T-2916

THE REMOVAL OF IRON FROM ALUMINUM CHLORIDE LEACH LIQUORS BY ION EXCHANGE

by

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A thesis submitted to the Faculty and Board of Trustees of the Colorado School of Mines in partial fulfillment of the requirements for the degree of Master of Science - Metallurgical Engineering

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Date May 22, 1984

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ABSTRACT

The sorption behavior of iron onto three anion exchange resins from simulated aluminum chloride leach liquors has been studied. Bench scale sorption isotherm experiments were performed at room temperature. The initial chloride concentrations of the simulated leach liquors ranged from 1M to 6M. No significant iron loading was observed for the Dowex WGR resin. Iron loading for the Dowex SBR and Dowex MWA-1 resins increased with increasing chloride concentrations. Maximum capacities observed for both resins were approximately 0.95 milliequivalents Fe per dry gram resin at an initial chloride concentration of 6M. The Dowex SBR resin sorbed noticeably greater amounts of iron than the MWA-1 resin at initial chloride concentrations of 4 and 5M. Iron stripping, however, was more difficult for the SBR resin than with the MWA-1 resin. This may lead to problems when applying the SBR resin to industrial use. Computer programs were written to predict the equilibrium distribution of species in various aqueous electrolytes. Correlation of computer results with published data indicated good qualitative correlations.

Strict quantitative conclusions may, however, be suspect. Comparison of computer program predictions and sorption isotherm results indicate that the species $Fe(Cl)_{3\ (aq)}$ may be the main species sorbed from the simulated leach liquors.

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ACKNOWLEDGEMENTS

The author would like to express his appreciation to Dr. Charles Natalie for his assistance and guidance throughout the course of this project.

Special thanks are extended to the Kroll Institute for Extractive Metallurgy and to the Department of Metallurgical Engineering for their financial support. Appreciation is extended to Dr. William Copeland for his assistance in this area.

Thanks also go to all the graduate students in the department for their assistance and advice, especially Stephanie Simons and Taie Li. Thanks are also extended to: Ramiro Camahuali, Enrique Elorza, Rod Leonard, Gary Hemphill, Brian Eberhard, Rick Woldow, Bruce Kelley, Tom Battle, and Elane Bruno for their friendship.

Finally, the author would like to acknowledge his parents, Anthony and Helen Gudeczauskas, and family for their love and support.

CHAPTER 1

INTRODUCTION

Over the past 15 years, the United States has witnessed a decreasing supply of domestic raw materials that are required for metals production. Some ores, namely those containing cobalt, chromium, and aluminum are domestically found in such small quantities that large amounts are imported to meet production needs. For this reason, the U.S. Bureau of Mines has been investigating (1-8) metals production from alternative domestic sources. One such possibility involves the production of cell-grade alumina from domestic kaolinitic clay deposits. The process involves leaching aluminum from the clay with hydrochloric acid and later crystallizing aluminum chloride from the leach liquor. The aluminum chloride is subsequently calcined to produce a pure alumina product. One of the drawbacks of this process, however, is the co-leaching of iron from the clay along with the aluminum.

The iron is present in sufficiently high quantities so as to leave an unacceptable impurity content in the cell-grade alumina. Ensuing tests were undertaken in an attempt to rid the leach liquor of the unwanted iron. One procedure investigated involved the use of solvent extraction. Pilot plant tests were conducted to study the feasibility and performance of the proposed process and results proved to be encouraging (1).

One disadvantage encountered during the use of solvent extraction involves the loss of organic solvent in the iron removal stage. The organics loss necessitated the implementation of a column containing activated carbon to insure that no organics proceded to the crystallization stage. The problem of emulsion formation and solvent loss is inherent in almost all solvent extraction operations and economic costs could be high.

Ion exchange has, therefore, been proposed to replace solvent extraction in the removal of iron from aluminum chloride leach liquors. Ion exchange has shown itself to be economically viable in the removal of low concentration impurities while keeping organic losses low. A two stage sequence can be used to describe the industrial ion exchange process:

1) ADSORPTION - an anionic or cationic resin is used to adsorb the desired metal ion or metal complex ion into the resin from an aqueous solution.

2) ELUTION - the recovery of the metal ion or metal complex ion in a different aqueous phase by using an appropriate eluant.

Industrially, ion exchange is performed in one of three ways: a fixed bed, a moving bed, or a resin-in-pulp reactor. A series of three or more fixed bed columns are usually run in series with descending flows of the solution through the columns. As a column becomes saturated with the desired species it is removed from the series and eluted. The following column in series subsequently becomes the first column to receive the pregnant solution, while the freshly eluted column becomes the last column in the series.

Moving bed circuits consist of specifically separate columns designed exclusively for adsorption, backwashing, and elution. Resins are transported between columns by hydraulic pressure to reduce resin attrition. In order to maintain steady state conditions in a plant, each stage usually contains a set of three identical columns; as the contents of one column becomes saturated, the resin can be transported without disrupting operations.

Resin-in-pulp circuits are normally used to avoid any filtration steps that may otherwise have been required. Banks of cells are used in series, with the pregnant solution feed being switched to another bank once the initial bank has been saturated. One factor that must be observed closely, however, is the resin attrition due to agitation in the cells.

Among all the resin types available for use, the synthetic ion exchange resins have been the most widely used. Synthetic ion exchange resins have attained the most recognition because their properties can be controlled and their loading capacities are high. This luxury does not exist with natural inorganic ion exchangers and, consequently, these resins are limited in applicability. Even though a large emphasis has been placed on the use of ion exchange to recover various metals for their economic worth, about 98% of the resins produced are still used in water treatment (9).

Since iron is a naturally occuring impurity in all kaolinitic clays, it appears quite obvious that iron removal is imperative when producing cell-grade alumina. Because ion exchange use generally involves low organic losses, it seems readily apparent that this unit operation would be an acceptable alternative to solvent extraction. Therefore, experimentation using ion exchange as a sorbent for iron impurities has been studied.

1.1) SCOPE

This project has dealt with the equilibrium capacity of ion exchangers for the removal of iron from aluminum chloride leach liquors. Also, the iron species that can be extracted onto the ion exchange resins, under varying conditions, is predicted. This study can be categorized into the group of separation systems called aqueous/organic phase systems.

The theoretical fundamentals applying to this system are soundly established in the literature (9-11). Many studies have been undertaken in the ion exchange field, but only two known studies have been conducted regarding the removal of iron by ion exchange (12,13). From these studies, it is difficult to draw conclusions concerning the equilibrium capacity of the ion exchangers in aluminum chloride leach liquors. The need for a series of tests regarding iron removal seems quite obvious. It also seems apparent that a computer program would be helpful in predicting which species will be present in solution at different chloride concentrations.

1.2) AIM OF STUDY

The principal contribution to aluminum extractive metallurgy expected from this work has been obtained from sorption isotherm results. Also, an attempt was made to compare these sorption isotherm results with results predicted by a computer simulation program. Eventually, the sorption isotherm results could be used to design a pilot plant scale circuit to test steady state ion exchanger performance.

The driving force for this investigation stemmed from the need to remove iron from aluminum chloride leach liquors. Ion exchange was chosen because the organic loss was expected to be lower than that with solvent extraction techniques. The foundation of the study was to perform sorption isotherm tests in the removal of iron at different aqueous chloride concentrations. The sorption isotherms were then compared with a computer program that predicts the concentration of species in solution. Conclusions could subsequently be drawn regarding the iron species that is extracted. Considerable contradictions have been found in the literature (14-16) concerning the iron species present in chloride solutions and this study has served to provide more data in this area.

Since there has only been a small amount of research performed in the area of iron removal by ion exchange, this study has served to provide a better understanding of the ion exchange process in this area. The experimental results, as mentioned before, could become a good foundation in the development of pilot plant scale tests for the removal of iron impurities.

1.4) ORGANIZATION OF THESIS

The present chapter has given a general overview of ion exchange technology and the role ion exchange may play in the production of aluminum from domestic kaolinitic clay sources. The need for ion exchange experimentation in the removal of iron from aluminum chloride leach liquors was also discussed. Chapter 2 will present a review of the technical literature pertaining to alternative aluminum production and iron removal by solvent extraction and ion exchange. The third Chapter discusses the theoretical considerations pertaining to the determination of activities of species in solution. Also, theoretical considerations regarding ion exchange equilibria is analyzed. Chapter 4 presents the experimental setups and procedures used in this study. The experimental results and discussion are presented in the fifth Chapter while Chapter 6 concludes with pertinent conclusions and suggestions for further experimental work.

CHAPTER 2

LITERATURE SURVEY

2.1) BACKGROUND

Although the properties of ion exchange have been used for centuries, the modern era for ion exchange began about 130 years ago. In 1850, Thompson and Way discovered that cultivated soil was capable of exchanging numerous ions. A sample of sandy clay that was treated with ammonium sulfate was placed in a glass cylinder and water was subsequently passed through the column. The effluent from the column was found to contain gypsum. The amount of calcium eluted from the column was determined to be proportional to the amount of ammonia present in the clay (9). Twenty years later, in 1870, Lemberg (11) leached luecite with a salt solution and observed that the leucite ($K_2O.Al_2O_3.4SiO_2$) had transformed to analcite ($Na_2O.Al_2O_3.4SiO_2.2H_2O$). When Lemberg washed the analcite with a potassium chloride solution he observed that luecite was again present. From this process, Lemberg was able to describe the stoichiometry and reversibility of ion exchange.

Experiments of this nature continued up until 1905 when Ganz succeeded in synthesizing inorganic ion exchangers. One such synthesized ion exchanger, sodium perutite, was determined to have practical uses in water treatment (9).

The next major development in ion exchange technology occurred in 1935 when Adams and Holmes found that crushed phonograph records showed reversible ion exchange properties. This discovery marked the beginning of the era in which organic resins were used for ion exchange in place of inorganic ion exchangers. It was then possible to vary the operating characteristics of an ion exchanger in an organized method so that scientific understanding could be increased (10).

Numerous advances have occurred in the ion exchange field in the last 50 years including the major fields of water softening, uranium extraction, deionization, and desiccation. The advances seen in ion exchange seem to be less numerous today, however, due to the vast knowledge already gained in this area.

Currently, bauxitic ores are used to produce almost all the world's aluminum with the dominant aluminum mineral being gibbsite ($Al(OH)_3.3H_2O$).

The Bayer process is presently used to purify alumina. The first stage in the Bayer process involves treating the ground ore with a sodium hydroxide solution in order to selectively dissolve the alumina.

$$Al_2O_3.xH_2O + 2NaOH = 2NaAlO_2 + (x+1)\ H_2 \qquad (2.1)$$

After a solid-liquid separation step, the reverse of equation 2.1 occurs with an aluminum trihydrate precipitate being formed.

$$2NaAlO_2 + 4H_2O = 2NaOH + Al_2O_3.3H_2O \qquad (2.2)$$

Lastly, the alumina trihydrate is calcined to make a pure alumina product which is reduced electrothermically to produce aluminum (17,18).

2.2) THE CLAY-HCL PROCESS

Since the United States imports about 93% of the bauxite used in domestic aluminum production, research has been conducted to investigate aluminum production from domestic resoures. The U.S. Bureau of Mines has been actively examining the feasibility of leaching kaolinite using hydrochloric acid. Kaolinite ($Al_2O_3.2SiO_2.2H_2O$) is commonly found in many areas of the United States. The current main domestic kaolin deposits are located in Georgia, Arkansas, and Oregon with total U.S. kaolin deposits amounting to 3350 million short tons (19). It is easily mined and crushed and environmental hazards from processing kaolinitic clay are low since the main gangue product is silica. Hydrochloric acid leaching was found to be preferable over nitric, sulfuric, and sulfurous acids mainly due to cost and energy considerations (5).

Figure 2.1 depicts the clay-HCl process as developed by the Bureau of Mines. Incoming ore is calcined at 750°C to render the kaolin more readily leachable. The calcined ore is then leached in a hot, strong hydrochloric acid solution in order to dissolve the aluminum (along with any iron present). The pregnant leach liquor is then filtered to remove all solids before proceeding to the chlorination step where almost all of the iron present is oxidized from Fe^{++} to Fe^{+++}. Solvent extraction is subsequently utilized to remove almost all iron impurities. The leach liquor is then evaporated resulting in a saturated $AlCl_3$ solution. HCl gas is then added to crystallize aluminum chloride hexahydrate ($AlCl_3.6H_2O$). Finally, the aluminum chloride hexahydrate crystals are decomposed in two stages at 250°C and 1000°C in order to obtain a pure, anhydrous alumina product suitable for Hall-Heroult electrolysis (3). HCl acid is recovered in

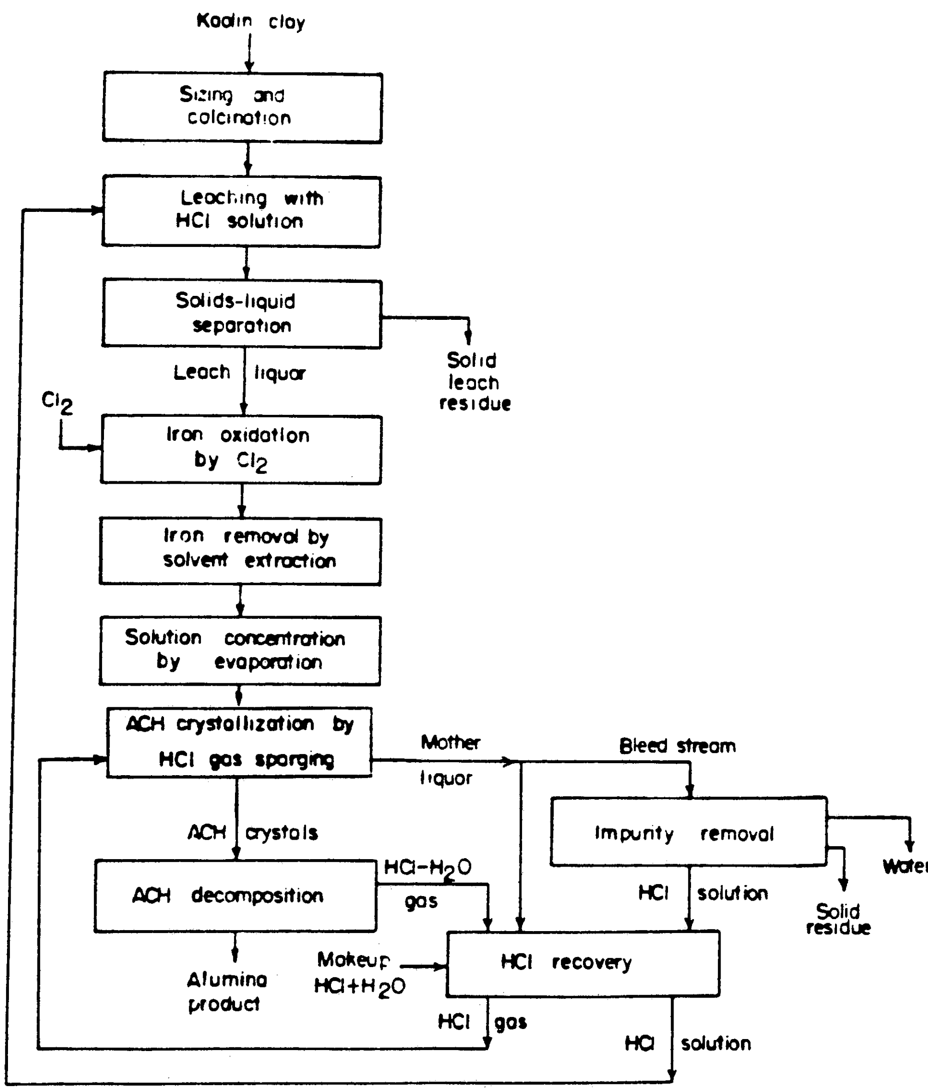

Figure 2.1 - The Clay-HCl Process as Developed by the U. S. Bureau of Mines (1).

the crystallization and decomposition steps and is recycled back to the leaching phase (3).

2.3) SPECIES IDENTIFICATION

One main concern encountered in the removal of iron from aluminum chloride leach liquors regards the iron chloride species that is extracted from the aqueous solution. The valence of the species plays an important role in solvent extraction and ion exchange since electrostatic forces are influential in species extraction.

Standley and Kruh (16) reported in 1960 that the main iron chloride species present in both "neutral" and acid solutions was $FeCl_4^-$. This conclusion was reached using x-ray diffraction in which varying amounts of ferric chloride and hydrochloric acid solutions were analyzed. The radial distribution method (20) was used in which a monochromatic x-ray beam was diffracted from a capillary tube containing the solution to be analyzed. The intensity of the diffracted x-rays was measured at different angles using a counter diffractometer. After correcting the intensities for various perturbations in measurements, the scattered intensities were re-calculated on an absolute scale for comparative purposes. Fourier analysis was then utilized in which a curve was drawn giving the average number of atoms between a distance r and r + dr from an atom. Based on the area analysis at a given atomic distance it was concluded that the ferric ion was surrounded by four chloride ions. In the absence of hydrochloric acid it was surmised that chloride ions were shared between iron atoms.

Brady, Robin, and Varimbi (14) contradicted the experimental results obtained by Standly and Kruh. Using nearly the same x-ray diffraction method as that of Standley and Kruh, Brady, Robin, and Varimbi deduced that three Fe-Cl bonds were present per ferric ion in neutral solutions. A neutral solution can be described as having no excess acid or base added to the solution. Data results also indicated that there were fewer than two $Fe-H_2O$ bonds per ferric ion. Even though an average of three Fe-Cl bonds per iron atom were found, they concluded that 75% of the iron present consisted of $FeCl_4^-$ while the remaining 25% of the iron was uncoordinated with any chloride atoms. When excess chloride was added as HCl, the coordination number around the ferric ion seemed to change from six to four and the main species appeared to be $FeCl_4^-$. Further experimentation using $HClO_4$ indicated that H^+ was instrumental in the coordination change of the iron ion since no excess chloride was added. The perchlorate was assumed not to complex with the ferric ion. As a result, it was concluded that the amount of $FeCl_4^-$ present in strongly acid solutions did not depend on the chloride concentration. Forty-eight percent of the iron present in concentrated $FeCl_3$ - concentrated acid solutions was deduced to be present as $FeCl_4^-$.

Earlier, in the year 1958, Friedman (15) used spectrophotometric experiments to determine the structure of iron-chloride species in strong HCl solutions. The absorption curve of a 0.68 M $FeCl_3$ solution in 16 M HCl was compared to the absorption curve for solid $KFeCl_4$ and an ether extract known to contain $FeCl_4^-$. The absorption curves closely resembled each other and it was therefore concluded that $FeCl_4^-$ was the main species present in 16 M HCl.

2.4) SOLVENT EXTRACTION OF IRON

Solvent extraction has been used by the U.S. Bureau of Mines and other researchers to remove iron from acid-aluminum chloride solutions with varying amounts of success. The U.S. Bureau of Mines (1,7) has investigated the use of several extractants for iron removal. Eisele et al (7) reported the use of Alamine 336 (a tertiary amine) and tri-butyl phosphate (TBP) on the separation from a simulated leach liquor containing 44.8 grams per liter Al, 5.85 gpl Fe, and 0.7 gpl H^+ as free chlorides. Distribution coefficients obtained ranged from 102 to 182 (increasing with a decrease in pH) for a 10% Alamine 336 extractant with a kerosine-Socal 335L diluent and from 0.40 to 8.31 for a 20% TBP extractant with the same diluent. Sorensen et al (1) performed a more detailed pilot plant study with Alamine 336 and found that a purified leach liquor could be continuously produced with iron levels of less than 7 ppm.

The extraction of iron(III) from chloride solutions in the absence of aluminum has also been researched extensively. Nelson and coworkers (21) reported in 1964 the use of tri-n-octylamine in the extraction of Fe(III) from aqueous HCl solutions. Their data supports the assumption that the ionic species $FeCl_4^-$ is found in the organic phase forming the ion pair $R_4NHFeCl_4$. The work of Good and Sristava (22) was undertaken to rectify any contradictions that were found in determining the extracted iron species. Conclusions regarding the extracted iron species reached by equilibrium data and spectral studies were contradictory in several previous studies and, as a result, Good and Sristava analyzed extracted iron species from a high molecular weight quaternary ammonium salt. All analyses (including infra-red spectroscopy) indicated that the extracted species was $FeCl_4^-$.

Ilic and Cattrall (23) indicated the presence of $FeCl_4^-$ in organic amine phases when extracting iron from a 6M HCl solution. Lindenbaum and Boyd (24) have also deduced that $FeCl_4^-$ is the main species present in 12 M HCl acid from the use of spectrophotometric measurements of organic amine phases. Ginsberg and Robin (25) have supported this same conclusion with their work with concentrated HCl solutions in which iron was extracted using pyridine.

2.5) ION EXCHANGE

The removal of iron using solid ion exchange resins has been studied less extensively than with solvent extraction. Khazanov (13) has reported the removal of iron from $AlCl_3$-HCl solutions by the use of EDE-10P (manufacturer unknown) ion exchange resin. Iron capacity was seen to increase with an increase in chloride and acid concentrations. Effluent iron concentrations were found to be less than 0.001 grams $FeCl_3$ per liter from an initial solution containing 281 grams $AlCl_3$ per liter and 18.5 grams $FeCl_3$ per liter.

The Dowex-1 (now known as Dowex-SBR) resin was used by Kraus and Moore (12) in order to remove iron from acid solutions ranging from 0.5 to 9.0 M HCl. Elution experiments were performed on the resin using an Fe 59 tracer and a 0.023 cm^2 column. Calculated distribution coefficients ranged from 0.16 at 0.5 M HCl to 5900 at 9.0 M HCl. The authors attributed the larger distribution coefficients to the formation of the probable $FeCl_4^-$ complex at higher acid concentrations. Further experimentation (using a resin column 10 cm high with an area of 0.024 cm^2) visually showed a good separation of iron impurities (30 mg/liter initially) from a 2 M aluminum chloride solution containing 3 M HCl.

2.6) ECONOMICAL WORTH

Presently, there is no economical cause to reclaim iron, for its value, by ion exchange mainly because iron can be more economically produced by conventional methods (26). Future developments may, however, require the recovery of iron by ion exchange due to changes in environmental pollution laws or to shortages of high-grade iron ores. If the availability of high-grade ores becomes small, the iron removed by ion exchange could be shipped in an upgraded state to an iron production site, thereby eliminating a tailings dam effluent problem while also recovering iron for production.

CHAPTER 3

THEORETICAL CONSIDERATIONS

As is the case in many areas of extractive metallurgy, ion exchange deals with the separation and/or concentration of certain species in solution. In many hydrometallurgical systems it is helpful to theoretically predict the activities of several species in solution.

This chapter is divided into two major sections. The first section will discuss the determination and prediction of activities of species in solution. The second section deals with the sorption of solutes by ion exchange and the resultant equilibria.

3.1) ACTIVITIES OF SPECIES IN SOLUTION

Normally, in dilute solutions, activity coefficients for ions rely on the solution ionic strength. However, at higher ionic strengths (greater than 0.1 molar), activity coefficients also become dependent on the type of ion in solution and simple theoretical calculations become inaccurate. Experimental values for mean activity coefficients are used at high ionic strengths, but even these values may be inaccurate since activity coefficients of ions in an electrolyte mixture may deviate greatly from the mean activity coefficient of a single electrolyte (27).

Mean ionic activity coefficients are, most times, measured either potentiometrically or from vapor pressure measurements. Single ion activity coefficients cannot be measured in such a manner since it is physically impossible to transfer a specific ion into a solvent. Even if it was feasible, the resulting solution would be electrically unbalanced and extra interactions would be introduced. Subsequently, mean activity coefficients are measured and single ion activity coefficients are derived from mean activity coefficient values.

Theoretically, all activity coefficient calculations are based on the thoery of Debye and Hückel (28). This theory is based on the assumption that all ions present in solution act like point charges in a continuous solution with a conductivity the same as that of the solvent. The mean activity coefficient of a binary electrolyte in dilute solutions was determined to be:

$$-\log \gamma_{\pm} = A z_{+} z_{-} \sqrt{I} \qquad (3.1)$$

where $\gamma_{\pm}$ = mean act. coeff. of the salt in question.

A = const. depending on the temperature and dielectric constant of the solvent.

$z_+ z_-$ = ionic valences of positively and negatively charged species in solution.

I = ionic strength of the solution.

The value for an individual activity coefficient in dilute solutions was derived to be:

$$-\log \gamma = Az^2\sqrt{I} \qquad (3.2)$$

where γ = activity coefficient of the species in question.

z = valence of the species in question.

Even though this equation is not immediately substantiated, it provides the proper results for calculation of the mean activity coefficient. As mentioned before, problems arise when attempting to predict activity coefficients at high ionic strengths. Several empirical extensions have, therefore, been brought forward to more accurately predict activity coefficients in strong electrolytes. One such extension was proposed by Davies(27):

$$-\log \gamma = Az^2\left(\frac{\sqrt{I}}{1 + \sqrt{I}}\right) - 0.2I \qquad (3.3)$$

Activity coefficients predicted from the Davies equation have been found to be accurate over a wide range of ionic strengths. The Davies equation was used (28) to predict the solubility product of AgCl in ionic strengths as strong as 5 moles/liter and calculated values were seen to match well with measured values. Errors from the use of the Davies equation were found to be less than the experimental error encountered when measuring the solubility product.

The Davies equation can, therefore, be used in conjunction with stepwise ionic complex equilibrium constants in order to predict the activities of species in strong electrolytes. The predictions would require the solution of several simultaneous equations, all of which can be linearized by transformation into log space. Subsequently, the mathematical method employed involves the use of the geometric-arithmetic equality for the solution. The formulation of the computer program used to predict equilibrium activities of species in solution is described in Appendix 2.

3.2) ION EXCHANGE

Ion exchange materials consist of two main parts, a structural fraction (polymer matrix) and a functional fraction (ion-active group) (9). Varying the proportions and types of these two parts results in the availability of various types of resins. Anion exchangers can be grouped into two general categories; strong-base exchangers and weak-base exchangers. The active groups for weak base exchangers always contain either primary, secondary, or tertiary amine groups. Strong base exchangers were more difficult to synthesize and were not successfully developed until 1950 (10). Typical functional groups for these types include quaternary amines, quaternary phosphonium groups, and tertiary sulfonium groups.

Generally, a functioning ion exchanger must meet certain requirements. Many of these requirements affect each other, however. As a result, changing an operating property in one area may well alter other characteristics.

Firstly, an ion exchanger should exhibit a high total capacity or low equivalent weight. A second requirement is that the ion exchange resin be chemically and physically stable in the operating environment. It should operate well in the necessary pH ranges and should exhibit a good selectivity for the species in question. Thirdly, the kinetic properties should be such that a high equilibrium capacity is obtainable in the alloted loading time. A fourth requirement is that the resin have an extremely low solubility. A main advantage of ion exchange is its low organic solubility along with its re-usability. The last requirement is that the resin be available at such a cost so as to make a process economically viable (11).

3.3) ION EXCHANGE EQUILIBRIA

Resin loading is found in ion exchange when an ion exchanger is put into a solution containing different counter ions. After an appropriate amount of time, a certain amount of counter ions in solution (B) will exchange with counter ions (A) initially present in the resin according to the reaction:

$$\bar{C}_A + C_B = \bar{C}_B + C_A \qquad (3.4)$$

where C_A= concentration of A in solution.

$\bar{C}_A$= concentration of A in ion exchange resin.

C_B= concentration of B in solution.

$\bar{C}_B$= concentration of B in ion exchange resin.

This type of ion exchange is usually reversible and, as a result, it should make no difference from which side the equilibrium was obtained.

3.3.1) GRAPHICAL EQUILIBRIUM EXPRESSIONS

The equilibria between different competing ions can be expressed in several different ways. There are, however, two well known graphical methods for depicting sorption equilibria.

The first method involves the use of sorption isotherms. Sorption isotherms describe, either functionally or graphically, the dependence of the equilibrium solute concentration in the ion exchange resin on the equilibrium solute concentration in the external solution. Customarily, it is preferred to express the concentrations in both phases either to wet unit weight in the phase or to unit volume in the phase. A typical sorption isotherm is shown in Figure 3.1.

Distribution coefficients, on the other hand, describe the ratio of the concentration of solute in the ion exchanger to the concentration of solute in the external solution. Individual distribution coefficients correspond to single points on sorption isotherms. As a result, it can be deduced that a distribution coefficient for a

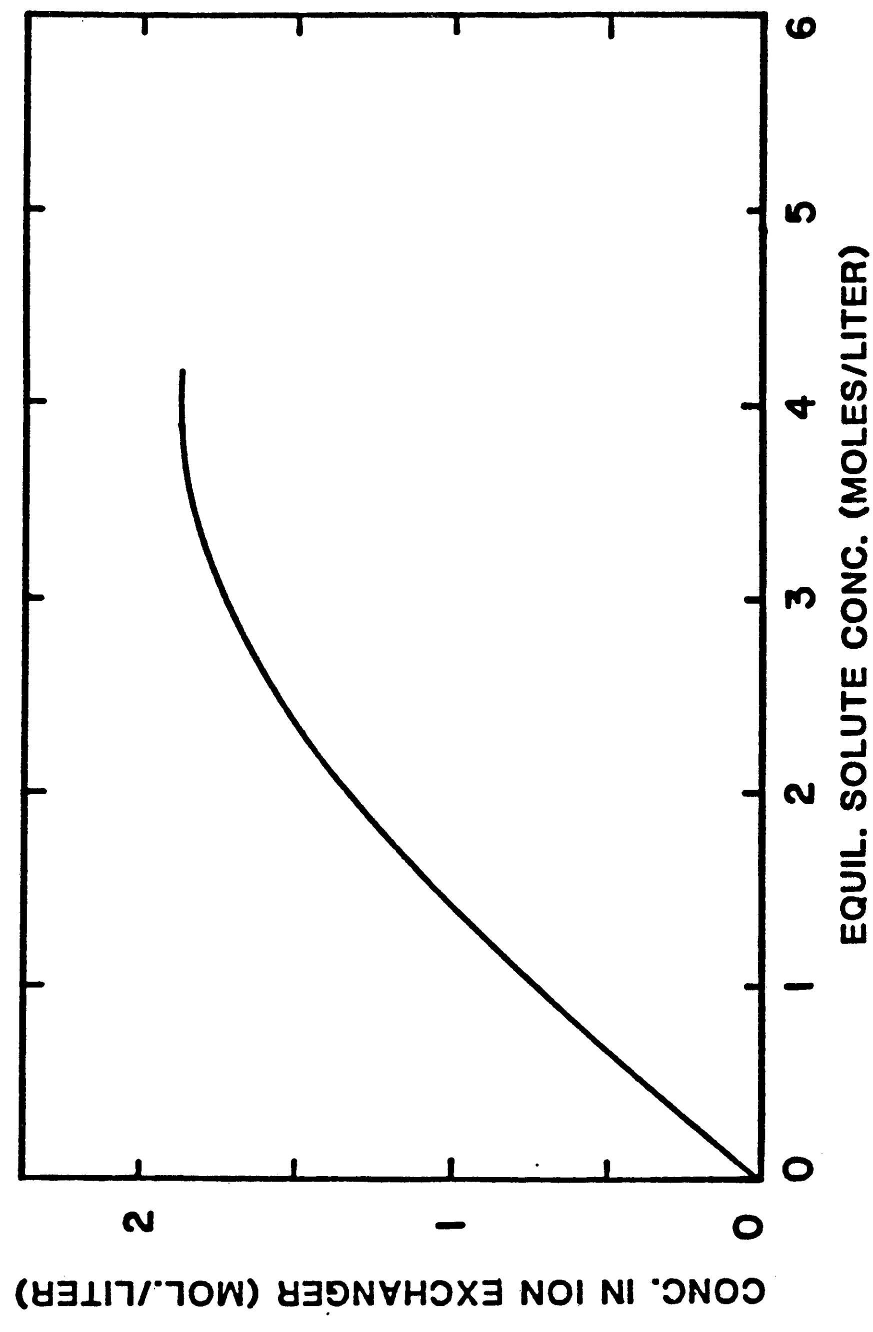

Figure 3.1 - Typical Sorption Isotherm Graph.

certain system will only be constant if the sorption isotherm graph for that system is linear. A typical distribution coefficient graph corresponding to the sorption isotherm of Figure 3.1 is shown in Figure 3.2.

3.3.2) OTHER EQUILIBRIUM EXPRESSIONS

There are also several other quantities used in describing ion exchange equilibria and these will be discussed below.

The separation factor describes the preference an ion exchanger has for one counter ion over another counter ion. If equation (3.4) represents the reaction occurring, the separation factor can be written as:

$$\alpha_A^B = \frac{\bar{C}_B C_A}{\bar{C}_A C_B} \qquad (3.5)$$

If the counter ion (B) is preferred to that of counter ion (A), then the value for the separation factor will be greater than unity. Since the separation factor is dimensionless, the choice of concentration units will have no affect on the numerical value obtained. Like the distribution coefficient, the separation factor is variable and depends on the total solution concentration.

The selectivity coefficient is used in many areas

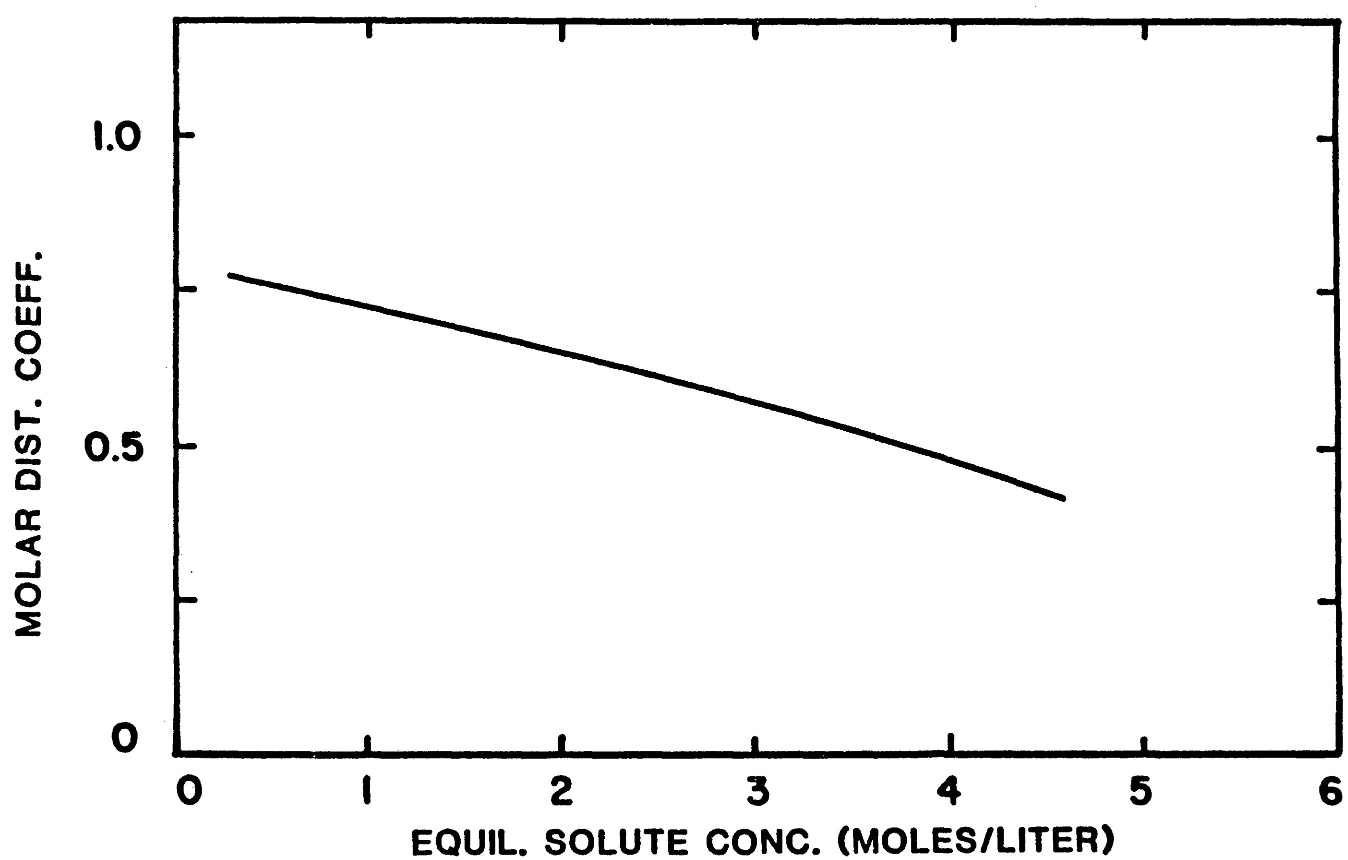

Figure 3.2 - Typical Distribution Coefficient Graph.

because it is more suitable for theoretical analysis. The molar selectivity coefficient is shown by the equation:

$$K'^{B}_{A} = \frac{\bar{C}_A^{|z_B|} \; C_B^{|z_A|}}{\bar{C}_B^{|z_A|} \; C_A^{|z_B|}} \tag{3.6}$$

where z_A = ionic valence of species A.

z_B = ionic valence of species B.

It should be noted that selectivity coefficients are not constants, but depend on the experimental conditions involved. Also when counter ions of different valences are involved, the choice of concentration units becomes important since exponential quantities are calculated.

One last expression that is occasionally used is the thermodynamic equilibrium constant. The thermodynamic equilibrium constant is found from the thermodynamic relation:

$$\Delta G = -RT\ln K^{B}_{A} \tag{3.7}$$

where ΔG = standard free energy change of the ion exchange.

R = ideal gas constant.

T = temperature in degrees Kelvin.

K_A^B = equilibrium constant.

The thermodynamic equilibrium constant, in contrast to the distribution coefficient, the separation factor, and the selectivity coefficient, is a true constant contingent on temperature only. As a result, this constant describes little regarding how any counter ions are distributed under other variable conditions.

Even though the above quantities have been shown to use concentration values, it must be noted that the concentration values can and should be replaced by the activities of the species in the ion exchanger and in the bulk solution. Activities are necessary to describe the effective concentration in equilibrium expressions.

3.3.3) SORPTION EQUILIBRIA THERMODYNAMICS

Rigorous thermodynamic treatment can describe the equilibrium between ion exchangers and solutions, but usually this treatment is rather general. The practical value of such a treatment is also somewhat restricted since many quantities described cannot be independently measured without taking other effects into consideration. Many models have been introduced (10) that explain the affect of certain properties on an ion exchange system, but such models depart from strict thermodynamic laws. A basic thermodynamic model developed by Donnan (10) will, however, be given to describe the relevent forces present.

According to Donnan's theory, equilibrium is reached when the electrochemical potential of an ionic species i is equal in both the ion exchange resin and in the bulk solution:

$$\eta_i \text{ (Resin)} = \eta_i \text{ (Solution)} \tag{3.8}$$

The electrochemical potential is related to the chemical potential by the expression:

$$\eta_i = \mu_i + z_i F \Phi \tag{3.9}$$

where η_i = electrochemical potential of species i.

μ_i = chemical potential of species i.

z_i = valence of species i (negative for anions, zero for nonelectrolytes).

F = Faraday constant.

Φ = electrical potential of species i.

Also, the chemical potential of a species can be further broken into its components:

$$\mu_i = \mu_i + RT\ln a_i + (P-P^o)\nu_i \qquad (3.10)$$

where μ_i = chemical potential of species i in standard state.

a_i = activity of species i.

P = measured isothermal pressure.

P^o = standard pressure.

ν_i = partial molar volume of species i.

The above equation assumes that the partial molar volume of species i is independent of composition and pressure and that the isothermal chemical potential can be split into two terms, one depending on composition and the other depending on pressure. One other quantity also needs to be defined at this time. The swelling pressure can be defined as the pressure difference between that in the resin and that in the external solution:

$$\Pi = \bar{P} - P \qquad (3.11)$$

where Π = swelling pressure.

Combining the last four equations, one obtains a relation for the potential difference between the ion excganger and the bulk solution:

$$\bar{\Phi} - \Phi = \frac{1}{z_i F_i}\left(RT \ln \frac{\bar{a}_i}{a_i} - \Pi \nu_i\right) \tag{3.12}$$

This equation applies to any mobile ionic species in solution assuming that the partial molar volume remains constant. When one mole of an electrolyte (AY) is added to solution, one obtains at equilibrium:

$$RT \ln \left(\frac{a_A}{\bar{a}_A}\right)^{\nu_A}\left(\frac{a_Y}{\bar{a}_Y}\right)^{\nu_Y} = \Pi \nu_{AY} \tag{3.13}$$

where ν_A = moles of ion A in solution.

ν_Y = moles of ion Y in solution.

ν_{AY} = partial molar volume of the electrolyte.

The general thermodynamic formulation of the Donnan equilibrium is finally determined to be:

$$\left(\frac{\bar{a}\pm}{a\pm}\right)^{\nu} = \left(\frac{\bar{a}_w}{a_w}\right)^{\nu_{AY}/\nu_w} \tag{3.14}$$

where $a\pm$ = mean activity of electrolyte AY.

a_w = activity of water.

ν_w = partial molar volume of water in the system.

Once again, it should be noted that such quantities defined in the derivation are very difficult to measure. Qualitative conclusions can be drawn, however, regarding relative amounts of adsorption.

The forces present to form equilibrium will now be qualitatively discussed. The tendency of fixed and mobile ions within the ion exchanger to form solvation shells will exert an expanding force on the resin matrix. Electrostatic repulsion of the fixed ions in the ion exchanger will also tend to expand the resin. The amount of crosslinking of the structured matrix in the ion exchanger also plays a large role in selectivity. Highly crosslinked resins will not be able to swell as greatly, and as a result, the size and solvation tendency of counter ions will be important. Weakly crosslinked resins, on the other hand, will swell more readily and the valence of the counter ions will be important due to electrochemical potential differences. Balancing the expanding forces in a resin are the tendencies for the resin to contract into a more natural configuration. This can be accomplished by allowing the counter ion with a smaller hydrated ionic radius or higher valence into the resin. As can be seen, counter ion sorption from complex electrolytes depends on many factors and may be difficult to predict without a great deal of detailed information concerning the ion exchanger and bulk solution.

CHAPTER 4

EXPERIMENTAL PROCEDURE

This chapter provides a description of the experimental equipment and setup used during this investigation. The analytical method used for iron determination in the aqueous phase is described in section 4.3. Diagrams have been included to aid in the description wherever possible.

4.1 EQUIPMENT

In this study equipment was used in two main areas:

i) Sorption Isotherms

ii) Resin Stripping

The procedure for producing sorption isotherms consisted of contacting the ion exchange resins with increasing amounts of solubulized iron in agitated reaction vessels containing either a simulated aluminum chloride leach liquor or a hydrochloric acid solution. The 500 ml reaction vessel contained four baffles spaced at 90 intervals to avoid vortex formation during experiment runs. The reaction vessel cover contained a teflon agitator equipped with a pulley. The agitator assembly was driven by a Sargent-Welch adjustable speed Bodine motor. A rubber pulley belt was used to connect the agitator drive to the agitator.

Resin stripping was performed using a 250 ml KIMAX buret with teflon stopcock. Before the addition of resin to the buret, approximately 1.3 cubic inches of spun glass wool was packed into the buret bottom to act as a porous medium through which solution could pass and resin beads could not. Hot, 1 M HCl liquid (heated by a Corning hot plate/magnetic stirrer) was pumped to the top of the column by a Cole-Parmer Masterflex pump drive (60 rpm) containing a Masterflex 7014 pump head and Tygon (0.0655" I.D. - 0.1945 " O.D.) tubing. A constant head was maintained above the resin bed in the column. The end of a gum rubber tube was placed above the resin bed to keep a one inch depth of liquor above the resin. The flow diagram is shown in Figure 4.1. Effluents from the column were collected in a 3 liter reaction vessel.

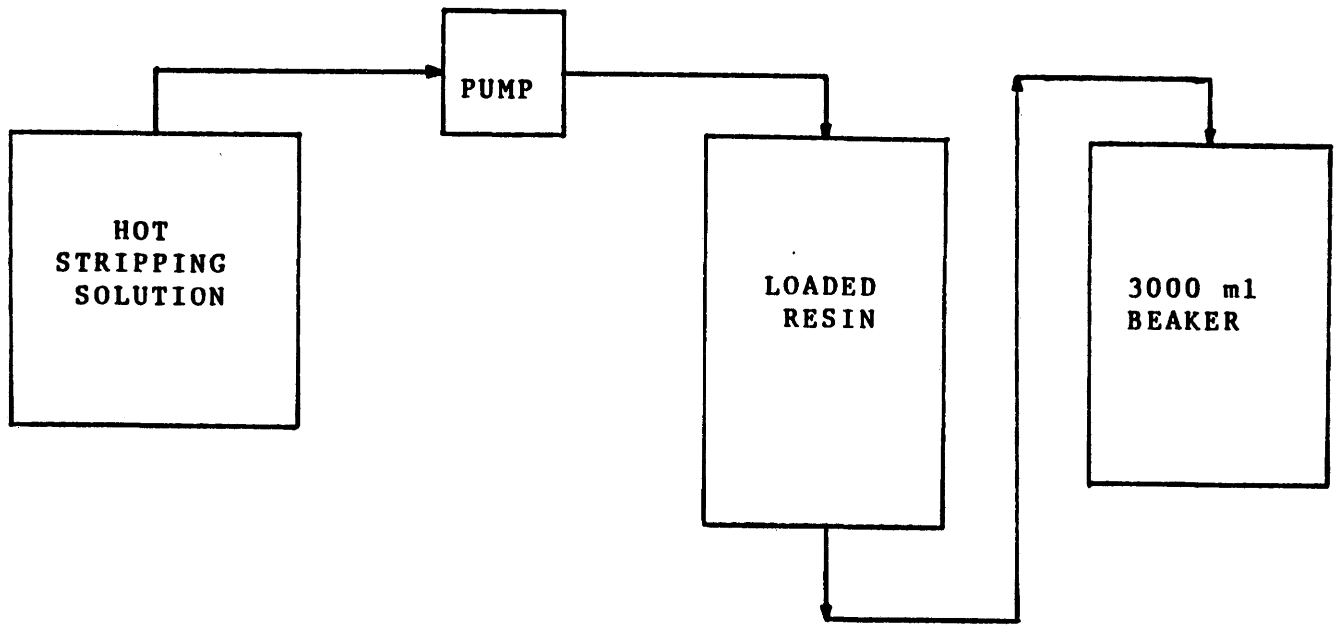

Figure 4.1 - Flow Diagram for Resin Stripping.

4.2 MATERIALS AND REAGENTS

Three types of anionic exchange resins were used. The specifications of each resin are shown in Table 4.1. Reagents used for preparation of the simulated leach liquor were standard reagent grade chemicals and their spcifications are listed in Table 4.2.

4.3 CHEMICAL ANALYSIS

In this investigation it was necessary to determine the amount of iron present in the aqueous phase after each equilibrium had been established during the construction of sorption isotherms. Iron concentrations were determined using a Perkin-Elmer model 306 Atomic Absorption Spectrophotometer. The linear working range for iron is 0-5 ppm. When dilutions were necessary, the samples and standards were diluted in a weak HCl solution in order to maintain the same matrix (background) for uniformity.

4.4 PROCEDURE

Initially, experiments were performed to determine the wet density of each resin in the chloride form. These values could be an important factor in equipment selection since resin beads with a density less than that of leach liquors can lead to difficulties in column operations. All

	RESIN		
	Dowex SBR	Dowex WGR	Dowex MWA-1
TYPE	Strongly Basic Anion Exch.	Weakly Basic Anion Exch.	Macroporous Weak Base Anion Exch.
ACTIVE GROUP	Trimethyl Benzyl Ammonium	EPI Amine	Tertiary Amine
STD. WET MESH SZ.	20-50	20-50	20-50
EFFECTIVE pH RANGE	0-14	0-7	0-7
THERMAL STAB.	Good to 150 °C	Good at 95 °C	Good to 100 °C

Table 4.1 - Ion Exchange Resin Specifications.

Table 4.2

Chemical Reagents Used and

Their Specifications

Hydrochloric Acid	-	36.5-38.0% HCl, Fisher Scientific Co.
Ferric Chloride	-	99.90% as $FeCl_3.6H_2O$, lump, Fisher Scientific Co.
Aluminum Chloride	-	99.90% as $AlCl_3.6H_2O$, crystals, Fisher Sci. Co.
Sodium Chloride	-	99.95% as NaCl, crystals, Fisher Scientific Co.

resins received were contacted with distilled water for at least 8 hours in order to insure maximum moisture uptake. Next, each resin was converted to the Cl^- form by first preparing 2000 ml of a 1 M HCl solution. The HCl was then pumped from a resevoir through the column for 8 hours. Effluents from the column were recirculated back to the resevoir to minimize acid waste.

Resin bead density experiments were performed using a 10 ml graduated cylinder. A small amount of distilled water was placed in the graduated cylinder and the cylinder mass and volume readings were recorded. Next, a small amount of resin that had excess surface water removed was placed in the cylinder and a new mass and volume were recorded. The bead densities were calculated from the equation:

$$\text{Bead Density} = (W(2)-W(1))/(V(2)-V(1))$$

where V(1)= Cylinder volume before resin addition.
V(2)= Cylinder volume after resin addition.
W(1)= Cylinder mass before resin addition.
W(2)= Cylinder mass aftyer resin addition.

Simulated leach liquors were prepared in different proportions depending on the desired total chloride concentration. Table 4.3 lists the amounts of reagents that were dissolved to a total 500 ml using 500 ml volumetric flasks for each desired chloride concentration.

Initially, it was attempted to perform all experiments with a leach liquor containing 45 gpl Al for all chloride concentrations because the U.S. Bureau of Mines used simulated leach liquors containing 45 gpl Al in their solvent extraction tests. This could only be accomplished for the 5 and 6 M chloride runs when using aluminum chloride as a reagent. The use of aluminum oxide (Al_2O_3) was attempted to satisfy the requirements for aluminum at lower chloride concentrations, but, it was found insoluble even in a boiling 4 M HCl solution. Consequently, only hydrochloric acid was used to meet the chloride concentration requirements at the 1, 2, and 3 M chloride runs. The 4 M chloride experiment was run at 35 gpl aluminum mainly because the aluminum concentration was fairly close to the initial target value. Upon dissolution of all reagents into the simulated leach liquor, the volumetric flask was shaken several times and then poured into the baffled reaction vessel. Resin to be added to the reaction vessel was first contacted for one hour with the same simulated leach liquor that was to be used in the

Initial Cl^- Conc. in Leach Liquor	grams $AlCl_3 \cdot 6H_2O$	grams NaCl	ml 12 M HCl
1	0	0	41.7
2	0	0	83.3
3	0	0	125.0
4	156.53	3.16	0
5	201.25	0	0
6	201.25	29.22	0

Table 4.3 - Reagent Amounts Used in Sorption Isotherm Tests.

experiment. This was necessary to minimize concentration changes caused by sorption and desorption of electrolytes from the ion exchanger. The resin was then placed in a Buchner funnel and vacuum filtered for 25 minutes in an attempt to rid the resin of excess solution adhering to bead surfaces. Following vacuum filtering, the resin was added to the reaction vessel using a spatula.

Equal amounts of ferric chloride were added to the reaction vessel at 8 hour intervals. 2.4192 grams of $FeCl_3 \cdot 6H_2O$ (weighed by Mettler H10 analytical balance) was added at each interval increasing the total amount of iron added to the vessel by 1 gpl Fe. Four milliliter leach liquor samples were taken at the end of each 8 hour interval before additional ferric chloride was added. Coarse filter paper (Schleicher and Schuell Sharkskin) was required to filter the sample from resin beads that were taken during sampling when the resin density was less than that of the simulated leach liquor. The experiments were run until 10 gpl Fe total was added to the reaction vessel.

Once the extraction isotherm was completed the agitated reaction vessel apparatus was dismantled. The loaded resin was then poured as a slurry into a 250 ml buret containing bottom packed glass wool. Two thousand milliliters of 1 M HCl was subsequently heated to slow boiling and then pumped to the buret top where it stripped the resin by descending gravity flow. Flow rates through the column were found to be 1890 ml/min.ft (15.33 ml/min.). The stripping procedure was repeated four times for each resin. The average stripping time was 105 minutes. This represents a disparity since an average of only 1610 ml was pumped through the column. Strip liquor loss was most likely due to evaporation since the strip liquor was in a slow boiling stage. Temperatures of the strip liquor in the top of the column were found to be approximately 65 °C which was due to heat loss through the Tygon tubing and the column itself. Following the fourth stripping cycle a sample of the effluent stripping liquor was taken for iron analysis.

The stripped resin and the packed glass wool were removed from the buret by means of forced air. Compressed air was forced up through the bottom of the buret and the resin and glass wool was discharged into a 2000 ml reaction vessel. Small amounts of resin adhered to the glass wool and were removed with a pair of tweezers.

After a series of sorption isotherm experiments were performed, the stripped resin was dried. The resin was first placed in a 600 ml Pyrex beaker and excess water was poured off. The resin was then placed on a hot plate at the lowest temperature setting for three days to facilitate evaporation. The semi-dry resin was then placed in a desiccator for two weeks in an atempt to rid the strongly bound water from the resin. No significant resin weight changes were seen between two and two and a half weeks. Dry resin weights were then recorded.

4.5 VISUAL OBSERVATIONS

In the experiments performed at 5 and 6 M chloride concentrations all three resins 'floated' to the top of the simulated leach liquor initially, and proceeded to sink after partial loading with iron.

After numerous loading cycles all resins showed signs of deterioration. Close inspection of the resin beads showed that some resin beads had lost their sphericity. Also, the leach liquor appeared cloudy and further experiments necessitated the use of previously unused resins.

CHAPTER 5

RESULTS AND DISCUSSION

The results obtained from experimental work and from the computer programs are shown in this chapter. The order of results presentation is as follows:

A) RESIN DENSITY MEASUREMENTS

B) SORPTION ISOTHERM TESTS

C) COMPUTER PROGRAM RESULTS

5.1) RESIN DENSITY MEASUREMENTS

Density measurements on each resin were easily carried out. All resins were in the chloride form when the tests were performed. The results are shown in Table 5.1.

5.2) SORPTION ISOTHERM TESTS

5.2.1) PRELIMINARY EXPERIMENTS

The first number of sorption isotherm runs were exploratory in nature. Familiarization was gained both

RESIN	DENSITY (grams/liter)
Dowex SBR	1.19
Dowex WGR	1.16
Dowex MWA-1	1.09

Table 5.1 - Wet Resin Densities in the Cl^- Form.

with the experimental apparatus used and with the range of reagent additions needed. As mentioned in Chapter 4, aluminum oxide was not used as an aluminum source since the material was not readily leachable. This may be due to refining techniques used in processing commercially available reagent grade aluminum oxide. Anhydrous ferric chloride ($FeCl_3$) was initially utilized in sorption isotherm experiments as the source for iron impurity, but it was found too reactive. Accurate weight measurements were found to be difficult to obtain. Hydrated ferric chloride ($FeCl_3.6H_2O$) was therefore used in following experiments. Beginning sorption isotherm experiments involved adding 0.1210 grams $FeCl_3.6H_2O$ to the simulated leach liquor at one hour intervals until 0.35 gpl Fe total was added. Atomic absorption iron analysis from the aqueous phase indicated low concentrations of iron. Sorption isotherms that were subsequently constructed indicated that the graphs were linear for all points calculated. This indicated that maximum loading had not been obtained and further additions were required. Additional tests were carried out by adding larger amounts of hydrated ferric chloride to the simulated leach liquor at one hour intervals and maximum loading was thought to be obtained after adding 7 gpl total Fe to the reaction vessel. It was later found, however, that one hour time intervals were insufficient to allow for equilibration. Finally, eight hour time intervals were determined to be sufficient for iron addition. No significant changes in aqueous Fe concentrations were found between an 8 hour and 36 hour time period. It was therefore deduced that 8 hour intervals were sufficient for equilibrium measurements. A total of 10 gpl Fe was also found to be required to attain a level of loading close to maximum.

5.2.2) SORPTION ISOTHERM RESULTS

After the initial tests were performed and the proper experimental procedure was decided upon, the actual sorption isotherm experiments were begun. All experiments were performed at room temperature. The laboratory air temperature fluctuated between 21 and 27 $^{\circ}$C. As a result, a mean temperature of 24 $^{\circ}$C was chosen to be the reported experimental temperature. Heats of reaction in ion exchange have been reported to be low in most cases (10) and the temperature fluctuations observed were not believed to have had a major effect on the sorption isotherms. Sorption isotherms for the Dowex MWA-1 resin are shown in Figures 5.1 through 5.6 while those for the Dowex SBR resin are depicted in Figures 5.7 through 5.11. Iron sorption was

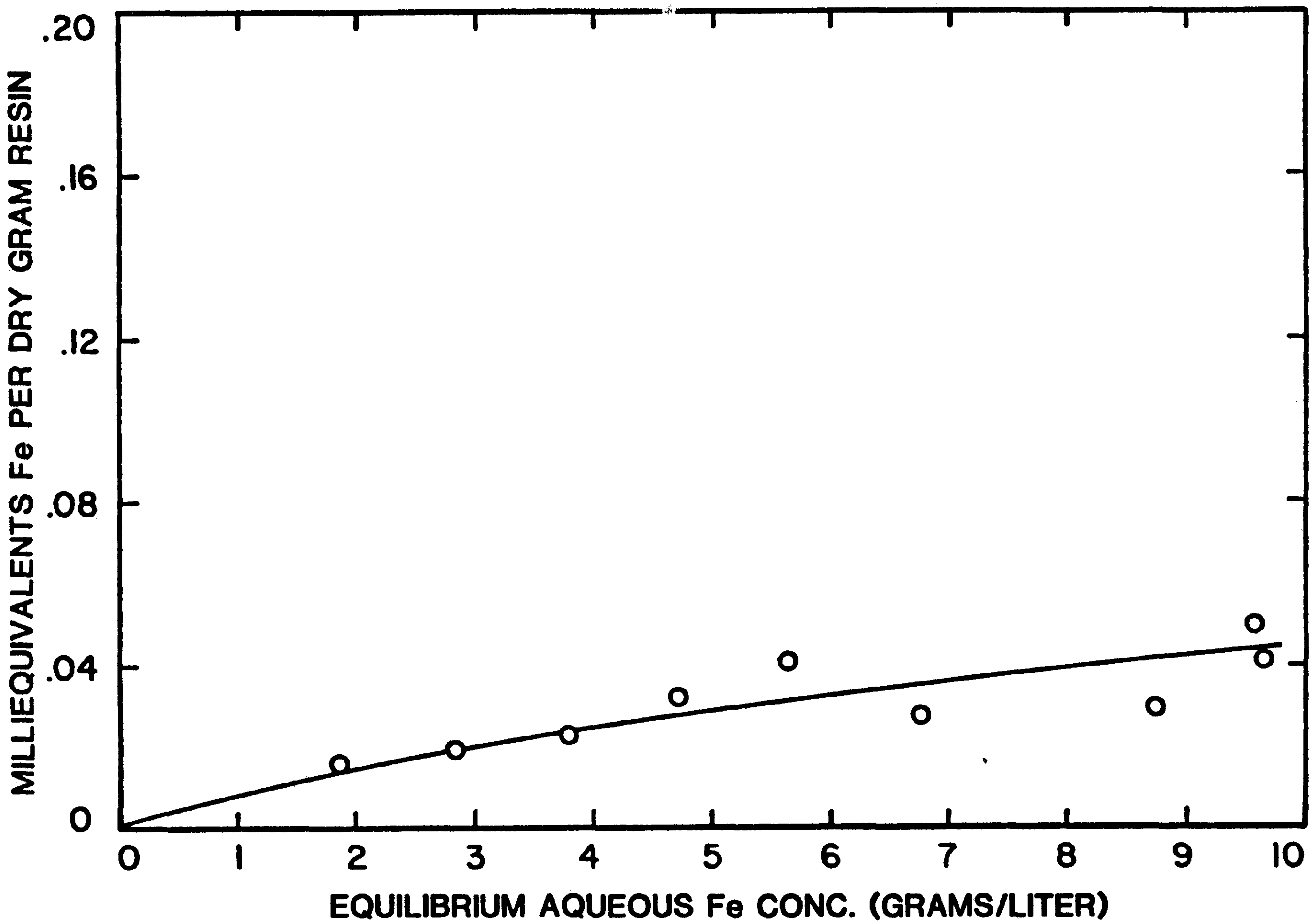

Figure 5.1 - Sorption Isotherm at 24 Deg. C for MWA-1 Resin.

Initial Cl conc. = 1M.

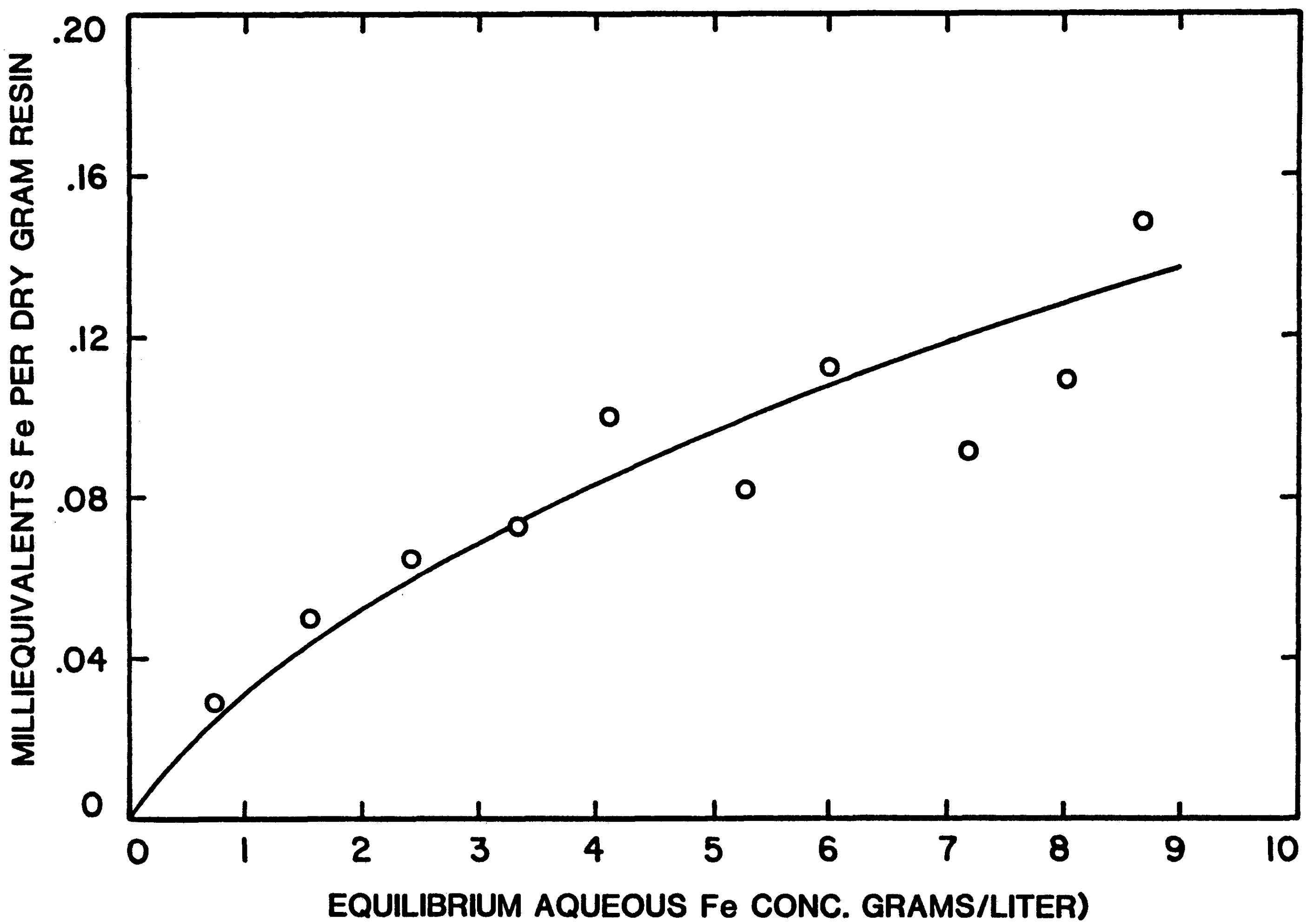

Figure 5.2 - Sorption Isotherm at 24 Deg. C for MWA-1 Resin.

Initial Cl conc. = 2M.

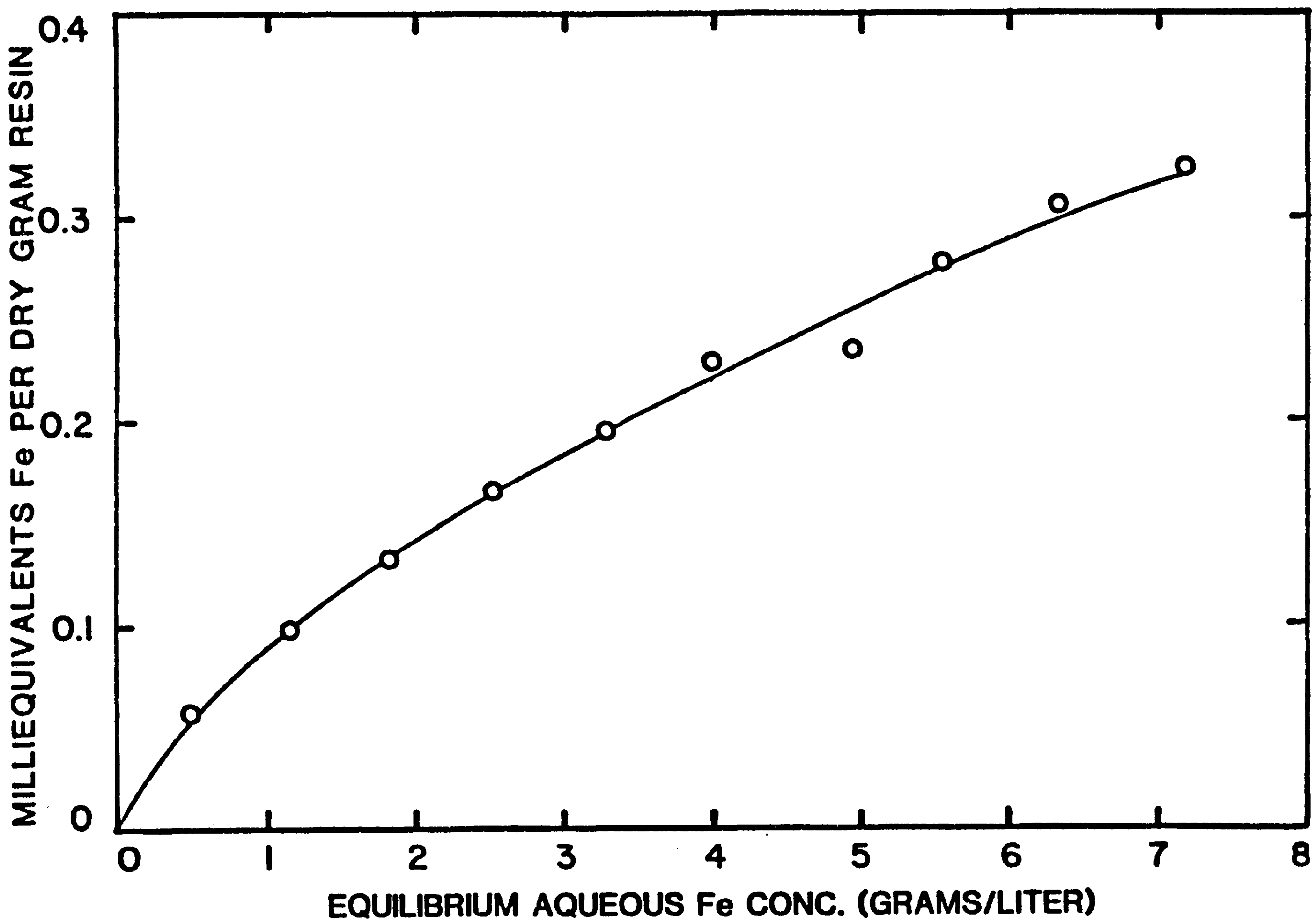

Figure 5.3 - Sorption Isotherm at 24 Deg. C for MWA-1 Resin.

Initial Cl conc. = 3M.

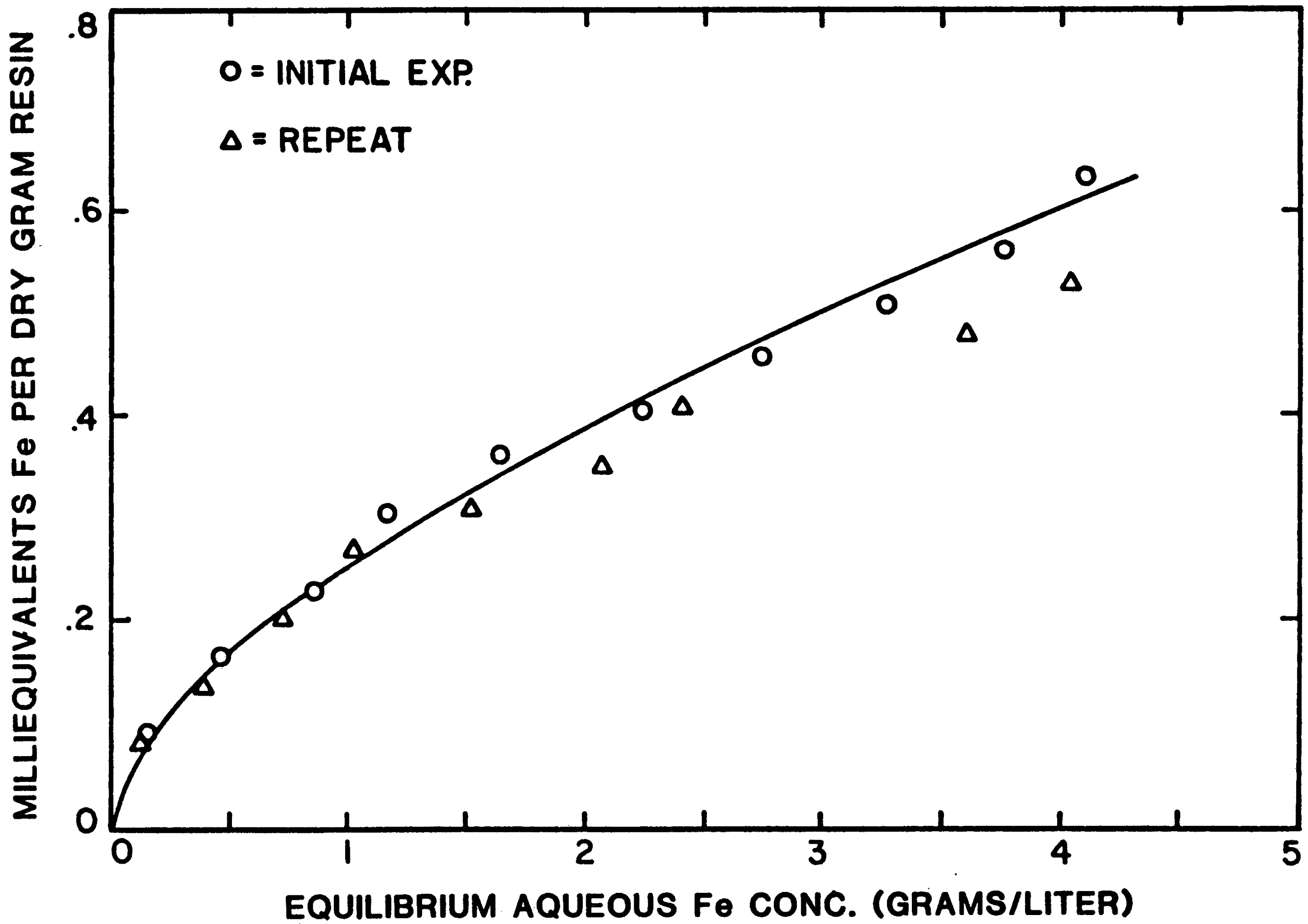

Figure 5.4 - Sorption Isotherm at 24 Deg. C for MWA-1 Resin.
Initial Cl conc. = 4M.

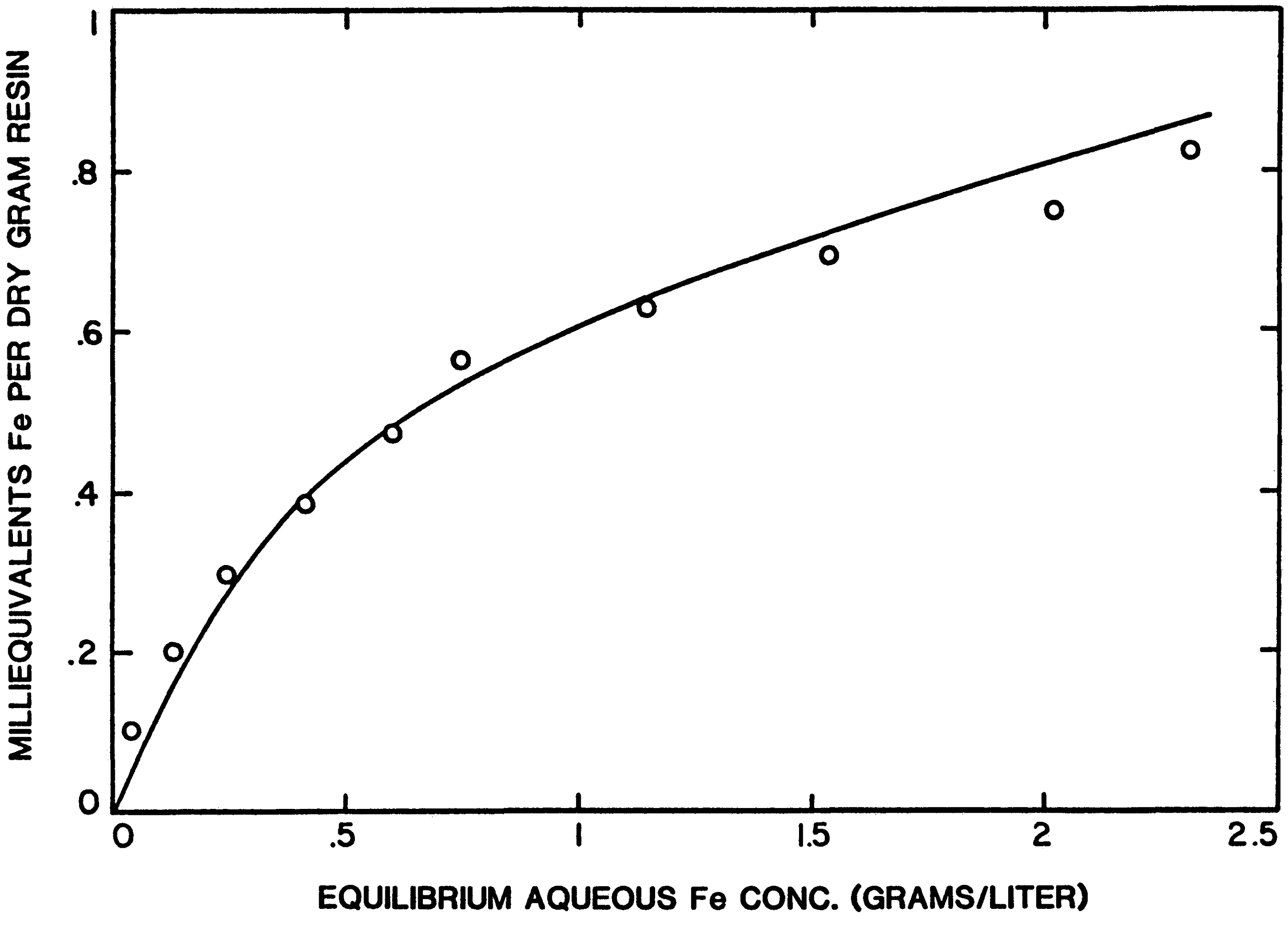

Figure 5.5 - Sorption Isotherm at 24 Deg. C for MWA-1 Resin.

Initial Cl conc. = 5M.

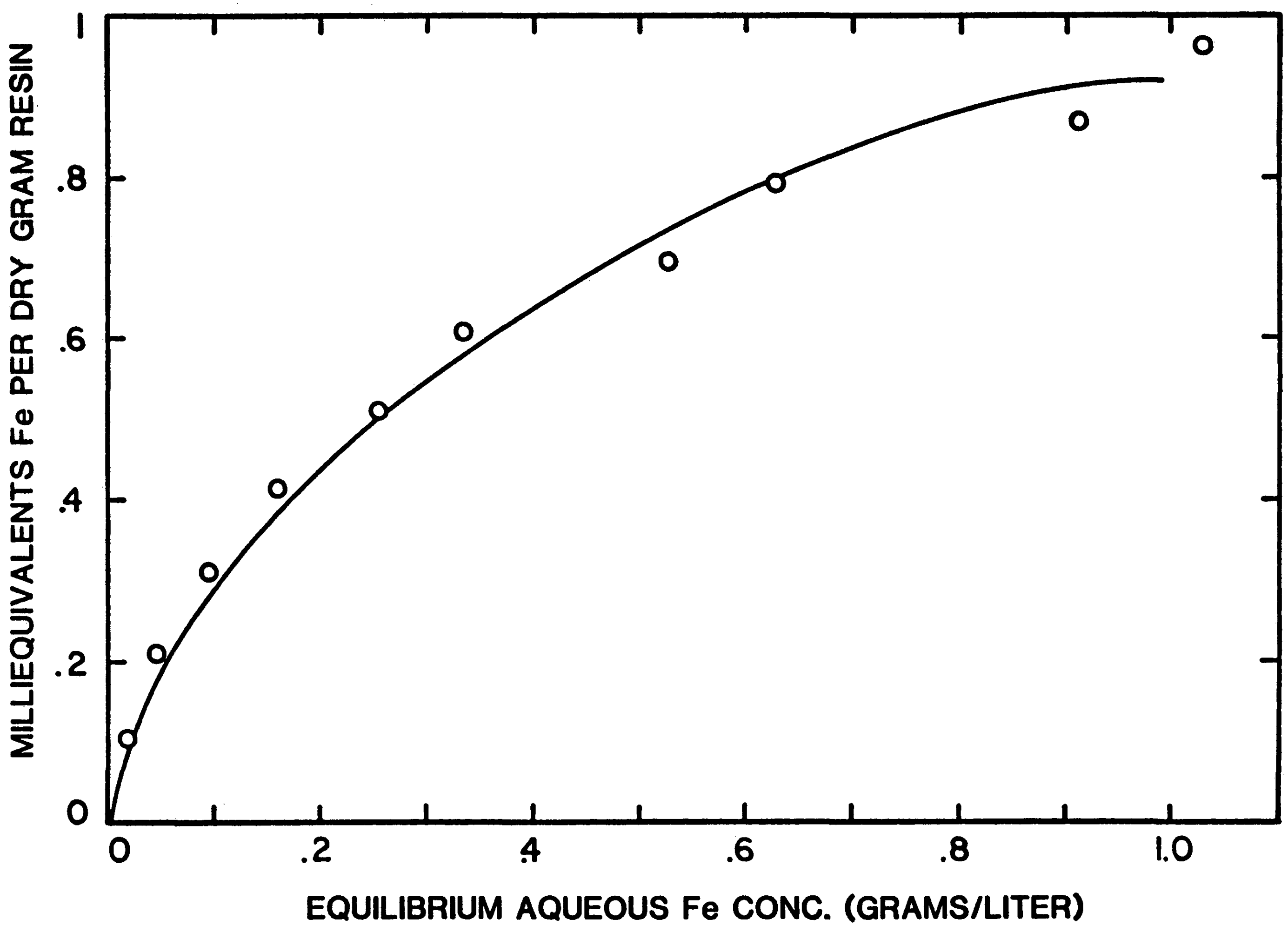

Figure 5.6 - Sorption isotherm at 24 Deg. C for MWA-1 Resin.

Initial Cl conc. = 6M.

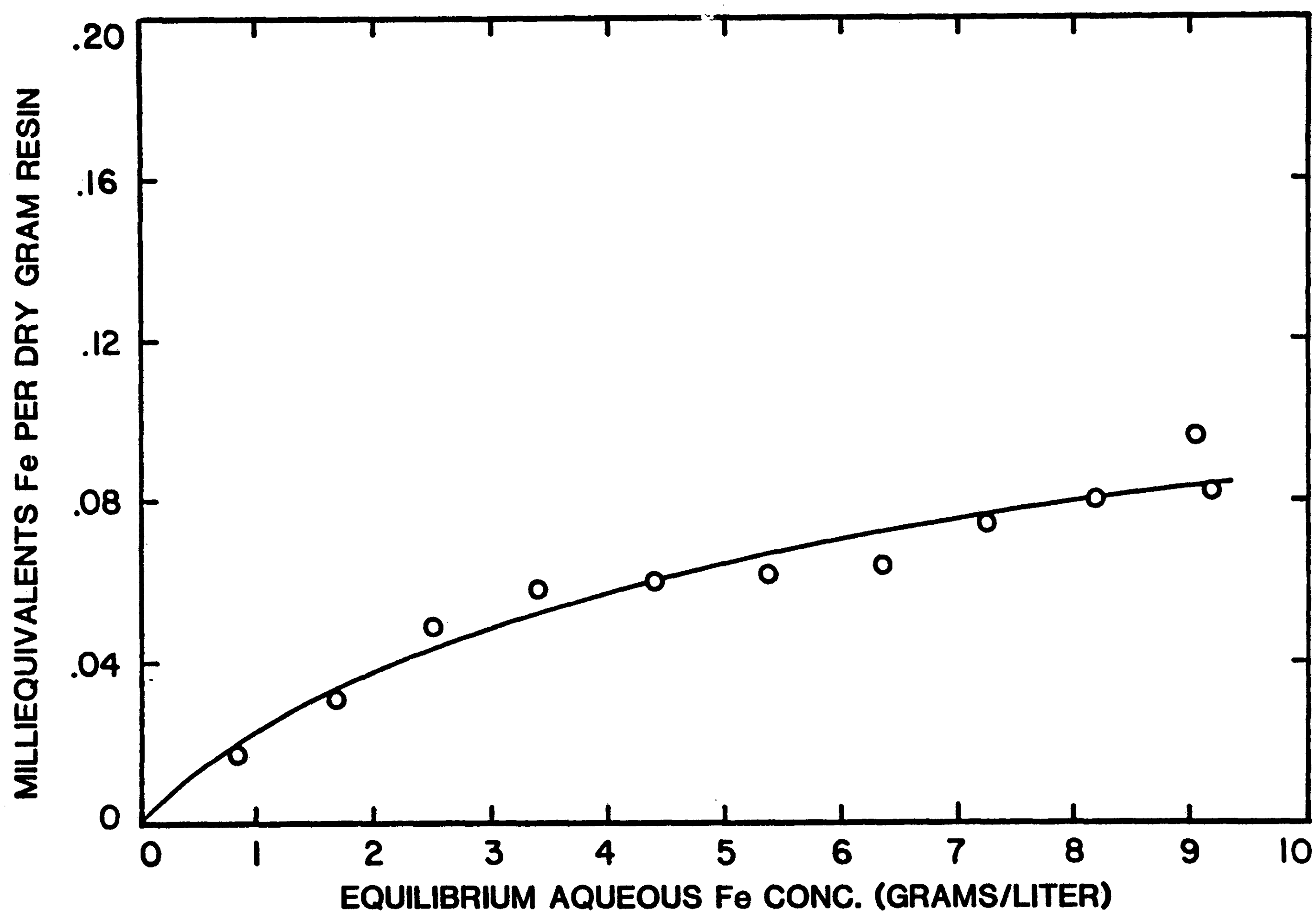

Figure 5.7 - Sorption Isotherm at 24 Deg. C for SBR Resin.

Initial Cl conc. = 2M.

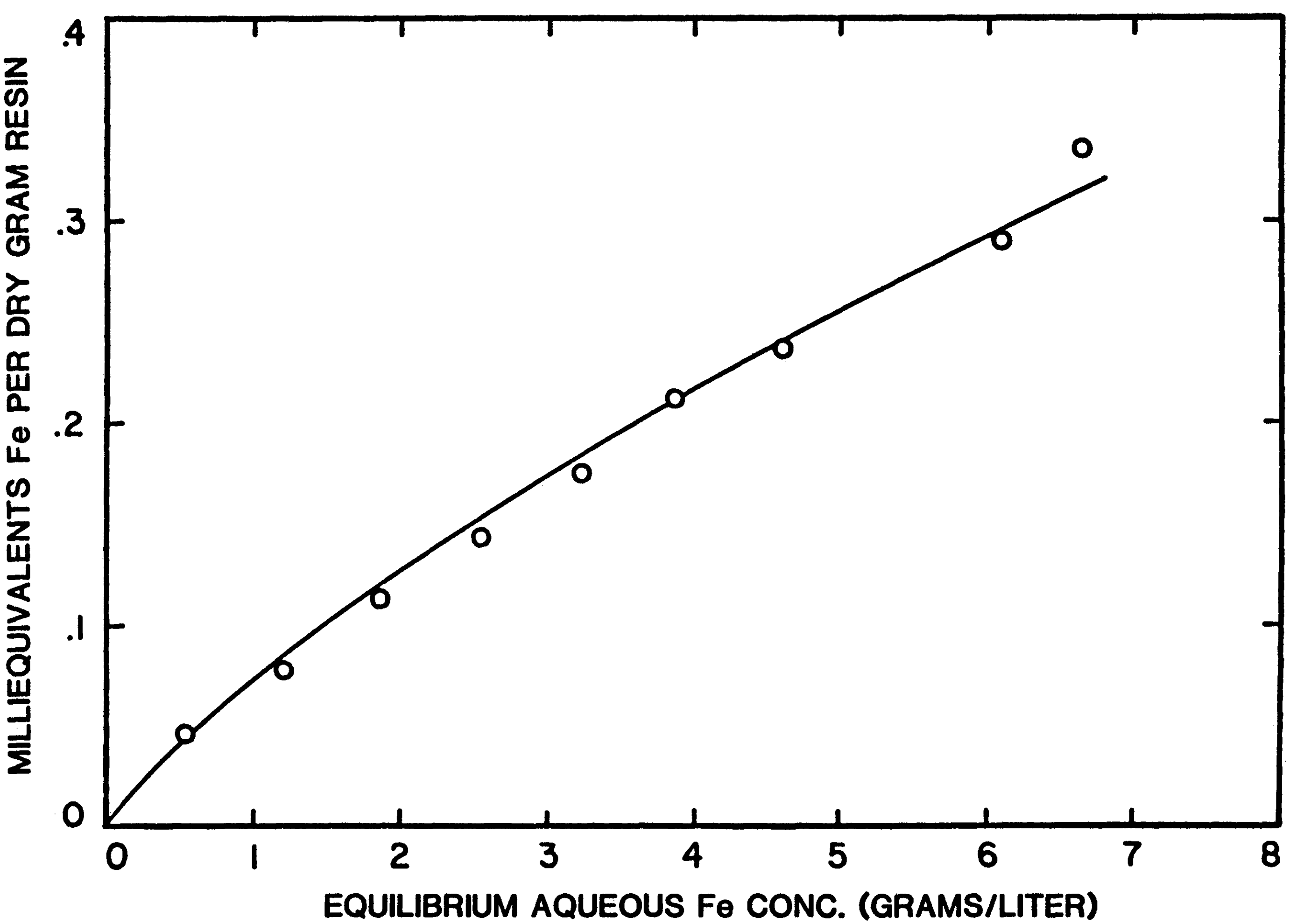

Figure 5.8 - Sorption Isotherm at 24 Deg. C for SBR Resin.

Initial Cl conc. = 3M.

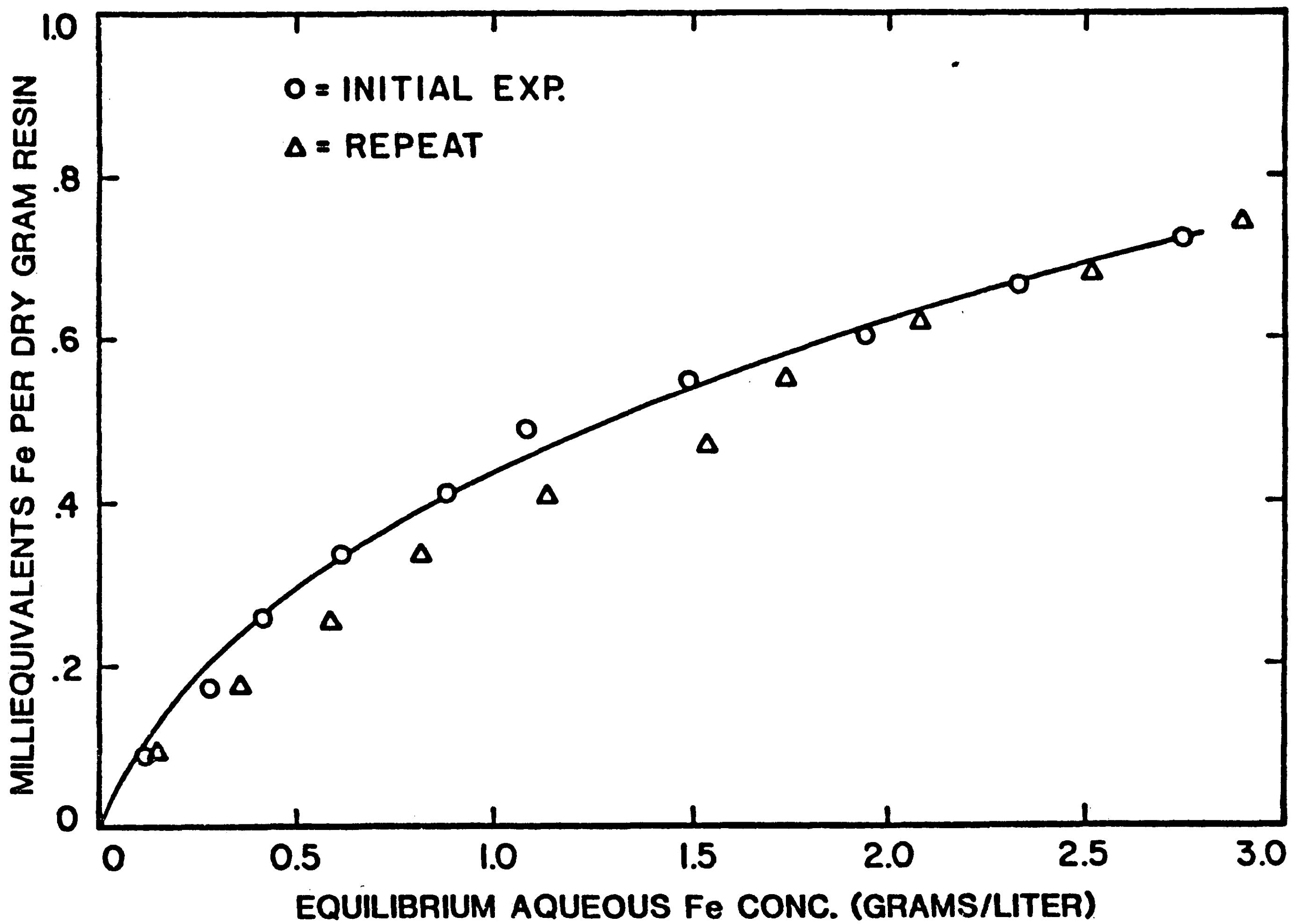

Figure 5.9 - Sorption Isotherm at 24 Deg. C for SBR Resin.

Initial Cl conc. = 4M.

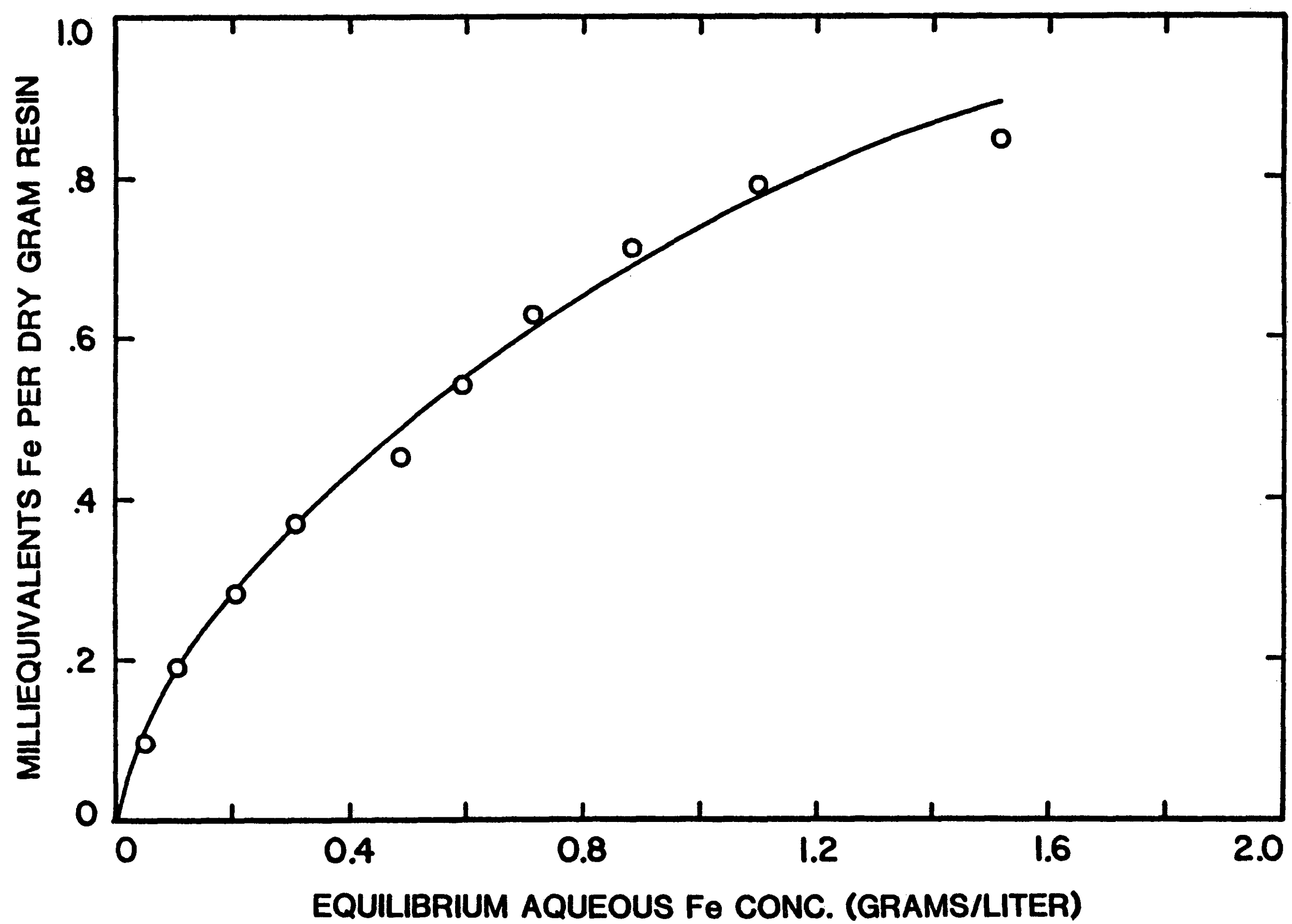

Figure 5.10 - Sorption Isotherm at 24 Deg. C for SBR Resin.
Initial Cl conc. = 5M.

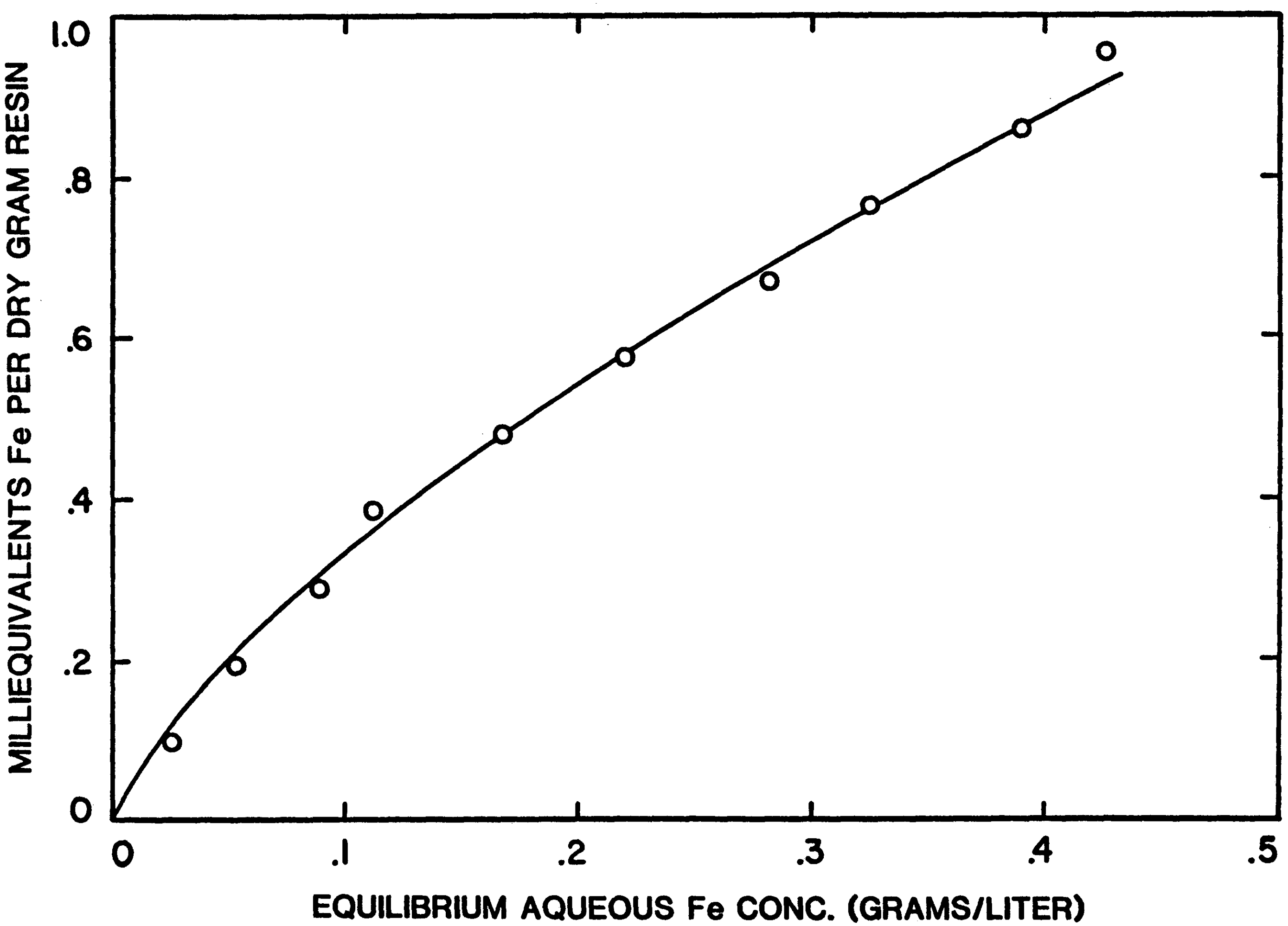

Figure 5.11 - Sorption Isotherm at 24 Deg. C for SBR Resin.

Initial Cl conc. = 6M.

not observed when using the Dowex WGR resin. Be it due to resin decay or an improper resin choice, this resin was deemed to be unacceptable for further use and was rejected.

Initial chloride concentrations used in the sorption isotherms ranged from 1M to 6M for the MWA-1 resin and from 2M to 6M for the SBR resin. A sorption isotherm was attempted for the SBR resin at an initial chloride concentration of 1M, but iron loading was not observed. It should be noted forthwith that the total chloride concentration of the simulated leach liquor increased in each experiment as each increment of hydrated ferric chloride was added. An addition of 10 gpl Fe would correspond to a chloride concentration increase of 0.54 M.

Figures 5.4 and 5.9 both contain data for duplicate runs. The duplicate experiments were run to test the reproducibility of the resin performance. The duplicate experiments were performed using resins from different commercial batches and total loading capacities may have been slightly different.

It can be seen that all sorption isotherms are parabolic in shape which is typical in such graphs. It can also be seen that the amount of iron sorbed increases with an increase in the total chloride concentration for both resins. This phenomenon is depicted graphically in Figures

5.12 and 5.13. Such diagrams could be important in the selection of the optimum operating chloride concentrations. Since final iron impurity concentrations are required to be less than 15 ppm in the purified alumina product (1), several ion exchange stages would likely be required for purification. If pilot plant tests were run at low chloride concentrations, several additional ion exchange stages may well be required.

From Figures 5.12 and 5.13 it can also be seen that the Dowex SBR resin loaded slightly greater amounts of iron than the Dowex MWA-1 resin at higher chloride concentrations. Since operating conditions were essentially the same for both resins, it may be deduced that the Dowex SBR resin was more efficient in iron removal.

Different results were obtained during resin stripping, however. Visually, the MWA-1 resin appeared to strip more rapidly than the SBR resin. Final strip liquor effluants from the SBR resin showed higher iron concentrations than from the MWA-1 resin. Average iron concentrations in effluant strip liquors was 2.86 ppm for the SBR resin while that for the MWA-1 resin was 2.32 ppm. Such a difference is not terribly large, but the fact that the SBR resin stripped slowly may be of concern in

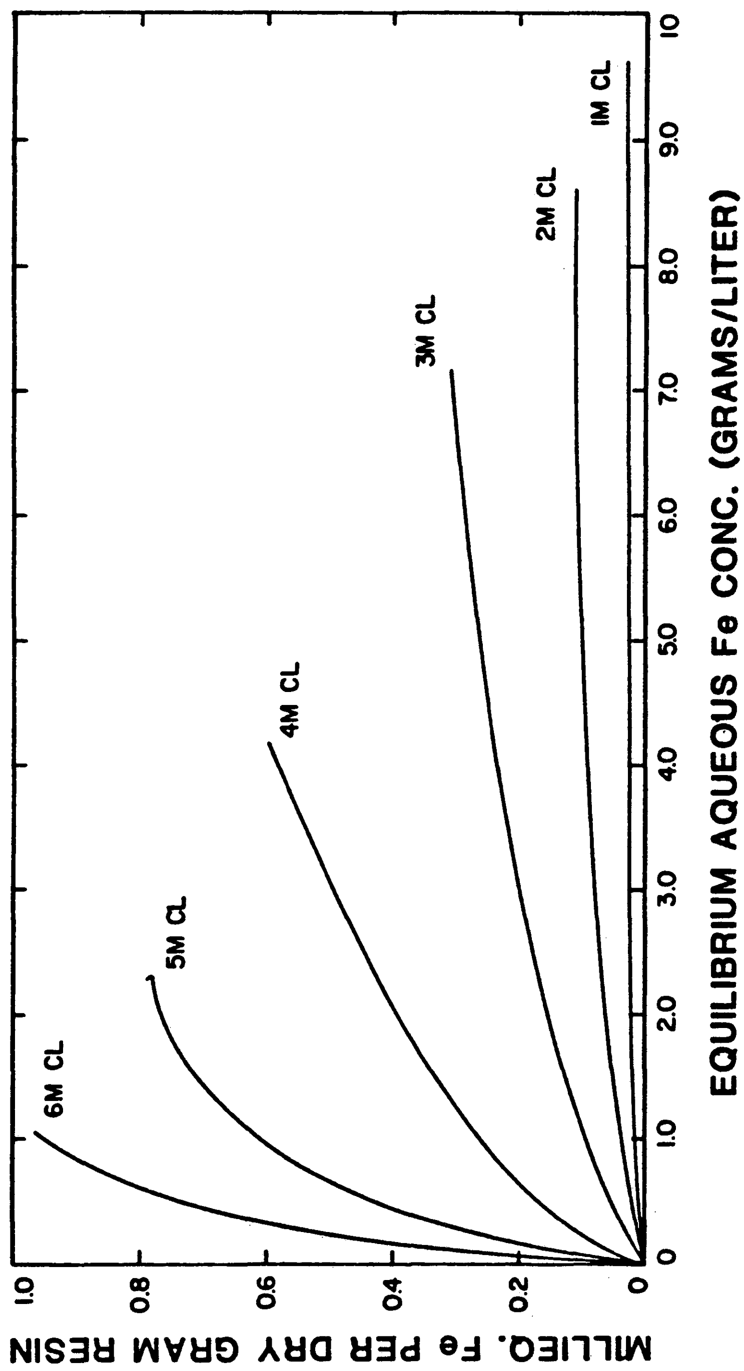

Figure 5.12 - Combination of Sorption Isotherms at 24 Deg. C for MWA-1 Resin.

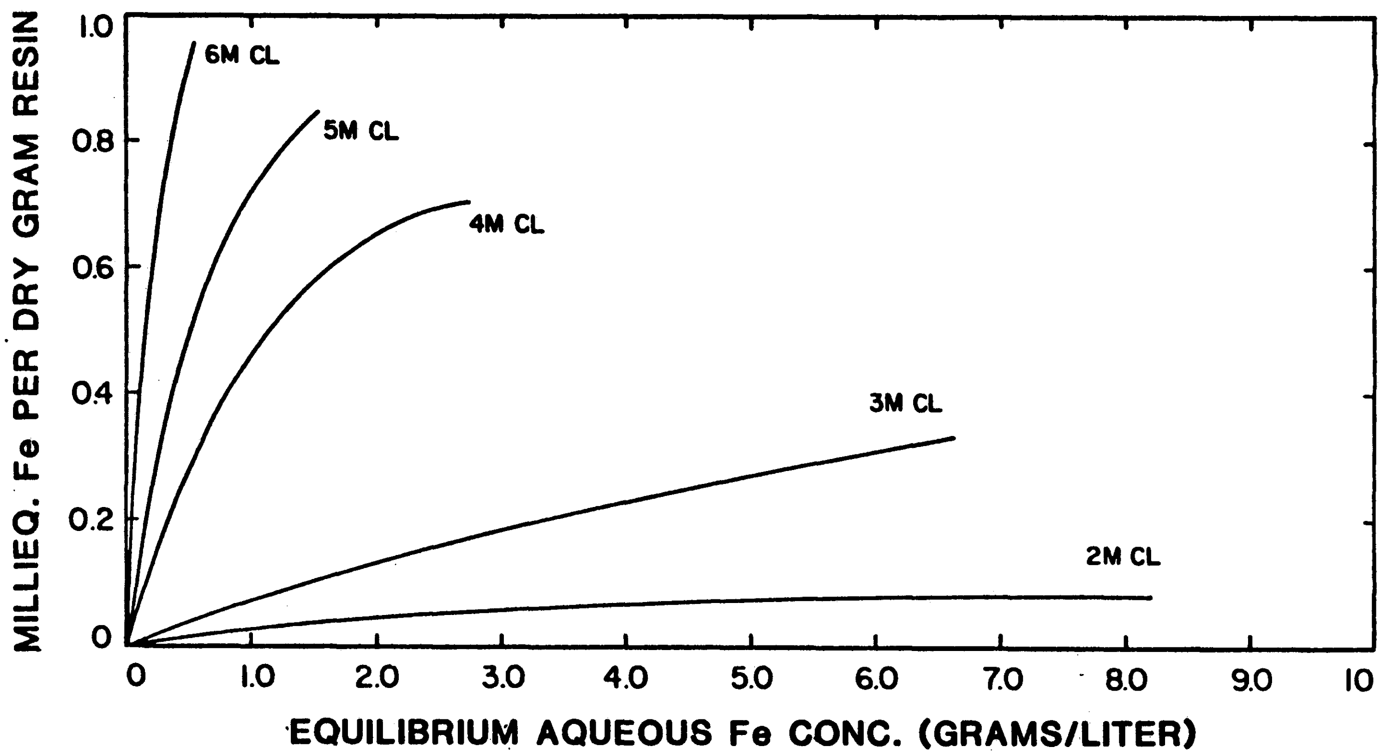

Figure 5.13 - Combination of sorption Isotherms at 24 Deg. C for SBR Resin.

industrial operations.

It must also be noted at this time that the total chloride concentration may not be the only factor affecting ion exchange loading capacity. The solution pH and aluminum concentration may also affect iron removal. As noted in Chapter 4, sorption isotherms performed at 1, 2 and 3 M initial chloride concentrations used hydrochloric acid as the source for chloride ions. The initial pH readings for all experiments are shown in Table 5.2. Since the readings for four of the experiments were unobtainable, it is difficult to draw conclusions regarding the effect of solution pH. The presence of aluminum may also affect the iron loading capacity since co-adsorption of aluminum-chloride ions would decrease the effective capacity for ferric-chloride adsorption. Evidence indicates, however, (29) that no anionic aluminum-chloride species exist. In an attempt to investigate the possibility of aluminum co-adsorption, an aluminum atomic absorption analysis was performed. Aqueous samples from the 4M chloride sorption isotherms were examined to test for concentration differences. Results showed a slight decrease in the aluminum concentration from 35 gpl Al before resin addition to 33.2 gpl Al after resin and iron additions. Aluminum concentrations were found to remain

SIMULATED LEACH LIQUOR INITIAL CL^- CONC. (M)	pH
1	0.35
2	NR
3	NR
4	1.05
5	NR
6	NR

Table 5.2 - Initial pH Readings for Simulated Leach liquors.

essentially constant as increasing amounts of hydrated ferric chloride were added.

Another effect aluminum may have on iron sorption is the amount of aluminum-chloride species formed. Aluminum may reduce the total amount of chloride ions available for iron complexation.

Two additional graphs are shown depicting the effect of chloride concentration on the equilibrium capacity of the ion exchange resins. Figure 5.14 applies to the MWA-1 resin at a constant aqueous Fe concentration of 0.9 gpl. Figure 5.15 represents loading for the SBR resin at a constant aqueous Fe concentration of 0.3 gpl. The sharp upswing in both graphs at higher chloride concentrations indicates the possibility that a new ferric-chloride species may have become prevalent.

5.3) COMPUTER PROGRAM RESULTS

A total of three computer programs were written in an effort to describe the equilibrium distribution of species present in the simulated leach liquors. As mentioned before, the formulation of the computer programs is described in Appendix 2 while stepwise formation constants are found in Appendix 1. The purpose for the computer simulation programs was to predict the major ferric

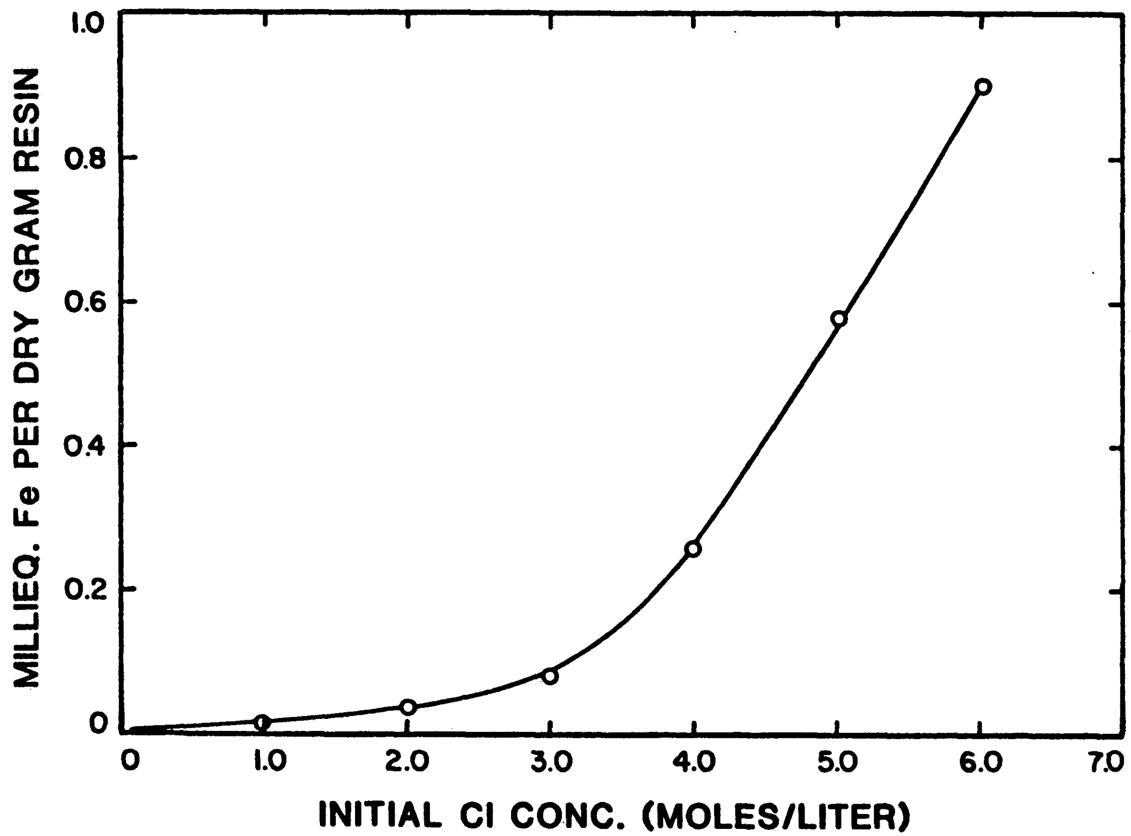

Figure 5.14 - Effect of Chloride Conc. on the Sorption of Iron into MWA-1 Resin. Aqueous Fe Conc. = 0.9 Grams/Liter.

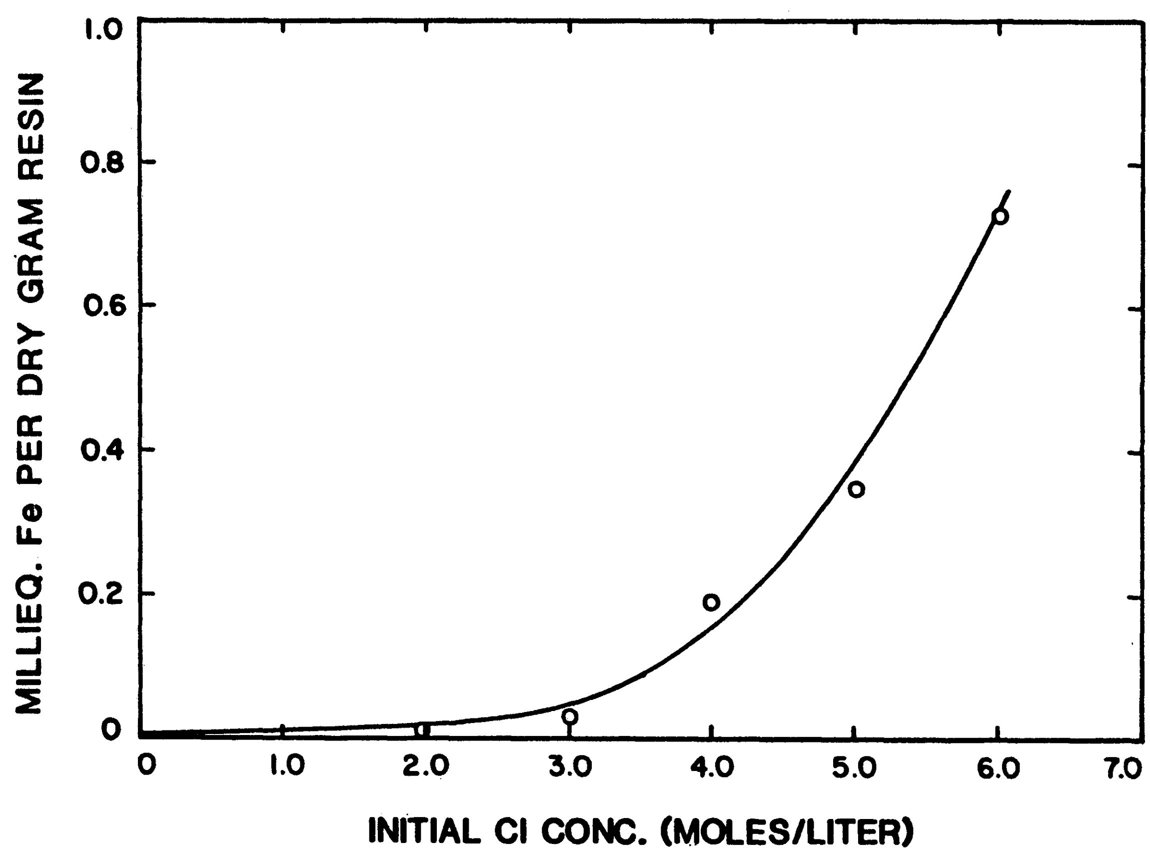

Figure 5.15 - Effect of Chloride Conc. on the Sorption of Iron into SBR Resin. Aqueous Fe Conc. = 0.3 Grams/Liter.

chloride species present in solution at different total chloride concentrations. Before drawing conclusions regarding the equilibrium species present, it was necessary to compare the computer results with published data concerning activities of ferric chloride and aluminum chloride species.

5.3.1) COMPARISON WITH PUBLISHED DATA

Very little activity data pertaining to Fe-Al-Cl-H_2O systems were found in the literature. Selected references have been found, however, (8,30,31,32) and these will be discussed further.

Since most studies were carried out to determine the mean activity coefficient of $AlCl_3$, the results presented will therefore pertain to aluminum chloride. All temperatures are reported at 25 °C.

Mason (31) has calculated the activity coefficients of $AlCl_3$ in molarity ranges from .047 to 1.751. Osmotic coefficients were used to mathematically predict aluminum chloride mean activity coefficients in aqueous solutions. Brown, et al (8) utilized a power series to determine mean ionic activity coefficients of $AlCl_3$. Bromley (32) has reported the mean activity coefficient of aluminum chloride in a strong electrolyte solution. These results are compared to the computer program predictions and all results are shown in Table 5.3. It can be seen that the computer prediction values are consistently higher than other tabulated values. It should also be noted, however, that predicted mean activity coefficients at higher molarities are in closer agreement. Since probable operating concentrations would be approximately 1.5 to 2.0 M $AlCl_3$, the computer program may have a practical application.

Even though several studies were performed investigating the structure of ferric chloride species present in aqueous solutions, data regarding species activities were scarce. Since the computer program prediction for $AlCl_3$ activity coefficients was relatively close to published data, it was also assumed that data obtained for ferric-chloride species would also be in good agreement. A distribution diagram for the Fe-Cl-H_2O system was subsequently produced and is shown in Figure 5.16. The distribution diagram was produced for a constant total iron concentration of 0.1 M. It can be seen that increasing the total chloride concentration in the system tends to increase the fractions of $Fe(Cl)_3$ and $Fe(Cl)_4^-$ present in solution. Also, the $Fe(Cl)_2^+$ concentration reaches a maximum at a chloride content of

Molarity	Mason	Brown	Bromley	Computer Prediction
0.049	0.436			0.56
.097	.384			.50
.195	.348	.305		.48
.292	.338			.49
.389	.357			.51
.486	.378			.55
.584	.406	.356		.60
.681	.442			.66
.778	.487			.72
.875	.542			.80
.973	.610	.539		.90
1.070	.689			1.00
1.167	.815			1.12
1.265	.918			1.26
1.362	.935	.936		1.41
1.459	1.253			1.59
1.556	1.610			1.80
1.654	1.773			2.03
1.751	2.131	1.819		2.29
3.29		10.251	10.42	16.76

Table 5.3 - Comparison of Mean Ionic Activity Coefficients for $AlCl_3$ in Water.

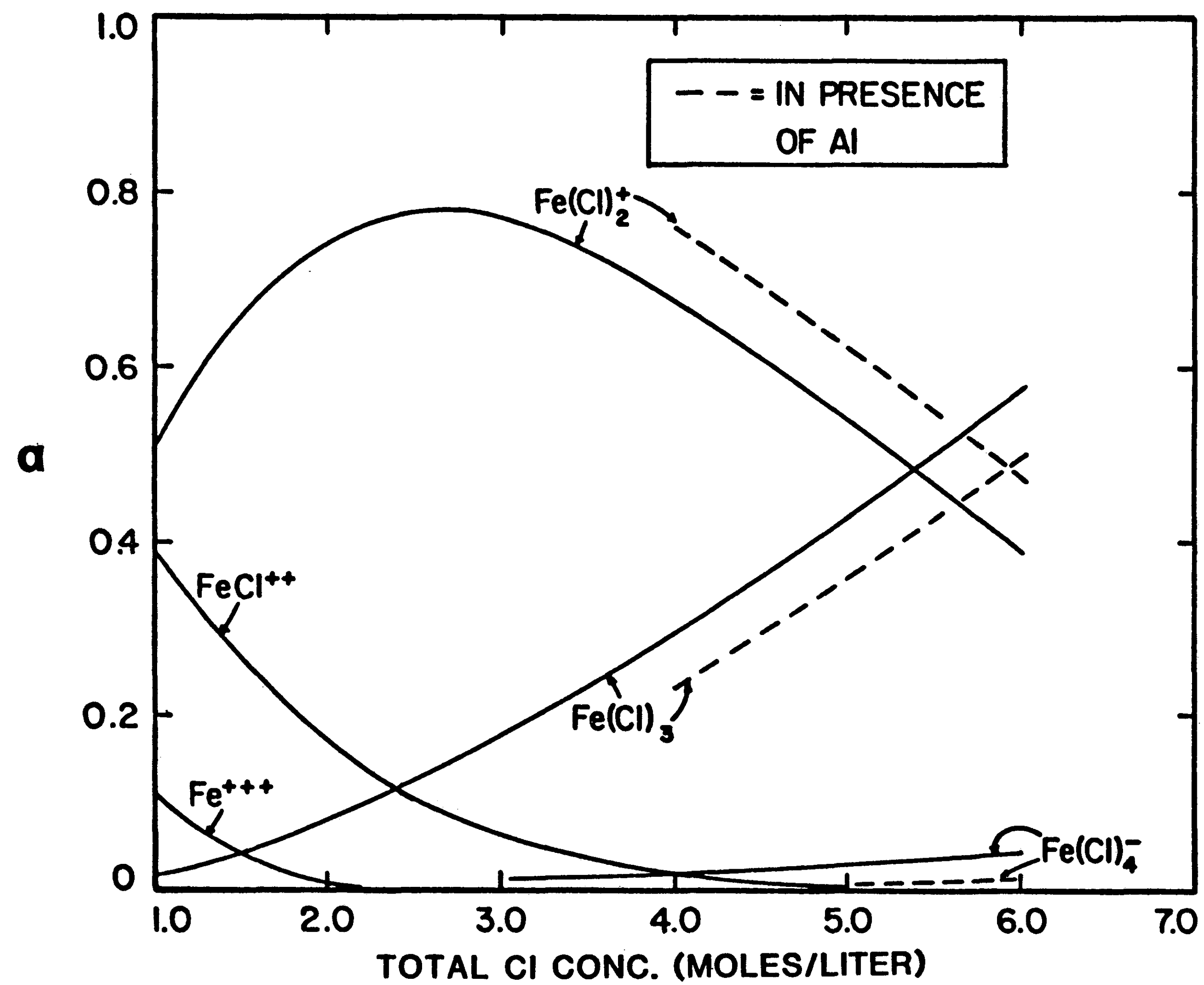

Figure 5.16 - Distribution Diagram for the Fe-Cl-H_2O System at 25 Deg. C According to Computer Program Prediction.

approximately 2.5 M and then begins to decrease.

5.3.2) COMPARISON WITH SORPTION ISOTHERMS

The distribution diagram shown in Figure 5.16 raises questions regarding the species that is extracted during sorption isotherm runs. At low chloride concentrations, smaller amounts of iron were sorbed while at higher chloride concentrations, iron loading was much greater. $Fe(Cl)_4^-$ does not seem to be present in a large enough fraction to facilitate iron removal. The fraction of $Fe(Cl)_3$, on the other hand, increases rapidly at chloride concentrations greater than 3 M. This corresponds to the shape of Figures 5.14 and 5.15 where iron sorption increases rapidly at chloride concentrations greater than 3 M. If $Fe(Cl)_3$ were the species removed from solution, the species, after diffusing into the resin, would complex with chloride counter ions already present in the resin according to the equation:

$$Fe(Cl)_3 + RCl = R(Cl)_4Fe \qquad (5.1)$$

where R = Functional group in the ion exchanger.

This proposed reaction would be contrary to a typical ion exchange reaction where counter ions displace each other. Such a reaction could be written as:

$$Fe(Cl)_4^- \quad + \quad RCl \quad = \quad RFe(Cl)_4 \quad + \quad Cl^- \qquad (5.2)$$

The proposed reaction is also contrary to the conclusions previously reached by researchers. Electrolyte conditions within an ion exchanger are nearly impossible to examine and the exact counter ion reactions for this system may not be known for a long period of time. The sorption of the $Fe(Cl)_3$ species is but one possible reaction out of several.

CHAPTER 6

CONCLUSIONS

This investigation will now be concluded with a brief discussion of the work undertaken. Conclusions will follow while the last section will consist of suggestions for future work.

6.1) SUMMARY

The research reported in this thesis was principally devoted to determining the operating characteristics of three ion exchange resins in the removal of iron from aluminum chloride leach liquors. The major experimental endeavor involved establishing sorption isotherms in which iron was removed from aluminum chloride leach liquors. Also, the wet density of the ion exchange resins in the Cl^- form was determined. The equilibrium distribution of various species in the aqueous electrolyte was predicted by a computational model developed for this goal.

6.2) CONCLUSIONS

The major conclusions reached will now be discussed.

1. Significant iron sorption was not observed with the Dowex WGR resin. This may be due to deterioration of the resin or to an improper chemical environment to which the resin was subjected. As a result, this resin was deemed unacceptable for iron sorption from aluminum chloride leach liquors.

2. Iron capacities for the Dowex SBR and Dowex MWA-1 resins were found to be less than 1 milliequivalent per dry gram resin. These capacities are low compared to the expected values. Such capacities may have a negative affect on possible industrial applications.

3. The amount of iron extracted by the Dowex SBR and Dowex MWA-1 resins seemed largely dependent on the chloride concentration present in solution. Maximum resin capacities were observed for both resins at the highest initial chloride concentration used.

4. The Dowex SBR resin seemed to have a slightly larger iron capacity than that for the MWA-1 resin at higher chloride concentrations. The capacity difference observed may, however, be within the experimental error observed for such experiments.

5. Iron was more easily stripped from the MWA-1 resin

than from the SBR resin. Visual observations indicated a more rapid color change in the resin and in the strip liquor with the MWA-1 resin than with the SBR resin. The final strip liquor effluents of the MWA-1 resin also contained a higher concentration of Fe than did the effluents of the SBR resin. Since smaller proportions of stripping liquor would likely be used industrially, the SBR resin may not operate as well.

6. Computer programs were written to predict the equilibrium distribution of species in solution. Activity coefficient data for $AlCl_3$ matched fairly well with other published data. As a result, although exact quantitative conclusions regarding the distribution of species may not be possible, qualitative conclusions may still be inferred.

7. The computer prediction program determined the possible formation of the $Fe(Cl)_{3\ (aq)}$ species in chloride molarities ranging from 4 to 6M in the Fe-Cl-H_2O system. The fraction of $Fe(Cl)_4^-$ predicted to be present at such chloride concentrations is small. Comparison of the computer prediction distribution diagram with sorption isotherm data indicates that the species $Fe(Cl)_{3\ (aq)}$ may be sorbed onto the anion exchange resins. A proposed expression for the reaction

may be written as:

$$Fe(Cl)_3 + RCl = RCl_4Fe$$

6.3) SUGGESTIONS FOR FURTHER WORK

It seems obvious from the data presented that several aspects may warrant further investigation:

A) The effective cycle life of both resins should be determined so that conclusions may be drawn regarding resistivity to the chemical environment.

B) Each resin should be subjected to steady state pilot plant tests to examine the effectiveness of iron removal. Such long contact times between resin and solution, as given in this study, may not be practical under industrial operations.

C) Critically assess the computer prediction programs and determine if any other activity coefficient equations produce more accurate results.

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APPENDIX 1

EQUILIBRIUM CONSTANT DATA FOR REACTIONS AT 25 °C (33,34,35)

	Reaction	LOG K
1)	$Al^{+++} + Cl^{-} = AlCl^{++}$	7.205
2)	$Fe^{+++} + Cl^{-} = FeCl^{++}$	1.525
3)	$Fe^{+++} + 2Cl^{-} = FeCl_2^{+}$	2.249
4)	$Fe^{+++} + 3Cl^{-} = FeCl_3$ (aq)	1.156
5)	$Fe^{+++} + 4Cl^{-} = FeCl_4^{-}$	-0.756
6)	$H^{+} + OH^{-} = H_2O$	14.0
7)	$Al^{+++} + OH^{-} = AlOH^{++}$	-4.74

APPENDIX 2

EQUILIBRIUM SPECIES CONCENTRATIONS IN THE Al-Fe-Cl-H_2O SYSTEM

The equilibrium constants approach has been utilized to predict the equilibrium species distribution in the given system. This mathematical method was developed by Baker (36) in 1980.

Data exists for a possible eleven species that can be formed from the five independent components (Al, Fe, Cl, O, and H). Seven equations are needed to predict the equilibrium in the system. The ensuing equations were chosen:

$$Al^{+++} + Cl^{-} = AlCl^{++} \qquad \text{(A2.1)}$$

$$Fe^{+++} + Cl^{-} = FeCl^{++} \qquad \text{(A2.2)}$$

$$Fe^{+++} + 2Cl^{-} = FeCl_2^{+} \qquad \text{(A2.3)}$$

$$Fe^{+++} + 3Cl^{-} = FeCl_3 \qquad (A2.4)$$

$$Fe^{+++} + 4Cl^{-} = FeCl_4^{-} \qquad (A2.5)$$

$$H^{+} + OH^{-} = H_2O \qquad (A2.6)$$

$$Al^{+++} + OH^{-} = AlOH^{++} \qquad (A2.7)$$

Thermodynamic equilibrium constants at 25°C were readily found in the literature (33,34,35). Sound thermodynamic data could not be found for further compounds involving aluminum chloride species, however. As a result another modified program was written excluding aluminum from solution.

A collection of non-linear equations results from the equilibrium reactions, and the common form of the equations is:

$$K_j = \prod_{i=1}^{N_j} (a_i)^{\nu_{ij}} \quad ; \; j = 1,2...7 \qquad (A2.8)$$

where K_j = the equilibrium constant for the reaction j.

ν_{ij} = the stoichiometric coefficient for species i and is positive if the species is a product or negative if the species is a reactant.

It is assumed that in this system the solution will not be saturated in $FeCl_3$ and $AlCl_3$ and precipitation will not be involved. Also, pH readings are assumed to be low enough to rule out possible iron hydroxide complexes formed. Five additional equations are subsequently needed to provide the necessary eleven required for the problem solution. Three equations will be provided from the molar balances on Al, Fe, and Cl. The last equation deals wih the electroneutrality condition (charge balance) since the electrolyte solution must be electroneutral.

Since the method used necessitated the use of the arithmetic-geometric inequality, it was determined useful to delegate a single unknown for the magnitude of the positive and negative charges in the system. Furthermore, the succeeding numbers were utilized for subscripts in describing the species:

$H^{+} \equiv 1$	$Fe^{+++} \equiv 5$	$FeCl_4^{-} \equiv 9$
$OH^{-} \equiv 2$	$FeCl^{++} \equiv 6$	$Cl^{-} \equiv 10$
$Al^{+++} \equiv 3$	$FeCl_2^{+} \equiv 7$	$AlOH^{++} \equiv 11$
$AlCl^{+} \equiv 4$	$FeCl_3 \equiv 8$	

Mass balances:

$$Cl_T = C9 = C_4 + C_6 + 2C_7 + 3C_8 + 4C_9 + C_{10} \quad (A2.9)$$

$$Al_T = C5 = C_3 + C_4 + C_{11} \quad (A2.10)$$

$$Fe_T = C4 = C_5 + C_6 + C_7 + C_8 + C_9 \quad (A2.11)$$

Charge Balances:

$$"+" = C_1 + 3C_3 + 2C_4 + 3C_5 + 2C_6 + C_7 + 2C_{11} \quad (A2.12)$$

$$"-" = C_2 + C_9 + C_{10} \quad (A2.13)$$

Mass Action Equations: The "molar action" equations may subsequently be expressed in terms of the concentration equilibrium constants so that they may be compatible with the molar balance equations:

$$K'_1 = \frac{C_4}{C_3 * C_{10}} \quad (A2.14)$$

$$K'_2 = \frac{C_6}{C_5 * C_{10}} \quad (A2.15)$$

$$K'_3 = \frac{C_7}{C_5 * C_{10} * C_{10}} \quad (A2.16)$$

$$K'_4 = \frac{C_8}{C_5 * C_{10}^3} \quad \text{(A2.17)}$$

$$K'_5 = \frac{C_9}{C_5 * C_{10}^4} \quad \text{(A2.18)}$$

$$K'_6 = \frac{1}{C_1 * C_2} \quad \text{(A2.19)}$$

$$K'_7 = \frac{C_{11}}{C_2 * C_3} \quad \text{(A2.20)}$$

where K'_j's are the reaction concentration-equilibrium constants and C_i's are the species concentrations. The above numbering of equations corresponds to the equations previously given. It is found from equation (A2.8) that:

$$K_j = K'_j \prod_{i=1}^{N_j} \gamma^{\nu_{ij}} \quad \text{(A2.21)}$$

from which the K_j estimates can be calculated when the species activity coefficient has been found.

SOLUTION OF THE MODEL EQUATIONS

In solving the model equations it was found suitable to normalize all the species in solution with regard to the highest concentration species present (the total chloride in this problem). As a result, the normalized equations assume the form:

$$\sum_{i=1}^{N_k} \alpha_{ik} * Y_i = A_k \ ; \quad k = 1,2,3 \tag{A2.22}$$

$$K_j' = \prod_{i=1}^{N_j} (Y_i * C_9)^{\nu_{ij}} \ ; \ j = 1,2\ldots7 \tag{A2.23}$$

where $Y_i = \frac{C_i}{C9}$ = the normalized concentration with respect to the total chloride concentration.

α_{ik} = the coefficient associated with Y in the kth molar balance.

N_k = the total number of species used in the balances.

The arithmetic-geometric equality is subsequently defined (36):

$$U_1 + \ldots U_N = \left(\frac{U_1}{\delta_1}\right)^{\delta_1} \left(\frac{U_2}{\delta_2}\right)^{\delta_2} \ldots \left(\frac{U_N}{\delta_N}\right)^{\delta_N} \tag{A2.24}$$

where U_i's are positive and real, and δ_i's are weighting factors (presently unknown) that are positive fractions that satisfy the following condition:

$$\sum_{i=1}^{N} \delta_i = 1 \qquad (A2.25)$$

which is guaranteed if:

$$\delta_i = \frac{U_i}{\sum_{i=1}^{N} U_i} \qquad (A2.26)$$

It is, therefore, possible to express the molar balances and charge balance as non-linear equations by use of the above equality. This is accomplished so that all equations will subsequently be non-linear so that a transformation into log space results in a group of linear equations.

The geometric form of the molar and charge balances has become:

$$\prod_{i=1} \left(\frac{\alpha_{ik} * Y_i}{w_{ik}} \right)^{w_{ik}} = A_k \; ; \; k = 1,2,3 \qquad (A2.27)$$

where:

$$w_{ik} = \frac{\alpha_{ik} * Y_i}{\sum_{i=1}^{N_k} \alpha_{ik} * Y_i} \qquad \text{(A2.28)}$$

The equilibrium can now be expressed as:

$$\frac{K'_j}{C9^{\Sigma \nu_{ij}}} = K''_j = \prod_{i=1}^{N_j} (Y_i)^{\nu_{ij}} \quad ; \; j = 1,2...7 \qquad \text{(A2.29)}$$

Taking logs of these equations gives a system of linear equations in log domain where the weighting factors (w's) are not initially known and must be determined iteratively. These linear equations subsequently resemble:

$$\sum_{i=1}^{N_k} w_{ik} * z_i = \sum_{i=1}^{N_k} w_{ik} \ln w_{ik} + \ln A_k \quad ; \; k=1,2,3,4 \qquad \text{(A2.30)}$$

$$\sum_{i=1}^{N_j} \nu_{ij} * z_i = \ln K''_j \quad ; \; j = 1,2...6 \qquad \text{(A2.31)}$$

where $z_i = \ln Y_i$

The system of linear equations with the unknown

z_i's is solved by using matrix routines in a BASIC computer program. Initially, all Y_i values are assigned a value of 1 and the subsequent w_{ik} values are calculated by taking exponentials. The new Y_i's are then used to re-calculate values. This iterative procedure is continued until all Y_i values converge within a given specification allowance. Normally, all Y_i's are required to converge to within at least 0.01%.

The computer program used is shown in the following pages along with a sample output. Subsequent programs omitting aluminum and adding sodium species are also shown following the first program.

SPECIES DISTRIBUTION IN THE Al-Fe-Cl-H_2O SYSTEM

```
5  REM          ********************************************
10  REM         **** EQUILIBRIUM DISTRIBUTION OF SPECIES****
20  REM         ****   IN THE AL-FE-CL-H2O SYSTEM       ****
30  REM         ****            AT 25 DEG. C            ****
40  REM         ****  PROGRAM USES ARITHMETIC-GEOMETRIC ****
50  REM         **** EQUALITY FOR SOLUTION IN LOG SPACE ****
60  REM         ********************************************
70  REM
80  REM   DIMENSIONING OF VARIABLES
90  DIM B$(14)
100  DIM H(25),I(25),F(12,12)
110  DIM W(30),C(12,12),E(12,12),Z(12,1),D(12,1),Y(20)
120  DIM K(10),J(10),X(25)
125  DIM R(20),G(15)
130  HOME
140  PRINT : PRINT : PRINT
150  INVERSE
160  PRINT "****************************************"
170  PRINT "*                                      *"
180  PRINT "*        DISTRIBUTION OF SPECIES       *"
190  PRINT "*     IN THE AL-FE-CL-H2O SYSTEM    *"
200  PRINT "*                                      *"
210  PRINT "****************************************"
220  NORMAL : PRINT : PRINT
230  PRINT "        HIT 'RETURN' TO CONTINUE       "
240  GET A$
250  HOME : PRINT : PRINT
260  INVERSE
265  PRINT "                                       "
270  PRINT "       INPUT THE CONCENTRATIONS        "
280  PRINT "        OF ELEMENTS IN SOLUTION        "
290  PRINT "           IN MOLES/LITER              "
300  PRINT "                                       "
310  NORMAL : PRINT : PRINT : PRINT
320  INPUT "    AL   = ";C5
330  INPUT "    FE   = ";C4
340  INPUT "    CL   = ";C9
360 N = 0
370 M = 12
374  REM
375  REM   READ LOG K VALUES
376  REM
380  FOR I = 1 TO 7
```

```
390  READ J(I)
400 K(I) = 10 ^ J(I)
410  NEXT I
420  DATA  7.205,1.525,2.249
430  DATA  1.156,-0.756,14.0
435  DATA  -4.74
440  FOR I = 1 TO M
450 Y(I) = 1
460  NEXT I
464  REM
465  REM  ZERO MATRICES
466  REM
470  & C = (0)
480  & E = (0)
490  & Z = (0)
500  & D = (0)
504  REM
505  REM  LOAD CONSTANTS INTO MATRIX
506  REM
510 C(1,1) =  - 1:C(1,2) =  - 1:C(2,12) =  - 1:C(3,2) =  -
1:C(3,3) =  - 1:C(3,11) = 1
520 C(4,3) =  - 1:C(4,4) = 1:C(4,10) =  - 1:C(6,5) =  -
1:C(6,6) = 1
530 C(6,10) =  - 1:C(7,5) =  - 1:C(7,7) = 1:C(7,10) =  -
2:C(8,5) =  - 1
540 C(8,8) = 1:C(8,10) =  - 3:C(9,5) =  - 1:C(9,9) =
1:C(9,10) =  - 4
545 C(12,12) =  - 1
550 S1 = Y(4) + Y(6) + 2 * Y(7) + 3 * Y(8) + 4 * Y(9) +
Y(10)
560 S2 = Y(5) + Y(6) + Y(7) + Y(8) + Y(9)
570 S3 = Y(3) + Y(4) + Y(11)
580 S4 = Y(1) + 3 * Y(3) + 2 * Y(4) + 3 * Y(5) + 2 * Y(6) +
Y(7) + 2 * Y(11)
584  REM
585  REM   LOAD WEIGHTING FACTORS
586  REM
590 S5 = Y(2) + Y(9) + Y(10)
610 W(1) = Y(4) / S1:W(2) = Y(6) / S1:W(3) = 2 * Y(7) / S1
620 W(4) = 3 * Y(8) / S1:W(5) = 4 * Y(9) / S1:W(6) = Y(10)
/ S1
630 W(7) = Y(5) / S2:W(8) = Y(6) / S2:W(9) = Y(7) / S2
640 W(10) = Y(8) / S2:W(11) = Y(9) / S2
650 W(12) = Y(3) / S3:W(13) = Y(4) / S3:W(14) = Y(11) / S3
670 W(15) = Y(1) / S4:W(16) = 3 * Y(3) / S4:W(17) = 2 *
Y(4) / S4
680 W(18) = 3 * Y(5) / S4:W(19) = 2 * Y(6) / S4:W(20) =
Y(7) / S4:W(21) = 2 * Y(11) / S4
```

```
700 W(22) = Y(2) / S5:W(23) = Y(9) / S5:W(24) = Y(10) / S5
710 C(2,2) = W(22):C(2,9) = W(23):C(2,10) = W(24)
720 C(5,5) = W(7):C(5,6) = W(8):C(5,7) = W(9):C(5,8) =
W(10):C(5,9) = W(11)
730 C(10,4) = W(1):C(10,6) = W(2):C(10,7) = W(3):C(10,8) =
W(4):C(10,9) = W(5)
740 C(10,10) = W(6):C(11,3) = W(12):C(11,4) =
W(13):C(11,11) = W(14)
750 C(12,1) = W(15):C(12,3) = W(16):C(12,4) = W(17):C(12,5)
= W(18):C(12,6) = W(19)
760 C(12,7) = W(20):C(12,11) = W(21)
770  REM
790  REM  LOAD D MATRIX
800  REM
840 D(1,1) =  LOG (K(6)) + 2 *  LOG (C9)
850 D(2,1) = 0
860  FOR I = 22 TO 24
870  IF W(I) = 0 THEN 890
880 D(2,1) = D(2,1) + W(I) *  LOG (W(I))
890  NEXT I
900 D(2,1) = D(2,1) -  LOG (C9)
910 D(3,1) =  LOG (K(7)) +  LOG (C9)
920 D(4,1) =  LOG (K(1)) +  LOG (C9)
930 D(5,1) = 0
940  FOR I = 7 TO 11
950  IF W(I) = 0 THEN 970
960 D(5,1) = D(5,1) + W(I) *  LOG (W(I))
970  NEXT I
980 D(5,1) = D(5,1) -  LOG (C9) +  LOG (C4)
990 D(6,1) =  LOG (K(2)) +  LOG (C9)
1000 D(7,1) =  LOG (K(3)) + 2 *  LOG (C9)
1010 D(8,1) =  LOG (K(4)) + 3 *  LOG (C9)
1020 D(9,1) =  LOG (K(5)) + 4 *  LOG (C9)
1030 D(10,1) = 0
1040  FOR I = 1 TO 6
1050  IF W(I) = 0 THEN 1070
1060 D(10,1) = D(10,1) + W(I) *  LOG (W(I))
1070  NEXT I
1075 D(10,1) = D(10,1) - W(3) *  LOG (2) - W(4) *  LOG (3)
- W(5) *  LOG (4)
1080 D(11,1) = 0
1090  FOR I = 12 TO 14
1100  IF W(I) = 0 THEN 1120
1110 D(11,1) = D(11,1) + W(I) *  LOG (W(I))
1120  NEXT I
1130 D(11,1) = D(11,1) -  LOG (C9) +  LOG (C5)
1140 D(12,1) = 0
1150  FOR I = 15 TO 21
```

```
1160  IF W(I) = 0 THEN 1180
1170 D(12,1) = D(12,1) + W(I) *  LOG (W(I))
1180  NEXT I
1190 D(12,1) = D(12,1) - W(16) *  LOG (3) - W(17) *  LOG
(2) - W(18) *  LOG (3)
1200 D(12,1) = D(12,1) - W(19) *  LOG (2) - W(21) *  LOG
(2) -  LOG (C9)
1220  & E = INV(C)
1230  & Z = E.D
1240 K = 0
1250  FOR I = 1 TO M
1260  IF Z(I,1) <  - 15 THEN Z(I,1) =  - 15
1270  IF Z(I,1) > 15 THEN Z(I,1) = 15
1280 X(I) =  EXP (Z(I,1))
1281  PRINT X(I) - Y(I),I
1290  IF  ABS (X(I) - Y(I)) < 1E - 3 THEN 1310
1300 K = K + 1
1310 Y(I) = X(I)
1320  IF I = M THEN 1360
1330  IF Y(I) < 1 THEN 1380
1340 Y(I) = 1
1350  IF I < M THEN 1380
1360  IF Y(I) < 10 THEN 1380
1370 Y(I) = 10
1380  NEXT I
1390 N = N + 1
1400  PRINT "ITERATION NO.  ";N
1410  PRINT " J=  ";J
1420  IF N > 100 THEN 1450
1430  IF K = 0 THEN 1490
1440  GOTO 550
1450  PRINT "SOLUTION DID NOT CONVERGE"
1460  GOTO 2000
1470  GOTO 550
1480  HOME : PRINT "  NO CONVERGENCE"
1490  FOR I = 1 TO M - 1
1500 R(I) = Y(I) * C9
1510  NEXT I
1520 J = J + 1
1530  IF J > 40 THEN 1550
1540  GOTO 1560
1550  PRINT "  NO CONVERGENCE J>40"
1554  REM
1555  REM  CALCULATE IONIC STRENGTH
1556  REM
1560 H(J) = R(1) + R(2) + 9 * R(3) + 4 * R(4) + 9 * R(5) +
4 * R(6)
1570 H(J) = H(J) + R(7) + R(9) + R(10) + 4 * R(11)
```

```
1580 I(J) = 0.5 * H(J)
1584  REM
1585  REM  CALCULATE GAMMAS
1586  REM
1590 G(8) = 1
1600 G1 = 10 ^ ( - .509 * ((I(J) ^ (.5) / (1 + I(J) ^
(.5))) - 0.2 * I(J)))
1610 G(1) = G1:G(2) = G1:G(7) = G1:G(9) = G1:G(10) = G1
1620 G2 = 10 ^ ( - .509 * 4 * ((I(J) ^ (.5) / (1 + I(J) ^
(.5))) - 0.2 * I(J)))
1630 G(4) = G2:G(6) = G2:G(11) = G2
1640 G3 = 10 ^ ( - .509 * 9 * ((I(J) ^ (.5) / (1 + I(J) ^
(.5))) - 0.2 * I(J)))
1650 G(3) = G3:G(5) = G3
1654  REM
1655  REM  CALCULATE K GAMMAS
1660 K9(1) = G(4) / (G(3) * G(10))
1666  REM
1670 K9(2) = G(6) / (G(5) * G(10))
1680 K9(3) = G(7) / (G(5) * G(10) ^ 2)
1690 K9(4) = G(8) / (G(5) * G(10) ^ 3)
1700 K9(5) = G(9) / (G(5) * G(10) ^ 4)
1710 K9(6) = 1 / (G(1) * G(2))
1715 K9(7) = G(11) / (G(2) * G(3))
1720 K(1) = 10 ^ (7.205) / K9(1)
1730 K(2) = 10 ^ (1.525) / K9(2)
1740 K(3) = 10 ^ (2.249) / K9(3)
1750 K(4) = 10 ^ (1.156) / K9(4)
1760 K(5) = 10 ^ ( - .756) / K9(5)
1770 K(6) = 10 ^ (14.0) / K9(6)
1775 K(7) = 10 ^ ( - 4.74) / K9(7)
1780  IF J = 1 THEN 550
1790  IF  ABS (I(J) - I(J - 1)) < 1E - 6 THEN 1810
1800  GOTO 550
1810  HOME : PRINT "JOB IS DONE"
1820  PRINT : PRINT
1830  PRINT "       SOLUTION HAS BEEN FOUND"
1840  PRINT " PH = "; - 1 *  LOG (Y(1) * C9 * G(1)) /  LOG
(10)
1900  PRINT  CHR$ (4);"PR#1"
1910  PRINT
1915  PRINT "  IONIC STRENGTH = ";I(J)
1920  PRINT : PRINT "ALUMINUM CONC. = ";C5;" M"
1930  PRINT : PRINT "     IRON CONC. = ";C4;" M       PH= ";
- 1 *  LOG (Y(1) * C9 * G(1)) /  LOG (10)
1940  PRINT : PRINT "CHLORIDE CONC. = ";C9;" M": PRINT :
PRINT
1950  PRINT " SPECIES        CONC.       ACT. COEFF.
```

```
ACTIVITY"
1960  PRINT " -------           -----          -----------
---------"
1970 A$ = "#########     #.######^^^^     #.######^^^^
#.######^^^^"
1980  PRINT
1990 B$(1) = "  H+  "
2000 B$(2) = " OH-  "
2010 B$(3) = " AL+++"
2020 B$(4) = "ALCL++"
2030 B$(5) = " FE+++"
2040 B$(6) = "FECL++"
2050 B$(7) = "FE(CL)2+"
2060 B$(8) = "FE(CL)3"
2070 B$(9) = "FE(CL)4-"
2080 B$(10) = " CL- "
2085 B$(11) = "AL(OH)++"
2090  FOR I = 1 TO 11
2100  &  PRINT USEA$;B$(I),Y(I) * C9,G(I),Y(I) * C9 * G(I)
2110  NEXT I
2120  PRINT  CHR$ (4);"PR#0"
```

Sample Computer Printout of Results for the

Al-Fe-Cl-H_2O System.

IONIC STRENGTH = 3.1320214

ALUMINUM CONC. = 1 M

IRON CONC. = .1 M PH= 1.53009529

CHLORIDE CONC. = 3.33 M

SPECIES	CONC.	ACT. COEFF.	ACTIVITY
H+	2.994291E-02	9.853959E-01	2.950562E-02
OH-	1.018655E-06	9.853959E-01	1.003778E-06
AL+++	1.018655E-06	8.759853E-01	8.923266E-07
ALCL++	1.000045E+00	9.428509E-01	9.428938E-01
FE+++	1.143008E-04	8.759853E-01	1.001258E-04
FECL++	7.444359E-03	9.428509E-01	7.018921E-03
FE(CL)2+	7.895576E-02	9.853959E-01	7.780268E-02
FE(CL)3	1.314374E-02	1.000000E+00	1.314374E-02
FE(CL)4-	3.418476E-04	9.853959E-01	3.368552E-04
CL-	2.123800E+00	9.853959E-01	2.092784E+00
AL(OH)++	1.018655E-06	9.428509E-01	9.604396E-07

SPECIES DISTRIBUTION IN THE $Fe-Cl-H_2O$ SYSTEM

```
05  REM    *******************************************
10  REM    *** EQUILIBRIUM DISTRIBUTION OF SPECIES ***
20  REM    ***   IN THE FE - CL - H2O SYSTEM       ***
30  REM    ***            PROGRAM USES             ***
40  REM    ***   ARITHMETIC-GEOMETRIC INEQUALITY   ***
45  REM    *******************************************
47  REM
50  REM  DIMENSIONING OF VARIABLES
80  DIM B$(9)
90  DIM H(20),I(20)
100  DIM F(9,9)
110  DIM W(20),C(9,9),E(9,9),Z(9,1),D(9,1),Y(15)
120  DIM K(10),J(10),X(20)
130  HOME
140  VTAB (4): INVERSE
150  PRINT "**************************************"
155  PRINT "*                                    *"
160  PRINT "*    IONIC EQUILIBRIA DISTRIBUTION   *"
170  PRINT "*      FOR THE FE-CL-H2O SYSTEM      *"
180  PRINT "*                                    *"
190  PRINT "*  PROGRAM USES ARITHMETIC-GEOMETRIC *"
200  PRINT "*  EQUALITY FOR SOLUTION IN LOG SPACE *"
220  PRINT "*                                    *"
230  PRINT "**************************************"
240  PRINT : PRINT
250  NORMAL : PRINT "       HIT 'RETURN' TO CONTINUE"
260  GET P$
270  HOME : PRINT : PRINT
280  INVERSE : PRINT "  ENTER THE CHLORIDE CONC.
(MOL./LITER)"
290  NORMAL : INPUT C9
295  PRINT : PRINT
300  INVERSE : PRINT "  ENTER THE IRON CONC. (MOL./LITER)
"
305  NORMAL : INPUT C4
310  HOME : VTAB (12): HTAB (13): PRINT "NOW EXECUTING"
320 N = 0
330 M = 9
334  REM
335  REM  READ LOG K VALUES
336  REM
340  FOR I = 1 TO 5
350  READ J(I)
360 K(I) = 10 ^ J(I)
```

```
370  NEXT I
380  DATA  1.525,2.249,1.156,-0.756,14.0
390  FOR I = 1 TO M
400 Y(I) = 1
410  NEXT I
414  REM
415  REM  ZERO MATRICES
416  REM
420  & C = (0)
430  & E = (0)
440  & Z = (0)
450  & D = (0)
454  REM
455  REM    LOAD CONSTANTS INTO MATRIX
456  REM
460 C(1,1) =  - 1:C(1,6) =  - 1:C(4,1) =  - 1:C(5,1) =  - 1
470 C(6,1) =  - 1:C(7,9) =  - 1:C(8,7) =  - 1:C(8,8) =  - 1
480 C(9,9) =  - 1:C(6,6) =  - 2:C(4,6) =  - 3:C(5,6) =  - 4
490 C(1,2) = 1:C(4,4) = 1:C(5,5) = 1:C(6,3) = 1
500 S1 = Y(2) + 2 * Y(3) + 3 * Y(4) + 4 * Y(5) + Y(6)
510 S2 = Y(1) + Y(2) + Y(3) + Y(4) + Y(5)
520 S3 = 3 * Y(1) + 2 * Y(2) + Y(3) + Y(7)
530 S4 = Y(5) + Y(6) + Y(8)
535  REM
540  REM    DEF'N OF W'S (WEIGHTING FACTORS)
550  REM
560 W(1) = Y(2) / S1:W(2) = 2 * Y(3) / S1:W(3) = 3 * Y(4) /
S1
570 W(4) = 4 * Y(5) / S1:W(5) = Y(6) / S1
580 W(6) = Y(1) / S2:W(7) = Y(2) / S2:W(8) = Y(3) / S2
590 W(9) = Y(4) / S2:W(10) = Y(5) / S2
600 W(11) = 3 * Y(1) / S3:W(12) = 2 * Y(2) / S3:W(13) =
Y(3) / S3:W(14) = Y(7) / S3
610 W(15) = Y(5) / S4:W(16) = Y(6) / S4:W(17) = Y(8) / S4
620 C(2,2) = W(1):C(2,3) = W(2):C(2,4) = W(3):C(2,5) = W(4)
630 C(2,6) = W(5):C(3,1) = W(6):C(3,2) = W(7):C(3,3) = W(8)
640 C(3,4) = W(9):C(3,5) = W(10):C(7,1) = W(11):C(7,2) =
W(12)
650 C(7,3) = W(13):C(7,7) = W(14):C(9,5) = W(15):C(9,6) =
W(16)
660 C(9,8) = W(17)
664  REM
665  REM  LOAD D MATRIX
666  REM
670 D(1,1) =  LOG (K(1)) +  LOG (C9)
680 D(2,1) = 0
690  FOR I = 1 TO 5
700  IF W(I) = 0 THEN 720
```

```
710 D(2,1) = D(2,1) + W(I) *  LOG (W(I))
720  NEXT I
730 D(2,1) = D(2,1) - W(2) *  LOG (2) - W(3) *  LOG (3) -
W(4) *  LOG (4)
740 D(3,1) = 0
750  FOR I = 6 TO 10
760  IF W(I) = 0 THEN 780
770 D(3,1) = D(3,1) + W(I) *  LOG (W(I))
780  NEXT I
790 D(3,1) = D(3,1) +  LOG (C4) -  LOG (C9)
800 D(4,1) =  LOG (K(3)) + 3 *  LOG (C9)
810 D(5,1) =  LOG (K(4)) + 4 *  LOG (C9)
820 D(6,1) =  LOG (K(2)) + 2 *  LOG (C9)
830 D(7,1) = 0
840  FOR I = 11 TO 14
850  IF W(I) = 0 THEN 870
860 D(7,1) = D(7,1) + W(I) *  LOG (W(I))
870  NEXT I
880 D(7,1) = D(7,1) -  LOG (C9) - W(11) *  LOG (3) - W(12)
*  LOG (2)
890 D(8,1) =  LOG (K(5)) + 2 *  LOG (C9)
900 D(9,1) = 0
910  FOR I = 15 TO 17
920  IF W(I) = 0 THEN 940
930 D(9,1) = D(9,1) + W(I) *  LOG (W(I))
940  NEXT I
950 D(9,1) = D(9,1) -  LOG (C9)
960  & E = INV(C)
970  & Z = E.D
980 K = 0
990  FOR I = 1 TO M
1000  IF Z(I,1) <  - 25 THEN Z(I,1) =  - 25
1010  IF Z(I,1) > 25 THEN Z(I,1) = 25
1020 X(I) =  EXP (Z(I,1))
1030  IF  ABS (X(I) - Y(I)) < 1E - 3 THEN 1050
1040 K = K + 1
1050 Y(I) = X(I)
1060  IF I = M THEN 1100
1070  IF Y(I) < 1 THEN 1120
1080 Y(I) = 1
1090  IF I < M THEN 1120
1100  IF Y(I) < 15 THEN 1120
1110 Y(I) = 15
1120  NEXT I
1130 N = N + 1
1140  PRINT "ITERATION NO. ";N
1150  PRINT "   J= ";J
1160  IF N > 30 THEN 1190
```

```
1170  IF K = 0 THEN 1230
1180  GOTO 500
1190  PRINT "  SOLUTION DID NOT CONVERGE"
1200  GOTO 1810
1210  GOTO 500
1220  PRINT "SOLUTION DID NOT CONVERGE"
1230  FOR I = 1 TO M - 1
1240 R(I) = Y(I) * C9
1250  NEXT I
1260 J = J + 1
1270  IF J > 40 THEN 1290
1280  GOTO 1300
1290  PRINT "  NO CONVERGENCE"
1294  REM
1295  REM   CALCULATE IONIC STRENGTH
1296  REM
1300 H(J) = 9 * R(1) + 4 * R(2) + R(3) + R(5) + R(6) + R(7)
+ R(8)
1310 I(J) = 0.5 * H(J)
1314  REM
1315  REM  CALCULATE GAMMAS
1316  REM
1320 G(4) = 1
1330 G1 = 10 ^ ( - .509 * ((I(J) ^ (.5) / (1 + I(J) ^
(.5))) - 0.2 * I(J)))
1340 G(3) = G1:G(5) = G1:G(6) = G1:G(7) = G1:G(8) = G1
1350 G2 = 10 ^ ( - .509 * 4 * ((I(J) ^ (.5) / (1 + I(J) ^
(.5))) - 0.2 * I(J)))
1360 G(2) = G2
1370 G3 = 10 ^ ( - .509 * 9 * ((I(J) ^ (.5) / (1 + I(J) ^
(.5))) - 0.2 * I(J)))
1380 G(1) = G3
1390 K9(1) = G(2) / (G(1) * G(6))
1400 K9(2) = G(3) / (G(1) * G(6) ^ 2)
1410 K9(3) = G(4) / (G(1) * G(6) ^ 3)
1420 K9(4) = G(5) / (G(1) * G(6) ^ 4)
1430 K9(5) = 1 / (G(7) * G(8))
1440 K(1) = 10 ^ (1.525) / K9(1)
1450 K(2) = 10 ^ (2.249) / K9(2)
1460 K(3) = 10 ^ (1.156) / K9(3)
1470 K(4) = 10 ^ ( - 0.756) / K9(4)
1480 K(5) = 10 ^ (14.0) / K9(5)
1490  IF J = 1 THEN 500
1500  IF  ABS (I(J) - I(J - 1)) < 1E - 6 THEN 1520
1510  GOTO 500
1520  HOME
1530  PRINT : PRINT
1540  PRINT " SOLUTION HAS BEEN FOUND"
```

```
1550  FOR B = 1 TO 3000
1560  NEXT B
1570  PRINT  CHR$ (4);"PR#1"
1580  PRINT : PRINT
1585  PRINT "  IONIC STRENGTH = ";I(J)
1586  PRINT
1590  PRINT "    CHLORIDE CONC. = ";C9;" MOL./LITER"
1600  PRINT
1610  PRINT "        IRON CONC. = ";C4;" MOL./LITER"
1620  PRINT : HTAB (15): PRINT " PH = "; - 1 *  LOG (Y(7) *
C9 * G(7)) /  LOG (10)
1624  PRINT
1625  HTAB (6): PRINT "IONIC STRENGTH = ";I(J)
1630  PRINT : PRINT
1640  PRINT " SPECIES          CONC.        ACT. COEFF.
ACTIVITY"
1650  PRINT " -------          -----        -----------
--------"
1660 A$ = "########     #.######^^^^     #.######^^^^
#.######^^^^"
1670  PRINT
1680 B$(1) = " FE+++"
1690 B$(2) = "FECL++"
1700 B$(3) = "FE(CL)2+"
1710 B$(4) = "FE(CL)3"
1720 B$(5) = "FE(CL)4-"
1730 B$(6) = "  CL- "
1740 B$(7) = "  H+  "
1750 B$(8) = "  OH- "
1760  FOR I = 1 TO 8
1770  &  PRINT USEA$;B$(I),Y(I) * C9,G(I),Y(I) * C9 * G(I)
1780  NEXT I
1790  PRINT  CHR$ (4);"PR#0"
1800  END
```

SPECIES DISTRIBUTION AND THE Al-Fe-Na-Cl-H_2O SYSTEM

```
5  REM         ********************************************
10  REM        **** EQUILIBRIUM DISTRIBUTION OF SPECIES****
20  REM        **** IN THE AL-FE-CL-NA-H2O SYSTEM      ****
30  REM        ****            AT 25 DEG. C            ****
40  REM        ****  PROGRAM USES ARITHMETIC-GEOMETRIC ****
50  REM        **** EQUALITY FOR SOLUTION IN LOG SPACE ****
60  REM        ********************************************
70  REM
80  REM    DIMENSIONING OF VARIABLES
90  DIM B$(14)
100  DIM H(25),I(25),F(12,12)
110  DIM W(30),C(12,12),E(12,12),Z(12,1),D(12,1),Y(20)
120  DIM K(10),J(10),X(25)
125  DIM R(20),G(15)
130  HOME
140  PRINT : PRINT : PRINT
150  INVERSE
160  PRINT "****************************************"
170  PRINT "*                                      *"
180  PRINT "*       DISTRIBUTION OF SPECIES        *"
190  PRINT "*    IN THE AL-FE-NA-CL-H2O SYSTEM     *"
200  PRINT "*                                      *"
210  PRINT "****************************************"
220  NORMAL : PRINT : PRINT
230  PRINT "        HIT 'RETURN' TO CONTINUE       "
240  GET A$
250  HOME : PRINT : PRINT
260  INVERSE
265  PRINT "                                       "
270  PRINT "       INPUT THE CONCENTRATIONS        "
280  PRINT "        OF ELEMENTS IN SOLUTION        "
290  PRINT "           IN MOLES/LITER              "
300  PRINT "                                       "
310  NORMAL : PRINT : PRINT : PRINT
320  INPUT "    AL  = ";C5
330  INPUT "    FE  = ";C4
340  INPUT "    CL  = ";C9
350  INPUT "    NA  = ";C6
360 N = 0
370 M = 12
380  FOR I = 1 TO 6
390  READ J(I)
400 K(I) = 10 ^ J(I)
410  NEXT I
```

```
420  DATA  7.205,1.525,2.249
430  DATA  1.156,-0.756,14.0
440  FOR I = 1 TO M
450 Y(I) = 1
460  NEXT I
470  & C = (0)
480  & E = (0)
490  & Z = (0)
500  & D = (0)
510 C(1,1) =  - 1:C(1,2) =  - 1:C(2,12) =  - 1:C(6,5) =  -
1:C(6,6) = 1
520 C(6,10) =  - 1:C(7,5) =  - 1:C(7,7) = 1:C(7,10) =  -
2:C(8,5) =  - 1
530 C(8,8) = 1:C(8,10) =  - 3:C(9,5) =  - 1:C(9,9) =
1:C(9,10) =  - 4
540 C(10,3) =  - 1:C(10,4) = 1:C(10,10) =  - 1:C(12,12) =
- 1
550 S1 = Y(4) + Y(6) + 2 * Y(7) + 3 * Y(8) + 4 * Y(9) +
Y(10)
560 S2 = Y(5) + Y(6) + Y(7) + Y(8) + Y(9)
570 S3 = Y(3) + Y(4)
580 S4 = Y(1) + 3 * Y(3) + 2 * Y(4) + 3 * Y(5) + 2 * Y(6) +
Y(7) + Y(11)
590 S5 = Y(2) + Y(9) + Y(10)
600 S6 = Y(11)
610 W(1) = Y(4) / S1:W(2) = Y(6) / S1:W(3) = 2 * Y(7) / S1
620 W(4) = 3 * Y(8) / S1:W(5) = 4 * Y(9) / S1:W(6) = Y(10)
/ S1
630 W(7) = Y(5) / S2:W(8) = Y(6) / S2:W(9) = Y(7) / S2
640 W(10) = Y(8) / S2:W(11) = Y(9) / S2
650 W(12) = Y(3) / S3
660 W(13) = Y(4) / S3
670 W(14) = Y(1) / S4:W(15) = 3 * Y(3) / S4:W(16) = 2 *
Y(4) / S4
680 W(17) = 3 * Y(5) / S4:W(18) = 2 * Y(6) / S4:W(19) =
Y(7) / S4
690 W(20) = Y(11) / S4
700 W(21) = Y(2) / S5:W(22) = Y(9) / S5:W(23) = Y(10) / S5
710 W(24) = Y(11) / S6
720 C(2,2) = W(21):C(2,9) = W(22):C(2,10) = W(23)
730 C(3,3) = W(12):C(3,4) = W(13):C(4,4) = W(1)
740 C(4,6) = W(2):C(4,7) = W(3):C(4,8) = W(4)
750 C(4,9) = W(5):C(4,10) = W(6)
760 C(5,5) = W(7):C(5,6) = W(8):C(5,7) = W(9)
770 C(5,8) = W(10):C(5,9) = W(11)
780 C(11,11) = W(24):C(12,1) = W(14):C(12,3) = W(15)
790 C(12,4) = W(16):C(12,5) = W(17):C(12,6) = W(18)
800 C(12,7) = W(19):C(12,11) = W(20)
```

```
810  REM
820  REM     LOAD D MATRIX
830  REM
840 D(1,1) =  LOG (K(6)) + 2 *  LOG (C9)
850 D(2,1) = 0
860  FOR I = 21 TO 23
870  IF W(I) = 0 THEN 890
880 D(2,1) = D(2,1) + W(I) *  LOG (W(I))
890  NEXT I
900 D(2,1) = D(2,1) -  LOG (C9)
910 D(3,1) = 0
920  FOR I = 12 TO 13
930  IF W(I) = 0 THEN 950
940 D(3,1) = D(3,1) + W(I) *  LOG (W(I))
950  NEXT I
960 D(3,1) = D(3,1) +  LOG (C5) -  LOG (C9)
970 D(4,1) = 0
980  FOR I = 1 TO 6
990  IF W(I) = 0 THEN 1010
1000 D(4,1) = D(4,1) + W(I) *  LOG (W(I))
1010  NEXT I
1020 D(4,1) = D(4,1) - W(3) *  LOG (2) - W(4) *  LOG (3) -
W(5) *  LOG (4)
1030 D(5,1) = 0
1040  FOR I = 7 TO 11
1050  IF W(I) = 0 THEN 1070
1060 D(5,1) = D(5,1) + W(I) *  LOG (W(I))
1070  NEXT I
1080 D(5,1) = D(5,1) +  LOG (C4) -  LOG (C9)
1090 D(6,1) =  LOG (K(2)) +  LOG (C9)
1100 D(7,1) =  LOG (K(3)) + 2 *  LOG (C9)
1110 D(8,1) =  LOG (K(4)) + 3 *  LOG (C9)
1120 D(9,1) =  LOG (K(5)) + 4 *  LOG (C9)
1130 D(10,1) =  LOG (K(1)) +  LOG (C9)
1140 D(11,1) = W(24) *  LOG (W(24)) -  LOG (C9) +  LOG (C6)
1150 D(12,1) = 0
1160  FOR I = 14 TO 20
1170  IF W(I) = 0 THEN 1190
1180 D(12,1) = D(12,1) + W(I) *  LOG (W(I))
1190  NEXT I
1200 D(12,1) = D(12,1) - W(15) *  LOG (3) - W(16) *  LOG
(2) - W(17) *  LOG (3)
1210 D(12,1) = D(12,1) - W(18) *  LOG (2) -  LOG (C9)
1220  & E = INV(C)
1230  & Z = E.D
1240 K = 0
1250  FOR I = 1 TO M
1260  IF Z(I,1) <  - 25 THEN Z(I,1) =  - 25
```

```
1270  IF Z(I,1) > 25 THEN Z(I,1) = 25
1280 X(I) =  EXP (Z(I,1))
1290  IF  ABS (X(I) - Y(I)) < 1E - 3 THEN 1310
1300 K = K + 1
1310 Y(I) = X(I)
1320  IF I = M THEN 1360
1330  IF Y(I) < 1 THEN 1380
1340 Y(I) = 1
1350  IF I < M THEN 1380
1360  IF Y(I) < 15 THEN 1380
1370 Y(I) = 15
1380  NEXT I
1390 N = N + 1
1400  HOME : VTAB (12): HTAB (12): PRINT "ITERATION NO.
";N
1410  PRINT "            J= ";J
1420  IF N > 40 THEN 1450
1430  IF K = 0 THEN 1490
1440  GOTO 550
1450  PRINT : PRINT "   SOLUTION DID NOT CONVERGE (N>40)"
1460  GOTO 2000
1470  GOTO 550
1480  HOME : VTAB (12): HTAB (12): PRINT "NO CONVERGENCE"
1490  FOR I = 1 TO (M - 1)
1500 R(I) = Y(I) * C9
1510  NEXT I
1520 J = J + 1
1530  IF J > 40 THEN 1550
1540  GOTO 1560
1550  PRINT "NO CONVERGENCE"
1554  REM
1555  REM     CALCULATE IONIC STRENGTH
1556  REM
1560 H(J) = R(1) + R(2) + 9 * R(3) + 4 * R(4) + 9 * R(5) +
4 * R(6)
1570 H(J) = H(J) + R(7) + R(9) + R(10) + R(11)
1580 I(J) = 0.5 * H(J)
1590 G(8) = 1
1600 G1 = 10 ^ ( - .509 * ((I(J) ^ (.5) / (1 + I(J) ^
(.5))) - 0.2 * I(J)))
1610 G(1) = G1:G(2) = G1:G(7) = G1:G(9) = G1:G(10) =
G1:G(11) = G1
1620 G2 = 10 ^ ( - .509 * 4 * ((I(J) ^ (.5) / (1 + I(J) ^
(.5))) - 0.2 * I(J)))
1630 G(4) = G2:G(6) = G2
1640 G3 = 10 ^ ( - .509 * 9 * ((I(J) ^ (.5) / (1 + I(J) ^
(.5))) - 0.2 * I(J)))
1650 G(3) = G3:G(5) = G3
```

```
1660 K9(1) = G(4) / (G(3) * G(10))
1670 K9(2) = G(6) / (G(5) * G(10))
1680 K9(3) = G(7) / (G(5) * G(10) ^ 2)
1690 K9(4) = G(8) / (G(5) * G(10) ^ 3)
1700 K9(5) = G(9) / (G(5) * G(10) ^ 4)
1710 K9(6) = 1 / (G(1) * G(2))
1720 K(1) = 10 ^ (7.205) / K9(1)
1730 K(2) = 10 ^ (1.525) / K9(2)
1740 K(3) = 10 ^ (2.249) / K9(3)
1750 K(4) = 10 ^ (1.156) / K9(4)
1760 K(5) = 10 ^ ( - .756) / K9(5)
1770 K(6) = 10 ^ (14.0) / K9(6)
1780  IF J = 1 THEN 550
1790  IF  ABS (I(J) - I(J - 1)) < 1E - 6 THEN 1810
1800  GOTO 550
1810  HOME
1820  PRINT : PRINT
1830  PRINT "       SOLUTION HAS BEEN FOUND"
1840  PRINT " PH = "; - 1 *  LOG (Y(1) * C9 * G(1)) /  LOG
(10)
1900  PRINT  CHR$ (4);"PR#1"
1910  PRINT
1920  PRINT : PRINT "ALUMINUM CONC. = ";C5;" M"
1930  PRINT : PRINT "    IRON CONC. = ";C4;" M       PH= ";
- 1 *  LOG (Y(1) * C9 * G(1)) /  LOG (10)
1935  PRINT : PRINT "  SODIUM CONC. = ";C6;" M"
1940  PRINT : PRINT "CHLORIDE CONC. = ";C9;" M": PRINT :
PRINT
1950  PRINT " SPECIES         CONC.        ACT. COEFF.
ACTIVITY"
1960  PRINT " -------         -----        -----------
---------"
1970 A$ = "########     #.######^^^^     #.######^^^^
#.######^^^^"
1980  PRINT
1990 B$(1) = "  H+  "
2000 B$(2) = " OH-  "
2010 B$(3) = " AL+++"
2020 B$(4) = "ALCL++"
2030 B$(5) = " FE+++"
2040 B$(6) = "FECL++"
2050 B$(7) = "FE(CL)2+"
2060 B$(8) = "FE(CL)3"
2070 B$(9) = "FE(CL)4-"
2080 B$(10) = " CL- "
2085 B$(11) = " NA+ "
2090  FOR I = 1 TO 11
2100  &  PRINT USEA$;B$(I),Y(I) * C9,G(I),Y(I) * C9 * G(I)
```

```
2110  NEXT I
2120  PRINT  CHR$ (4);"PR#0"
```