass balance. In the business world any comparison of alternatives must include financial considerations, so there is a chapter on the costs involved in the operation. A chapter on the optimisation of the process by examination of the operating variables is included.

Some aspects of the plant do not greatly affect the mass balances or the kinetics and are not included as processes in the model. These include losses of water vapour and ammonia through evaporation and stripping in open pipes and tanks; crystallisation of salts like manganese sulphate and ammonium sulphate; costs of pumping; the reduction of the iron concentration in the leach with aeration and aluminium sulphate; use of reagents for pH control and other similar functions. Since these factors do influence the profitability of the operation they are included in an empirical way in the costing. Mostly they are taken to be fixed costs, or to vary linearly with the factors that influence them. They are discussed in greater detail in the chapter on costs. However, these costs are small in comparison to the cost of power and the cost of manganese ore and do not have as large an effect on the profitability of the operation.

As the ammonia and the sulphate in the solution are not consumed or produced in any of the reactions, their levels are assumed to be constant throughout the circuit. Provided it is ensured, via the plant operators, that there are make-up streams of ammonia and sulphate to account for losses of these species in the cake of the filter press, and other sundry losses, then this assumption is valid. These make-up streams must be included in the operating cost of the plant.

The loss of manganese in crystallised salts is not modelled. The input of manganese is in the ore, the output is the plated manganese and the losses are the MnS in the precipitation section, the production of manganese dioxide in the cells and the loss of manganese in the solution trapped in the leach filter cake. The subsequent treatment of the MnS with acid to retrieve the manganese is not modelled and all the MnS is assumed lost for the purposes of a mass balance over the precipitation

section. The addition on the plant of this recovered manganese to the leach tanks is small and will affect the ore feed rate, but only to an insignificant degree.

It is also assumed that all the sulphide added as ammonium sulphide in the precipitation section is precipitated out as metal sulphides. Tests done by Bijsterveld (1983) on the plant electrolyte subsequent to the sulphide precipitation show very low levels of sulphur in solution, so this assumption is accurate.

The production of hydrogen in the cells ultimately causes a loss of water but this is small and together with evaporation losses is covered by any other water addition, or if needs be a make-up stream. The production of oxygen in the cells is covered by this same water loss plus the oxygen that arrives in the manganese ore.

An energy balance on the plant is not attempted as the energy losses from the pipes and tanks are large. Temperatures for the model are taken to be typical values from the plant.

The pHs of the solutions entering the precipitation tank and the cell house are controlled to the desired values by the addition of ammonium hydroxide or concentrated sulphuric acid. As the flow rate in the plant, which leads to the leach tanks, is kept constant the pH in the leach is controlled by the addition rate of the ore. The higher the rate the higher the pH.

The culmination of this dissertation is a computer program, including all the assumptions and mathematics, that accurately describes the function-

ing of the manganese electrowinning plant. The program structure has been designed to facilitate change and extension by other users. The codes for distinct sections are written separately in subroutines. This permits them to be changed easily at one place only. To aid in the understanding of the logic flow a large amount of commentary is included between program lines. This dissertation also acts as a manual to which reference can be made. It provides greater detail to the manipulative steps giving rise to the forms of the equations used. Sections in the program refer directly to the relevant sections in the dissertation. The naming of variables in the dissertation may appear clumsy at times, this is because the exact same names are used as appear in the program. This results in greater comprehension when referring to the program listings.

A flow chart of the model logic is presented in Figure 2 on page 9. It shows the steps in the procedure for calculating the complete model. Calculating the model in the order shown results in the elimination of any loops in the mass balance procedure. This is mainly a result of the way the leach is controlled on the plant and is more fully discussed in Section 2.3. The flow charts for each subroutine are presented in the appropriate chapters.

A listing of the computer program, in the BASIC language used by the Hewlett-Packard HP-87 computer is presented in Appendix N at the rear of this dissertation. Copies of the program in the FORTRAN 77 language are also available.

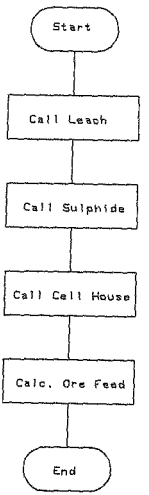


Figure 2. Model Flowchart

2 MANGANESE LEACH SECTION

2.1 Manganese Leach Introduction

Jones (1983) has investigated the kinetics of the leach reactions involved and has shown experimentally that the rates of reaction are high in comparison to the residence times involved on the plant (≈5 hrs). This permits one to use equilibrium and mass balance considerations only in calculating the leach. The tank itself is assumed to behave as an ideal CSTR.

The manganese ore comes from a calciner and consists mostly of MnO with a small amount of Mn_2O_3, together with the gangue and the impurities. The ore is added to the acid as it enters the leach tank. The manganese oxide in the ore reacts with the acid to form manganese sulphate and water, and hence decreases the strength of the acid. Therefore the greater the manganese concentration in solution the lower the acidity, or the greater the pH. As the regenerated acid from the cell house is pumped back to the manganese leach at a constant rate, the pH in the leach tank can be controlled through the addition rate of manganese ore. The higher the addition rate the higher the leach pH.

There is another leach tank in series with the first and its purpose is to control the amount of iron which is also leached. Air is sparged through this tank and aluminium sulphate is added. The Fe^{2+} ions are oxidised to Fe^{3+} which then drop out of solution with the aluminium sulphate. This process does not affect the manganese concentration directly unless the pH in the tank falls to a low value that reduces the

efficiency of the iron removal o[illegible]ally. This process is therefore not modelled.

The leach conditions are calculated for the conditions in the second (final) tank. Settling tanks then concentrate the gangue and the precipitates which are sent to a belt filter and removed. Some of the solution which contains manganese is also lost here and this is the point of major loss of all chemicals in the circuit.

The leach efficiency is the fraction of total manganese added that ends up in solution. Nearly all the MnO gets leached. At the lower end of the pH range (6.0 - 7.2) the Mn_2O_3 disproportionates into MnO and MnO_2. The former leaches while the latter does not. Hence the leach efficiency increases with lower pH and asymptotes toward a value determined by the amount of MnO_2 produced by the complete disproportionation of the Mn_2O_3. At a higher pH the efficiency is lower since only the MnO is leached. However a high pH means more manganese is in solution so the leach pH is also one of the process variables that can be optimised. An equation has been fitted to plant and experimental data to give the leach efficiency as a function of the leach pH. It is presented in Appendix A.

To determine the leach one makes use of a mass balance across the leach tank to give the total concentrations of substances, and then one uses the solution equilibria to calculate the individual species. There is a precipitation reaction between the Mn^{2+} ion and water to give manganese hydroxide and hydrogen ions. Manganese hydroxide is not soluble and covers the surface of the ore preventing further leaching. This reaction represents a maximum limit on the concentration of manganese for a given pH. The calculated manganese concentration is therefore compared to the maximum equilibrium value allowed. If this is exceeded then the calculation must be repeated for some other desired point of operation, usually

a lower leach pH. If on the plant one attempts to obtain an operating pH occurring at a manganese concentration greater than the equilibrium allowed, by increasing the flowrate of ore, then the extra manganese that is added does not leach but is removed in the filter and the leach efficiency appears to drop suddenly.

The regenerated acid returning from the cell house contains sulphuric acid, sulphate, manganese and ammonia with insignificant impurities. In the tanks the iron and aluminium sulphate are neglected since they are removed in the belt filter anyway, and the impurities of the cobalt type are neglected since they are present in small concentrations (≈ 50 ppm).

It must be noted that to calculate the solution equilibria only three degrees of freedom are available. Of the four quantities in the precipitation tanks, which include the total concentrations in kmole/m^3 of manganese (MAN_T), sulphate ($SULPH_T$) and ammonia (AMM_T), as well as the pH, only three may be specified and the remaining value can be calculated. The specified quantities are AMM_T, $SULPH_T$, and pH. Hence knowing the total concentrations of manganese, sulphate, pH and the equilibrium equations, the species in solution may be calculated, and hence the manganese concentration is known. The species present in the leach are the same as those identified by Bijsterveld (1983) in the sulphide section and are:

$$Mn^{2+},\ MnSO_4,\ SO_4^{2-},\ NH_4^+,\ NH_4SO_4^-,\ NH_3,\ MnNH_3^{2+},\ MnNH_3SO_4$$

The manganese-ammonia complexes have been restricted to the simple form with only one associated ammonia molecule. Tilak, Rajagopalan and Reddy (1962) report this to be the most likely association for pHs below 8. Above this one finds increasing substitution of the water molecules sur-

rounding the hydrated molecule by ammonia, but the simple complex may be used to represent the trends of these interactions.

To solve the solution equilibrium one requires reaction equilibrium equations and individual component balance equations, as set out in the following section.

2.2 Leach Equilibrium

The important equations for the solution equilibria are as follows:

Note: Writing Mn, NH_4 etc implies concentration in kmole/m³ thereof.

$$AMM_T = NH_4 + NH_3 + MnNH_3 + NH_4SO_4 + MnNH_3SO_4$$
(Amm component balance) 2.1

$$SULPH_T = MnSO_4 + SO_4 + NH_4SO_4$$ (Sulph component balance) 2.2

$$2Mn + 2MnNH_3 + NH_4 = 2SO_4 + NH_4SO_4$$
(Electroneutrality, H=0) 2.3

$$MnSO_4/(Mn \times SO_4) = K_1$$ ($Mn^{2+} + SO_4^{2-} \equiv MnSO_4$) 2.4

$$NH_4/(H \times NH_3) = K_2$$ ($H^+ + NH_3 \equiv NH_4^+$) 2.5

$$NH_4SO_4/(NH_4 \times SO_4) = K_3 \qquad (NH_4^+ + SO_4^{2-} \equiv NH_4SO_4^-) \qquad 2.6$$

$$MnNH_3/(Mn \times NH_3) = K_4 \qquad (Mn^{2+} + NH_3 \equiv MnNH_3^{2+}) \qquad 2.7$$

$$MnNH_3SO_4/(MnNH_3 \times SO_4) = K_5 \qquad (MnNH_3^{2+} + SO_4^{2-} \equiv MnNH_3SO_4) \qquad 2.8$$

And $H = 10^{-pH}$ 2.9

The above equilibrium equations are based on equilibrium ratios which use concentrations and not activities. The only values available are equilibrium constants, which are based on activities, so it is necessary to convert these to ratios using activity coefficients. The equilibrium constants are calculated as functions of temperature from standard thermodynamic data in Appendix A. The method of Morris (1983) is used to obtain the activity coefficients. The method is based on the Debye-Huckel equation with some modifications that tailor it for strong electrolytes. The method is detailed in Appendix B. The activity coefficients of hydrogen and all uncharged species are taken to be unity, while those for charged species are calculated. It is necessary to know the concentrations of the species to calculate the activity coefficients hence an iterative procedure is adopted. Initial values of the coefficients are taken, the solution equilibria calculated and then new values of the coefficients found. The entire process is then repeated until convergence is reached.

The equations using equilibrium constants have the same form as those using ratios except that the concentrations have activity coefficients pre-multiplied into them. An example of this is shown in Appendix B.

In solving the eight equations 2.1-2.8 in eight unknowns for the solution equilibria an iterative procedure is again adopted. A flow sheet showing the procedure is presented in Figure 3 on page 16. The two species involving free ammonia are minor species and have initial concentrations of zero. This leaves six equations in six unknowns which are solved. The two minor species can then be calculated and the total concentrations of ammonia and sulphate are adjusted as well as the equation of electroneutrality. The six major equations are solved again and the process is repeated until convergence is attained. This algorithm works well if the pH is not too high. At a high pH (> 7.5) the $MnNH_3^{2+}$ and $MnNH_3SO_4$ species start to become major species and the algorithm fails. The detailed equations and algorithm for the leach solution equilibrium are presented in Appendix C.

Once all the concentrations have been found the Mn^{2+} concentration is compared to the maximum equilibrium concentration. This is found from:

$$Mneq = H^2/Kmneq \qquad 2.10$$

Kmneq is the solubility product ratio found from the activity coefficients and the solubility product constant, which is presented in Appendix A. If Mn > Mneq then the chosen pH is too high and the model must be restarted with different values for the variables.

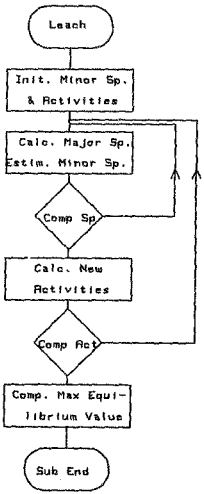


Figure 3. Flowchart of Leach Section.

2.3 Ore Feed to Leach

The ore feed rate that is required to give the chosen pH for a given flowrate and concentration of solution can be calculated from:

$$Fr = \frac{(Mnexit - Mnin) \times Q + Mnlost}{Leff \times Mfrac} \qquad 2.11$$

where:

Fr	=	Ore feed rate.	(kg/hr)
Mnexit	=	Total Mn conc. in leach.	(kg/m^3)
Mnin	=	Total Mn conc. cell exit.	(kg/m^3)
Mnlost	=	Soluble Mn lost in filter cake.	(kg/hr)
Q	=	Total solution flowrate.	(m^3/hr)
Leff	=	Leach efficiency.	
Mfrac	=	Total Mn fraction in ore.	

This may only be done once Mnin is known, i.e. only when the cell house has been calculated. The fact that the ore feed rate is calculated to give the chosen leach pH instead of specifying the feed rate and calculating the pH means that the overall mass balance on the plant need only be done once. Normally this would have to be calculated in an iterative way which could then have convergence stability problems, and would also require much more computation time. It is fortunate for the model that the plant operates in this fashion as it has greatly simplified the calculation.

3 SULPHIDE PRECIPITATION SECTION

3.1 Sulphide Introduction

The method used to purify the solution at this point is precipitation. The impurities are reacted with ammonium sulphide to form metal sulphides which are insoluble and are removed in the settling tanks. Most of the cobalt and other impurities are knocked out in this way.

Bijsterveld (1983) studied the kinetics of the precipitation and found that the precipitation is auto-catalysed by the presence of metal sulphides. Once started the reactions proceed rapidly to completion within minutes. As the residence time on the plant is much greater than this (≈ 2 hrs), the reaction may be assumed to go all the way to equilibrium. Bijsterveld also found that the the concentrations of sulphide species in solution after precipitation were minute, meaning that essentially all the sulphide was precipitated. Furthermore, since the concentration of cobalt is low (≈ 15 ppm) it is also assumed that the molar amount of MnS that is formed is equal to the molar amount of sulphide added.

The solution comes from the leach containing manganese, sulphate and ammonia in water. Ammonium sulphide and a recycle stream from the underflow of the sulphide precipitation settling tanks, which contains metal sulphides, is added to the pipe just after the leach section. When the solution reaches the sulphide settling tanks the reaction is complete.

It must be noted that, as in the leach, to calculate the solution equilibria only three degrees of freedom are available. i.e. of the three concentrations in the precipitation tanks MAN_T, $SULPH_T$, AMM_T, and the pH only three may be specified and the remaining value can be calculated. The specified quantities are MAN_T, $SULPH_T$, and pH. It must be noted that the total ammonia concentration has been changed by the addition of ammonium sulphide. Also the individual species concentrations are different to those in the leach because the pH and the temperatures are different. Hence knowing the total concentrations of manganese, sulphate, pH and the equilibrium equations, the species in solution may be calculated. According to Bijsterveld (1983) the species present are:

$$Mn^{2+},\ MnSO_4,\ SO_4^{2-},\ NH_4^+,\ NH_4SO_4^-,\ NH_3,\ MnNH_3^{2+},\ MnNH_3SO_4$$

together with the cobalt species, which are found once the above have been calculated, and the hydrogen ion concentration which is defined to be 10 to the power of the negative pH. The ammonia complexes are discussed in Section 2.1.

To solve the solution equilibrium one requires reaction equilibrium equations and individual component balance equations, as set out in the following sections.

3.2 Sulphide Equilibrium

There are thus eight unknowns and eight equations as follows:

Note: Writing Mn, NH_4 etc implies concentration in kmole/m^3 thereof.

$MAN_T = Mn + MnSO_4 + MnNH_3$ (Mn component balance) 3.1

$SULPH_T = MnSO_4 + SO_4 + NH_4SO_4$ (Sulph component balance) 3.2

$2Mn + 2MnNH_3 + NH_4 = 2SO_4 + NH_4SO_4$ (Electroneutrality, I=0) 3.3

$MnSO_4/(Mn \times SO_4) = K_1$ $(Mn^{2+} + SO_4^{2-} \equiv MnSO_4)$ 3.4

$NH_4/(H \times NH_3) = K_2$ $(H^+ + NH_3 \equiv NH_4^+)$ 3.5

$NH_4SO_4/(NH_4 \times SO_4) = K_3$ $(NH_4^+ + SO_4^{2-} \equiv NH_4SO_4^-)$ 3.6

$MnNH_3/(Mn \times NH_3) = K_4$ $(Mn^{2+} + NH_3 \equiv MnNH_3^{2+})$ 3.7

$MnNH_3SO_4/(MnNH_3 \times SO_4) = K_5$ $(MnNH_3^{2+} + SO_4^{2-} \equiv MnNH_3SO_4)$ 3.8

and $H = 10^{-pH}$ 3.9

As in Section 2.2 it is necessary to find the equilibrium ratios from the equilibrium constants. The procedure is identical to that followed in the leach, except that the equations of solution equilibrium are manipulated

differently. This is due to the change in the variables held constant according to the degrees of freedom available. The detailed equations and algorithm used to calculate the sulphide section are presented in Appendix D. A flowchart of the procedure is given in Figure 4 on page 22.

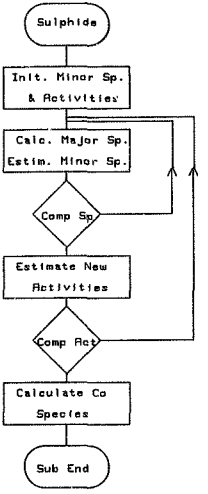


Figure 4. Flowchart of Sulphide Section.

3.3 Sulphide Impurities

Once the manganese species have been found it is possible to calculate the cobalt species. Since their concentrations are small they do not affect the concentrations of the major species. It is shown in Appendix D that provided both MnS and CoS are precipitating then the following equation holds:

$$\frac{Co}{Mn} = \frac{Ksc}{Ksm} \qquad 3.10$$

where Ksc and Ksm are the solubility product constants that are obtained as functions of temperature in Appendix A, and *Co* and *Mn* are the concentrations of Co^{2+} and Mn^{2+} respectively. Hence it is possible to find the Co^{2+} concentration and then the concentrations of the following species:

$CoSO_4$, $CoNH_3^{2+}$, $CoNH_3SO_4$

The equilibrium equations are:

$$CoSO_4/(Co \times SO_4) = K_6 \qquad (Co^{2+} + SO_4^{2-} \rightleftharpoons CoSO_4) \qquad 3.11$$

$$CoNH_3/(Co \times NH_3) = K_7 \qquad (Co^{2+} + NH_3 \rightleftharpoons CoNH_3^{2+}) \qquad 3.12$$

$$CoNH_3SO_4/(CoNH_3 \times SO_4) = K_8 \qquad (CoSO_4 + NH_3 \rightleftharpoons CoNH_3SO_4) \qquad 3.13$$

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$$CoNH_3SO_4/(CoNH_3 \times SO_4) = K_8 \qquad (CoSO_4 + NH_3 \equiv CoNH_3SO_4) \qquad 3.13$$

Again the above equations are in terms of equilibrium ratios which have been obtained from the constants by multiplying in the activity coefficients.

Once these cobalt species have been found the total cobalt concentration is then the sum of all of them, and the precipitation section has been calculated. The details of this section are presented in Appendix D.

4 CELL HOUSE SECTION

4.1 Cell House Introduction

The cell house is the most important operation for it is here that the actual function of the plant is fulfilled. The manganese that has been leached and purified is now electro-plated into the product that is sold to obtain the revenue for the plant. Apart from the cost of the ore in the leach section, the cell house is the most costly section of the plant to run. This is due to the great deal of power required to carry out the electrowinning. This cost of power is about fifty times more than any other operating cost. The cell house consists of a number of electro-plating cells, in parallel to the flow of solution, and in a combination of parallel and series to the flow of current.

Each cell block contains 72 cathodes and corresponding anodes. The cathodes slip down into wooden supports which hold the membranes, and so separate the cathode compartments from the anode compartments. Each cathode is allowed to plate manganese for approximately 24-48 hours after which it is removed from its box and a new cathode is slipped in. The entire cell block gets drained and cleaned about once every three weeks. After this period of time the membranes have started to become blinded by the deposition of manganese hydroxide.

The five major potential electrochemical reactions that may occur in the cells, and their standard electrochemical potentials given by Weast (1976), are as follows:

Reaction	Potential	
$Mn^{2+} + 2e^- \equiv Mn$	-1.029v	4.1
$2H^+ + 2e^- \equiv H_2$	0.000v	4.2
$2H_2O + 2e^- \equiv H_2 + 2OH^-$	-0.828v	4.3
$O_2 + 4H^+ + 4e^- \equiv 2H_2O$	+1.229v	4.4
$MnO_2 + 4H^+ + 2e^- \equiv 2H_2O + Mn^{2+}$	+1.208v	4.5

The first three will occur on the cathode as reduction reactions and the last two will occur on the anode as oxidation reactions. It is not completely clear which of the two reactions 4.2 and 4.3 actually taker place in the cathode. In definite acidic solutions reaction 4.2 occurs only, but at higher pHs the second reaction gains in importance. Bockris (1954:241) estimates that the relative importance of the two reactions changes in the pH range 8-9 which includes the operating pH of the plant. This estimate however is based on purely thermodynamic grounds. Vetter (1967) states that kinetic considerations are important and that the metal on the cathode influences the hydrogen evolution greatly. Bryson in an early unpublished modelling exercise included both reactions in a kinetic study, and found that the model was insensitive to even an order of magnitude change in the parameter related to reaction 4.3. For these reasons Rodrigues (1983) excluded reaction 4.3 from his kinetic study of the hydrogen evolution.

Therefore one is left with only the first two reactions occurring on the cathode. Of course any metal impurity more noble than manganese will plate out preferentially to manganese, and must therefore be eliminated from the electrolyte solution. This is why so much emphasis is placed on the purification of the solution, especially in the case of cobalt.

The MnO_2 that is produced at the anode is not only a waste of manganese, but it comes out of the solution, falls to the bottom of the cell and blocks up the pipes and fittings. It is therefore desirable to reduce this as much as possible. This reaction is mass-transfer limited so that the higher the current density on the anode the more oxygen will be produced and the less MnO_2. Typically on the plant the current density is kept at 1000 amps/m^2 and the production of oxygen accounts for 99% of the current.

4.2 Electro-plating Cell

As is shown schematically in Figure 5 on page 29 each electro-plating cell consists of the following sections:

1. A feed stream which flows into a cathode compartment.

2. A cathode compartment containing the cathode onto which the manganese is plated out. Hydrogen gas is also produced at the cathode; this is the major cause of inefficient current usage. The hydrogen bubbles off from the cathode and is released into the atmosphere. This bubbling action ensures that the solution in the cathode compartment is well mixed, and hence may be considered an ideal CSTR. The hydrogen gas is saturated with water vapour and ammonia gas, so small quanti-

ties of these species are lost. These losses are important for the operation of the cell but have a very small cost value.

3. A diaphragm, separating the cathode compartment from the anode compartment, through which the solution flows from cathode to anode. This diaphragm acts to separate the solution in the cathode from that in the anode, and in particular to reduce the flux of hydrogen ions that diffuse back into the cathode and which then cause the current inefficiency. The diaphragm is not ion selective but works physically to block ion migration into the cathode against the flow of solution.

4. The anode compartment containing the anode that produces the oxygen which is the primary co-product of the manganese. Some MnO_2 is also produced in the anode as an inefficiency. Under normal operating conditions the amount produced is not large, and usually drops to the bottom of the cell and is removed during routine cell maintenance. The oxygen strips out water vapour from the anode compartment, but not ammonia since there is no aqueous NH_3 in the anode owing to the low pH.

5. An exit stream that is then pumped back to the leach. Flow through the cell is maintained by gravity with the feed coming from constant head tanks.

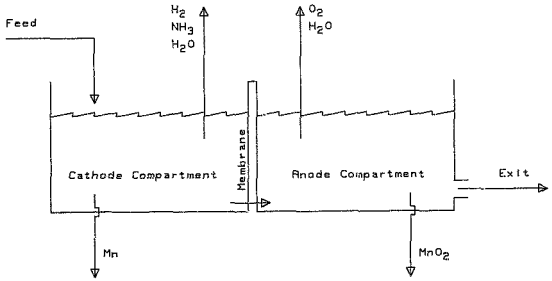


Figure 5. Schematic Diagram of Cell Geometry.

Rodrigues (1983) has examined the kinetics and equilibria occurring in the cell and has modelled these processes on the assumption that the following species only are present:

$$Mn^{2+},\ SO_4^{2-},\ NH_4^+,\ H^+,\ NH_3,\ MnNH_3^{2+}$$

This is not consistent with the rest of the plant. However as the equations used have been fitted to this assumption the inconsistencies can be avoided. It would be possible to change all the equations to be consistent but this would mean that new fitting parameters in the equations would have to be found.

A flowchart of the procedure followed in calculating the cell house is given in Figure 6 on page 31. The procedure is examined in greater detail in the following sections.

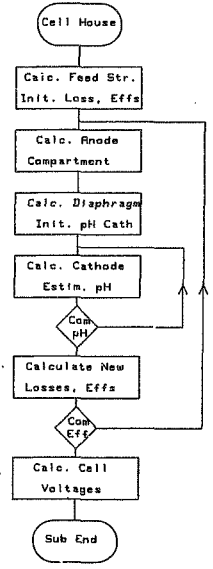


Figure 6. Flowchart of Cell House Section.

4.3 Feed Stream

The equilibrium of species in the feed stream needs to be explicitly calculated since the concentrations of the free ammonia species are important for the hydrogen-ion balance in the cell. It also gives an idea of the concentrations to be expected inside the cell based on the new assumption about the species present.

There are two important equilibrium reactions, which together with the electroneutrality equation and the manganese component balance equation enable one to calculate the concentrations of the species in the feed, provided the total manganese and sulphate concentrations, and the pH of the feed are known. These equations are:

$$MAN_T = Mn + MnNH_3 \qquad \text{(Mn component balance)} \qquad 4.6$$

$$NH_4 + 2MAN_T = 2SULPH_T \qquad \text{(electroneutrality, H = 0)} \qquad 4.7$$

$$(H \times MnNH_3)/(Mn \times NH_4) = Kc \qquad (Mn^{2+} + NH_4^+ \equiv MnNH_3^{2+} + H^+) \qquad 4.8$$

$$NH_4/(H \times NH_3) = Ka \qquad (NH_3 + H^+ \equiv NH_4^+) \qquad 4.9$$

In this case the K values are still equilibrium ratios, but Rodrigues (1983) has determined these experimentally on the basis of concentrations and has fitted these to temperature, so it is not necessary to find activity coefficients. The K values are presented in Appendix A. The al-

gorithm for calculating the equilibrium species is presented in Appendix E.

4.4 Anode Compartment

Given particular values for current efficiencies and the losses of ammonia and water in the cathode and anode it is possible to perform a mass balance over the complete cell to find the flowrate and total concentrations of manganese, ammonia and sulphate in the exit stream. A mass balance envelope for this is shown in Figure 7 on page 35. As the evolution of oxygen in the anode results in good mixing of the solution, it may be assumed that the anode compartment behaves like a CSTR. This implies that the solution in the anode compartment has the same composition as the exit stream. Hence knowing the exit stream, conditions at the anode may be calculated. The anode solution is regenerated acid at a low pH (< 1) and contains the following species:

Mn^{2+}, NH_4^+, H^+, SO_4^{2-}, HSO_4^-

There is no aqueous NH_3 present and the H^+ concentration is significant. To calculate the individual concentrations the following equations are used:

$MAN_T = Mn$	(Mn component balance)	4.10
$AMM_T = NH_4$	(Am component balance)	4.11
$SULPH_T = SO_4 + HSO_4$	(Sulph component balance)	4.12
$2Mn + NH_4 + H = 2SO_4 + HSO_4$	(electroneutrality)	4.13
$(H \times SO_4)/HSO_4 = Kh$	$(HSO_4^- \equiv H^+ + SO_4^{2-})$	4.14

Again, Rodrigues has modelled the equilibrium ratio Kh as a function of temperature. It is presented in Appendix A. The equations and algorithm used in this section are presented in Appendix F.

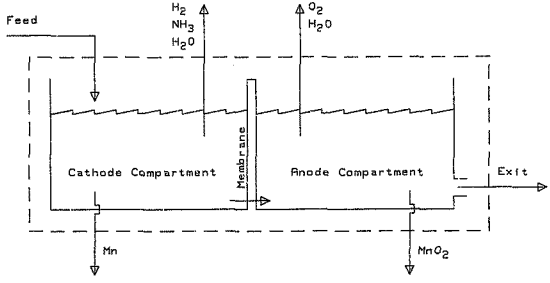


Figure 7. Anode Mass Balance Envelope.

4.5 Diaphragm

To calculate the cathode compartment conditions it is important to know the molar fluxes of species across the membrane. Bryson and Lawrence (1980) have developed an equation that may be used for this purpose. It is not necessary to calculate the sulphate flux as the sulphate concentration is not used in the cathode. As it is observed in practice that the manganese concentration in the cathode equals that in the anode it is also not necessary to know the manganese flux.

The assumption is also made that no bisulphate ion is present in the membrane, in other words it is assumed that these ions dissociate at the surface of the membrane on the anode side. The bisulphate ion only exists at low pHs and would readily dissociate as the pH in the membrane increases towards the cathode. The two important fluxes are thus H^+ and NH_4^+. The flux equation for the two species is presented in Appendix G. The derivation is not given and may be found in the paper of Bryson and Lawrence (1980), or in the dissertation of Rodrigues (1983). The manipulation of the equation into a useable form is given. The flux of hydrogen is from the anode to the cathode. The flux of ammonia is from the cathode to the anode, and the result of this is a higher concentration of ammonia in the cathode than in the anode.

The membrane is made of polypropylene with a 2x2 twilled Dutch weave. Cook (1978) has studied this membrane and reports an average thickness of 1.37 mm and a void fraction of 0.67. He obtained the latter value from the mass per unit area of the membrane, the thickness and the material density. He reports values for the above of 415 g/m^2 and 0.91 g/cm^3. The total area per cell bath depends on the number of cathodes per bath as well as the dimensions of the wooden supports and the level of the

electrolyte in the cathode. The value used is presented with the other process constants in Appendix J.

4.6 Cathode Compartment

Using the diaphragm equation the ammonia gives the total concentration of ammonia in the cathode compartment. The total concentration of manganese is known to be the same as in the anode so it is now possible to calculate the equilibrium concentrations as a function of pH. The species present are the same as in the feed stream. As the pH is in the region 6-8, the actual hydrogen ion concentration is small and may be neglected in the electroneutrality equation and in the hydrogen ion balance over the cathode compartment. The equations used to calculate the equilibria are:

$$MAN_T = Mn + MnNH_3 \qquad \text{(Mn component balance)} \qquad 4.15$$

$$AMM_T = NH_4 + NH_3 + MnNH_3 \qquad \text{(Amm component balance)} \qquad 4.16$$

$$2MAN_T + NH_4 = 2SO_4 \qquad \text{(electroneutrality, H=0)} \qquad 4.17$$

$$(H \times MnNH_3)/(Mn \times NH_4) = Kc \qquad (Mn^{2+} + NH_4^+ \rightleftharpoons H^+ + MnNH_3^{2+}) \qquad 4.18$$

$$NH_4/(H \times NH_3) = Ka \qquad (NH_3 + H^+ \rightleftharpoons NH_4^+) \qquad 4.19$$

Including:

$$H = 10^{-pH} \qquad 4.20$$

A mass balance on the hydrogen ion around the cathode compartment is performed. A mass balance envelope for this is shown in Figure 8 on page 41. The important point to note is that there is no free ammonia species present in the anode. Therefore all the free ammonia species that are pre[illegible]he feed stream, less the amount of NH_3 that gets stripped by [illegible]as at the cathode, must react with hydrogen ions before they [illegible]compartment. The assumption, similar to that in Section [illegible]d. th[illegible] this reaction occurs at the surface of the membrane on [illegible] cathode s[illegible], i.e. no free ammonia species exist in the membrane. This reaction reduces the net hydrogen flux to the cathode compartment. Under steady-state conditions, and neglecting the actual hydrogen ion concentration in the feed, the net flux of hydrogen into the cathode compartment must equal the amount of hydrogen that is evolved at the cathode.

Rodrigues (1983) made an error in this section when he assumed that the reduction in flux is caused by the flow, through the membrane to the anode, of all the free ammonia species in the cathode compartment. As the pH inside the cathode compartment is greater than the pH of the feed stream, the equilibria of the reactions between the free ammonia species and the ammonium ion species in solution change, resulting in a much greater concentration of free ammonia species in the cathode compartment. Therefore as the feed stream enters the cathode compartment with its higher pH, hydrogen ions are released into the solution. This is an extra source of hydrogen ions that Rodrigues did not take into account. The correct way to account for these processes is as described in the previous paragraph.

Rodrigues has modelled the kinetics of the current efficiency in the cathode compartment as a function of the local properties and has obtained the following equation:

$$\xi_c = 1/(1 + C1 \times J1 \times J2 \times J3 \times H/Mn) \quad 4.21$$

Where:

$$J1 = 1 + (C2 \times Co_T/Mn) \quad 4.22$$

$$J2 = 1 + \exp(12300/Tc - 40.53) \quad 4.23$$

$$J3 = 1 - 1.213\times10^{-4} \times(I_c - 550) + 1.278\times10^{-5} \times(I_c - 550)^2 \quad 4.24$$

And where:

C1	=	A constant	
C2	=	A constant	
Tc	=	Temperature	°C
I_c	=	Current Density	amps/m²
H	=	Hydrogen ion conc.	kmole/m³
Mn	=	Manganese conc.	kmole/m³
Co_T	=	Total Co conc.	kmole/m³

The number of moles of hydrogen evolved may also be calculated from the current efficiency and the total current if hydrogen gas is the only other product at the cathode. Using the above equation, the current efficiency is a function of pH (Mn is a function of pH via the equilibria). It is then possible to find the particular pH in the cathode compartment that balances the amount of hydrogen evolution, via the current efficiency equation and the total current, with the net flux of hydrogen into the

compartment. An algorithm for doing this based on a Newton-Raphson scheme is implemented and is presented in Appendix H.

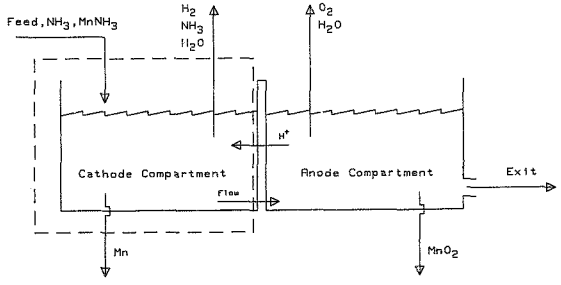


Figure 8. Cathode Hydrogen Ion Balance Envelope.

4.7 Complete Cell

To advance to this point in the model it has been necessary to take values for the current efficiencies and water and ammonia losses. This was done to calculate the mass balance over the cell and to then obtain the anode conditions. It is now possible to calculate these values from the newly found details of the cathode and anode.

The new cathode current efficiency is calculated from the amount of hydrogen gas evolved with the following equation using the Faraday constant.

$$\xi_c = 1 - BB \times Hprod \qquad 4.25$$

where $BB = 9.65 \times 10^7 / I$ s/kmole

Hprod is the production rate of hydrogen gas and is in kmole of hydrogen atoms per second.

The new anode current efficiency is estimated from the equation presented by Rodrigues (1983):

$$\xi_a = 1 - 1.58 \times Mn / [I_a]^{\frac{1}{2}} \qquad 4.26$$

where I_a is 1000 amps/m^2 on the plant.

The losses of water and ammonia from the catholyte and the anolyte are obtained by assuming that the hydrogen and oxygen that are evolved are

saturated with the appropriate species. In the anode there are is no free ammonia, so:

$$\text{(moles } H_2O \text{ lost)/(moles } O_2 \text{ evolved)} = g_w/(1-g_w) \qquad 4.27$$

In the cathode both ammonia and water vapour are lost in the hydrogen as it evolves, so the equations are:

$$\text{(moles } H_2O \text{ lost)/(moles } H_2 \text{ evolved)} = y_w/(1-y_w-y_n) \qquad 4.28$$

$$\text{(moles } NH_3 \text{ lost)/(moles } H_2 \text{ evolved)} = y_n/(1-y_w-y_n) \qquad 4.29$$

where the y_i and g_i are the mole fractions in the evolving gases for water vapour(w) and ammonia(n). Rodrigues (1983) has fitted the following equation from steam tables for the water vapour.

$$y_w = -1.267 + 0.00428 \times T \qquad 4.30$$

The same equation is used for g_w. For the ammonia equilibrium, it is assumed that Henry's Law applies. Thus the mole fraction of ammonia in the gas is proportional to the concentration of the ammonia in the solution. The proportionality constant is calculated in Appendix K, using data from Perry and Chilton (1973). The equation becomes:

$$y_n = 0.0367 \times [NH_3 + NH_4] \qquad 4.31$$

Thus new values for the losses of water and ammonia are found. The entire calculation is then repeated with the new values in an iterative manner until the the values used equal those calculated, and convergence occurs. At this point all equations are satisfied.

In the calculations of the cell house it is also necessary to know the densities of the solutions in the feed stream, the anode compartment and the cathode compartment. These values have been measured on the plant and are 1185, 1160 and 1165 kg/m^3 respectively. They are taken to be constants, i.e. independent of temperature or concentration.

In this way all the important ope[illegible] e cell house are determined. The concentration of Mn^{2+} in the [illegible]partment must now be compared with the maximum allowed by the hydrox[illegible] precipitation reaction. The equation used is:

$$Mneq = H^2/Kmn \qquad 4.32$$

where Kmn is the solubility product ratio presented in Appendix A. If Mn > Mneq then manganese hydroxide precipitation will occur, and conditions calculated by the model are incorrect. The model must be rerun with different variables.

4.8 Cell Voltage

The cell voltage is the sum of five components, namely:

1. The potential between the anode and the anode electrolyte, which consists of the the standard electrochemical potential plus the overpotential for the reaction.

2. The ohmic potential drop across the anode electrolyte from the anode to the membrane.

3. The ohmic potential drop across the membrane from the anode side to the cathode side.

4. The ohmic potential drop across the cathode solution from the membrane to the cathode.

5. The potential between the cathode electrolyte and the cathode. This consists of the standard electrochemical potential plus the overpotential.

4.8.1 Cathodic and Anodic Potentials

The total electrode potentials are the sum of these equilibrium values and the overpotentials. The electrochemical potential drops are given by

$$E_i = E_i^o + RT\ln\{I_i/(C_i \times I_i^{ex})\}/F \qquad 4.33$$

where E_i^o are the standard electrochemical potentials given in Section 4.1, I_i are the current densities and C_i is the concentration of the charged reacting specie, i.e. H^+ at the anode and Mn^{2+} at the cathode.

Nicol (1976) gives a value for the exchange current density for oxygen evolution on a lead anode of:

$$I_a^{ex} = 10^{-12} \text{ amps/m}^2 \qquad 4.34$$

Hurlen and Valand (1964) show that the exchange current density for the cathode reaction is a function of temperature and is given by:

$$I_c^{ex} = 7.1\times10^{10} \times T \times \exp(-6300/RT) \quad \text{amps/m}^2 \qquad 4.35$$

The ohmic potential drop across the membrane has proved too difficult to be modelled. The value measured on the plant varies between 1.0-1.5 volts. In the model it is taken to be 1 volt. The absolute cell voltage value is not very important as it is mainly used for comparisons between different operating points.

4.8.2 Ohmic Potential Drops

The ohmic equation is:

$$V_i = (L_i \times I_i)/\kappa_i \qquad 4.36$$

The average distances between the cathode and membrane, L_c, and the membrane and anode, L_a, on the plant are about 3×10^{-2} m.

Tozawa, Sasaki and Umetsu (1982) present the following equation giving the electrical conductance (mhos/m) of an electrolyte containing sulphuric acid, as a function of the hydrogen ion concentration.

$$\kappa_a = (17.6 \times H) + 34.7 \qquad 4.37$$

Karelov, Doroshkevich, Khudyakov and Gryaznukhina (1980) present an equation obtained by regression giving the electrical conductance (mhos/m) of an ammonium sulphate electrolyte.

$$\kappa_c = -4.00 - 0.28 \times NH_3 + 10.19 \times NH_4 + 4.03 \times Mn + 2.27 \times (T-273) \qquad 4.38$$

The equation was developed for zinc and copper, but assuming that manganese behaves similarly to zinc enables one to use it. The variables in the above equation are the concentrations of NH_3, NH_4^+ and Mn^{2+}, and the temperature in °K.

5 OVERALL PLANT BALANCE

The complete plant model may now be calculated. To do this values for certain operating variables must be chosen. It is by the judicious choice of these variables that the overall process may be optimised. These variables are the following:

1. Flowrate of solution. Assumed constant throughout plant.

2. Total current supplied to the cell house.

3. Concentration of sulphate. Assumed constant throughout plant.

4. Concentration of ammonia.

5. Leach pH, in the range 6.0-7.2 .

6. Sulphide section pH, in the range 6.0-7.2 .

7. Cell house feed pH, in range 6.0-8.0

8. Ammonium sulphide addition rate in sulphide section.

The model uses the concentrations of sulphate and ammonia species to calculate the solution equilibria in the various sections. These two concentrations are, unfortunately, not easy to visualise, and are not normally used on the plant. The people who operate the plant prefer to think in terms of the total ammonium sulphate concentration, in kg/m^3, and the total manganese concentration in the leach, in kg/m^3, and would therefore like to specify these values. Unfortunately they are direct outputs of the model, and one would therefore be trying to specify the

outputs and calculate the inputs. This is not how a true model should work. A compromise can be made however. From specifications of the concentrations in kg/m^3 of ammonium sulphate and manganese in the leach, it is possible to estimate the concentrations of ammonia and sulphate species in solution. Using these estimated values as given values the actual concentrations of manganese and ammonium sulphate can be calculated. These values will not be too far from the specified values. Therefore the model has been changed to accommodate this: instead of points 3 and 4 above being specified, the concentrations of ammonium sulphate and manganese in the leach are specified in kg/m^3.

The pH values in the sulphide section and the cell feed are not properly independent as they are mostly decided by the leach pH. Therefore values are chosen to be those experienced on the plant relative to the leach pH. The temperatures in the plant are difficult to control to absolute values and for the model plant values are used. It has been shown by Rodrigues (1983) that the optimum temperature in the cell house for the cathode current efficiency is 39°C.

A standard set of operating variables is used to give a reference operating state to which comparison may be made. This set of variables has been chosen to mimic the operating conditions on the plant as far as possible, to make this standard set as more meaningful, and potential improvements more relevant. The set of operating variables is given in Appendix J.

There are also several constants in the various equations used whose values may be varied so that the model results compare to the actual operating data. These include diffusion coefficients for the hydrogen and ammonium ions, constants in the equations describing the kinetics of various processes as well as the equilibrium constants and ratios. Once

they have been determined to give the closest agreement to the plant they must not be changed. The values used for the constants are also given in Appendix J.

The procedure then followed in calculating the model is as follows: first the leach section is solved. The ore feed rate can only be determined once the cell house return stream is known, but this is not required for the leach conditions. The sulphide precipitation section is then calculated and the level of impurities found (Co_T). The impurity level prior to the sulphide section is not known and hence the efficiency of the precipitation is not known. This is not attempted as the Co level is of importance only in the cell house where it influences the kinetics of the plating. The cell house section is then calculated to find the production rates of products and waste products, and the concentrations in the cell house return stream to the leach. The leach efficiency is then calculated and hence the ore feed rate can be found, allowing for the loss of manganese in the solution entrapped in the leach filter cake. The amount of this loss is proportional to the concentration of the manganese in the solution.

In order to understand the procedure more fully, reference may be made to the logic flow diagram in Figure 2 on page 9. Thus all values have been found that have bearing on the profitability of the plant.

6 COSTING

The following operating costs have been modelled to obtain a reasonable total operating cost and hence net operating profit:

1. The cost of ore. The manganese ore is bought from an outside source and is then treated on the plant before being used. One can then find a cost per ton of ore that reflects this. The cost of the ore is the biggest cost of the operation.

2. Cost of power. The current used to plate the manganese carries a power cost. This can be estimated by calculating the volt drops across the cathode, cathode solution, diaphragm, anode solution and the anode. The total volt drop together with the current gives a power that can be costed at so many cents per kilowatt hour. The cost of power is the second biggest cost and is of the order of the cost of the ore. The equations for estimating the volt drops may be examined in Section 4.8.1.

3. Cost of make-up ammonia. Ammonia is lost in the cathode compartment and in the solution lost in the leach filter cake. All ammonia lost must be made up. Some is accounted for in the streams of ammonium hydroxide that are used in pH control. Estimating the loss in the solution in the filter cake to be proportional to the ammonia concentration and adding in the cathode loss gives a value that may be costed at current selling prices of ammonia.

4. Cost of make-up sulphate. Sulphate is also lost in the filter cake. This loss is estimated in the same way as the ammonia lost in the filter cake.

The revenue for the plant comes from the sale of the plated manganese. A value for this per ton of manganese can be found from the London Metals Exchange. The net profit can be calculated from the revenue minus the sum of all costs. This gives units of R/hr. It is also possible to divide this value by the production rate of manganese to give R/ton of manganese produced. This is more a measure of the efficiency of production. The values used in the costing of the plant are given in Appendix I.

The net profit value obtained is used as the objective function in the optimisation routine. It must be emphasised that this value is useful only for a comparison between two situations as to which of them is "better" than the other. It can not be used in an absolute sense at all as there is much costing information that is ignored, such as fixed costs, interest costs and labour costs etc.

7 OPTIMISATION

7.1 Introduction

An optimisation problem can be thought of as the maximising or minimising of some value, called the objective function, which is a function of some variables, by judicious choice of those variables. In this model the objective function is to be maximised and is either the net profit, or the profit per unit manganese produced, as discussed in Section 6.

The variables are, in general, those listed in Section 5. As an optimisation problem gets more difficult with an increase in the number of variables, it is desirable to reduce this number as much as possible.

The addition rate of ammonium sulphide, determined from equilibrium and mass balance considerations, need only be enough for the precipitation of the impurities and therefore need not be very much. Actually, more than this is required for kinetic reasons. As the model is not based on kinetic considerations in this area it is unable to make relevant predictions about this particular variable. Therefore the ammonium sulphide addition rate is taken as the actual rate on the plant and is held constant.

Although there is pH control on the solutions in the sulphide tanks and on the solution flowing into the cell house, the pHs in these two area are not truly independent variables. The values are largely determined by the pH in the leach tank, the pH control can only fine tune the value. For instance it would be impossible to have a pH in the leach of 7.2 and

one in the cell house feed stream of 6.0 without massive amounts of acid being added. It is observed on the plant that the pH in the sulphide tank is about 0.35 units higher than that in the leach tank. This is mostly due to the temperature difference between the leach and the sulphide section which affects the equilibria. The pH in the feed stream is normally slightly lower than in the sulphide tank as SO_2 is added to plate manganese in the desired crystalline form.

For these reasons the pH in the leach is kept as an independent variable and the pHs in the sulphide tank and the feed stream are allowed to vary linearly with this pH as follows:

$$pH_s = pH_l + 0.35 \qquad 7.1$$

$$pH_f = pH_s - 0.02 \qquad 7.2$$

The total number of independent variables is thus reduced from eight to five, consequently reducing the difficulty of the optimisation problem.

Two approaches to the optimisation problem are tried. The first, discussed in Section 7.2, considers the model as a "black box" with several inputs, the variables, and one output, the objective function. No information about the structure of the model is used, but the effect of all variables is considered. The second approach, discussed in Section 7.3, uses information about the structure of the model to concentrate on a few variables and their affect on a particular section of the model only.

7.2 Overall Model Optimisation

The problem is increased in difficulty since most of the variables that affect the system are constrained to lie within specific ranges and may not vary outside those ranges. Should an optimum point lie on one of these boundaries, finding it with a numeric algorithm is not easy.

The constraints that occur include that on the leach pH. Should it go too high, the algorithm calculating the leach equilibria fails. Another real limit in the leach occurs when the calculated manganese concentration exceeds the equilibrium value. This is similar to a process in the cathode where the solubility product for $Mn(OH)_2$ can be exceeded, resulting in precipitation which clogs up the diaphragm. None of these constraints are constant or independent, they are all functions of the other variables and may not be violated.

Most efficient optimisation algorithms make use of derivative information about the objective function to aid in finding the optimum point. Since analytic derivatives are not available from the model, the next best class of optimisation algorithm uses numerical estimates of the slopes. Most optimisation routines in this class can only work with unconstrained regions. To handle the constraint it is possible to return a zero function evaluation for those points beyond it. This results in a very ill-conditioned shape for the objective function with an effective infinite slope at the constraint. It is impossible to smooth the curve at this point since the position of the constraint can only be found by trial and error, and if one is beyond this point it is not known how far one is from it. Hence should the optimum point lie close to or on the constraint then the routine may calculate very large slopes which will send it completely out of the region, and the routine will fail. This is true of the method of Powell (1964) and the quasi Newton-Raphson method which were tried.

A method that appears to work on a limited scale is the Simplex method of Nelder and Mead (1965). The method does not use any slope information at all. This makes it very inefficient for "nice" problems, but has the advantage here in that it cannot get confused by spurious slopes. The method appears to work when applied to two variables at a time, but has trouble dealing with large numbers of variables. The algorithm is taken straight from Nelder and Mead (1965) and is not presented as a better algorithm was obtained.

When applied to three or more variables the Simplex routine does not converge to the same optimum when started from different initial simplexes. It converges when striking a constraint instead of proceeding along the constraint to a better point. A variation of the Simplex routine, called the Complex algorithm developed by Box (1965) for constrained optimisation problems was then applied. This method consistently finds *the same optimum point from* different initial configurations, and is therefore recommended. A FORTRAN 77 program listing of this algorithm is presented in Appendix L.

The approach in this section consisted of obtaining the objective function value for a standard set of variables. This standard set represents the actual plant operating conditions as closely as possible, and is tabled in Appendix J. The standard function value is then compared to those obtained from the optimisation routine for various limits on the explicit variable constraints. For instance in one case the flow rate may be allowed to vary within ten percent of the standard value, and in another case it may be allowed to only vary by a maximum of five percent.

Various combinations of variables and explicit limits are tried. In some cases some of the variables are held constant to see the affect on the others. In this way it possible to obtain an idea of the sensitivity of the model to the various parameters.

As there are two potential objective function values, namely in units of R/hr or R/ton manganese produced, the above strategy is followed for both. Optimising the first value is akin to making as much money as possible without caring about the efficiency of the operation. This would be desirable, for instance, where the demand for the product exceeded the supply and there was no shortage of ore. Optimising the second value is useful when economic competition is strong and one wishes to minimise costs and produce as efficiently as possible.

7.3 Cell House Optimisation

Instead of examining the model in its entirety one can use results from the model to identify areas of importance. From the costs involved it is clear that the two major factors involved are the leach efficiency and the current efficiency on the cathode. The leach efficiency is primarily a function of the pH as discussed in Section 2.1. The current efficiency only will be discussed here.

The pH in the cathode compartment varies so as to balance the hydrogen evolved with the net hydrogen flux as discussed in Section 4.6. An increase in the net flux causes the concentration of hydrogen ions to increase, lowering the pH, which results in an increase of hydrogen evolution and the cell reaches a steady state at a lower, and more inefficient, pH. A reduction in the net flux means the hydrogen ion concentration

gets reduced and the rate of hydrogen evolution is also reduced, hence more manganese is plated.

The easiest way to control the hydrogen flux through the membrane is to vary the flowrate through the membrane. An increase in the flowrate decreases the hydrogen flux and vice versa. (Note that the direction of flux is counter to that of the flow.) It is therefore obvious that a high flowrate through the membrane is desirable. Unfortunately as the pH in the cathode compartment rises to effect the above strategy it reaches the point of manganese hydroxide precipitation, which blinds the membrane and has a disastrous effect on the cell performance. One can therefore say that the optimum flowrate lies on the constraint of manganese hydroxide production. This constraint also determines the maximum pH at which the cell may operate.

The question that now requires examination is what is the best manganese concentration in the cell. The kinetics of plating, and hence the hydrogen evolution rate, is dependent on the manganese concentration. The pH at which manganese hydroxide forms is also dependent on the manganese concentration. Is it best to have a low manganese concentration and a high optimum pH, or a high manganese concentration and a low optimum pH? One can analyse the kinetic equation governing the cathode subject to the constraint that we have the onset of manganese hydroxide precipitation. This gives us the following two equations:

$$\xi_a = 1/(1 + C1 \times (1 + C2/Mn) \times H/Mn) \qquad 7.3$$

where

$H = H^+$ concentration

Mn = Mn^{2+} concentration

$C1, C2$ = constants

and

$$Kmn = H^2/Mn \qquad 7.4$$

which is the equilibrium equation for the reaction:

$$Mn^{2+} + 2H_2O \equiv Mn(OH)_2 + 2H^+$$

using the equilibrium ratio.

Substitute equation 7.4 into 7.3 to get an equation for current efficiency as a function of manganese concentration. Taking the derivative with respect to Mn and putting equal to zero one can solve for the Mn values. There are two solutions of Mn. One is negative and of no practical use, the other has:

$$Mn^{-3/2} = 0$$

This implies a maximum as Mn tends to infinity. It is therefore shown that it is best to have a high manganese concentration inside the cells. In practice there are other constraints on this such as the quality of the metal produced etc. The above analysis has ignored the effect of a higher manganese concentration elsewhere in the process, such as the losses in the filter cake, and the effect on the conductivities of the solutions. It should therefore be checked using the whole model.

8 RESULTS AND DISCUSSION

8.1 Introduction

The first thing that must be realised about the model is that it is a steady-state model. This implies that it can only make statements about the average performance of the plant. It cannot predict the intermediate unsteady conditions in the plant immediately after a change, only the final steady state. Hence from a control point of view it could be used to determine the set points that would then be used in a control strategy. The model is also, in a sense, non-unique: levels of performance in the plant can be achieved by various sets of variables. In answer to the question "The plant is operating badly, what must I do?", the model can't give an answer. The answer must be found elsewhere, then it can be checked using the model.

The model can be used to identify which of the operating variables the plant is most sensitive to. These variables would most probably require the most control. A qualitative help to controlling the plant could also be obtained in situations where it is unclear how the plant will react. Using the model to predict the outcome of a change will help in either preventing or encouraging such change as the case may be. The model has therefore been designed so that these problems can be quickly and easily solved once they arise.

The model's most important value, however, lies in being able to predict normal steady-state operation at a particular set of operating variables, and to compare this operation with the operation at a standard set of variables. A comparison of this nature could provide information on

whether it is worth trying to improve a section at a particular cost. Conversely, the amount of effort worth expending to improve performance given the expected improvement may be determined. This sort of sensitivity analysis is examined with greater detail in the following sections on Optimisation.

When deriving a model it is usual to have some kind of comparison between predicted values and corresponding measured values, in order to see how accurate the model is. Many comparisons of this type have been made in the development of the model and they have been concerned with the particular sections involved. With respect to the model as a whole there are some parameters, tabled in Appendix J, together with some equilibrium constants, in Appendix A, that have been fitted to give a close agreement between the model and the experimental, or plant, values. Unfortunately to test these fitted parameters, and hence the model, it is necessary to have experimental values at some different conditions to compare with what the model would predict for that situation. These experimental values are not available. As a pilot plant is not available for such tests it would entail changing the operation of the full scale plant for a period of time. This is obviously impractical, and the model, as a whole, is therefore untested, even though its parts may be well founded.

8.2 General Model Results

There are number of aspects to the model that can provide insight into the functioning of the plant, especially when contrasted with the normal intuitive operating philosophy about the plant.

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8.2 General Model Results

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A great deal of effort is expended on the plant in maintaining a constant strip. The strip is defined as the difference in total manganese concentration between the cell house feed stream and the cathode compartment. It is believed that this must be maintained at a constant value for correct operation. From the point of view of the model, the strip has no physical effect by itself. It does reflect the rate of production of manganese but only in its relation to the flowrate. It is the concentrations in the cathode compartment that are far more important, and it is conceivable to have two situations with the same manganese concentrations, but with differing flowrates and strips having the same production rates and current efficiencies.

A typical graph of the leach efficiency vs the leach pH from plant data shows the leach efficiency decreasing gradually as the pH increases up to a particular value. Above this value the leach efficiency decreases suddenly and rapidly as the pH increases. This curve is easily explained as the result of two different processes dominating in two regions. As discussed in Section 2.1 the gently sloping section on the left of the curve is caused by the disproportionation of Mn_2O_3 into MnO which can leach, and MnO_2 which does not leach. The sudden steep drop of the leach efficiency occurs when the desired operating pH of the leach is too high. As more manganese ore is added to react with the solution to increase the pH to this point, the manganese in solution approaches the equilibrium maximum with respect to the manganese hydroxide precipitation reaction. The manganese in the ore is unable to leach into solution and the leach efficiency appears to drop suddenly.

The following point indicates that the solution equilibria used in the model accurately indicate the trends of the species in solution. It is observed on the plant that the solution emerges from the final leach tank at a pH of about 6.55 at a temperature of about 50°C. It then cools down to about 44°C at a pH of 6.9 in the sulphide tanks. Although this stream

does have ammonium hydroxide added to it for pH control, much of the difference is due to the temperature change. This was confirmed by measuring the pH of a sample of solution from the cathode compartment at 40°C and then at 20°C after it cooled down. The pH increased by an amount that corresponds to a drop in the hydrogen ion concentration to a fourth of its initial value. On heating the solution back up to 40°C the pH increased again. The solution chemistry used in the model predicts this phenomenon merely from the temperature dependance of the equilibrium constants used.

The cell voltages predicted by the model are compared with those measured on the plant, and are found to agree fairly well except for the volt drop over the membrane. Under the standard set of plant operating variables the predicted cathode potential, anode potential, cathode compartment volt drop and anode compartment volt drop of 1.69v, 2.22v, 0.48v and 0.66v compare favourably with the corresponding values, measured by the author, of 1.6v, 2.0v, 0.45v and 0.55v respectively. The average volt drop across the membrane is 1v. The model is unable to predict this on the simple basis of an average solution conductivity in the membrane.

The volt drops on the plant were measured with a Luggin capillary filled with saturated KCl solution, a multimeter and a calomel electrode. It was necessary to add or subtract the standard electrode potential associated with the calomel electrode from the measured values. They are not very accurate as the capillary had to be inserted into the compartments concerned and moved about from electrode to membrane. The lack of space between the wooden frames that support the two compartments made it difficult to know where the tip of the capillary was.

To complement the voltage measurements, samples from the cathode and the anode compartments were taken and their conductivities measured. These

values agreed within 5% with the values calculated for the sample conditions using the conductivity equations presented in Section 4.8.2. These values are not presented as the sample temperature in the laboratory was not the same as on the plant and therefore the measured conductivities are not applicable.

The costs that are included in the model are intended to reflect the expenses and profit of the production only. Overheads such as wages, interest on capital, and costs of departments such as marketing and sales are not included. Other costs which are not included but which do relate to production are cost of maintenance and cost of pumping. For these reasons the profit value returned by the model means nothing by itself. Its only use is as a means of comparison between different plant operating conditions. Even then the absolute difference is all that may have meaning. Differences measured in percentage change are irrelevant since the base value may be very different.

8.3 Single Variable Optimisation

The model makes a clear statement that the greater the flow rate in the cell, the higher the pH in the cathode compartment, and the better the cathode current efficiency. Rodrigues (1983) has already raised this point, but it bears repetition for emphasis. A greater flow through the membrane reduces the back migration of hydrogen ions. As hydrogen is stripped from the cathode compartment the pH increases, reducing the stripping rate until it equals the net hydrogen flux again. This balance is described in more detail in Section 4.6. A lower stripping rate in effect means a better current efficiency. The limiting factor in raising the flowrate is that eventually the pH increases to the point where precipitation of manganese hydroxide occurs.

As there is a great deal of variation in the values found from the literature for the solubility product constant describing the reaction producing manganese hydroxide, it was decided to fit this value within the range of the literature values. The value chosen together with the standard set of operating variables results in a predicted operation just within the limit set by this reaction. This has been done to mimic the procedure on the plant. There the major control variable in the cell house is the flowrate to each cell. The flowrate is usually held as high as possible, with the maximum value being determined by the onset of manganese hydroxide precipitation. The plant operator does keep a margin of safety, but this does not affect the argument.

This operation close to a physical limit has some interesting results for the effect of changing one variable at a time only. (The results of changing more than one variable simultaneously are examined in Section 8.4 below.) Keeping the remaining variables at their values set out in Appendix J, one gets:

1. The behaviour of the flowrate (Q) in the model is described above. Its best value is high, and is constrained by the precipitation in the cells.

2. The concentration of ammonium sulphate (AMSLPH) in the solution also follows this trend. Its best value is a maximum value and is constrained by the same precipitation reaction. If the concentration goes above this limit then more manganese in the cell is complexed with the ammonia and is not available for plating. This reduces the current efficiency which causes more hydrogen to be evolved. The pH then rises more than the Mn^{2+} concentration falls and precipitation of manganese hydroxide occurs.

3. The pH in the leach tank (PHLCH), and hence the pHs in the sulphide tanks (PHSUL) and the cell house feed stream (PHF) which are linked to it, follows the same trend. It has an optimum maximum value which is determined by the precipitation of manganese hydroxide. The reason for this is not clear as the pH has a subtle effect via the relationship between manganese and ammonia upon which it has a large influence.

4. The manganese concentration in the leach (MANGAN) determines the concentration in the cathode compartment provided the flowrate is constant. Therefore, as examined in Section 7.3, the higher the manganese concentration in the plant, and hence in the cathode compartment, the better. Of course other constraints not taken into account here may exist which limit the concentration. A surprising result from the model is that the manganese concentration must be greater than some minimum value to prevent manganese hydroxide formation. As described above with respect to the effect of ammonium sulphate, a low Mn^{2+} concentration results in a pH increase to cause the precipitation.

5. The total current (I) has two effects. It must be greater than some lower limit or else precipitation occurs in the cells. A lower current produces less manganese which results in a higher manganese level in the cells and precipitation occurs. At this lower limit the plant will be running most efficiently. An increase in current reduces the efficiency, but increases the production rate of manganese. This increase is greater than the decrease in efficiency and the plant will make more money at the higher current.

The only variables that can be changed individually on the plant to improve performance are therefore: increasing the manganese concentration or increasing the current. It must be stated however that in practice variations in the other variables can be tolerated as a result of the

margin of safety kept by the plant operator. This analysis holds when there is no safety margin at all. Hence the five variables involved in the analysis are at their respective limits in the standard set of variables listed in Appendix J.

The limits on the variables are not constant. They depend on the values of the other variables. Hence by changing the variables simultaneously, the limits on the individual variables are changed, permitting the changes to occur beyond the previous limits.

8.4 Multi-Variable Optimisation

The results of the optimisation runs are tabled at the end of this section. Optimisation by choice of five variables is presented in Table 1, by choice of four variables in Table 2, by choice of three variables in Table 3 and by choice of two variables in Table 4. The variables used in the optimisation are the five variables isolated in Section 7.1. The pH used is that in the final leach tank, although it must be remembered that for the purposes of the optimisation runs the pHs in the sulphide tanks and the cell house feed stream are determined by the leach pH from the equations 7.1 and 7.2.

In each table the separate combinations of variables are grouped together and the group numbered. Within each group the results of optimising the objective function with units of R/hr are listed first, and then the results of the objective function with units R/ton. These latter values also have a "t" written after them. A "c" after a variable in a table indicates that it was held constant, an "l" after a variable indicates that it lies on the lower limit of its explicit range and a "u" indicates that it lies

on the upper limit of its range. Some runs were repeated with different explicit limits to check trends.

The explicit limits referred to here are not of the same type as those referred to in Section 8.3. Those are real limits imposed by the model and are only defined for changes in one particular variable at a time. The explicit limits mentioned in this section are arbitrary constraints on the range of values that the variables are allowed to take.

A detailed output of the model for the standard set of operating variables and parameters is presented in Table 5. The standard objective function values taken from this table are 3081.35 R/hr and 1035.55 R/ton. These values are the bases for the comparisons of the plant's performance.

The analysis of the optimisation exercise starts by looking at the case where all five variables were allowed to vary by 10% on either side of their standard values. This is group 1 in Table 1 at the end of this chapter. In the case of the first objective function, abbreviated F., in (R/hr) it can be seen that the flowrate Q, the current I and the manganese concentration in the leach are all at their upper limits. The ammonium sulphate concentration stands at its lower limit, while the pH in the leach, and hence in the sulphide tanks and the cell house feed stream, is higher than its standard value. The F. value is 3592.06 which is better than the normal value of 3081.35. This situation is contrasted by that which arises when using the second objective function (R/ton). Here the flowrate and the manganese concentration are still at their upper limits, but the current is at its lower limit. The ammonium sulphate concentration is also at its lower limit and the pH is lower than normal. The F. value is 1053.03 compared to 1035.55.

The two other groups in Table [illegible] runs for differing limits of the variables show similar trends, as do the combinations of four variables, with PHLCH or I held constant, in Table 2, except for group 1 in Table 2. Here the pH is fixed so that the ammonium sulphate increases to a model-determined limit to increase performance.

To see the relationship between the flowrate, the ammonium sulphate concentration and the pH, several runs were done with current, I, and manganese concentration, MANGAN, held constant. These runs are presented in group 1 of Table 3. Again for both objective functions the flowrate increased to its explicit limit. The ammonium sulphate concentration decreased to its lower limit. The pH increased to a model-determined limit. These results show no change in behaviour from those for the full five variable optimisation. The remainder of runs in Table 3 agree with results as found.

To obtain a better idea of the relationships between the variables, they were taken two at a time for the most interesting cases and the results are listed in Table 4 and discussed below:

1. In group 1 for Q vs AMSLPH the flowrate increased to its upper limit whilst the ammonium sulphate concentration decreased, for both objective functions. The values for AMSLPH are not at their lower explicit limits and therefore indicate that the values are at a maximum real limit defined by the model. The effect of the higher flowrate is to lower the maximum (and best) concentration when compared to the standard set of variables. The net result is a better operating condition.

2. In group 2, AMSLPH is varied against MANGAN. The results are similar to those in group 1 and MANGAN behaves in a similar fashion to Q in the above paragraph. In this case the model-determined limit on AMSLPH

is above its standard value. In groups 1 and 2 therefore the ammonium sulphate concentration is not as important as the flowrate or the manganese concentration.

3. In group 3, Q is varied against MANGAN. Here the manganese concentration is more important than the flowrate since the manganese goes to its upper limit and it is left to the flowrate to be subjected to the model-determined limit.

4. In group 4, AMSLPH is varied against the leach pH. For both of the objective functions the ammonium sulphate concentration decreases to its lower explicit limit and the pH increases to a model-determined limit. This indicates that the ammonium sulphate concentration has a greater effect on the performance than the pH.

5. MANGAN is varied against leach pH in group 5. As expected the manganese increases to its upper limit and the pH is model-determined to a value greater than the standard value.

6. Group 6 presents Q vs I. For the first objective function the current increased to its limit and for the second the current decreased to its limit. In both cases the flowrate was model-determined although the limiting value for the flowrate in the first case was greater than in the second. This indicates that the total current is more important than the flowrate. The two variables where then allowed to vary to a greater degree when optimising the second objective function. A true optimum point was found, i.e. it does not lie on an explicit limit. The maximum however was very shallow, having the same value to six significant figures as the constrained optimum.

7. In group 7, I is varied against AMSLPH. The current stands at its upper limit for the first F. and at its lower limit for the second F.. In the first case the model determined limit for the ammonium sulphate concentration was slightly higher than the standard value.

In the second case this limit was driven downwards by the current, with a resulting low ammonium sulphate concentration. The benefits of a low current out-weigh those a high ammonium sulphate concentration.

The case of the second objective function (R/ton) in point 6 above is interesting in that it is the only case where at least one of the variables is not at an explicit limit. The values for the flowrate and the current are at model-determined limits within their permitted ranges. This implies that the relationship between these two variables does have a true optimum point that is within the range of feasible operation. The relationships between the other variables all indicate that the best conditions lie far away from the standard one. Such conditions in practice will introduce extra constraints and features not covered by the model and therefore the model may break down. Therefore these variables must be artificially constrained. This is the reason for the introduction of the explicit limits. In these cases the model is indicating directions that may be fruitfully pursued, but it is not clear exactly how far one may proceed in each direction. In the particular case of the flowrate vs the total current for most efficient operation, a best point does exist, although its position still depends on the values of the other variables.

Examining the above results enables one to determine the order of importance of the variables with respect to their influences on the objective function. In decreasing order they are : MANGAN, I, Q, AMSLPH and pH. This says that where a beneficial change in one variable can only occur at the expense of a non-beneficial change for some other variable, then the change that causes the better operation will occur to the variable of higher order. An example of this is point 3 where the manganese concentration must be explicitly restrained, and the maximum value of the flowrate is determined by the manganese. The manganese therefore has a higher order than the flowrate.

The ranking also gives the order of sensitivity of the plant to each variable. For instance the plant will have a greater reaction to a 5% change in the manganese concentration than it will to a 5% change in the ammonium sulphate concentration.

To understand more clearly the differing effects of the variables in relation to the two objective functions, the two runs in group 1 of Table 4 are presented in greater detail in Tables 6 and 7. It is easy to see why high flowrates and manganese concentrations benefit both of the objective functions. A high flowrate increases the current efficiency and hence improves the second F.. It also means a greater production rate of manganese, which benefits the first F.. The manganese has such a large effect on the efficiency of the process that this effect must be included in the first F.. Of course there is a difference inside the cell. The optimum point for the second F. (R/ton) has a higher manganese concentration and a lower strip than the optimum point for the first F. (R/hr).

The current differs greatly between the two. It is high to boost production and hence revenue for the first F.. It is low when optimising the second F.. This may be strange at first sight since Rodrigues (1983) has already shown that the optimum current density in the cells is 550 amps/m^2. The current density at 46800 amps is lower than this (= 513 amps/m^2) and is therefore not as efficient as it could be. The overriding effect is again the manganese concentration. The low current strips less manganese from the cells and a higher concentration results. This has a very positive effect on the cell house performance. However, even if this effect is removed by restricting the manganese concentration in the cells to be less than 13 kg/m^3 say, the current still drops to its lower explicit limit.

The leach pH is of lesser order than any of the other variables, and hence although its optimum value always tends higher, the maximum limit is always determined by the other variables.

This leaves the ammonium sulphate concentration for discussion. Although this value is always tending higher to improve the operation, the movements of the other variables tend to drive down the maximum value that the ammonium concentration can take. This implies that the secondary effect of the ammonium sulphate through its influence on the other species is more important than its direct effect in the conductivity of the solution. The corresponding high leach pH that is usually associated with a low ammonium sulphate concentration also implies that its effect on the equilibria is more important than its effect on the leach efficiency.

8.5 Conclusions

The model appears to predict the behaviour of the plant well without any obvious contradictions. Its predictions in many cases agree with standard plant operating procedure, but the model also highlights some aspects which were not realised previously. It has some important suggestions to make with respect to the plant operating variables:

1. A high manganese concentration is desirable. The improvement in the cell house out-weighs any increase in loss of manganese in crystallised salts, or in the belt filter residue. Constraints on this variable such as the quality of manganese produced and the possibility of flaking of the metal from the cathodes could be more closely examined in order to eliminate them.

2. The flowrate should be as high as can be tolerated. This variable is the most easily controlled of the variables, and as the model predicts a fair sensitivity to it, strict control of this variable must be maintained.

3. Depending on whether maximum performance or efficiency of operation is desired, two distinct set points can be suggested for the the total current. For maximum performance the current must be kept high, and for maximum efficiency and reduced costs of operation the current must be low.

4. The ammonium sulphate concentration must be kept low. The increase in ohmic potential drop through the solution is not as important as its effect on the manganese complexes.

5. The pH in the leach tank must be kept as high as possible, the level being determined by the other variables. A low leach pH and hence good leach efficiency is not as important as the effect the pH has on the cell house.

No	Q m^3/hr	I amps	AMSLPH kg/m^3	MANGAN kg/m^3	PHLCH	F Value R/hr, R/Ton
1)	176.0(u)	57200(u)	112.5(ℓ)	34.10(u)	6.737	3592.06
	176.0(u)	46800(ℓ)	112.5(ℓ)	34.10(u)	6.5867	1053.03(t)
2)	168.0(u)	54600(u)	118.8(ℓ)	32.55(u)	6.659	3344.79
3)	192.0(u)	42452	100.0(ℓ)	37.20(ℓ)	6.4821	1058.28(t)

Table 1. Optimisation with Five Variables

No	Q m^3/hr	I amps	AMSLPH kg/m^3	MANGAN kg/m^3	PHLCH	F Value R/hr, R/Ton
1)	176.0(u)	57200(u)	128.0	34.10(u)	6.55(c)	3506.07
	176.0(u)	46802(ℓ)	115.7	34.09(u)	6.55(c)	1052.80(t)
	176.0(u)	45527	112.5(ℓ)	34.10(u)	6.55(c)	1053.84(t)
2)	176.0(u)	52000(c)	112.5(ℓ)	34.10(u)	6.6921	3429.27
	176.0(u)	52000(c)	112.5(ℓ)	34.10(u)	6.6922	1047.73(t)

Table 2. Optimisation with Four Variables

No	Q m^3/hr	I amps	AMSLPH kg/m^3	MANGAN kg/m^3	PHLCH	F Value R/hr, R/Ton
1)	176.0(u)	52000(c)	112.5(ℓ)	31(c)	6.6231	3279.72
	168.0(u)	52000(c)	118.8(ℓ)	31(c)	6.5888	3185.42
2)	176.0(u)	52000(c)	112.5(u)	31(c)	6.6232	1042.81(t)
	168.0(u)	52000(c)	118.8(ℓ)	31(c)	6.5888	1039.54(t)
3)	160(c)	52000(c)	100.0(ℓ)	37.20(u)	6.9538	3512.63
	160(c)	52000(c)	100.0(ℓ)	37.20(u)	6.9538	1048.55(t)
	160(c)	52000(c)	112.5(ℓ)	34.10(u)	6.7897	1043.31(t)
4)	176.0(u)	52000(c)	124.9	34.10(u)	6.55(c)	3370.35
	176.0(u)	52000(c)	124.9	34.10(u)	6.55(c)	1046.70(t)

Table 3. Optimisation with Three Variables

No	Q m^3/hr	I amps	AMSLPH kg/m^3	MANGAN kg/m^3	PHLGH	F Value R/hr, R/Ton
1)	192.0(u)	52000(c)	110.3	31(c)	6.55(c)	3395.00
	176.0(u)	52000(c)	118.0	31(c)	6.55(c)	3252.55
	192.0(u)	52000(c)	110.3	31(c)	6.55(c)	1047.20(t)
	176.0(u)	52000(c)	118.0	31(c)	6.55(c)	1042.36(t)
2)	160(c)	52000(c)	133.5	34.10(u)	6.55(c)	3207.63
	160(c)	52000(c)	129.5	32.55(u)	6.55(c)	3146.88
	160(c)	52000(c)	133.5	34.10(u)	6.55(c)	1040.92(t)
	160(c)	52000(c)	129.5	32.55(u)	6.55(c)	1038.43(t)
3)	175.8	52000(c)	125(c)	34.10(u)	6.55(c)	3368.48
	168.0(u)	52000(c)	125(c)	32.55(u)	6.55(c)	3229.16
	175.8	52000(c)	125(c)	34.10(u)	6.55(c)	1046.64(t)
	168.0(u)	52000(c)	125(c)	32.55(u)	6.55(c)	1041.69(t)
4)	160(c)	52000(c)	100.0(£)	31(c)	6.8740	3216.37
	160(c)	52000(c)	112.5(£)	31(c)	6.7175	3148.07
	160(c)	52000(c)	100.0(£)	31(c)	6.8740	1038.20(t)
	160(c)	52000(c)	112.5(£)	31(c)	6.7175	1037.02(t)
5)	160(c)	52000(c)	125.0(c)	34.10(u)	6.6496	3250.88
	160(c)	52000(c)	125(c)	34.10(u)	6.6495	1041.98(t)
6)	162.3	57200(u)	125(c)	31(c)	6.55(c)	3199.85
	147.1	46638	125(c)	31(c)	6.55(c)	1038.89(t)
	147.7	46804(£)	125(c)	31(c)	6.55(c)	1038.89(t)
7)	160(c)	57200(u)	123.8	31(c)	6.55(c)	3169.79
	160(c)	46800(£)	118.9	31(c)	6.55(c)	1044.43(t)

Table 4. Optimisation with Two Variables

PROCESS VARIABLES.

1. TEMP. OF CATHODE COMPARTMENT (C)	=	40.00
2. PH OF CELLHOUSE FEED	=	6.880
3. FLOWRATE (m3/hr)	=	160.0
4. TOTAL CURRENT (amps)	=	52000.
5. NO OF CELLS	=	82.
6. PH OF LEACH TANKS	=	6.550
7. PH OF SULPHIDE TANKS	=	6.900
8. TEMP. OF LEACH (C)	=	51.0
9. TEMP. OF SULPHIDE. TANKS (C)	=	44.0
10. AMMONIUM-SULPHATE IN LEACH. (g/l)	=	125.0
11. DESIRED MN IN LEACH. (g/l)	=	31.0
12. AMMONIUM-SULPHIDE ADD. (l/min)	=	4.200

LEACH SECTION.

MANGANESE	=	31.06	g/l
AMMONIA	=	1.934	kmole/m3
SULPHATE	=	1.510	kmole/m3
AMM-SULPHATE	=	124.9	g/l
LC EFFIC	=	0.865	

SULPHIDE SECTION.

MANGANESE	=	30.80	g/l
COBALT	=	1.004	ppm

CELLHOUSE.

MN OUT	=	12.02	g/l
ACID OUT	=	30.95	g/l
CUR. EFF.	=	0.681	
PH CATHODE	=	8.209	
MN Safety	=	0.000	
PROD MN	=	2975.56	kg/hr
CELL VOLTAGE	=	6.08	volts

COSTS.

PROFIT	=	3081.35	R/hr	1035.55	R/ton
AMMONIA COST	=	16.41	R/hr	5.51	R/ton
SULPHATE COST	=	52.33	R/hr	17.59	R/ton
MANGAN COST	=	795.12	R/hr	267.22	R/ton
POWER COST	=	518.14	R/hr	174.13	R/ton
REVENUE	=	4463.34	R/hr		

Table 5. Model Output: Standard Variable Set

PROCESS VARIABLES.

1. TEMP. OF CATHODE COMPARTMENT (C)	=	40.00
2. PH OF CELLHOUSE FEED	=	7.067
3. FLOWRATE (m3/hr)	=	176.0
4. TOTAL CURRENT (amps)	=	57200.
5. NO OF CELLS	=	82.
6. PH OF LEACH TANKS	=	6.737
7. PH OF SULPHIDE TANKS	=	7.087
8. TEMP. OF LEACH (C)	=	51.0
9. TEMP. OF SULPHIDE. TANKS (C)	=	44.0
10. AMMONIUM-SULPHATE IN LEACH. (g/l)	=	112.5
11. DESIRED MN IN LEACH. (g/l)	=	34.1
12. AMMONIUM-SULPHIDE ADD. (l/min)	=	4.200

LEACH SECTION.

MANGANESE	=	34.86	g/l
AMMONIA	=	1.740	kmole/m3
SULPHATE	=	1.472	kmole/m3
AMM-SULPHATE	=	110.7	g/l
LCH EFFIC	=	0.855	

SULPHIDE SECTION.

MANGANESE	=	34.63	g/l
COBALT	=	1.286	ppm

CELLHOUSE.

MN OUT	=	14.78	g/l
ACID OUT	=	31.07	g/l
CUR. EFF.	=	0.719	
PH CATHODE	=	8.125	
MN SAFETY	=	0.000	
PROD MN	=	3457.22	kg/hr
CELL VOLTAGE	=	6.23	volts

COSTS.

PROFIT	=	3592.06	R/hr	1039.00	R/ton
AMMONIA COST	=	15.82	R/hr	4.58	R/ton
SULPHATE COST	=	56.11	R/hr	16.23	R/ton
MANGAN COST	=	937.72	R/hr	271.24	R/ton
POWER COST	=	584.11	R/hr	168.96	R/ton
REVENUE	=	5185.82	R/hr		

Table 6. Model Output: First Objective Function Optimum Point

PROCESS VARIABLES.

1. TEMP. OF CATHODE COMPARTMENT (C)	=	40.00
2. PH OF CELLHOUSE FEED	=	6.917
3. FLOWRATE (m3/hr)	=	176.0
4. TOTAL CURRENT (amps)	=	46801.
5. NO OF CELLS	=	82.
6. PH OF LEACH TANKS	=	6.587
7. PH OF SULPHIDE TANKS	=	6.937
8. TEMP. OF LEACH (C)	=	51.0
9. TEMP. OF SULPHIDE. TANKS (C)	=	44.0
10. AMMONIUM-SULPHATE IN LEACH. (g/l)	=	112.5
11. DESIRED MN IN LEACH. (g/l)	=	34.1
12. AMMONIUM-SULPHIDE ADD. (l/min)	=	4.200

LEACH SECTION.

MANGANESE	=	34.36	g/l
AMMONIA	=	1.740	kmole/m3
SULPHATE	=	1.472	kmole/m3
AMM-SULPHATE	=	111.9	g/l
LCH EFFIC	=	0.863	

SULPHIDE SECTION.

MANGANESE	=	34.13	g/l
COBALT	=	1.109	ppm

CELLHOUSE.

MN OUT	=	16.76	g/l
ACID OUT	=	27.65	g/l
CUR. EFF.	=	0.766	
PH CATHODE	=	8.078	
MN SAFETY	=	0.000	
PROD MN	=	3013.84	kg/hr
CELL VOLTAGE	=	6.00	volts

COSTS.

PROFIT	=	3173.66	R/hr	1053.03	R/ton
AMMONIA COST	=	14.52	R/hr	4.82	R/ton
SULPHATE COST	=	56.11	R/hr	18.62	R/ton
MANGAN COST	=	816.03	R/hr	270.76	R/ton
POWER COST	=	460.45	R/hr	152.78	R/ton
REVENUE	=	4520.76	R/hr		

Table 7. Model Output: Second Objective Function Optimum Point

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APPENDIX A THERMODYNAMIC DATA

A.1 Equilibrium Constants

Equilibrium constants, where possible, have been obtained from the literature for the reactions concerned. There is a great deal of confusion in the literature concerning equilibrium constants, and many authors publish values that are not true equilibrium constants, but include activity coefficients. Martell and Smith (1976,1982) in particular report Log K values at different ionic strengths. In some cases the variation between dilute solutions and concentrated solutions may be 2 units. Since the definition of the equilibrium constant K is

$$K = \exp(\Delta G^{\circ}/RT) \qquad A.1$$

it may not vary with concentration. The reported variations must reflect the changes in activity coefficients. Assuming that these reported values are equilibrium ratios typified in equation B.3, one may proceed as follows. As concentrations decrease and approach very dilute solutions, non-idealities decrease and solutions become more ideal. Therefore it may be assumed that the activity coefficients approach one. In consequence in very dilute solutions the equilibrium ratio may be taken to have the same numerical value as the equilibrium constant.

To estimate the equilibrium constants at various temperatures from values at a known temperatures, the integrated form of the Gibbs-Helmholtz equation, with ΔH assumed constant, is used.

$$\ln(K_j/K_i) = (1/T_i - 1/T_j) \times \Delta H_r/R \qquad A.2$$

The data values and resulting expressions that were used in the model are presented below.

1. $Mn^{2+} + SO_4^{2-} \equiv MnSO_4$

   LogK = 2.26, 25°C, I.Strength = 0.0

   LogK = 0.60, 25°C, I.S. = 2.0

   ΔH_r = 2.1 kcal/mole, 25°C, I.S. = 0; Martell and Smith (1982)

   ΔH_r = 3.37 kcal/mole, 25°C; Nair and Nancollas (1959)

   $K_1 = \exp(5.204 + 2100(1/298 - 1/T)/1.987)$ A.3

2. $H^+ + NH_3 \equiv NH_4^+$

   LogK = 9.244, 25°C, I.S. = 0.0

   LogK = 9.40, 25°C, I.S. = 1.0

   LogK = 9.45, 25°C, I.S. = 2.0

   ΔH_r = -12.45 kcal/mole, 25°C, I.S. = 0

   ΔH_r = -13.51 kcal/mole, 25°C, I.S. = 3; Martell and Smith (1976)

   $K_2 = \exp(21.29 - 13000(1/298 - 1/T)/1.987)$ A.4

3. $NH_4^+ + SO_4^{2-} \equiv NH_4SO_4^-$

   LogK = 0.94, 25°C, I.S. = 0; Martell and Smith (1982)

   However Oblad (1975) reports values that Bijsterveld used to fit the equation:

   $K_3 = 10^{(1.05 + 0.0053(t - 273))}$ A.5

4. $Mn^{2+} + NH_3 \equiv MnNH_3^{2+}$

   LogK = 1.00, 20°C, I.S. = 2; Martell and Smith (1976)

   No value at dilute concentrations could be found.

No data for temperature extrapolation could be found.

$$K_4 = 10 \qquad A.6$$

5. $MnNH_3^{2+} + SO_4^{2-} \equiv MnNH_3SO_4$

No data could be found, so the equilibrium constant is taken to be the same as for the reaction in 1 above.

$$K_5 = K_1 \qquad A.7$$

6. $Co^{2+} + SO_4^{2-} \equiv CoSO_4$

LogK = 2.34, 25°C, I.S. = 0

LogK = 0.23, 25°C, I.S. = 3

ΔH_r = 1.4 kcal/mole, 25°C, I.S. = 0; Martell and Smith (1982)

ΔH_r = 1.74 kcal/mole, 25°C, I.S. = 0; Nair and Nancollas (1959)

$$K_6 = \exp(5.388 + 1400(1/298 - 1/T)/1.987) \qquad A.8$$

7. $Co^{2+} + NH_3 \equiv CoNH_3^{2+}$

LogK = 2.10, 30°C, I.S. = 2

LogK = 1.99, 20°C, I.S. = 0; Martell and Smith (1976)

But from Bjerrum (1957) one obtains the following constant and equation:

K = 104 at 25°C

$$K_7 = 10^{(2\,017 + 0.005(298 - T))} \qquad A.9$$

8. $CoSO_4 + NH_3 \equiv CoNH_3SO_4$

No data could be found for this complex so the equilibrium constant is taken to be the same as for the reaction in 6 above.

$K_8 = K_6$ A.10

9. $MnS \equiv Mn^{2+} + S^{2-}$

LogK = -10.5, 25°C, I.S. = 0; Martell and Smith (1976)

ΔH_r = 6200 cal/mole; Naumov, Ryzhenko and Khodakovsky (1974)

Ksm = exp(-24.177 + 62000(1/298 - 1/T)/1.987) A.11

10. $CoS \equiv Co^{2+} + S^{2-}$

ΔH_r = 16900 cal/mole; Naumov et al (1974)

The equilibrium constant for this reaction at 25°C is fitted to agree with the level of cobalt concentration on the plant. Hoover Bijsterveld (1983) calculated the permissible range to be from 3×10^{-16} to 3×10^{-14}. The value used is:

$K = 1.1\times10^{-16}$

Ksc = exp(-36.746 + 16900(1/298 - 1/T)/1.987) A.12

11. $Mn^{2+} + 2H_2O \equiv Mn(OH)_2 + 2H^+$

ΔH_r = 25930 cal/mole

ΔG_r = 20174 cal/mole; calculated from data in Perry and Chilton (1973), and Garrels and Christ (1965).

This gives $K_{298} = 1.59\times10^{-15}$

The actual value used at 298°K is changed to agree with the LogK value given in Pourbaix (1974).

Kmneq = 4.9×10^{-16} × exp(25930(1/298 - 1/T)/1.987) A.13

A.2 Equilibrium Ratios

The following ratios have been fitted by Rodrigues (1983) to experimental data for the temperature range 295-330 K.

1. $Mn^{2+} + NH_4^+ \equiv MnNH_3^{2+} + H^+$

$$Kc = \exp(-34.57 + 0.051 \times T) \qquad A.14$$

2. $NH_3 + H^+ \equiv NH_4^+$

$$Ka = \exp(40.32 - 0.064 \times T) \qquad A.15$$

3. $HSO_4^- \equiv H^+ + SO_4^{2-}$

$$Kh = \exp(8.339 - 0.0294 \times T) \qquad A.16$$

4. $Mn^{2+} + 2H_2C \equiv Mn(OH)_2 + 2H^+$

Rodrigues used the expression found by Jones (1983) which best fitted Jones's data.

$$Kmn = \exp(-66.00 + 0.1025 \times T) \qquad A.17$$

This equation does not fit the plant data, possibly because Rodrigues never tried it for pHs above 7.8. Above this pH the ratio of $Mn/MnSO_4$ changes dramatically. Rodrigues, however, did not account for the presence of $MnSO_4$. The equation used which best fitted the data is:

$$Kmn = \exp(-67.15 + 0.1025 \times T) \qquad A.18$$

A.3 Leach Efficiency

Very little explicit data is available for an accurate idea of the way the leach efficiency varies with the leach pH. The following equation is fitted to plant data and is very approximate, but it does decrease with the pH as experienced on the plant:

$$Leff = 0.8 + 0.0727 \times pH - 0.00959 \times pH^2 \qquad A.19$$

APPENDIX B ACTIVITY COEFFICIENTS

A useful and general result from thermodynamics holds that for a reaction at equilibrium of the following type:

$$S_1 + S_2 \rightleftharpoons S_3 + S_4$$

one may write the equation:

$$K = a_3 \times a_4 / (a_1 \times a_2) \qquad B.1$$

where K is defined by equation A.1. Using activity coefficients and concentrations instead of activities, one may write:

$$K = \gamma_3 c_3 \times \gamma_4 c_4 / (\gamma_1 c_1 \times \gamma_2 c_2) \qquad B.2$$

and hence obtain:

$$K' = c_3 \times c_4 / (c_1 \times c_2) \qquad B.3$$

This new variable K' is known as the equilibrium ratio to distinguish it from K the equilibrium constant. It includes the information on the activity coefficients, and permits one to solve for the concentrations. The K values are obtainable from thermodynamic data, and hence what is required are the activity coefficients.

Neutral species in solution are generally close to ideality, i.e. their activity coefficients are close to unity, and are therefore taken to be unity in this dissertation. A common convention in electrochemistry is to take the hydrogen ion concentration to be ten to the power of the negative pH. This also implies that the activity coefficient of the hy-

drogen ion equals one. Hence the only species that one need examine are the charged species.

Note: The activity of a pure substance in its standard state is one, e.g. H_2O, $Mn(OH)_{2,s}$. The method of Morris (1983) to calculate activity coefficients in strong electrolytes is as follows:

$$\mu = 0.5 \times \Sigma c_j z_j^2 \qquad \text{B.4}$$

$$-\ln \gamma_j = A z_j^2 \mu^{\frac{1}{2}} / (1 + B p_j \mu^{\frac{1}{2}}) \qquad \text{B.5}$$

in which $$A = Ao - \beta J \qquad \text{B.6}$$

$$J = \Sigma c_k \qquad \text{B.7}$$

$$B = Bo \times (A/Ao)^{1/3} \qquad \text{B.8}$$

where	Ao	= Normal solvent constant.	$(m^3/kmole)^{\frac{1}{2}}$
	A	= Modified solvent constant.	$(m^3/kmole)^{\frac{1}{2}}$
	Bo	= Normal solvent constant.	$(m^3/kmole)^{\frac{1}{2}}/Ang$
	B	= Modified solvent constant.	$(m^3/kmole)^{\frac{1}{2}}/Ang$
	c_j	= Conc. of charged species j.	$kmole/m^3$
	c_k	= Conc. of uncharged species k.	$kmole/m^3$
	z_j	= Unit charge of species j.	
	p_j	= Effective ion diameter parameter.	Angstroms.
	μ	= Solution ionic strength.	
	γ_j	= Activity coefficient of species j.	
	β	= Empirical dielectric constant.	$(m^3/kmole)^{\frac{1}{2}}$

and for sulphate solutions $\beta = 0.3$ Morris (1983).

The following two expressions give Ao and Bo for water as functions of temperature. They have been fitted to data from Manov, Bates, Hamer and Acree as reported by Kortum (1965). The "goodness" of fit can be examined in Figure 9 on page 93.

$$Ao = 0.4882 + 7.598\times10^{-4}Tc + 2.948\times10^{-6}Tc^2 + 1.185\times10^{-8}Tc^3 \qquad B.9$$

$$Bo = 0.3241 + 1.649\times10^{-4}Tc + 6.579\times10^{-7}Tc^2 + 1.030\times10^{-9}Tc^3 \qquad B.10$$

where $Tc = T - 273.15$

The ion size parameters that are used are given in Table 8 at the end of this appendix.

Molecule	z_j	p_j, Ang.	Reference
Mn^{2+}	2	6	1
$MnNH_3^{2+}$	2	6	*
Co^{2+}	2	6	1
$CoNH_3^{2+}$	2	6	*
NH_4^+	1	3	1
SO_4^-	2	4	1
S^{2-}	2	5	1
$NH_4SO_4^-$	1	4	2

1 Barner and Scheuerman (1978)

2 Oblad (1975)

* Estimated by comparison with other complexes due to lack of data.

Table 8. Molecular Parameters.

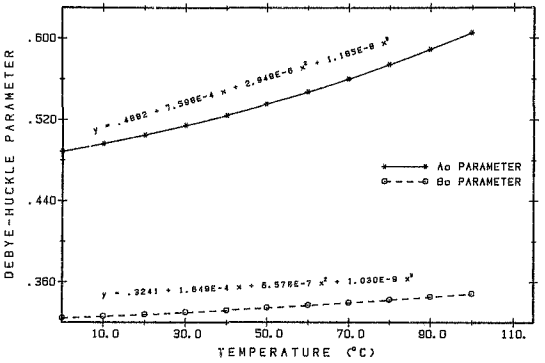


Figure 9. Debye-Huckle Constants.

APPENDIX C LEACH EQUILIBRIUM

Given the equilibrium ratios, this algorithm uses two nested iterative loops to determine the solution equilibria. The total number of variables, including the concentrations of NH_3, $MnNH_3^{2+}$ and $MnNH_3SO_4$, is nine. As these three species are minor, the algorithm starts by assuming their concentrations are zero. This leaves six unknowns to be found. Neglecting the terms for the above species in the equations describing the component balances (2.1, 2.2) gives:

$$AMM = NH_4 + NH_4SO_4 \qquad C.1$$

$$SULPH = MnSO_4 + SO_4 + NH_4SO_4 \qquad C.2$$

The electroneutrality equation retains the term for the manganese ammonia complex, and this term takes an initial value of zero. The pH is specified and therefore the hydrogen ion concentration is known. The initial values of AMM and SULPH are the specified values AMM_T and $SULPH_T$. Typical values for these specified constants are included in Appendix J.

Now substituting C.1 into 2.6 gives:

$$SO_4 = (AMM/NH_4 - 1)/K_3 \qquad C.3$$

and substituting 2.4 and C.1 into C.2 gives:

$$Mn = (SULPH - SO_4 - AMM + NH_4)/K_1 \qquad C.4$$

therefore substituting C.4 into 2.3 gives:

$$SO_4 = (-B + SQRT(B^2 - 4AC))/2A \qquad C.5$$

where $A = K_1$

$B = 1 - K_1(NH_4 + MnNH_3 - AMM/2)$

$C = AMM - SULPH - NH_4$

It is now possible to solve equations C.3 and C.5 simultaneously for SO_4 and NH_4. This is done iteratively using the Newton-Raphson scheme. Subtracting C.3 from C.5 gives a function of NH_4 that will have zero value at the solution of the system.

The function is:

$$f = (-B + SQRT(B^2 - 4AC)/2A) - (AMM/NH_4 - 1)/K_3 \qquad C.6$$

The derivative is:

$$f' = K_1/(2A) + (-2K_1B + 4A)/(4A \times DELTA) + AMM/(K_3(NH_4)^2) \qquad C.7$$

where $DELTA = SQRT(B^2 - 4AC)$.

Successively more accurate values of NH_4 are found from an initial guess according to:

$$NH_{4,i+1} = NH_{4,i} - (f/f')_i \qquad C.8$$

Once the desired accuracy in the value of NH_4 has been obtained, the remaining concentrations are easily found: SO_4 from C.3, NH_4SO_4 from C.1, $MnSO_4$ from C.2 and Mn from 2.4. These are the major species that are then used to find the concentrations of the minor species: NH_3 from 2.5, $MnNH_3$ from 2.7 and $MnNH_3SO_4$ from 2.8.

These minor concentrations are used to modify the the total component concentrations that were used in the above equations, to account for the presence of the minor species. The changes are

$$AMM = AMM_T - NH_3 - MnNH_3 \qquad C.9$$

$$SULPH = SULPH_T - MnNH_3SO_4 \qquad C.10$$

and the new value of $MnNH_3$ in the electro-neutrality equation 2.3.

The algorithm then branches back to the beginning and repeats the above procedure until the desired degree of accuracy is obtained. The two nested loops are thus an inner loop that does the Newton-Raphson iteration, and a loop around this that converges to the correct concentrations of the minor species. There is yet another loop outside these two that iterates for the activity coefficients. The initial coefficients are a guess to obtain the equilibrium ratios from the equilibrium constants. The solution equilibria is determined as above to give the concentrations. The concentrations are used to find better values of the activity coefficients as described in Appendix B, and the algorithm repeats itself.

Once complete conversion has occurred to the desired tolerances the total manganese concentration may be determined from:

$$MAN_T = Mn + MnSO_4 + MnNH_3 + MnNH_3SO_4 \qquad C.11$$

APPENDIX D SULPHIDE EQUILIBRIUM

D.1 Electrolyte Species

The algorithm used here is similar to that used in Appendix C. The differences between the two methods lie in the equations that are used, and the presence of the cobalt species. As the concentrations of the cobalt species are very small (< 5 ppm), the assumption is made that they do not influence the concentrations of the other species. The equations for the electrolyte species are derived as follows: One has

$$MAN = Mn + MnSO_4 \qquad D.1$$

in the place of C.1, where MAN takes the initial value of MAN_T, which is the total concentration of manganese in the leach less the amount of sulphide added as ammonium sulphide. Modifying equation C 11 with the sulphide addition rate gives:

$$MAN_T = MAN_{T,leach} - Q_s \times (NH_4)_2S \qquad D.2$$

where Q_s is the flowrate of the ammonium sulphide addition, and the concentration of ammonium sulphide refers to this stream. Now substituting D.1 into 3.4 gives:

$$Mn = MAN/(1 + K_1 \times SO_4) \qquad D.3$$

and substituting D.1 and 3.6 into C.2 gives:

$$NH_4 = (SULPH - MAN + Mn - SO_4)/(K_3 \times SO_4) \qquad D.4$$

which, when substituted together with 3.6 into 3.3 gives:

$$SO_4 = (-B + SQRT(B^2 - 4AC))/2A \qquad D.5$$

where $A = K_3$

$B = 1 - K_3(MAN + Mn - SULPH + 2MnNH_3)$

$C = MAN - Mn - SULPH$

It is now possible to solve equations D.3 and D.5 simultaneously for Mn and SO_4. The method used is successive substitution. An initial guess for the value of the Mn concentration is taken. A value for SO_4 is then found from equation D.5. This value is substituted into equation D.3 to give a new value for Mn. This process is repeated until the successive values of Mn or SO_4 differ by less than an appropriate amount. This indicates that convergence has occurred.

Once the desired accuracy in the values of Mn and SO_4 has been obtained, the remaining concentrations are easily found: $MnSO_4$ from D.1, NH_4SO_4 from C.2 and NH_4 from 3.6. These are the major species that are then used to find the concentrations of the minor species: NH_3 from 3.5, $MnNH_3$ from 3.7 and $MnNH_3SO_4$ from 3.8

These minor concentrations are used to modify the the total component concentrations, that were used in the above equations, to account for the presence of the minor species. The changes are

$$MAN = MAN_T - MnNH_3 - MnNH_3 \qquad D.6$$

$$SULPH = SULPH_T - MnNH_3SO_4 \qquad D.7$$

and the new value of $MnNH_3$ in the electro-neutrality equation 3.3.

The algorithm then follows the same procedure as that described in Appendix C concerning the leach equilibrium, with respect to the convergence and the activity coefficients.

D.2 Cobalt Species

The assumption made at the beginning of this appendix means that it is not necessary to account for effects of the cobalt concentrations on the total component concentrations or the electro-neutrality equation. This results in the cobalt concentrations being easily found. Provide that both Mn^{2+} and Co^{2+} have reached their solubility limits with respect to sulphide(S^{2-}), i.e. that there is both MnS and CoS being precipitated, then one has:

$$Ksm = Mn \times S \qquad (MnS \equiv Mn^{2+} + S^{2-}) \qquad D.8$$

$$Ksc = Co \times S \qquad (CoS \equiv Co^{2+} + S^{2-}) \qquad D.9$$

Note that the activities of the solid precipitates are taken to be unity since they are virtually pure and in their standard states.

Dividing D.9 by D.8 results in

$$Co/Mn = Ksc/Ksm \qquad D.10$$

The cobalt ion is very similar to the manganese ion so the method predicting the activity coefficients gives the same value for both Mn^{2+} and Co^{2+}. The activity coefficient of the sulphide species appears in both the Ksc and the Ksm equilibrium ratios. Therefore it is not necessary to use the equilibrium ratios in equation D.10, instead the equilibrium constants can be used.

Once the Co^{2+} concentration has been found using equation D.10 the other cobalt species can be found thus: $CoSO_4$ from equation 3.11, $CoNH_3$ from equation 3.12 and $CoNH_3SO_4$ from equation 3.13.

APPENDIX E CELL FEED EQUILIBRIUM

The species and governing equations for this calculation are presented in Section 4.3. The determination of the equilibria in the feed stream of the cell house is an easier calculation than in the leach or in the sulphide section because equilibrium ratios are available instead of constants, and the number of species is smaller. In fact no iterative procedures need be adopted at all.

Substituting equation 4.6 into 4.8 gives:

$$Mn = (H \times MAN_T)/(NH_4 \times (Kc + H/NH_4)) \qquad E.1$$

The pH, and hence the hydrogen ion concentration, is known. The ammonium ion concentration NH_4 is found from equation 4.7, the manganese concentration Mn is found from E.1, then $MnNH_3$ is found from 4.6 and NH_3 is found from 4.9.

APPENDIX F CELL ANOLYTE EQUILIBRIUM

The species and governing equations for this calculation are presented in Section 4.4. A new reaction is introduced at the low pH in the anolyte. It is the equilibrium between sulphate and bi-sulphate. No free ammonia species are present in solution because of the high acidity. The hydrogen ion concentration is significant and must be included in the electro-neutrality equation.

Substituting 4.10, 4.11 and 4.12 into 4.13 and solving for SO_4 gives:

$$SO_4 = 2MAN_T + H + AMM_T - SULPH_T \qquad F.1$$

Substituting F.1 back into 4.12 results in:

$$HSO_4 = 2SULPH_T - MAN_T - H - AMM_T \qquad F.2$$

Substituting F.1 and F.2 into 4.14 gives a quadratic in H which solves as

$$H = (-U + SQRT(U^2 + 4V))/2 \qquad F.3$$

where $U = 2MAN_T + AMM_T - SULPH_T + Kh$

$$V = (2SULPH_T - 2MAN_T - AMM_T) \times Kh$$

Once H has been determined from F.3 it is easy to get SO_4 from F.1 and HSO_4 from 4.12, since Mn and NH_4 are obtained from equations 4.10 and 4.11 directly.

APPENDIX G DIAPHRAGM FLUXES

G.1 General Equation

Bryson and Lawrence (1980) have developed an equation giving the flux of a species through the diaphragm of a chlor-alkali cell. This equation may be used for the similar situation found in the manganese electrowinning cell. There is very little data available in the manganese case so the interactive effect included in the chlor-alkali cell is dropped and the interaction coef[illegible] assumed zero. The diffusion coefficients are determined fro[illegible] Hence the mass flowrate of species j (kmole/s) through the diaph[illegible] distance x from the catholyte can be expressed as:

$$W_j = Q_m C_j(x) - IFD_j z_j C_j(x)/RT\kappa^* - \varepsilon A_m D_j \frac{d}{dx} C_j(x) \qquad G.1$$

where κ^*	= Average conductance of the solution.	mhos/m
Q_m	= Flowrate through membrane.	m^3/s
C_j	= Conc. of species j at x in membrane.	$kmole/m^3$
I	= Current.	amps
F	= Faraday's constant 96500.	coul/mole
A_m	= Area of flow through membrane.	m^2
D_j	= Diffusion coefficient species j.	m^2/s
R	= Gas constant 8.314.	J/(mole.K)
T	= Temperature.	° K
ε	= Voidage.	
z_j	= Unit charge on species j.	
d	= Thickness of membrane.	m

Integrating G.1 with boundary conditions:

$$C_j(0) = Y_j \; ; \; C_j(d) = Z_j$$

results in the equation:

$$W_j = -\alpha_j D_j \{Z_j - Y_j \exp(-\alpha_j d/\varepsilon A_m)\}/\{1 - \exp(-\alpha_j d/\varepsilon A_m)\} \qquad G.2$$

where

$$\alpha_j = (IFz_j/RTk^*) - (Q_m/D_j)$$

G.2 Hydrogen Flux

The hydrogen ion concentration in the anode compartment has been found, so Y_h takes this value. The pH in the cathode compartment is in the region of 8 so the hydrogen ion concentration, Z_h, may be taken as zero. Equation G.2 becomes:

$$W_h = \alpha_h D_h Y_h/\{\exp(\alpha_h d/\varepsilon A_m) - 1\} \qquad G.3$$

G.3 Ammonium Flux

In this case the ammonium concentration in the anode compartment has been determined, but the concentration in the cathode compartment not known

and is not insignificant. From mass balance considerations around the anode compartment it can be seen that the ammonium flux through the diaphragm is in the opposite direction to the hydrogen flux, and is equal to the flux of ammonium out of the anode compartment in the exit stream; this is a known value. Therefore using Y_a and W_a, one can calculate Z_a. This is the total concentration of ammonia and ammonium in the cathode compartment, since the ammonia species are assumed to react with hydrogen ions to form ammonium at the surface of the diaphragm (x=d). The equation for the total ammonia concentration is then:

$$Z_a = Y_a \exp(\alpha_a d/\varepsilon A_m) + W_a(\exp(\alpha_a d/\varepsilon A_m) - 1)/\alpha_a D_a \qquad G.4$$

The flux W_a is:

$$W_a = Q_a \times Y_a \qquad G.5$$

APPENDIX H CATHOLYTE DETERMINATION

H.1 Solution Chemistry

To calculate conditions in the catholyte the following values are used:

1. The total manganese concentration in the catholyte. This is the same as in the anolyte.

2. The total ammonia concentration which is found from the flux equations.

3. The flux of hydrogen ions into the cathode compartment through the diaphragm. This is also determined from the flux equations.

4. The flux of free ammonia flowing into the cathode compartment with the feed stream. This is obtained by multiplying the total free ammonia concentration by the flowrate.

Taking the equations listed in Section 4.6 one may manipulate them to give:

Substituting equations 4.18 and 4.19 into 4.16 results in:

$$AMM_T = NH_4 \times (1 + 1/H \times Ka + Kc \times Mn/H) \qquad H.1$$

Substituting 4.18 into 4.17, and then substituting H.1 into the resulting equation produces:

$$MAN_T = Mn + Mn \times AMM_T/(H/Kc + 1/KaKc + Mn) \qquad H.2$$

Letting XX = H/Kc and YY = 1/KaKc and solving for Mn in H.2 gives:

$$Mn = \{-B + SQRT(B^2 + 4MAN_T \times (XX + YY))\}/2 \qquad H.3$$

where $B = XX + YY + AMM_T - MAN_T$

The Mn^{2+} concentration is then explicitly found from equation H.3. The other concentrations can be found as follows: $MnNH_3$ from 4.17, NH_4 from 4.18 and NH_3 from 4.19 provided the pH is known.

H.2 pH Determination

The pH is determined by balancing the rate of hydrogen evolution, which is dependant on the pH, with the net rate of hydrogen flux onto the cathode compartment. This idea is more fully examined in Section 4.6.

Equation H.3 has Mn as a function of the hydrogen ion concentration only. Taking the derivative of this function results in the equation:

$$\frac{dMn}{dH} = [-1/Kc + \tfrac{1}{2}\{B^2 + 4MAN_T(XX + YY)\}^{-\frac{1}{2}} \times DUM]/2 \qquad H.4$$

where $DUM = 2B/Kc + 4MAN_T/Kc$

A hydrogen ion balance is now performed over the cathode compartment, noting that at steady state there can be no accumulation of hydrogen ions in the compartment. With reference to the discussion given in Section 4.6 one obtains:

$$Hnet = W_h - \{Q_f \times (NH_{3,f} + MnNH_{3,f}) - NH_{3,lost}\} \qquad H.5$$

and for steady state there must be:

$$Hnet = Hprod \qquad H.6$$

Hprod is the production rate of hydrogen gas, and Hnet and Hprod are in kmole/s per cell. They refer to individual atoms or ions.

Now the current efficiency $\xi_{c\&h.}$ is related to the rate of hydrogen production Hprod by:

$$\xi_c = 1 - BB \times Hprod \qquad H.7$$

where $BB = 9.65 \times 10^7 / I$ s/kmole

Hprod is the rate of hydrogen production at the cathode and refers to hydrogen atoms not molecules. Substituting H.7 into 4.21 and rearranging produces:

$$Hprod = [1 - AA/\{AA + (1 + CC/Mn) \times H/Mn\}]/BB \qquad H.8$$

where $CC = C2 \times Co_h$ from 4.22
and $AA = 1/(C1 \times J2 \times J3)$ from 4.21

It is necessary to know how Hprod varies with the hydrogen ion concentration. Equation H.8 actually shows Hprod as a function of H only since the manganese concentration Mn is a function of H only via equation H.3. Taking the derivative of H.8 with respect to H gives:

$$\frac{dHprod}{dH} = AA \times \{(1 + CC/Mn) \times (Mn - H\frac{dMn}{dH})/Mn^2 + H/Mn \times (1 - CC/Mn)\}/DUM \qquad \ldots H.9$$

where $DUM = BB \times \{AA + (1 + CC/Mn) \times H/Mn\}^2$

and $\frac{dMn}{dH}$ is obtained from equation H.4.

Taking equation H.6 and writing both terms on the same side gives a function of pH that must have zero value when the left hand side of H.6 equals the left. This function is then used in the Newton-Raphson to find the catholyte pH. The function is:

$$F(pH) = Hprod - Hnet \qquad H.10$$

Hflux is not influenced by the conditions in the catholyte, therefore from equation H.5 it can be seen that Hnet is not a function of the pH in the catholyte. It is a constant as far as conditions in the cathode compartment are concerned. The derivative of equation H.5 is then:

$$F'(pH) = \frac{dHprod}{dH} \times \frac{dH}{dpH} \qquad H.11$$

now $$H = 10^{-pH} \qquad H.12$$

so $$\frac{dH}{dpH} = -\ln 10 \times e^{-\ln 10 \times pH} \qquad H.13$$

The Newton-Raphson scheme becomes:

$$pH_{i+1} = pH_i - (F(pH)/F'(pH))_i \qquad H.13$$

A suitable initial guess is taken to start the iteration, which continues until the values for the pH converge to the chosen tolerance. The final value is then taken as the pH of the catholyte. This value enables all the concentrations in the cathode compartment to be calculated; Mn from H.3 and then the other species from equations 4.15 to 4.20. The cathode current efficiency is then calculated from equation 4.21. Note the discussion in Section 4.7, this value need not be exactly the same as the value already used.

APPENDIX I COSTING

The costs that are used in the model to obtain a financial value that can be used for comparisons include

1. Ammonia as NH_3 at R96 per ton.

2. Sulphate as sulphuric acid at R92 per ton of concentrated acid.

3. Manganese in the reduced ore from the calciner, costed at a rate of R216 per ton of pure manganese.

4. Power, which is costed at 2 cents per kilowatt hour.

The revenue for the plant is obtained from the sale of the electrolytic manganese on the world market. A representative cost of R1500 per ton of manganese is taken.

A profit value is obtained by subtracting the four costs from the revenue. This gives units of R/hr. If this value is again divided by the appropriate manganese production rate, a profit value in units of R/ton Mn is obtained. In arriving at the above two values no fixed costs, or variable costs not directly related to the production, are used as the information is not available.

APPENDIX J MODEL VARIABLES AND PARAMETERS

Apart from the equilibrium constants and ratios which are dealt with in Appendix A, there are two kinds of numbers that are important in the model. The first kind are values such as flowrates, total concentrations, areas and temperatures. They are the model variables that may be changed at will by the user, even though it may be impossible to do the same on the plant. The second kind are the model parameters. These values have been chosen to achieve agreement between the model and the plant, and may not be changed. They include various diffusion constants. Typical variables are tabled in Table 10, and the parameters are tabled in Table 9, below.

Parameter	Name	Value	Units
H^+ Diffusion	HDIFF	1.16×10^{-8}	m^2/s
NH_4^+ Diffusion	ADIFF	6.10×10^{-10}	m^2/s
H_2 Evolution const.	CONST	2.70×10^{6}	
Impurity Effect const.	CONST2	1850	

Table 9. Model Parameters.

Variable	Name	Value	Units
Flowrate	QFEED	160	m^3/hr
Ammonium Sulphate conc.	AMSLPH	125	kg/m^3
Manganese conc.	MANGAN	31	kg/m^3
Amm-Sulphide addition	NH42SQ	4.2	l/min
Current	I	52000	amps
pH Cell Feed	PHF	6.88	
pH Leach Tank	PHLCH	6.55	
pH Sulphide Tank	PHSUL	6.90	
Temp. of Catholyte	TCC	40	°C
Temp. of Leach	TCLCH	51	°C
Temp. of Sulphide	TCSUL	44	°C
No. of Cells	CELLNO	82	
Cathode Area	CAREA	91.2	m^2
Diaphragm Area	DAREA	88.4	m^2
Diaphragm Thickness	DTHICK	1.37×10^{-3}	m
Diaphragm Voidage	VOID	0.67	

Table 10. Model Variables.

APPENDIX K AMMONIA GAS-LIQUID EQUILIBRIUM

The hydrogen gas evolving at the cathode is taken to be saturated with ammonia gas. If the assumption is made that Henry's Law applies then the following equation is applicable:

$$y_n = K_H \times [\text{Total ammonia conc.}] \qquad K.1$$

Perry and Chilton (1973) give values of partial pressure for ammonia in air at 40°C above solutions of ammonia in water. Table 11 below was drawn up from this data. It shows values of K_h at various concentrations from which an average value is calculated.

The Henry's Law constant is thus:

$$K_H = 0.0367 \ \text{m}^4/\text{kmole}$$

w/100w	NH_3 kmole/m^3	Pi mmHg, 40°C	Pi/760	K_H m^3/kmole
1.2	0.656	18.3	0.024	0.0366
1.6	0.871	24.1	0.032	0.0367
2.0	1.08	30.0	0.039	0.0361
2.5	1.35	37.6	0.049	0.0363
3.0	1.61	45.0	0.059	0.0366
4.0	2.13	60.8	0.080	0.0376

Table 11. Henry's Law Constant for Ammonia.

APPENDIX L PROGRAM LISTING OF COMPLEX ALGORITHM

```
C  THIS PROGRAM APPLIES THE SIMPLEX METHOD OF NELDER AND MEAD
C  (COMPUTER J. (1965) VOL.7,P.308) TO A USER DEFINED OBJECTIVE
C  FUNCTION OF NVAR NUMBER OF VARIABLES.
C  THE FUNCTION SUBPROGRAM MUST HAVE THE FOLLOWING FORM:
C
C     FUNCTION OBJECT(NVAR,X,NFEVAL)
C     IMPLICIT REAL*8 (A-Z)
C     INTEGER NVAR,NFEVAL
C     DIMENSION X(10)
C     NFEVAL=NFEVAL+1
C     IF (NFEVAL.GT.200) STOP
C     OBJECT= FUNCTION OF X'S
C     RETURN
C     END
C
C
      IMPLICIT REAL*8 (A-Z)
      REAL*4 GGUBFS
      INTEGER I,J,II,JJ,K,M,H,L,NVAR,NPOINT,NFEVAL
      DIMENSION X(15,15),FVALUE(15),XPOINT(15),XCENT(15),XREFL(15)
     C,XEXPA(15),XCONTR(15),UPPER(15),LOWER(15),V(15)
      NFEVAL=1
C  THE FOLLOWING CONSTANT IS THE REFLECTION COEFFICIENT
      A=1.1D0
C  THE NUMBER OF VARIABLES IS NVAR, AND THE NUMBER OF POINTS
C  IS NPOINT.
      NVAR=5
      K=5
      DSEED=2
      NPOINT=NVAR+1+K
      LOWER(1)=.90D0
      UPPER(1)=1.10D0
      LOWER(2)=.90D0
      UPPER(2)=1.10D0
      LOWER(3)=.90D0
      UPPER(3)=1.10D0
      LOWER(4)=0.90D0
      UPPER(4)=1.10D0
      LOWER(5)=0.90D0
      UPPER(5)=1.10D0
C  THE ALGORITHM REQUIRES NVAR+1+K INITIAL POINTS, IN THE SHAPE OF
C  A SIMPLEX TO START. THE VARIABLES ARE SCALED AND THE INITIAL
C  POINTS ARE GENERATED WITHIN STEP OF THE POINT ALL X'S=1 IN
C  THE DIRECTIONS OF THE MAJOR AXES. CONVERGENCE MAY BE AFFECTED
C  BY THE ORIENTATION OF THE INITIAL SIMPLEX.
C  THE NVAR+1 POINTS ARE STORED ROW BY ROW IN THE POSITION MATRIX.
      DO 15 J=1,NVAR
      X(1,J)=1
15    CONTINUE
      DO 25 I=2,NPOINT
```

```
      DO 20 J=1,NVAR
      X(I,J)=LOWER(J)+GGUBFS(DSEED)*(UPPER(J)-LOWER(J))
20    CONTINUE
25    CONTINUE
      DO 40 I=1,NPOINT
      DO 30 J=1,NVAR
      XPOINT(J)=X(I,J)
30    CONTINUE
      FVALUE(I)=OBJECT(NVAR,XPOINT,NFEVAL)
      COUNT=1
32    IF (FVALUE(I).LT.10) THEN
      IF (COUNT.GT.30) THEN
      WRITE (2,*) 'CENTROID OF REMAINING POINTS IS NOT FEASIBLE.'
      STOP
      END IF
      COUNT=COUNT+1
      DO 35 JJ=1,NVAR
      XCENT(JJ)=0
      M=I-1
      DO 34 II=1,M
      XCENT(JJ)=XCENT(JJ)+X(II,JJ)
34    CONTINUE
      XCENT(JJ)=XCENT(JJ)/(I-1)
35    CONTINUE
      DO 37 JJ=1,NVAR
      X(I,JJ)=(XCENT(JJ)+X(I,JJ))/2
      XPOINT(JJ)=X(I,JJ)
37    CONTINUE
      FVALUE(I)=OBJECT(NVAR,XPOINT,NFEVAL)
      GO TO 32
      END IF
40    CONTINUE
C  THIS IS THE STARTING POINT OF THE ITERATION PROCEDURE. THE MAXIMUM
C  AND MINIMUM FUNCTION VALUES ARE FOUND TOGETHER WITH THEIR CORRE-
C  SPONDING POINTS IN THE POSITION MATRIX.
42    H=1
      FMAX=FVALUE(1)
      L=1
      FMIN=FVALUE(1)
      DO 45 I=1,NPOINT
      IF (FVALUE(I).LT.FMIN) THEN
         FMIN=FVALUE(I)
         L=I
      ELSE IF (FVALUE(I).GT.FMAX) THEN
         FMAX=FVALUE(I)
         H=I
      END IF
45    CONTINUE
C CHECK FOR CONVERGENCE. STOP IF DIFFERENCE BETWEEN LOWEST AND HIGHEST
C FUNCTION EVALUATIONS DIFFER BY LESS THAN 0.001
      IF (DABS(FVALUE(H)-FVALUE(L)).LT.1D-3) THEN
      DO 47 I=1,NVAR
      V(I)=X(H,I)*V(I)
47    CONTINUE
```

```
      WRITE (1,7) (X(H,J),V(J), J=1,NVAR),FVALUE(H)
C     WRITE (1,7) (X(H,J), J=1,NVAR),FVALUE(H)
 7    FORMAT((1X,F12.6,10X,F12.6))
      STOP
      END IF
C  THE CENTROID OF THE NVAR POINTS EXCLUDING THE POINT OF LOWEST
C  VALUE IS THEN FOUND.
      DO 60 J=1,NVAR
      XCENT(J)=0
      DO 50 I=1,NPOINT
      IF (I.NE.L) XCENT(J)=XCENT(J)+X(I,J)
50    CONTINUE
      XCENT(J)=XCENT(J)/(NPOINT-1)
60    CONTINUE
C  THE REFLECTION OF THE LOWEST POINT ABOUT THE CENTROID AND ITS
C  VALUE IS FOUND.
      DO 70 J=1,NVAR
      XPOINT(J)=XCENT(J)*(1+A)-X(L,J)*A
      IF (XPOINT(J).LT.LOWER(J)) XPOINT(J)=LOWER(J)+1D-9
      IF (XPOINT(J).GT.UPPER(J)) XPOINT(J)=UPPER(J)-1D-9
70    CONTINUE
C     WRITE (2,*) 'R'
      FREFL=OBJECT(NVAR,XPOINT,NFEVAL)
72    IF (FREFL.LT.10) THEN
      DO 75 JJ=1,NVAR
C CHANGE XCENT(JJ) TO X(L,JJ)
C     XPOINT(JJ)=(XPOINT(JJ)+XCENT(JJ))/2
      XPOINT(JJ)=(2*XPOINT(JJ)+X(L,JJ))/3
75    CONTINUE
C     WRITE (2,*) 'RX'
      FREFL=OBJECT(NVAR,XPOINT,NFEVAL)
      GO TO 72
      END IF
C  IF THE REFLECTION IS BETTER THAN THE WORST POINT BY A SIGNIFICANT
C  DEGREE THEN REPLACE IT WITH THE REFLECTION.
      IF ((FREFL-FVALUE(L)).GT.(0.01D0*(FVALUE(H)-FVALUE(L)))) THEN
          DO 140 J=1,NVAR
          X(L,J)=XPOINT(J)
140       CONTINUE
          FVALUE(L)=FREFL
          GO TO 42
      END IF
C  SINCE THE REFLECTION POINT IS NOT GOOD WE FIND A CONTRACTION POINT
C  IN THE DIRECTION OF THE CENTROID POINT.
145   DO 150 J=1,NVAR
      XPOINT(J)=(X(L,J)+XCENT(J))/2
150   CONTINUE
C     WRITE (2,*) 'C'
      FCONTR=OBJECT(NVAR,XPOINT,NFEVAL)
152   IF (FCONTR.LT.10) THEN
      DO 155 JJ=1,NVAR
C CHANGE XCENT(JJ) TO X(L,JJ)
C     XPOINT(JJ)=(XPOINT(JJ)+XCENT(JJ
```

```
      XPOINT(JJ)=(XPOINT(JJ)+X(L,JJ))/2
155   CONTINUE
C     WRITE (2,*) 'CX'
      FCONTR=OBJECT(NVAR,XPOINT,NFEVAL)
      GO TO 152
      END IF
C  IF THE CONTRACTION IS STILL WORSE THAN THE WORST POINT WE CONTRACT
C  THE ENTIRE SIMPLEX CLOSER TO THE BEST POINT AND REPEAT THE ITERATION.
      IF ((FCONTR-FVALUE(L)).LE.(1D-2*(FVALUE(H)-FVALUE(L)))) THEN
      DO 170 I=1,NPOINT
      DO 160 J=1,NVAR
      X(I,J)=(X(I,J)+X(H,J))/2
      XPOINT(J)=X(I,J)
160   CONTINUE
C     WRITE (2,*) 'B'
      FVALUE(I)=OBJECT(NVAR,XPOINT,NFEVAL)
162   IF (FVALUE(I).LT.10) THEN
      DO 164 JJ=1,NVAR
      X(I,JJ)=(X(I,JJ)+X(H,JJ))/2
      XPOINT(JJ)=X(I,JJ)
164   CONTINUE
C     WRITE (2,*) 'BX'
      FVALUE(I)=OBJECT(NVAR,XPOINT,NFEVAL)
      GOTO 162
      END IF
170   CONTINUE
      GOTO 42
      END IF
C  ELSE IF THE CONTRACTION IS BETTER THAN THE WORST POINT THEN REPLACE
C  IT WITH THE CONTRACTION POINT AND REPEAT THE ITERATION.
      DO 190 J=1,NVAR
      X(L,J)=XPOINT(J)
190   CONTINUE
      FVALUE(L)=FCONTR
      GO TO 42
      END
```

APPENDIX M BASIC LISTING OF THE MODEL

```
10010     ! THIS PROGRAM MODELS THE PERFORMANCE OF THE SOLUTION CIRCUIT OF A
10020     ! MANGANESE ELECTROWINNING PLANT. IT INCLUDES A SUBROUTINE THAT AP-
10030     ! PROXIMATES THE COSTS INVOLVED IN THE OPERATION TO ESTABLISH A
10040     ! BASIS OF COMPARISON FOR THE PLANT.
10050       !
10060       !
10070     ! SECTION LOCATION TABLE:
10080       !
10090       ! SECTION:                                                  LINE NO:
10100       ! --------                                                  --------
10110       !
10120       ! INTRODUCTION & LINE NUMBERING ..... 10000
10130       ! MAJOR VARIABLES, UNITS, MOLAR MASSES ..... 10330
10140       ! CONTROL OF DATA RETRIEVAL/SELECTION ..... 12000
10150       ! SUBROUTINES TO CHANGE VARIABLES ..... 16100
10160       ! CONTROL OF CALCULATION SUBROUTINES ..... 20000
10170       ! DATA STORAGE, PROGRAM END ..... 20840
10180       ! CELLHOUSE SUBROUTINE ..... 22000
10190       ! SULPHIDE SUBROUTINE ..... 25000
10200       ! LEACH SUBROUTINE .. ..... 28000
10210       ! COSTS SUBROUTINE ..... 30000
10220       ! LEACH EFFICIENCY SUBROUTINE ..... 31000
10230       ! EQUILIBRIUM CONSTANTS SUBROUTINE ..... 32000
10240       ! EQUILIBRIUM RATIOS SUBROUTINE ..... 33000
10250       ! ACTIVITY CO-EFFICIENTS SUBROUTINE ..... 34000
10260       ! LEACH PRINT SUBROUTINE ..... 35000
10270       ! SULPHIDE PRINT SUBROUTINE ..... 36000
10280       ! VARIABLES PRINT SUBROUTINE ..... 37000
10290       ! CELLHOUSE PRINT SUBROUTINE ..... 38000
10300       ! C[illegible]S PRINT SUBROUTINE ..... 39000
10310       !
10320       !
10330     ! THE FOLLOWING LIST SETS OUT THE NAMES AND UNITS OF THE VARIABLES
10340     ! ENCOUNTERED AT THE BEGINNING OF THE PROGRAM.
10350       !
10360     ! VARIABLES RELATED TO COMPLETE PLANT.
10370       ! QFEED    = TOTAL SOLUTION FLOWRATE IN PLANT              m3/hr
10380       ! AMMONIA  = TOTAL AMM. CONC. IN SOLUTION                  kmole/m3
10390       ! SULPHATE = TOTAL SULPHATE CONC IN SOLUTION               kmole/m3
10400       ! MNFEED  = TOTAL MN IN ORE FED TO LEACH                  kg/hr
10410       ! MNPRT   = TOTAL MN PRODUCTION                           kg/hr
10420       ! MOPRT   = TOTAL MN DIOXIDE PRODUCTION                   kg/hr
10430       ! NH3CLT  = TOTAL NH3 LOSS FROM CELLS                     kg/hr
10440     ! VARIABLES RELATED TO CELL HOUSE
10450       ! EFFC    = CATHODE CURRENT EFFICIENCY
10460       ! EFFG    = INITIAL VALUE CATH. CURR. EFF.
10470       ! TFC     = TEMPERATURE OF CELL HOUSE FEED                 C
10480       ! PHF     = PH OF CELL HOUSE FEED
10490       ! CELLNO  = NO OF CELLS IN CELL HOUSE
10500       ! CAREA   = CATHODE PLATE AREA                             m2
```

```
10510       ! DAREA     = DIAPHRAGM AREA                                    m2
10520       ! VOID      = VOIDAGE OF MEMBRANE
10530       ! DTHICK    = THICKNESS OF DIAPHRAGM                            m
10540       ! AMMCEX    = TOTAL AMM. CON. CELL HOUSE EXIT                   kmole/m3
10550       ! VOLT      = VOLT DROP PER CELL                                volts
10560       ! I         = TOTAL CURRENT SUPPLIED TO CELLS                   amps
10570     ! PARAMETERS OF THE CELL HOUSE.
10580       ! HDIFF     = PARAMETER- H+ DIFF. CO-EFF.                       m2/s
10590       ! ADIFF     = PARAMETER- NH4+ DIFF. CO-EFF.                     m2/s
10600       ! CONST     = CONSTANT IN CURR. EFF. EQUATION
10610       ! CONST2    = CONSTANT IN IMPURITY EFFECT EQUATION
10620     ! VARIABLES OF THE LEACH TANKS.
10630       ! PHLCH     =    IN LEACH EXIT
10640       ! TKLCH     = TEMPERATURE IN LEACH TANKS                        k
10650     ! VARIABLES OF THE SULPHIDE PRECIP. TANKS.
10660       ! NH42S     = ADD. RATE OF (NH4)2S IN SULPHIDE PRECIP.          kmole/hr
10670       ! TKSUL     = TEMPERATURE IN SULPHIDE PRECIP. TANKS             k
10680       ! PHSUL     = PH IN SULPHIDE PRECIP. TANKS
10690     ! OTHER PARAMETERS INCLUDE THE EQUILIBRIUM CONSTANTS AND RATIOS.
10700     ! THESE AFFECT THE SOLUTION EQUILIBRIA, AND ARE PRESENTED IN THE
10710     ! SUBROUTINES KRATIO AND KCONSTANT.
10720     !
10730     ! MOLAR MASSES USED IN MODEL.
10740       ! Mn                          =  54.938
10750       ! NH4                        =  18.039
10760       ! SO4                        =  96.060
10770       ! Co                         =  58.933
10780       ! H                          =   1.008
10790       ! O                          =  15.999
10800       ! NH4OH                      =  35.046
10810       ! NH3                        =  17.031
10820       ! HSO4                       =  97.068
10830       ! H2SO4                      =  98.076
10840       ! NH4SO4                     = 114.099
10850       ! (NH4)2SO4                  = 132.138
10860       ! MnO2                       =  86.936
10870       ! Mn(OH)2                    =  88.952
10880       ! H2O                        =  18.015
10890       ! H2                         =   2.016
10900       ! O2                         =  31.998
10910       ! NH42S                      =  68.142
10920     !
12010 CLEAR
12020 PRINTER IS 704
12030 DISP "DO YOU WISH TO RUN THE STANDARD SET OF OPERATING CONDITIONS,"
12040 DISP "OR THE SET LAST USED?"
12050 DISP "ENTER S/L"
12060 CONDITIONS:
12070 INPUT X$
12080 IF X$ <> "S" AND X$ <> "L" THEN GOTO CONDITIONS
12090 IF X$="S" THEN ASSIGN# 1 TO  "NEWS-DATA"
12100 IF X$="L" THEN ASSIGN# 1 TO  "NEWL-DATA"
12110 READ# 1 ; EFFG,TCC,PHF,QFEED,I,HDIFF,ADIFF,CELLNO,CAREA,DAREA
12130 READ# 1 ; CONST,CONST2,DTHICK,VOID,PHLCH,TCLCH,AMMSULPHATE,MANGAN
```

```
12140 READ# 1 ; NH42SQ,TCSUL,PHSUL
12150 CLEAR
12160 DISP "DO YOU WISH TO CHANGE THE FITTED PARAMETERS TO THE MODEL?"
12170 DISP "NOTE: THIS SHOULD ONLY BE DONE IF THE PHYSICAL NATURE OF THE"
12180 DISP "CELL HOUSE IS CHANGED."
12190 DISP
12200 DISP "ENTER Y TO CHANGE, OR 'END LINE' TO CONTINUE."
12210 INPUT X$
12220 IF X$="Y" THEN GOSUB PARAMETERS
12230 SCREEN:
12240 PAGESIZE 24
12250 CLEAR
12252 DISP "PROCESS VARIABLES."
12254 DISP
12260 DISP USING 12270 ; TCC
12270 IMAGE "1.  TEMP. OF CATHODE COMPARTMENT (c)      = ",DDD.D
12280 DISP USING 12290 ; PHF
12290 IMAGE "2.  PH OF CELLHOUSE FEED                  = ",DD.DDD
12300 DISP USING 12310 ; QFEED
12310 IMAGE "3.  FLOWRATE (m3/hr)                      = ",DDDD.D
12320 DISP USING 12330 ; I
12330 IMAGE "4.  TOTAL CURRENT (amps)                  = ",DDDDDD
12340 DISP USING 12350 ; CELLNO
12350 IMAGE "5.  NO OF CELLS                           = ",DDD
12360 DISP USING 12370 ; PHLCH
12370 IMAGE "6.  PH OF LEACH TANKS                     = ",DD.DD
12380 DISP USING 12390 ; PHSUL
12390 IMAGE "7.  PH OF SULPHIDE TANKS                  = ",DD.DD
12400 DISP USING 12410 ; TCLCH
12410 IMAGE "8.  TEMP. OF LEACH (C)                    = ",DDD.D
12420 DISP USING 12430 ; TCSUL
12430 IMAGE "9.  TEMP. OF SULPHIDE. TANKS (C)          = ",DDD.D
12440 DISP USING 12450 ; AMMSULPHATE
12450 IMAGE "10. AMMONIA-SULPHATE IN LEACH. (g/l)      = ",DDDD.D
12460 DISP USING 12470 ; MANGAN
12470 IMAGE "11. DESIRED MN IN LEACH. (g/l)            = ",DDD.D
12480 DISP USING 12490 ; NH42SQ
12490 IMAGE "12. AMMONIUM-SULPHIDE ADD. (l/min)        = ",DD.DDD
12500 DISP
12510 DISP "TO CHANGE THE VALUE OF ANY OF THE ABOVE VARIABLES, ENTER ITS NO."
12520 DISP "TO SEE THE LIST AGAIN, ENTER 'A'."
12530 DISP "TO CONTINUE WITH MODEL, PRESS 'END LINE'."
12540 CHANGE:
12550 INPUT X$
12560 IF X$="A" THEN GOTO SCREEN
12570 IF X$="" THEN GOTO INITIAL
12580 IF LEN (X$)>2 THEN GOTO CHANGE
12590 IF LEN (X$)=1 THEN GOTO ONE
12600 IF X$[1,1]<"1" OR X$[1,1]>"2" THEN GOTO CHANGE
12610 IF X$[2,2]<"0" OR X$[2,2]>"9" THEN GOTO CHANGE
12620 GOTO VALUE
12630 ONE:
12640 IF X$<"1" OR X$>"9" THEN GOTO CHANGE
12650 VALUE:
```

```
12660 X=VAL (X$)
12670 IF X>12 THEN GOTO CHANGE
12680 PAGESIZE 16
12690 ON X GOSUB
16200,16300,16400,16500,16600,17500,17800,17600,17700,17900,18000,18100
12700 GOTO SCREEN
12710 PARAMETERS:
12720 CLEAR
12722 DISP "MODEL PARAMETERS."
12726 DISP USING 12728 ; EFFG
12728 IMAGE "1.  INITIAL CURRENT EFFICIENCY          = ",D.DD
12730 DISP USING 12740 ; CAREA
12740 IMAGE "2.  CATHODE AREA (m2)                   = ",DDD.DD
12750 DISP USING 12760 ; DAREA
12760 IMAGE "3.  DIAPHRAGM AREA (m2)                 = ",DDD.DD
12770 DISP USING 12780 ; DTHICK
12780 IMAGE "4.  DIAPHRAGM THICKNESS (m)             = ",MD.DDE
12790 DISP USING 12800 ; VOID
12800 IMAGE "5.  DIAPHRAGM VOIDAGE                   = ",D.DD
12810 DISP USING 12820 ; HDIFF
12820 IMAGE "6.  H DIFF. CO-EFF. (m2/s)              = ",MD.DDDE
12830 DISP USING 12840 ; ADIFF
12840 IMAGE "7.  NH4 DIFF. CO-EFF. (m2/s)            = ",MD.DDDE
12850 DISP USING 12860 ; CONST
12860 IMAGE "8.  CONSTANT FOR CUR. EFF.              = ",MD.DDE
12870 DISP USING 12880 : CONST2
12880 IMAGE "9.  CONST2 FOR IMP. EFFECT.             = ",DDDUD
12890 DISP
12900 DISP "TO CHANGE THE VALUE OF ANY OF THE ABOVE VARIABLES, ENTER ITS NO."
12910 DISP "TO SEE THE LIST AGAIN, ENTER 'A'."
12920 DISP "TO CONTINUE WITH MODEL, PRESS 'END LINE'."
12930 CHANGE2:
12940 INPUT X$
12950 IF X$="A" THEN GOTO PARAMETERS
12960 IF X$="" THEN RETURN
12970 IF LEN (X$)>2 THEN GOTO CHANGE2
12980 IF LEN (X$)=1 THEN GOTO ONE2
12990 IF X$[1,1]<"1" OR X$[1,1]>"2" THEN GOTO CHANGE2
13000 IF X$[2,2]<"0" OR X$[2,2]>"9" THEN GOTO CHANGE2
13010 GOTO VALUE2
13020 ONE2:
13030 IF X$<"1" OR X$>"9" THEN GOTO CHANGE2
13040 VALUE2:
13050 X=VAL (X$)
13060 IF X>9 THEN GOTO CHANGE2
13070 ON X GOSUB 16100,16700,16800,16900,17000,17100,17200,17300,17400
13080 GOTO PARAMETERS
16100 CLEAR
16110 DISP "INITIAL VALUE OF CATHODE CURRENT EFFICIENCY."
16120 DISP "THIS IS JUST A VALUE USED TO START THE CELLHOUSE ROUTINE."
16130 DISP "IT MUST ALWAYS BE GREATER THAN THE EXPECTED CURRENT EFFICIENCY."
16140 DISP "THERE IS NO REAL ADVANTAGE TO BE HAD BY CHANGING THIS VALUE."
16150 DISP "OLD CURRENT EFF. = ",EFFG
16160 DISP "ENTER NEW CATHODE CURR. EFF."
16170 INPUT EFFG$
```

```
16175 IF EFFG$="" THEN RETURN
16180 EFFG=VAL (EFFG$)
16190 RETURN
16200 CLEAR
16210 DISP "CELL HOUSE CATHODE COMPARTMENT TEMP . (c)"
16220 DISP "OLD TEMP = ";TCC
16230 DISP "ENTER NEW TEMP."
16240 INPUT TCC$
16250 IF TCC$="" THEN RETURN
16260 TCC=VAL (TCC$)
16270 RETURN
16300 CLEAR
16310 DISP "CELL HOUSE FEED STREAM pH"
16320 DISP "OLD PH = ";PHF
16330 DISP "ENTER NEW PH"
16340 INPUT PHF$
16350 IF PHF$="" THEN RETURN
16360 PHF=VAL (PHF$)
16370 RETURN
16400 CLEAR
16410 DISP "TOTAL FLOWRATE OF SOLUTION THROUGH PLANT (m3/hr)"
16420 DISP "OLD FLOWRATE = ";QFEED
16430 DISP "ENTER NEW FLOWRATE"
16440 INPUT QFEED$
16450 IF QFEED$="" THEN RETURN
16460 QFEED=VAL (QFEED$)
16470 RETURN
16500 CLEAR
16510 DISP "TOTAL CURRENT SUPPLIED IN CELL HOUSE (amps)"
16520 DISP "OLD CURRENT = ";I
16530 INPUT I$
16540 IF I$="" THEN RETURN
16550 I=VAL (I$)
16560 RETURN
16600 CLEAR
16610 DISP "NUMBER OF CELLS IN CELL HOUSE"
16620 DISP "OLD NUMBER = ";CELLNO
16630 DISP "ENTER NEW NUMBER"
16640 INPUT CELLNO$
16650 IF CELLNO$="" THEN RETURN
16660 CELLNO=VAL (CELLNO$)
16670 RETURN
16700 CLEAR
16710 DISP "CATHODE AREA (m2)"
16720 DISP "OLD AREA = ";CAREA
16730 DISP "ENTER NEW AREA"
16740 INPUT CAREA$
16750 IF CAREA$="" THEN RETURN
16760 CAREA=VAL (CAREA$)
16770 RETURN
16800 CLEAR
16810 DISP "DIAPHRAGM AREA (m2)"
16820 DISP "OLD AREA = ";DAREA
16830 DISP "ENTER NEW AREA"
```

```
16840 INPUT DAREA$
16850 IF DAREA$="" THEN RETURN
16860 DAREA=VAL (DAREA$)
16870 RETURN
16900 CLEAR
16910 DISP "DIAPHRAGM THICKNESS (m)"
16920 DISP "OLD THICKNESS = ";DTHICK
16930 DISP "ENTER NEW THICKNESS"
16940 INPUT DTHICK$
16950 IF DTHICK$="" THEN RETURN
16960 DTHICK=VAL (DTHICK$)
16970 RETURN
17000 CLEAR
17010 DISP "DIAPHRAGM VOIDAGE.  RATIO OF EMPTY SPACE TO TOTAL SPACE."
17020 DISP "OLD VOIDAGE = ";VOID
17030 DISP "ENTER NEW VOIDAGE"
17040 INPUT VOID$
17050 IF VOID$="" THEN RETURN
17060 VOID=VAL (VOID$)
17070 RETURN
17100 CLEAR
17110 DISP "H+ ION DIFFUSION PARAMETER. (m2/s)"
17120 DISP "THIS VALUE HAS BEEN FITTED TO PRODUCE THE BEST AGREEMENT BETWEEN"
17130 DISP "THE MODEL AND THE PLANT. IT SHOULD NOT BE CHANGED UNLESS SOME-"
17140 DISP "THING FUNDAMENTAL IN THE PROCESS, SUCH AS A DIAPHRAGM CHARAC-"
17150 DISP "TERISTIC, IS CHANGED."
17160 DISP "OLD DIFF CO-EFF = ";HDIFF
17170 DISP "ENTER NEW CO-EFF"
17180 INPUT HDIFF$
17183 IF HDIFF$="" THEN RETURN
17186 HDIFF=VAL (HDIFF$)
17190 RETURN
17200 CLEAR
17210 DISP "NH4+ ION DIFFUSION PARAMETER. (m2/s)"
17220 DISP "THIS VALUE HAS BEEN FITTED TO PRODUCE THE BEST AGREEMENT BETWEEN"
17230 DISP "THE MODEL AND THE PLANT. IT SHOULD NOT BE CHANGED UNLESS SOME-"
17240 DISP "THING FUNDAMENTAL IN THE PROCESS, SUCH AS A DIAPHRAGM CHARAC-"
17250 DISP "TERISTIC, IS CHANGED."
17260 DISP "OLD DIFF CO-EFF = ";ADIFF
17270 DISP "ENTER NEW CO-EFF"
17280 INPUT ADIFF$
17283 IF ADIFF$="" THEN RETURN
17286 ADIFF=VAL (ADIFF$)
17290 RETURN
17300 CLEAR
17310 DISP "T^5 CONSTANT IN THE CURRENT EFFICIENCY EQUATION"
17320 DISP "IT HAS BEEN FITTED TO OBTAIN THE BEST FIT BTWEEN THE MODEL AND "
17330 DISP "THE PLANT. IT SHOULD NOT BE CHANGED."
17340 DISP "STANDARD VALUE IS 0.95E7"
17350 DISP "OLD CONSTANT = ";CONST
17360 DISP "ENTER NEW CONSTANT"
17370 INPUT CONST$
17373 IF CONST$="" THEN RETURN
17376 CONST=VAL (CONST$)
```

```
17380 RETURN
17400 CLEAR
17410 DISP "THE CONSTANT IN THE IMPURITY EFFECT FACTOR."
17420 DISP "IT HAS BEEN FITTED TO OBTAIN THE BEST FIT BTWEEN THE MODEL AND "
17430 DISP "THE PLANT. IT SHOULD NOT BE CHANGED."
17435 DISP "STANDARD VALUE IS 1850."
17440 DISP "OLD CONSTANT = ";CONST2
17450 DISP "ENTER NEW CONSTANT"
17460 INPUT CONST2$
17470 IF CONST2$="" THEN RETURN
17480 CONST2=VAL (CONST2$)
17490 RETURN
17500 CLEAR
17510 DISP "pH IN LEACH TANKS."
17520 DISP "OLD pH = ";PHLCH
17530 DISP "ENTER NEW PH"
17540 INPUT PHLCH$
17550 IF PHLCH$="" THEN RETURN
17560 PHLCH=VAL (PHLCH$)
17570 RETURN
17600 CLEAR
17610 DISP "TEMPERATURE IN LEACH TANKS IN CENTIGRADE."
17620 DISP "OLD TEMP = ";TCLCH
17630 DISP "ENTER NEW TEMP"
17640 INPUT TCLCH$
17650 IF TCLCH$="" THEN RETURN
17660 TCLCH=VAL (TCLCH$)
17670 RETURN
17700 CLEAR
17710 DISP "TEMPERATURE IN SULPHIDE TANKS IN CENTIGRAL.
17720 DISP "OLD TEMP = ";TCSUL
17730 DISP "ENTER NEW TEMP"
17740 INPUT TCSUL$
17750 IF TCSUL$="" THEN RETURN
17760 TCSUL=VAL (TCSUL$)
17770 RETURN
17800 CLEAR
17810 DISP "pH IN SULPHIDE TANKS."
17820 DISP "OLD pH = ";PHSUL
17830 DISP "ENTER NEW PH"
17840 INPUT PHSUL$
17850 IF PHSUL$="" THEN RETURN
17860 PHSUL=VAL (PHSUL$)
17870 RETURN
17900 CLEAR
17910 DISP "TOTAL AMMONIUM-SULPHATE CONC. IN LEACH. (g/l)"
17920 DISP "OLD CONC. = ";AMMSULPHATE
17930 DISP "ENTER NEW CONC."
17940 INPUT AMMSULPHATE$
17950 IF AMMSULPHATE$="" THEN RETURN
17960 AMMSULPHATE=VAL (AMMSULPHATE$)
17970 RETURN
18000 CLEAR
18010 DISP "DESIRED MANGANESE CONC. IN LEACH SOLUTION. (g/l)."
```

```
18020 DISP "OLD CONC. = ";MANGAN
18030 DISP "ENTER NEW CONC."
18040 INPUT MANGAN$
18050 IF MANGAN$="" THEN RETURN
18060 MANGAN=VAL (MANGAN$)
18070 RETURN
18100 CLEAR
18110 DISP "ADDITION OF 20% AMMONIUM-SULPHIDE (l/min)."
18120 DISP "OLD RATE. = ";NH42SQ
18130 DISP "ENTER NEW RATE."
18140 INPUT NH42SQ$
18150 IF NH42SQ$="" THEN RETURN
18160 NH42SQ=VAL (NH42SQ$)
18170 RETURN
20000    !
20010    !
20020 INITIAL:
20025    ! OBTAIN THE MOLAR FLOWRATE OF NH42S. ASSUME S.G. =1, AND 20% BY MASS.
20030 NH42S=NH42SQ*60*.2/68.142
20034    ! AS THE MODEL USES SULPHATE AND AMMONIA AS INPUTS INDIVIDUALLY, AND
20035    ! NOT AMMONIUM-SULPHATE, WE FIND VALUES OF THE FORMER THAT WILL GIVE,
20036    ! ULTIMATELY, AN APPROXIMATELY CORRECT AMMSULPHATE VALUE.
20040 AMMONIA=AMMSULPHATE/132.138*2*1.022
20050 SULPHATE=MANGAN/54.938+AMMSULPHATE/132.138
20060 TKLCH=TCLCH+273.15
20070 TKSUL=TCSUL+273.15
20080    ! INITIAL ACTIVITY CO-EFFICIENT VALUES.
20090 PAGESIZE 16
20100 CLEAR
20110 TIME1=TIME
20120 GMN2=.25
20130 GNH4=.6
20140 GSO4=.2
20150 GNH4SO4=.65
20160 GS2=.2
20170 GMNNH3=.25
20180 GCO2=.25
20190 GCONH3=.25
20200    !
20210    ! CALL LEACH SUBROUTINE. INPUT TKLCH,PHLCH,AMMONIA,SULPHATE AND
20220    ! OUTPUT MANL.
20230 DISP
20240 DISP "CALCULATING LEACH..."
20250   GOSUB PVARIABLES
20270   GOSUB LEACH
20280 AMMSUL=((NH4L-NH4SO4L)/2+NH4SO4L)*132.142
20290   GOSUB LPRINT
20350    !
20360    ! CALL SULPHIDE SUBROUTINE. INPUT MANL, SULPHATE, TKSUL, PHSUL,
20370    ! NH42S. OUTPUT CORS, MANS, AMMS.
20380 DISP
20390 DISP "CALCULATING SULPHIDE..."
20440   GOSUB SULPHIDE
20450 MANSM=MANS*54.938
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20460   GOSUB SPRINT
20520    ! CALL CELL SUBROUTINE. INPUT MANS, SULPHATE, COBS. OUTPUT MANCEX,
20530    ! AMMCEX.
20540 DISP
20550 DISP "CALCULATING CELL HOUSE..."
20600   GOSUB CELLHOUSE
20610 MANAM=MANCEX*54.938
20620 ACID=((HA-HSO4A)/2+HSO4A)*98.076
20630   GOSUB CPRINT
20710    ! CALL COSTS SUBROUTINE.
20720    !
20730 DISP
20740 DISP "CALCULATING COSTS..."
20790   GOSUB COST
20800   GOSUB PPRINT
20830 DISP
20840 FINISH:
20845 TIME2=TIME
20880 DISP "FINISHED"
20890 TIMEABS=TIME2-TIME1
20910 DISP USING 20920 ; TIMEABS
20920 IMAGE "TIME FOR CALCULATION  =",MDDDD.D," secs."
20930 BEEP 60,50
20940 DISP
20950 DISP USING 20960
20960 IMAGE "TO STORE THE CURRENT DATA SET AS THE STANDARD SET ENTER 'S',"
20970 DISP USING 20980
20980 IMAGE "ELSE PRESS 'ENDLINE' TO STORE AS THE SET LAST USED."
20990 INPUT X$
21000 IF X$ <> "S" THEN GOTO LAST
21010 ASSIGN# 2 TO   "NEWS-DATA"
21020 PRINT# 2 ; EFFG,TCC,PHF,QFEED,I,HDIFF,ADIFF,CELLNO,CAREA,DAREA
21030 PRINT# 2 ; CONST,CONST2,DTHICK,VOID,PHLCH,TCLCH,AMMSULPHATE,MANGAN
21040 PRINT# 2 ; NH42SO,TCSUL,PHSUL
21060 BEEP 50,60
21070 END
21075 LAST:
21076 ASSIGN# 2 TO   "NEWL-DATA"
21080 PRINT# 2 ; EFFG,TCC,PHF,QFEED,I,HDIFF,ADIFF,CELLNO,CAREA,DAREA
21090 PRINT# 2 ; CONST,CONST2,DTHICK,VOID,PHLCH,TCLCH,AMMSULPHATE,MANGAN
21100 PRINT# 2 ; NH42SO,TCSUL,PHSUL
21110 BEEP 40,60
21120 END
22000    !
22010    !
22020 CELLHOUSE:
22030    ! THIS SUBROUTINE CALCULATES THE CELL HOUSE SECTION OF THE PLANT.
22040    ! IT USES THE FEED CONCENTRATIONS OF MN, SULPHATE AND COBALT AND
22050    ! THE FEED FLOWRATE, TOGETHER WITH THE TEMPERATURE (t) AND THE
22060    ! CURRENT (amps) SUPPLIED TO THE CELLS TO CALCULATE THE OPERATION
22070    ! OF THE CELLS.
22080    !
22090    ! SET THE CATHODE CURRENT EFFICIENCY TO THE INITIAL VALUE, AND THE
22100    ! ANODE CURRENT EFFICIENCY TO 0.99, AS WELL AS ZERO A DUMMY VARIABLE.
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22110 EFFC=EFFG
22120 EFFA=.99
22130 EFFD=EFFG
22140     ! SET THE DENSITIES OF SOLUTION (kg/m3) IN THE FEED, CATHODE, ANODE.
22150 DENF=1185
22160 DENC=1165
22170 DENA=1160
22180     ! INITIALISE THE LOSSES OF NH3 IN CATHODE, H2O IN CATHODE AND ANODE.
22190 NH3CL=0
22200 H2OCL=0
22210 H2OAL=0
22220     ! GET THE IMPURITY LEVEL (kmole/m3), FEED FLOWRATE PER CELL (m3/s),
22230     ! FEED TEMPERATURE (k), CURRENT DENSITY (amps/m3), EQUIVALENT CUR-
22240     ! RENT (mole/s), MASS OF MN IN FEED (kg/m3).
22250 IMP=COBS
22260 QF=QFEED/3600/CELLNO
22270 TC=TCC+273.15
22275 TF=TC-1
22280 CD=I/CAREA
22290 IEQV=I/96500
22300 MNF=MANS
22310 MNFM=MNF*54.938
22320 SULPHF=SULPHATE
22330     ! CALL THE SUBROUTINE THAT CALCULATES THE EQUILIBRIUM RATIOS AS
22340     ! FUNCTIONS OF TEMPERATURE.
22350 TEMPK=TF
22360 GOSUB KRATIO
22370     ! CALCULATE THE EQUILIBRIUM COMPOSITION OF THE FEED STREAM. FOR THE
22380     ! EQUATIONS SEE SECTION 4.3.
22390 HF=10**(-PHF)
22400 NH4F=2*(SULPHF-MNF)
22410 MN2F=MNF/(NH4F*(KMNNH3/HF+1/NH4F))
22420 MNNH3F=MNF-MN2F
22430 NH3F=NH4F/(KAMM*HF)
22440 AMMF=NH4F+NH3F+MNNH3F
22450 SO4F=SULPHF
22460 H2OF=DENF-54.938*MN2F-18.039*NH4F-71.969*MNNH3F-17.031*NH3F-96.06*SO4F
22470 H2OF=H2OF/18.015
22480     ! START OF LOOP TO CALCULATE THE ANODE COMPARTMENT FROM MASS BALANCE
22490     ! AND EQUILIBRIA, GIVEN VALUES OF CURRENT EFFICIENCIES, WATER AND
22500     ! AMMONIA LOSSES.
22510 FOR ICOUNT=1 TO 100
22520     ! CALCULATE MN AND OTHER PRODUCTION RATES PER CELL (kg/s).
22530 MNPR=.054938*EFFC*IEQV/2
22540 H2PR=.002016*(1-EFFC)*IEQV/2
22550 O2PR=.031998*EFFA*IEQV/2
22560 MOPR=.086936*(1-EFFA)*IEQV/2
22570     ! PERFORM A MN AND AMMONIA MASS BALANCE OVER ENTIRE CELL.
22580     ! QA     = FLOWRATE OF SOLUTION EXITING EACH CELL            (m3/s)
22590     ! MNANM = MASS OF MN IN ANODE COMPARTMENT                   (kg/m3)
22600     ! AMMAN = TOTAL CONC. OF AMMONIA IN ANODE COMPARTMENT       (kmole/m3)
22610     ! TA    = TEMPERATURE IN ANODE COMPARTMENT                  (k)
22620 QA=(QF*DENF-MNPR-H2PR-O2PR-MOPR-H2OCL-H2OAL-NH3CL)/DENA
22630 MNANM=(MNFM*QF-MNPR-MOPR*54.938/86.936)/QA
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22640 AMMAN=(AMMF*QF-NH3CL/17.031)/QA
22650 TA=TF+3.5
22660    ! CALL THE SUBROUTINE TO CALCULATE THE EQUILIBRIUM RATIOS AT THE
22670    ! ANODE TEMPERATURE.
22680 TEMPK=TA
22690 GOSUB KRATIO
22700    ! CALCULATE THE EQUILIBRIUM COMPOSITION OF THE ANODE COMPARTMENT.
22710    ! FOR THE EQUATIONS SEE SECTION 4.4.
22720 SULPHA=QF*SO4F/QA
22730 MN2A=MNANM/54.938
22740 NH4A=AMMAN
22750 U=2*MN2A+NH4A-SULPHA+KSO4
22760 V=(2*SULPHA-2*MN2A-NH4A)*KSO4
22770 HA=(-U+SQR (U*U+4*V))/2
22780 SO4A=2*MN2A+HA+NH4A-SULPHA
22790 HSO4A=SULPHA-SO4A
22800 H2OA=DENA-54.938*MN2A-1.008*HA-18.039*NH4A-96.06*SO4A-97.068*HSO4A
22810 H2OA=H2OA/18.015
22820    ! TC    = CATHODE COMPARTMENT TEMPERATURE                    (k)
22830    ! MNC   = TOTAL MN CONC. IN CATHODE COMP.                    (kmole/m3)
22840 TC=TF+1
22850 MNC=MNANM/54.938
22860    ! CALCULATE MOLAR DIFFUSION RATES THROUGH MEMBRANE, FROM MASS BALANCE
22870    ! AROUND THE ANODE SECTION. KMOLE/S
22880 ZH2O=QA*H2OA+H2OAL/18.015+EFFA*IEQV/2000+(1-EFFA)*IEQV/1000
22890 ZMN=QA*MN2A+(1-EFFA)*IEQV/2000
22900 ZAMM=CA*NH4A
22910    ! DETERMINE THE TOTAL AMM CONC. IN THE CATHODE, AND THE H+ ION BACK
22920    ! DIFFUSION FROM MEMBRANE TRANSPORT MODEL.
22930    ! SEE SECTION 4.5 FOR THE EQUATIONS.
22940    ! THE AVERAGE MEMBRANE CONDUCTIVITY IS TAKEN TO BE 14 (mhos/m).
22950 J6A=I*96500/(8.314*14*TC)-ZH2O*18.015/(1000*ADIFF)
22960 TEST=J6A*DTHICK/(VOID*DAREA)
22970    ! CHECK FOR UNDERFLOW.
22980 IF TEST<-50 THEN TEST=-50
22990 J7A=EXP (TEST)
23000 AMMC=AMMAN*J7A+ZAMM*(J7A-1)/(J6A*ADIFF)
23010 J6H=I*96500/(8.314*14*TC)-ZH2O*18.015/(1000*HDIFF)
23020 J7H=EXP (-(J6H*DTHICK/(VOID*DAREA)))
23030 HFLUX=J6H*HDIFF*HA/(1-J7H)
23040    ! START OF THE LOOP TO SOLVE THE TWO SIMUTANEOUS EQUATIONS FOR
23050    ! THE CATHODE PH AND THE NET HYDROGEN EVOLVED. A NEW VALUE FOR
23060    ! THE PH IS OBTAINED FROM AN OLD VALUE USING A NEWTON-RAPHSON
23070    ! SCHEME. THIS REQUIRES THE FIRST DERIVATIVE OF THE FUNCTION THAT
23080    ! RESULTS FROM THE SUBSTITUTION OF THE ONE EQUATION INTO THE OTHER.
23090    ! SEE SECTION 4.6 FOR THE EQUATIONS.
23100 PHDUM=7.5
23110    ! CALL THE EQUILIBRIUM RATIO SUBROUTINE.
23120 TEMPK=TC
23130 GOSUB KRATIO
23140 FOR IPH=1 TO 100
23150 PHC=PHDUM
23160 HC=10**(-PHC)
23170 YY=1/(KAMM*KMNNH3)
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23180 XX=HC/KMNNH3
23190 MN2C=(-(XX+YY+AM    HC)+SQR ((XX+YY+AMMC-MNC)**2+4*MNC*(XX+YY)))/2
23200 MNNH3C=MNC-MN2C
23210 NH4C=HC*KNNH3C/(KM_ ^*KMNNH3)
23220 NH3C=MNNH3C/(MN2C*KMNNH3*KAMM)
23230 SOLUB=HC**2/KMNOH-MN2C
23240 SO4C=MN2C+.5*NH4C+MNNH3C
23250 H2OC=DENC-MN2C*54.938-NH4C*18.039-MNNH3C*71.969-NH3C*17.031-SO4C*96.06
23260 H2OC=H2OC/18.015
23270    ! THE NET HYDROGEN EVOLVED IS THE DIFFERANCE BETWEEN THAT WHICH
23280    ! DIFFUSES BACK THROUGH THE MEMBRANE, AND THAT WHICH REACTS WITH
23290    ! THE NH3 SPECIES TO FORM NH4 SPECIES.
23300 HNET=HFLUX-(QF*(NH3F+NNNH3F)-NH3CL/17.031)
23310    ! IF THE NET H EVOLVED IS NEGATIVE THEN STOP THE PROGRAM.
23320 IF HNET>0 THEN GOTO PROCEED
23330 PRINT "HNET IS NEGATIVE",HNET,HFLUX
23335 DISP "HNET IS NEGATIVE",HNET,HFLUX
23340 PRINT "CANNOT CONTINUE WITH PROGRAM AS THE MODEL IS OUTSIDE"
23345 DISP "CANNOT CONTINUE WITH PROGRAM AS THE MODEL IS OUTSIDE"
23350 PRINT "THE PERMISSABLE REGION. THERE IS NOT ENOUGH H DIFFUSING BACK."
23355 DISP "THE PERMISSABLE REGION. THERE IS NOT ENOUGH H DIFFUSING BACK."
23360 GOTO FINISH
23370 PROCEED:
23380    ! IMPURITY EFFECT ON CATHODE CURRENT EFFICIENCY.
23390 J1=1+CONST2*IMP/MN2C
23400    ! TEMPERATURE EFFECT ON CATHODE CURRENT EFFICIENCY.
23410 J2=1+EXP (12300/TC-40.953)
23420    ! CURR. DENSITY EFFECT ON THE CATHODE CURRENT EFFICIENCY.
23430 J3=1-.0001213*(CD-550)+.00001278*(CD-550)**2
23440    ! SOME DUMMY VARIABLES.
23450 AA=1/(CONST*J2*J3)
23460 BB=1000/ISCY
23470 CC=CONST2*IMP
23480 DET=(XX+YY+AMMC-MNC)**2+4*MNC*(XX+YY)
23490 SROOT=SQR (DET)
23500    ! THE RATE OF CHANGE OF MN2 CONC. WITH HYDROGEN CONCENTRATIO.
23510 DMNDH=((-1)/KMNNH3+.5/SROOT*(2*(XX+YY+AMMC-MNC)/KMNNH3+4*MNC/KMNNH3))/2
23520 HPR=(1-1/(1+1/AA*(1+CC/MN2C)*HC/MN2C))/BB
23530 FUNCHPR=HPR-HNET
23540 DHPRDH=AA/BB*((1+CC/MN2C)*(MN2C-HC*DMNDH)/MN2C**2+HC*(1-CC/MN2C**2))
23550 DHPRDH=DHPRDH/(AA*(1+CC/MN2C)*HC/MN2C)**2
23560 FDERIV=-(DHPRDH*2.303*EXP (-(2.303*PHC)))
23570 FNCOLD=PHC
23580 PHDUM=PHC-FUNCHPR/FDERIV
23590 IF ABS (PHDUM-PHC)<.00001 THEN GOTO EFFICIENCY
23990 NEXT IPH
24000 PRINT "LOOP FOR PH IN CATHODE NOT CONVERGED AFTER 100 ITERATIONS."
24005 DISP "LOOP FOR PH IN CATHODE NOT CONVERGED AFTER 100 ITERATIONS."
24010 GOTO FINISH
24020 EFFICIENCY:
24030    ! CALCULATE THE NEW CATHODE CURRENT EFFICIENCY AND COMPARE WITH THE
24040    ! OLD VALUE. THE NEW VALUE IS TAKEN TO BE 30% OF THE OLD VALUE PLUS
24050    ! 70% OF THE VALUE THAT CORRESPONDS TO THE H2 EVOLUTION.
24060    ! THIS PREVENTS THE ITERATIONS FROM GOING UNSTABLE.
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24070 EFFD2=EFFD
24080 EFFD=EFFC
24090 EFFC=.7*(1-BB*HNET)+.3*EFFC
24100 CED=ABS (EFFD-EFFC)
24104    ! CALCULATE THE H2 PRODUCED AT THE NEW CATHODE CURRENT EFFICIENCY.
24105 H2DUM=.002016*(1-EFFC)*IEQV/2
24110    ! IF THE DIFFERANCE IS WITHIN TOLERANCE THEN CONTINUE WITH MODEL, ELSE
24120    ! ESTIMATE AMMONIA LOSS IN CATHODE , AND WATER LOSSES IN CATHODE AND
24130    ! ANODE, THEN RETURN TO STOP IF THERE HAVE BEEN TOO MANY ITERATIONS.
24140 IF CED<.00002 THEN GOTO CELLEND
24180    ! GET THE WATER MOLE FRACTION IN THE H2 GAS AT CATHODE.
24190 H2OFRC=-1.267+.00428*TC
24200    ! OBTAIN THE MOLE FRACTIONS OF THE LOST GASSES. SEE SECTION 4.7
24210    ! GET THE WATER MOLE FRACTION IN THE O2 GAS AT ANODE.
24220 H2OFRA=-1.267+.00428*TA
24230    ! GET THE NH3 MOLE FRACTION IN THE H2 GAS AT THE CATHODE.
24240 NH3FRC=.0367*(NH4C+NH3C)
24250    ! CALCULATE THE NEW AMMONIA CATHODE LOSS, AND THE WATER CATHODE AND
24260    ! ANODE LOSSES PER CELL (kg/s).
24265    ! FOR CATHODE LOSSES USE NEW H2 PRODUCTION RATE.
24270 NH3CL=NH3FRC/(1-H2OFRC-NH3FRC)*H2DUM*17.031/2.016
24280 H2OCL=H2OFRC/(1-H2OFRC-NH3FRC)*H2DUM*18.015/2.016
24290 H2OAL=H2OFRA/(1-H2OFRA)*O2FR*18.015/31.998
24300    ! CALCULATE ANODE CURRENT EFFICIENCY. ASSUMED MASS TRANSFER LIMITED.
24310    ! SEE SECTION 4.7 FOR THE EQUATION.
24320    ! ANODE CURRENT DENSITY IS ASSUMED TO BE 1000 amps/m2.
24330 EFFA=1-1.58*MN2A/1000**.5
24340    ! CONTINUE WITH CURRENT EFFICIENCY LOOP, OR STOP IF THERE HAVE BEEN
24350    ! TOO MANY ITERATIONS.
24360 NEXT ICOUNT
24370 PRINT "CURRENT EFFICIENCY LOOP NOT CONVERGED AFTER 100 ITERATIONS."
24375 DISP "CURRENT EFFICIENCY LOOP NOT CONVERGED AFTER 100 ITERATIONS."
24380 GOTO FINISH
24390 CELLEND:
24400    ! CONVERSION OF CELL HOUSE ROUTINE. CALCULATE SUNDRY VALUES.
24410    !
24420    ! CALCULATE THE RATE OF CHANGE OF H EVOLVED WITH A CHANGE IN H CONC.
24430 DUMMY=MNC**2+(MNC+CC)*HC/AA
24440 DHEVDH=MNC**2*(MNC+CC)/AA
24450 DHEVDH=DHEVDH/(BB*DUMMY*2)
24460    ! CALCULATE THE TOTAL ANODE EXIT FLOW. (m3/s)
24470 QANOD=QA*3600*CELLNO
24480    ! CALCULATE TOTAL WATER LOSS PER CELL. (kg/s)
24490 H2OLS=H2OCL+H2OAL
24500    ! CALCULATE TOTAL PRODUCTION RATES FOR PLANT.    (kg/hr)
24510 MNPRT=MNPR*3600*CELLNO
24520 MOPRT=MOPR*3600*CELLNO
24530 H2PRT=H2PR*3600*CELLNO
24540    ! CALCULATE TOTAL LOSSES FROM CELL HOUSE.        (kg/hr)
24550 H2OLST=H2OLS*3600*CELLNO
24560 NH3CLT=NH3CL*3600*CELLNO
24570    ! GET NN AND AMMONIA CONC. RELATIVE TO QFEED.
24580 MANCEX=MN2A*QANOD/QFEED
24590 AMMCEX=NH4A*QANOD/QFEED
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24600     ! EVALUATE THE TOTAL CELL VOLT DROP.
24610     ! CALCULATE MEMBRANE CONDUCTIVITY.                    (mhos/m)
24620 DCOND=1000*96500**2/8.314/TC*(NDIFF*(HC+HA)/2+4*ADIFF*(NH4C+NH4A)/2)
24630     ! CALCULATE ANODE COMPARTMENT CONDUCTIVITY.           (mhos/m)
24640 ACOND=17.6*HL+34.7
24650     ! CALCULATE CATHODE COMPARTMENT CONDUCTIVITY.         (mhos/m)
24660 CCOND=-4-.28*NH3C+10.19*NH4C-.03*MNC+.27*(TC-273)
24670     ! EVALUATE CATHODE POTENTIAL.                         (volts)
24680 EC=1.18+8.314*TC/96500*LOG (CW/(HC*710000000000*TC*EXP (-(63400/8.314/TC))))
24690     ! EVALUATE ANODE POTENTIAL.
24700 EA=1.23+8.314*TA/96500*LOG (1000/(HA*.000000000001))
24710     ! EVALUATE OHMIC POTENTIAL DROP.
24720 ER=CD*(.03/ACOND+.03/CCOND+DTHICK/(DCOND*VOID))
24730     ! GET TOTAL VOLT DROP. INCLUDE 1v FOR MEMBRANE LOSS.
24740 VOLT=EA+ER+EC+1
24750 RETURN
25000     !
25010     !
25020     !
25030 SULPHIDE:
25040     ! THIS SUBROUTINE CALCULATES THE SULPHIDE SECTION OF THE PLANT.
25050     ! IT REQUIRES THE SULPHIDE PH, TEMPERATURE (K), AND THE TOTAL
25060     ! CONCENTRATIONS (kmole/m3) OF MANGANESE AND SULPHATE. AS WELL
25070     ! AS THE ADDITION FLOWRATE OF AMMONIUM-SULPHIDE (kmole/hr).
25080     ! IT RETURNS THE TOTAL MN CONCENTRATION FROM THE MASS BALANCE
25090     ! AND THE SOLUTION CHEMISTRY.
25100 HS=10**(-PHSUL)
25110     ! INITIALISE ACTIVITY CONVERGENCE CHECK, AND THE INITIAL VALUES
25120     ! FOR MINOR AND MN2+ CONENTRATIONS. CALCULATE TOTAL MN AFTER PRECIP.
25130 MUDLD=0
25140 MINOR=0
25150 MN2S=.1
25160 TMAN=MANL-NH42S/QFEED
25170 MANS=TMAN
25180 SULPHS=SULPHATE
25190     ! CALL THE SUBROUTINE THAT CALCULATES THE EQUILIBRIUM CONSTANTS.
25200 TEMPK=TKSUL
25210 GOSUB KCONST
25220     ! START LOOP FOR ACTIVITY CO-EFFICIENTS.
25230 FOR L=1 TO 40
25240     ! CALCULATE THE EQ, RATIOS FROM THE EQ. CONSTANTS AND THE ACTIVITY
25250     ! CO-EFFICIENTS.
25260 K1=GMN2*GSO4*K1I
25270 K2=K2I/GNH4
25280 K3=GNH4*GSO4*K3I/GNH4SO4
25290 K4=GMN2*K4I/GMNNH3
25300 K5=GMNNH3*GSO4*K5I
25310 K6=GCO2*GSO4*K6I
25320 K7=GCO2*K7I/GCONH3
25330 K8=GCONH3*GSO4*K8I
25340 KSM=KSMI/(GMN2*GS2)
25350 KSC=KSCI/(GCO2*GS2)
25360     ! INITIALISE AND START LOOP FOR MINOR SPECIES. SET UP TOTAL CON-
25370     ! CENTRATIONS OF MAJOR SPECIES.
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25380 MINOLD=0
25390 FOR K=1 TO 40
25400     ! INITIALISE MN2+ CONVERGENCE CHECK.
25410 MN2OLD=0
25420     ! SOLVE FOR MN2+ CONCENTRATION AS A MAJOR SPECIES BY SUCCESIVE
25430     ! ITERATION. SEE SECTION 3.2 FOR THE EQUATIONS.
25440 FOR J=1 TO 100
25450 A=K3
25460 B=1-K3*(MANS+MN2S-SULPHS+2*MINOR)
25470 C=MANS-MN2S-SULPHS
25480 SO4S=(-B+SQR (B^B-4*A*C))/(2*A)
25490 MN2S=MANS/(1+K1*SO4S)
25500     ! IF SUCCESIVE VALUES OF MN2S DIFFER BY LESS THAN 1E-6 THEN
25510     ! CONTINUE WITH MODEL, ELSE REPEAT ROUTINE OR STOP IF THERE HAVE
25520     ! BEEN TOO MANY ITERATIONS.
25530 IF ABS (MN2S-MN2OLD)<.000001 THEN GOTO MAJRS
25540 MN2OLD=MN2S
25550 NEXT J
25560 PRINT "SULPHIDE INSIDE LOOP NOT CONVERGED AFTER 100 ITERATIONS."
25565 DISP "SULPHIDE INSIDE LOOP NOT CONVERGED AFTER 100 ITERATIONS."
25570 GOTO FINISH
25580 MAJRS:
25590     ! CALCULATE THE REMAINING MAJOR SPECIES, FOR EQUATIONS SEE SECTION 3.2
25600 MNSO4S=MANS-MN2S
25610 NH4SO4S=SULPHS-MNSO4S-SO4S
25620 NH4S=NH4SO4S/(K3*SO4S)
25630 NH3S=NH4S/(K2*HS)
25640     ! CALCULATE MINOR SPECIES.
25650 MNNH3S=K4*MN2S*NH3S
25660 MNAMSS=K5*MNNH3S*SO4S
25670     ! MODIFY THE TOTAL CONCENTRATIONS OF MAJOR SPECIES WITH THE CONCEN-
25680     ! TRATIONS OF THE MINOR SPECIES.
25690 MINOR=MNNH3S
25700 MANS=TMAN-MNNH3S-MNAMSS
25710 SULPHS=SULPHATE-MNAMSS
25720 AMMS=NH4S+NH4SO4S+NH3S+MNNH3S+MNAMSS
25730 ENEGS=2*SO4S+NH4SO4S
25740 EPOSS=2*MN2S+NH4S+2*MINOR
25750     ! CHECK FOR CONVERGENCE OF LOOP FOR MINOR SPECIES. CONTINUE WITH
25760     ! MODEL IF CONVERGED, ELSE REPEAT LOOP OR STOP IF TOO MANY ITERATIONS
25770     ! HAVE OCCURED.
25780 IF ABS (MINOR-MINOLD)<.000001 THEN GOTO ACTIVS
25790 MINOLD=MINOR
25800 NEXT K
25810 PRINT "SPHIDE LOOP FOR MINOR SPECIES NOT CONVERGED AFTER 40 ITERATIONS."
25815 DISP "SPHIDE LOOP FOR MINOR SPECIES NOT CONVERGED AFTER 40 ITERATIONS."
25820 GOTO FINISH
25830 ACTIVS:
25840     ! CALCULATE THE IONIC STRENGTH MU, AND THE SOLVENT STRENGTH JJ.
25850 MU=.5*(4*(MN2S+MNNH3S)+NH4S+NH4SO4S+4*SO4S)
25860 JJ=MNSO4S+MNAMSS+NH3S
25870     ! CHECK FOR CONVERGENCE OF ACTIVITY CO-EFFICIENTS BY EXAMINING THE
25880     ! IONIC STRENGTH, CONTINUE WITH MODEL IF CONVERGED.
25890 IF ABS (MUOLD-MU)<.00001 THEN GOTO COBALT
```

```
25900 MUOLD=MU
25910    ! CALL THE SUBROUTINE THAT CALCULATES THE NEW ACTIVITY CO-EFFICIENTS.
25920 GOSUB ACT_COEFFS
25930    ! REPEAT LOOP OR STOP IF THERE HAVE BEEN TOO MANY ITERATIONS.
25940 NEXT L
25950 PRINT "SULPHIDE LOOP FOR ACTIVITIES NOT CONVERGED AFTER 40 ITERATIONS."
25955 DISP "SULPHIDE LOOP FOR ACTIVITIES NOT CONVERGED AFTER 40 ITERATIONS."
25960 GOTO FINISH
25970 COBALT:
25980    ! ONCE THE MN SPECIES HAVE BEEN FOUND THEN CALCULATE THE COBALT
25990    ! SPECIES. FOR THE EQUATIONS SEE SECTION 3.3
26000 CO2S=MN2S*KSC/KSM
26010 COSO4S=K6*KSC/KSM*MN2S*SO4S
26020 CONH3S=K7*CO2S*NH3S
26030 COAMSS=K8*K7*KSC/KSM*MN2S*NH4S/(HS*K2)*SO4S
26040 COBS=CO2S+COSO4S+CONH3S+COAMSS
26050 COBPPM=COBS*53933
26060 MANS=TMAN
26100 RETURN
28000    !
28010    !
28020    !
28030 LEACH:
28040    ! THIS SUBROUTINE CALCULATES THE LEACH SECTION OF THE PLANT.
28050    ! IT REQUIRES THE LEACH PH, TEMPERATURE (k), AND THE TOTAL
28060    ! CONCENTRATIONS (kmol/m3) OF AMMONIA AND SULPHATE. IT THEN
28070    ! RETURNS THE TOTAL MN CONCENTRATION FROM THE MASS BALANCE AND
28080    ! THE SOLUTION CHEMISTRY.
28090 HL=10**(-PHLCH)
28100    ! INITIALISE THE CHECKS FOR CONVERGENCE, AND SET UP THE TOTAL
28110    ! CONCENTRATIONS OF MAJOR SPECIES.
28120 NH4G=.8
28130 MNOLD2=0
28140 MINOR=0
28150 AMML=AMMONIA
28160 SULPHL=SULPHATE
28170    ! CALL THE SUBROUTINE THAT CALCULATES THE EQUILIBRIUM CONSTANTS.
28180 TEMPK=TKLCH
28190 GOSUB KCONST
28200    ! START LOOP FOR ACTIVITY CO-EFFICIENTS.
28210 FOR L=1 TO 40
28220    ! CALCULATE THE EQ. RATIOS FROM THE EQ. CONSTANTS AND THE ACTIVITY
28230    ! CO-EFFICIENTS.
28240 K1=GMN2*GSO4*K1I
28250 K2=K2I/GNH4
28260 K3=GNH4*GSO4*K3I/GNH4SO4
28270 K4=GMN2*K4I/GMNNH3
28280 K5=GMNNH3*GSO4*K5I
28290 KMNEQ=KMNEQI*GMN2
28300    ! INITIALISE AND START LOOP FOR MINOR SPECIES.
28310 MNOLD=0
28320 FOR K=1 TO 100
28330    ! INITIALISE CONVERGENCE CHECK FOR NEWTON-RAPHSON.
28340 NH4DM=0
```

```
28350     ! START OF NEWTON-RAPHSON SCHEME. SEE SECTION 2.2 FOR EQUATIONS.
28360 FOR J=1 TO 100
28370 A=K1
28380 B=1-K1*(NH4G+MINOR-AMML/2)
28390 C=AMML-SULPHL-NH4G
28400 FUNNH4=(-B+SQR (B**2-4*A*C))/(2*A)-(AMML/NH4G-1)/K3
28410 FUNDERV=K1/(2*A)+((-(2*K1*B)+4*A)/(4*A*SQR (B**2-4*A*C)))+AMML/(K3*NH4G**2)
28420 NH4G=NH4G-FUNNH4/FUNDERV
28425     ! CHECK FOR CONVERGENCE OF NEWTON-RAPHSON ROUTINE.
28430 IF ABS (NH4G-NH4DM)<.000000001 THEN GOTO MAJR
28440 NH4DM=NH4G
28450 NEXT J
28460 PRINT "LEACH INSIDE LOOP NOT CONVERGED AFTER 100 ITERATIONS."
28465 DISP "LEACH INSIDE LOOP NOT CONVERGED AFTER 100 ITERATIONS."
28470 GOTO FINISH
28480 MAJR:
28490     ! CALCULATE THE REMAINING MAJOR SPECIES, FOR EQUATIONS SEE SECTON 2.2
28500 NH4L=NH4G
28510 SO4L=(AMML/NH4L-1)/K3
28520 NH4SO4L=AMML-NH4L
28530 MNSO4L=SULPHL-SO4L-NH4SO4L
28540 MN2L=MNSO4L/(K1*SO4L)
28550 NH3L=NH4L/(K2*HL)
28560     ! CALCULATE MINOR SPECIES.
28570 MNNH3L=K4*MN2L*NH3L
28580 MNAMSL=K5*MNNH3L*SO4L
28590 MINOR=MNNH3L
28600     ! MODIFY THE TOTAL CONCENTRATIONS OF MAJOR SPECIES WITH THE CONCEN-
28610     ! TRATIONS OF THE MINOR SPECIES.
28620 MANL=MN2L+MNSO4L+MNNH3L+MNAMSL
28625 MANLM=MANL*54.958
28630 SULPHL=SULPHATE-MNAMSL
28640 AMML=AMMONIA-NH3L-MNNH3L-MNAMSL
28650 ENEGL=2*SO4L+NH4SO4L
28660 EPOSL=2*MN2L+NH4L+2*MINOR
28670     ! CHECK FOR CONVERGENCE OF LOOP FOR MINOR SPECIES. CONTINUE WITH
28680     ! MODEL IF CONVERGED, ELSE REPEAT LOOP OR STOP IF TOO MANY ITERATIONS
28690     ! HAVE OCCURED.
28700 IF ABS (MNOLD-MANL)<.00001 THEN GOTO ACTIVITY
28710 MNOLD=MANL
28720 NEXT K
28730 PRINT "LEACH LOOP FOR MINOR SPECIES NOT CONVERGED AFTER 100 ITERATIONS."
28735 DISP "LEACH LOOP FOR MINOR SPECIES NOT CONVERGED AFTER 100 ITERATIONS."
28740 GOTO FINISH
28750 ACTIVITY:
28760     ! CHECK FOR CONVERGENCE OF ACTIVITY CO-EFFICIENTS BY EXAMINING THE
28770     ! MN CONCENTRATION, CONTINUE WITH MODEL IF CONVERGED.
28780 IF ABS (MANL-MNOLD2)<.0001 THEN GOTO MANEQ
28790 MNOLD2=MANL
28800     ! CALCULATE THE IONIC STRENGTH MU, AND THE SOLVENT STRENGTH JJ.
28810 MU=.5*(4*(MN2L+MNNH3L)+NH4L+NH4SO4L+4*SO4L)
28820 JJ=MNSO4L+MNAMSL+NH3L
28830     ! CALL THE SUBROUTINE THAT CALCULATES THE NEW ACTIVITY CO-EFFICIENTS.
28840 GOSUB ACT_COEFFS
```

```
28850     ! REPEAT LOOP OR STOP IF THERE HAVE BEEN TOO MANY ITERATIONS.
28860 NEXT I
28870 PRINT "LEACH ACTIVITIES LOOP NOT CONVERGED AFTER 40 ITERATIONS."
28875 DISP "LEACH ACTIVITIES LOOP NOT CONVERGED AFTER 40 ITERATIONS."
28880 GOTO FINISH
28890 MANEQ:
28892     ! CALCULATE THE LEACH EFFICIENCY. EQUATION IS FITTED TO PLANT DATA.
28894 GOSUB LCHEFF
28900     ! CALCULATE THE EQUILIBRIUM MN CONCENTRATION. THIS IS THE MAXIMUM
28910     ! ALLOWED MN CONCENTRATION FOR THE CHOSEN LEACH PH.
28920 MN2EQL=HL^*2/KMNEQ
28930 IF MN2EQL>MN2L THEN RETURN
28940 PRINT "MN CONCENTRATION LARGER THEN EQ. VALUE, CHOOSE LOWER LEACH PH"
28945 DISP "MN CONCENTRATION LARGER THEN EQ. VALUE, CHOOSE LOWER LEACH PH"
28950 PRINT "MN2EQ ";MNEQL,"MN2+ ";MN2L
28955 DISP "MN2EQ ";MNEQL,"MN2+ ";MN2L
28960 RETURN
30000 COST:
30010     !
30020     !
30030     ! THIS SUBROUTINE EVALUATES THE COSTS AND PROFIT INVOLVED IN THE
30040     ! OPERATION OF THE PLANT.
30050     ! CALL THE SUBROUTINE THAT EVALUATES THE LEACH EFFICIENCY.
30060 GOSUB LCHEFF
30070     ! THE REVENUE IS R1500 PER TON OF MN PRODUCED.
30080 MNPROF=1.5*MNPRT
30090     ! AMMONIA IS LOST IN THE CATHODE COMPARTMENT AND IN THE FILTER CAKE.
30100     ! THE FILTER CAKE LOSS IS ASSUMED TO BE 2.4% OF THE AMMONIA MASS
30110     ! FLOWRATE. THE COST IS R96 PER TON AMMONIA.
30120 AMCOST=.096*(.024*17.031*AMMCEX*QFEED+NH3CLT)
30130     ! SULPHATE IS LOST IN THE FILTER CAKE. THIS IS ASSUMED TO BE 2.4%
30140     ! OF THE SULPHATE MASS FLOWRATE. COST IS R92 PER TON SULPHATE.
30150 SCOST=.092*.024*98.076*SULPHATE*QFEED
30160     ! THE COST OF MANGANESE IN THE ORE IS R216 PER TON OF MN.
30170     ! THE MASS FLOWRATE OF MN IN THE ORE IS THAT REQUIRED BY THE
30180     ! MASS BALANCE PLUS THAT WHICH IS LOST IN THE FILTER CAKE (2.4%),
30185     ! DIVIDED BY THE LEACH EFFICIENCY.
30186 MNREQUIRED=(MANL-MANCEX+.024*MANL)*QFEED*54.938/LCHEFF
30190 MNCOST=.216*MNREQUIRED
30200     ! THE POWER COST IS TAKEN AS 2 CENTS PER KILOWATT HOUR.
30210 PCOST=.00002*CELLNO*VOLT*I
30220     ! CALCULATE THE PROFIT IN R/HR.
30230 PROFIT=MNPROF-(AMCOST+SCOST+MNCOST+PCOST)
30240     ! CALCULATE THE PROFIT IN R/TON MN.
30250 PROFTN=PROFIT*1000/MNPRT
30260 RETURN
31000 LCHEFF:
31010     ! THIS SUBROUTINE EVALUATES THE LEACH EFFICIENCY AS A FUNCTION
31020     ! OF PH. THIS IS A FITTED EQUATION TO PLANT DATA AND HOLDS PRO-
31030     ! VIDED THAT NO MN(OH)2 PRECIPITATION IS OCCURING.
31040  LCHEFF=.84-.0727*PHLCH-.00959*PHLCH**2
31050  ! LCHEFF=0.43+0.22*PHLCH-0.0232*PHLCH**2
31060 RETURN
32000 KCONST:
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32010     ! THIS SUBROUTINE EVALUATES THE EQUILIBRIUM CONSTANTS, USED IN THE
32020     ! LEACH AND SULPHIDE SECTIONS, AS FUNCTIONS OF TEMPERATURE (k).
32030     ! THE EQUATIONS ARE GIVEN IN SECTION APPENDIX A.
32040     ! EQ. CONSTANT FOR        MN2+  +  SO42-  =  MNSO4
32050  K1I=EXP (5.204+2100/1.987*(1/298.15-1/TEMPK))
32060     ! EQ. CONSTANT FOR        NH3   +  H+  =  NH432070  K2I=EXP (21.29-
(13000/1.987*(1/298.15-1/TEMPK)))
32080     ! EQ. CONSTANT FOR        NH4+  +  SO42-  =  NH4SO4-
32090  K3I=10**(1.05+.0053*(TEMPK-273.15))
32100     ! EQ. CONSTANT FOR        MN2+  +  NH3  =  MNNH3232110  K4I=10
32120     ! EQ. CONSTANT FOR        MNNH32+  +  SO42-  =  MNNH3SO4
32130  K5I=K1I
32140     ! EQ. CONSTANT FOR        CO2+  +  SO42-  =  COSO4
3215`  K6I=EXP (5.388+1400/1.987*(1/298.15-1/TEMPK))
32160     ! EQ. CONSTANT FOR        CO2+  +  NH3  =  CONH3232170
K7I=10**(2.017+.005*(298.15-TEMPK))
32180     ! EQ. CONSTANT FOR        CONH32+  +  SO42-  =  CONH3SO4
32190  K8I=K6I
32200     ! EQ. CONSTANT FOR        MNS  =  MN2+  +  S2-
32210  KSMI=EXP (-24.177+6200/1.987*(1/298.15-1/TEMPK))
32220     ! EQ. CONSTANT FOR        COS  =  CO2+  +  S2-
32230  KSCI=1.1E-16*EXP (16900/1.987*(1/293.15-1/TEMPK))
32240     ! EQ. CONSTANT FOR        MN2+ + 2H2O  =  MN(OH)22+  +  2H32245     !
CHANGED FROM 1.59E-15 TO 4.90E-16 TO FIT POURBAIX DIAGRAM.
32246     ! SEE KCONST.
32250  KMNEQI=4.9E-16*EXP (25930/1.987*(1/298.15-1/TEMPK))
32260 RETURN
33000 KRATIO:
33010     ! THIS SUBROUTINE EVALUATES THE EQUILIBRIUM RATIOS AS FUNCTIONS
33020     ! OF TEMPERATURE (K) FOR USE IN THE CELL HOUSE.
33030     ! THESE EQUILIBRIUM RATIOS HAVE BEEN FITTED BY RODRIGUES(1983).
33040     ! NOTE THAT THEY HAVE NO UNITS AS THE CONCENTRATIONS ARE DIVIDED
33050     ! BY THE UNIT OF CONCENTRATION Kmole/cM.
33060     ! EQ, RATIO FOR    MN2+  +  NH4+  =  MNNH32+  +  H33070 KMNNH3=EXP (-
34.57+.051*TEMPK)
33080     ! EQ. RATIO FOR    NH3  +  H+  =  NH433090 KAMM=EXP (40.32-.064*TEMPK)
33100     ! EQ. RATIO FOR    MN2+  +  2H2O  =  MN(OH)2  +  2H33110 KMNOH=EXP (-
67.15+.1025*TEMPK)*GMN2
33120     ! EQ. RATIO FOR    HSO4-  =  H+  +  SO42-
33130 KSO4=EXP (8.339-.0294*TEMPK)
33140 RETURN
34000 ACT_COEFFS:
34010     ! THIS SUBROUTINE CALCULATES THE ACTIVITY CO-EFFICIENTS AS FUNCTIONS
34020     ! OF TEMPERATURE (c), IONIC STRENGTH AND SOLVENT STRENGTH.
34030 TCENT=TEMPK-273.15
34040     ! THESE ARE THE DEBYE-HUCKEL PARAMS. FOR PURE WATER AS A FUNC OF TEMP.
34050 A0=.4882+.0007598*TCENT+.000002948*TCENT**2+.00000001185*TCENT**3
34060 B0=.3241+.0001649*TCENT+.0000006579*TCENT**2+.00000000103*TCENT**3
34070 A=A0-.3*JJ
34080 IF A<0 THEN A=0
34090 B=B0*(A/A0)**(1/3)
34100     ! ACT. CO-EFF FOR MN2+           Z=2          P=6
34110 GMN2=A*4*SQR (MU)/(1+B*6*SQR (MU))
34120     ! ACT CO-EFF FOR NH4+            Z=1          P=3
34130 GNH4=A*1*SQR (MU)/(1+B*3*SQR (MU))
34140     ! ACT CO-EFF FOR SO4+            Z=2          P=4
34150 GSO4=A*4*SQR (MU)/(1+B*4*SQR (MU))
34160     ! ACT CO-EFF FOR NH4SO4-         Z=1          P=4
34170 GNH4SO4=A*1*SQR (MU)/(1+B*4*SQR (MU))
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34180     ! ACT CO-EFF FOR S2-                Z=2         P=5
34190 GS2=A*4*SQR (MU)/(1+B*5*SQR (MU))
34200 GMN2=10**(-GMN2)
34210 GNH4=10**(-GNH4)
34220 GSO4=10**(-GSO4)
34230 GNH4SO4=10**(-GNH4SO4)
34240 GS2=10**(-GS2)
34250     ! ACT CO-EFF FOR MNNH32+             Z=2         P=6     (SIMILAR TO MN2)
34260 GMNNH3=GMN2
34270     ! ACT CO-EFF FOR CO2+                Z=2         P=6     (SIMILAR TO MN2)
34280 GCO2=GMN2
34290     ! ACT CO-EFF FOR CONH3+              Z=1         P=6     (SIMILAR TO MN2)
34300 GCONH3=GMN2
34310 RETURN
35000 LPRINT:
35010 PRINT
35020 PRINT "LEACH SECTION."
35030 PRINT "--------------"
35040 PRINT USING 35060 ; MANLM,AMMSUL,SULPHATE
35050 DISP USING 35060 ; MANLM,AMMSUL,SULPHATE
35060 IMAGE "MANGANESE     = ",DDD.DD,"  g/l",/,"AMM-SULPH      = ",DDDD.D,"
g/l",/,"SULPHATE      = ",MD.DDD,"  kmole/m3"
35070 PRINT USING 35090 ; AMMONIA,LCHEFF
35080 DISP USING 35090 ; AMMONIA,LCHEFF
35090 IMAGE "AMMONIA       = ",MD.DDD,"  kmole/m3",/,"LCH EFF        = ",MD.DDD
35100 PRINT
35110 PRINT
35120 RETURN
36000 SPRINT:
36010 ~RINT
36020 PRINT "SULPHIDE SECTION."
36030 PRINT "-----------------"
36040 PRINT USING 36060 ; MANSM,COBPPM
36050 DISP USING 36060 ; MANSM,COBPPM
36660 IMAGE "MANGANESE     = ",DDD.DD,"  g/l",/,"COBALT         = ",MD.DDD,"  ppm"
36100 PRINT
36110 PRINT
36120 RETURN
37000 PVARIABLES:
37010 PRINT
37070 PRINT "PROCESS VARIABLES."
37080 PRINT "------------------"
37090 PRINT USING 12270 ; TCC
37100 IMAGE "1.  TEMP. OF CATHODE COMPARTMENT (c)      = ",DDD.D
37110 PRINT USING 12290 ; PHF
37120 IMAGE "2.  PH OF CELLHOUSE FEED                  = ",DD.DDD
37130 PRINT USING 12310 ; QFEED
37140 IMAGE "3.  FLOWRATE (m3/hr)                      = ",DDDD.D
37150 PRINT USING 12330 ; I
37160 IMAGE "4.  TOTAL CURRENT (amps)                  = ",DDDDDD
37170 PRINT USING 12350 ; CELLNO
37180 IMAGE "5.  NO OF CELLS                           = ",DDD
37190 PRINT USING 12370 ; PHLCH
37200 IMAGE "6.  PH OF LEACH TANKS                     = ",DD.DD
37210 PRINT USING 12390 ; PHSUL
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37220 IMAGE "7.  PH OF SULPHIDE TANKS                    = ",DD.DD
37230 PRINT USING 12410 ; TCLCH
37240 IMAGE "8.  TEMP. OF LEACH (C)                      = ",DDD.D
37250 PRINT USING 12430 ; TCSUL
37260 IMAGE "9.  TEMP. OF SULPHIDE. TANKS (C)            = ",DDD.D
37270 PRINT USING 12450 ; AMMSULPHATE
37280 IMAGE "10. AMMONIA-SULPHATE IN LEACH. (g/l)        = ",DDDD.D
37290 PRINT USING 12470 ; MANGAN
37300 IMAGE "11. DESIRED MN IN LEACH. (g/l)              = ",DDD.D
37310 PRINT USING 12490 ; NH42SO
37320 IMAGE "12. AMMONIUM-SULPHIDE ADD. (l/min)          = ",DD.DDD
37330 PRINT
37340 PRINT
37350 RETURN
38000 OPRINT:
38010 PRINT
38020 PRINT "CELLHOUSE."
38030 PRINT "----------"
38040 PRINT USING 38060 ; MNANM,ACID,EFFC
38050 DISP USING 38060 ; MNANM,ACID,EFFC
38060 IMAGE "MN OUT          = ",DDD.DD,"  g/l",/"ACID OUT      = ",DDD.DD,"
g/l",/,"CUR. EFF.    = ",DD.DDD
38062 PRINT USING 39066 ; PHC
38064 DISP USING 39066 ; PHC
38066 IMAGE "pH CATHODE     = ",DD.DDD
38070 PRINT USING 38090 ; SOLUB
38080 DISP USING 38090 ; SOLUB
38090 IMAGE "MN SOLUBILITY LIMIT = ",DD.DDD
38100 PRINT
38110 PRINT
38120 RETURN
39000 PPRINT:
39001    !
39002    ! THIS SUBROUTINE PRINTS AND DISPLAYS THE COSTS.
39010 PRINT
39020 PRINT "COSTS."
39030 PRINT "------"
39040 PRINT USING 39060 ; PROFIT,PROFTN
39050 DISP USING 39060 ; PROFIT,PROFTN
39060 IMAGE "PROFIT          = ",DDDD.D,"  R/hr",/,"PROFIT          = ",DDDD.D,"
 R/ton"
39080 PRINT USING 39100 ; MNPRT,MNREQUIRED,MNCOST
39090 DISP USING 39100 ; MNPRT,MNREQUIRED,MNCOST
39100 IMAGE "MN PROD.        = ",DDDD.D,"  kg/hr",/,"MN REQUIRED   = ",DDDD.D,"
 kg/hr",/,"MN COST       = ",DDDD.D,"  R/hr"
39110 PRINT USING 39130 ; VOLT,PCOST
39120 DISP USING 39130 ; VOLT,PCOST
39130 IMAGE "VOLTAGE         = ",DDD.DD,"  v/cell",/,"POWER COST    = ",DDDD.D,"
 R/hr"
39140 PRINT
39150 PRINT
39160 PRINT
39170 PRINT
39180 PRINT
39190 RETURN
```

APPENDIX N NOMENCLATURE

Note: Concentrations of species, such as Mn^{2+} and $NH_4SO_4^-$, are written as Mn and NH_4SO_4 without the charges, and have units of kmole/m³. Total component concentrations are written as MAN_T, AMM_T and $SULPH_T$ in the same units.

Symbol	Meaning	Units
A_m	Area of flow through membrane	m²
Ao	Normal solvent constant.	$(m^2/kmole)^{\frac{1}{2}}$
A	Modified solvent constant.	$(m^2/kmole)^{\frac{1}{2}}$
Bo	Normal solvent constant.	$(m^2/kmole)^{\frac{1}{2}}$/Ang
B	Modified solvent constant.	$(m^2/kmole)^{\frac{1}{2}}$/Ang
c_j	Concentration of charged species j.	kmole/m³
c_k	Concentration of uncharged species k.	kmole/m³
C_i	Concentration of species i.	kmole/m³
C_j	Concentration of species j in membrane.	kmole/m³
Co_T	*Total Co concentration.*	kmole/m³
C1	Constant in cathode kinetic equation.	
C2	Constant in impurity effect expression.	
d	Thickness of membrane.	m
D_j	Diffusion coefficient of species j	m²/s
E_i^o	Standard electrochemical potential.	volts
E_i	Electrochemical potential drop.	volts
F	Faraday's constant = 96500.	coul/mole
F	Faraday's constant = 96500000.	coul/kmole
Fr	Ore feed rate.	kg/hr
g_i	Mole fraction in oxygen gas.	
H	Hydrogen ion concentration.	kmole/m³

I	Total current.	amps
I_i	Current density.	amps/m^2
K_j	Equilibrium constants.	
Ksm,Ksc,Kmneq	Solubility product constants.	
Kc,Ka,Kh	Experimentally determined equilibrium ratios.	
Kmn	Fitted solubility product ratio.	
L_i	Distance over current path.	m
Leff	Leach efficiency.	
Mfrac	Total Mn fraction in ore.	
Mn	Manganese concentration.	kmole/m^3
Mnexit	Total Mn concentration in leach.	kg/m^3
Mnin	Total Mn concentration in cell exit.	kg/m^3
Mnlost	Mn lost in filter cake.	kg/hr
P_j	Effective ion diameter parameter.	Angstroms.
Q	Total solution flowrate.	m^3/hr
Q_i	Flowrate per cell in section i.	m^3/s
Q_s	Flow of ammonium sulphide per m^3 solution.	m^3/m^3 soln.
R	Gas constant ≈ 8.314.	J/(mole.K)
R	Gas constant ≈ 1.987.	cal/(mole.K)
T	Temperature.	°K
Tc	Temperature ins de cathode compartment	°C
V_i	Ohmic volt drop.	volts
W_j	Molar flux species j.	kmole/s
y_j	Mole fraction in hydrogen gas.	
z_j	Unit charge on species j.	
β	Empirical dielectric constant.	$(m^3/kmole)^{\frac{1}{2}}$
γ_j	Activity coefficient of species j.	
ε	Voidage in membrane.	
κ_i	Solution conductance.	mhos/m
κ^*	Average solution conductance in membrane.	mhos/m
μ	Solution ionic strength.	kmole/m^3
ξ	Current efficiency as a fraction.	

Subscripts

a	Anode or Anode compartment.
c	Cathode or cathode compartment.
f	Feed stream.
h	Hydrogen.
i	General characteristic.
j	Charged specie.
k	Uncharged specie.
ℓ	Leach.
m	Membrane.
n	Ammonia.
s	Sulphide.
T	Total.
w	Water.

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