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**SIMULTANEOUS SULFATE AND CHLORIDE REMOVAL FROM MHD
SPENT SEED USING ANION-EXCHANGE RESIN**

A Thesis

Presented for the

Master of Science

Degree

The University of Tennessee, Knoxville

Santhanam Parthasarathy

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DEDICATION

This thesis is dedicated to my parents

Mr. K.R. Santhanam
(திரு. கே. ஆர். சந்தானம்)

and

Mrs. Vasantha Santhanam
(திருமதி. வசந்தா சந்தானம்)

for their love, affection and blessings.

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ABSTRACT

At the University of Tennessee Space Institute, (UTSI) a process to simultaneously remove sulfates and chlorides from spent seed material from a coal-fired magnetohydrodynamics (MHD) power plant has been developed. This process uses commercially available weak-base anion-exchange resin and can be used to regenerate the spent seed. In this thesis, results from batch and fixed-bed experiments conducted at UTSI to simultaneously remove sulfates and chlorides from MHD spent seed are discussed. Three commercially available anion-exchange resins were tested in batch mode experiments to study the sulfate and chloride removal efficiency. Process variables that affect the percentage removal like, the solution-to-resin ratio, solution concentration and multi-stage operation were studied. For the fixed-bed tests, experiments were conducted using two different resin carbonation procedures. One procedure involved carbonating the ion-exchange resin simultaneously during exhaustion and in the other procedure precarbonated resin was used. Results from the fixed-bed experiments performed by the latter procedure were explained by the Antonson's model that assumes intraparticle diffusion to be the overall rate controlling step. A kinetic model assuming reaction rate as the rate controlling step was used to analyze the simultaneous carbonation/exhaustion runs.

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LIST OF SYMBOLS

- A_1 : first Langmuir constant for reaction kinetics model (dimensionless)
- A_2 : second Langmuir constant for reaction kinetics model (ml_r/meq)
- a_1 : first Langmuir constant for Antonson's model (dimensionless)
- a_2 : second Langmuir constant for Antonson's model (ml_r/meq)
- A : area under $(1 - C/C_0)$ versus time curve, (min.)
- C : concentration of anions in the bulk phase, (meq/ml_s)
- C_C : chloride concentration in the bulk phase, (meq/ml_s)
- C_s : sulfate concentration in the bulk phase, (meq/ml_s)
- C_0 : initial concentration of anions in bulk phase, (meq/ml_s)
- C_s : concentration of anions in the fluid-solid interface, (meq/ml_s)
- C_T : total available ion-exchange sites in resin phase, (meq/ml_r)
- D : intraparticle diffusion coefficient, ($\text{cm}^2/\text{sec.}$)
- F : volumetric flow rate, ($\text{ml.}/\text{min.}$)
- h_1 : sulfate-to-chloride equivalents ratio, (dimensionless)
- h_2 : sulfate concentration in feed solution, (meq/l)
- h_3 : chloride concentration in feed solution, (meq/l)
- k_L : liquid film mass transfer coefficient, ($\text{cm.}/\text{min.}$)
- K_a : adsorption or forward reaction rate constant, ($\text{ml}_s/\text{min.} \cdot \text{meq}$)
- K_d : desorption or backward reaction rate constant, ($1/\text{min.}$)
- K_1 : rate constant for carbonation reaction, [$\text{cm}^2/(\text{Kg.} \cdot \text{min.})$]

- K_2 : rate constant for chloride exchange reaction, $[\text{ml}_s/(\text{meq} \cdot \text{min.})]$
 K_3 : rate constant for sulfate exchange reaction, $[(\text{ml}_s \cdot \text{ml}_r)/\text{meq}^2]$
 m : ratio of void fraction-to-the particle fraction, (dimensionless)
 P : CO_2 pressure, (Kg./cm^2)
 q : concentration of anions in resin phase, (meq/ml_r)
 q_c : chloride concentration in the resin phase, (meq/ml_r)
 q_s : sulfate concentration in the resin phase, (meq/ml_r)
 q_i : local resin phase concentration of anions, (meq/ml_r)
 q_s : concentration of anions at the fluid-solid interface, (meq/ml_r)
 q_∞ : equilibrium concentration of anions in the resin phase, (meq/ml_r)
 R : characteristic length of the resin particle, (cm.)
 r : radial coordinate in spherical particles, (cm.)
 s : effective surface area of the resin, $(\text{cm}^2/\text{gm. resin})$
 t : time, (min)
 v : superficial velocity in the resin bed, (cm./sec.)
 V : volumetric flow rate defined in equation (3.5) , $(\text{ml}_s/\text{sec.})$
 V_R : volume of resin, (ml_r)
 x : weight of resin traversed in the bed defined in equation (3.5), (gm.)
 X^* : z/mv (sec)
 X : $3Da_1z_T/mvR^2$ (dimensionless)
 y : volume of effluent from the fixed-bed defined in equation (3.5), (ml)
 z : axial position, (cm.)

z_T : height of the resin bed (cm.)

λ : dummy variable of integration

ϕ : $\frac{C}{C_0}$ (Dimensionless)

θ^* : $(t - \frac{z}{v})$ (sec.)

θ : $\frac{2D}{R^2}(t - \frac{z_T}{v})$ (Dimensionless)

CHAPTER I

INTRODUCTION

With the rising costs of energy, it is becoming apparent that a more efficient use of coal to produce electricity would be both economically and environmentally attractive. One of the methods that will yield more electricity per pound of coal is based on the Magnetohydrodynamics (MHD) principle.

In the MHD technology, hot combustion gases at temperatures up to 5000° F are seeded with a potassium salt, usually potassium carbonate (K_2CO_3). By thermal ionization at the high temperature of combustion, the potassium salts provide necessary electrons that increase the electrical conductivity of the "plasma", which is nothing but a slightly ionized gas. The plasma is then passed through a magnetic field at a high velocity which generates an electrical potential by Faraday's principle. The partially combusted coal, after passing through the MHD channel, is then combusted to completion as in a conventional coal-fired power plant and additional electricity is produced from the traditional steam-turbine/generator setup.

In a coal-fired open-cycle MHD power plant, the potassium seed that is added to increase the electrical conductivity of the plasma also provides

sufficient potassium to react with the sulfur-and chlorine-containing species in coal. Thus it reduces the SO_2 and HCl/Cl_2 emissions from the gaseous effluent and helps meet the EPA-approved emission limits for acid gases.

For the MHD process to be economically attractive, most of the potassium introduced as seed should be recycled as sulfur-free salt to minimize the fresh addition of potassium carbonate. The potassium in the seed on reacting with the sulfur-and chlorine-containing species in coal is converted to K_2SO_4 and KCl respectively. It is collected along with the flyash particles in the particulate collection devices such as the electrostatic precipitator and the baghouse filter. For recycle and reuse, potassium from such a mixture of spent seed needs to be regenerated to a sulfur-and chlorine-free form. This step of sulfur and chlorine removal is called seed regeneration.

Spent seed regeneration plays an important role in MHD performance and in the commercialization of this technology. From an economic standpoint, efficient recovery and regeneration is vital to the MHD system because the spent seed contains large quantities of soluble potassium. From an environmental point of view, the spent seed cannot be easily disposed of in a conventional unlined landfill. Alkali metal salts are water-soluble and would pose a problem of leaching into the groundwater. Surface run-off from such disposal sites can also alter the soil pH, which may not be acceptable. Hence, the spent seed needs to be recovered and recycled to the system for

both economic and environmental reasons.

EFFECTS OF THE BUILD-UP OF SULFUR-AND CHLORINE-CONTAINING SPECIES IN MHD SYSTEM

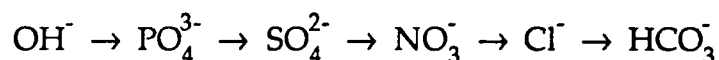
Recycling the spent seed without regeneration in to the MHD combustor would cause several operational and materials related problems. The corrosion rate of anodic surfaces in MHD generator, and rates of chemical attack on boiler tubes, refractory and other materials of construction are found to increase with an increase in sulfur concentration. The build-up of chloride in the MHD system is also a cause for grave concern. It would contribute to the corrosion of superheater tubes and steam generator/air heater surfaces in MHD system. The chlorine atom is electro-negative, which causes loss of electrons in the combustion fluid and therefore, a reduction in the electrical conductivity of the plasma. Chlorine can attack both metals and ceramics. Chlorine-containing species react with the refractory materials and lower their eutectic temperature, thereby reducing their mechanical strength and life, and make them prone to further chemical attack by other corrosive agents. Thus the build-up of sulfur-and chlorine-containing species in an MHD system if not controlled below an acceptable level, can significantly reduce the overall MHD performance and its attractiveness.

To simultaneously dechlorinate and desulfurize the spent seed

without losing a significant quantity of potassium, an ion-exchange resin-based concept has been developed at the University of Tennessee Space Institute (UTSI). This concept is simple, and uses commercially available weak-base anion-exchange resin to simultaneously desulfurize and dechlorinate aqueous solutions of alkali metal sulfates and chlorides. The involved process chemistry is similar to water softening operation and offers an attractive option to carry out dechlorination and desulfurization of the MHD spent seed simultaneously.

ION-EXCHANGE RESIN-BASED SEED REGENERATION CONCEPT

In the ion-exchange resin-based seed regeneration concept, the solution containing potassium sulfate and potassium chloride, is passed through a column packed with weak-base anion-exchange resin. The resin, Amberlite IRA-68, is a gel type, weakly basic anion-exchange resin possessing tertiary amine functionality in a cross-linked acrylic matrix. Weak-base anion-exchange resins have a strong affinity for hydroxide ions and their affinity for other anions decrease in the following order.



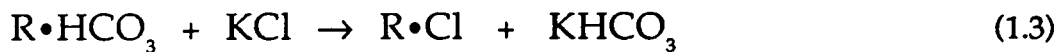
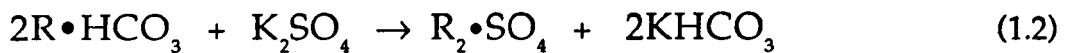
Any anion in the above affinity chart can easily replace the subsequent member(s) lying to the right in an exchange reaction as a general rule.

However, the resin can invert its affinity to any subsequent anion down the chart, if the concentration of that particular anion is increased substantially.

For the seed regeneration process, the sulfate and the chloride ions are to be removed from an aqueous solution containing K_2SO_4 and KCl respectively. To accomplish this, the resin supplied by the manufacturer in the free base form (i.e, in OH form), has to be converted to the bicarbonate form (HCO_3 form) so that it can be exchanged with the sulfate and the chloride ions in the solution. This task of carbonating the resin, i.e. converting it to the active bicarbonate form can be accomplished by contacting the resin with CO_2 gas as described by Equation (1.1).



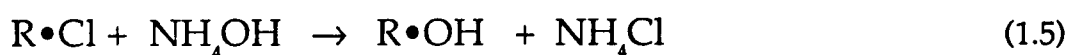
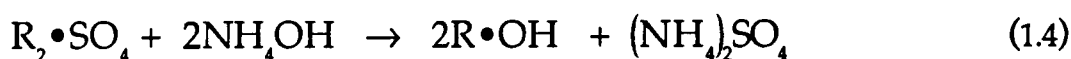
where R represents complex cation groups present in the resin. After the resin is converted to the bicarbonate form, it can be exhausted by contacting the resin with the aqueous solution containing a mixture of sulfate and chloride salts of potassium, as shown in equations (1.2) and (1.3).



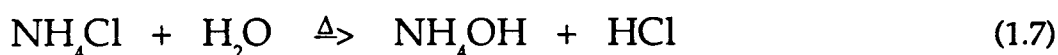
The potassium bicarbonate solution that is obtained as a product stream from the ion-exchange process can then be converted to a mixture of K_2CO_3 and

KHCO₃ during evaporation/concentration step and returned to the MHD combustor in a dry powder form.

To facilitate further use of the resin, it must be regenerated to its active form. Treating the resin with a 4% (by weight) ammonia solution would restore the resin to its R•OH form by the following reactions:



The products of regeneration, ammonium sulfate and ammonium chloride can then be either sold as fertilizer or thermally decomposed in an optional step at 200-250°C to give ammonia (NH₃) for recycle and respective acids (H₂SO₄ and HCl) for sale. The reactions involved are given in equations (1.6) and (1.7).



The resin thus restored to the free base form is then carbonated to convert it to the bicarbonate form before being used in the next cycle.

In previous investigations [1,2,3] , the seed regeneration was limited to removing only sulfates from the spent seed. Butler [1] , carried out proof-of-concept testing to remove sulfates from the spent seed using both bench scale

batch mode and fixed-bed mode experiments. Modeste [2], continued the work of Butler working with IRA-68, the weak-base anion-exchange resin. He modified the three-step process of exhaustion, regeneration and carbonation tested by Butler [1], to a two-step process by combining the exhaustion and carbonation steps.

Strevel [3], used the two-step process developed by Modeste [2], to remove only sulfates from the spent seed. His study included batch mode experiments to select three best weak-base anion-exchange resins suitable for further process variables study. He also evaluated the performance of these three resins, IRA-35, IRA-68, & IRA-93 selected from the batch mode experiments using a fixed-bed setup. The process variables used in the fixed-bed evaluations included, static CO₂ pressure, solution concentration, product inhibition, resin bed height, dissolved impurities, and superficial velocity.

In the present study, bench scale experiments were performed to evaluate the simultaneous removal of sulfate and chloride ions by the candidate anion-exchange resins. The process variables studied in the batch mode experiments include, effect of solution concentration, effect of solution-to-resin volumetric ratio, effect of multi-stage operation and effect of carbonate ion on simultaneous sulfate and chloride removal. Fixed-bed experiments with IRA-68 resin were then performed using both bicarbonate and the hydroxide form of resin under static CO₂ pressure to evaluate the resin's ability to simultaneously remove sulfates and chlorides.

Experiments were also carried out with the bicarbonate form of resin with no static CO₂ pressure. The process variables studied in the fixed-bed experiments include, sulfate-to-chloride equivalent ratio, solution concentration and degree of carbonation of the resin.

The Langmuir isotherm correlating the resin's capacity and the solution concentration will be used in this study for sulfates and chlorides separately. The non-linear equilibrium model developed by Antonson [4] , will be applied in this study to determine the resin phase diffusion coefficients for the fixed-bed runs. The effect of the fixed-bed process variables on the diffusion coefficients of sulfate and chloride ions will be discussed in detail.

CHAPTER II

LITERATURE REVIEW

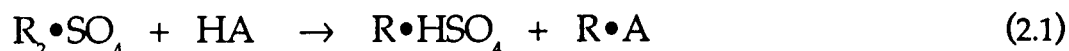
The literature reviewed consists of processes that use ion-exchange techniques to separate single or multiple ions from solutions and the mathematical models that describe the ion-exchange process. A significant amount of work has been reported in the literature on the application of ion-exchange resins in deionization of water, treatment of boiler feed water, treatment of acid mine discharges and desalination of brackish waters.

In the water deionization processes, the total amount of anions to be removed by the anion-exchange resin is about 500 ppm. In this process, first the raw water containing both cations and anions is passed through a strongly acidic cation-exchange column, where the cations are removed. The effluent from this column contains anions such as, sulfates, chlorides, nitrates and carbonates in the form of their respective acids. This effluent is then passed through a weak-base anion-exchange column, where most of the undesirable anions are removed. The effluent from the weak-base anion-exchange column can be further processed through a strong-base anion-exchange resin column to remove silicates if very high quality deionized water is desired.

The Kunin process [DESAL] was developed by the Rohm & Haas

Company, to remove about 3000 ppm of salinity from brackish water. The key aspect of the process was the discovery that Amberlite IRA-68 resin (which is the same resin used in this investigation), when converted by carbon dioxide to the bicarbonate form, has a high selectivity and exchange capacity for the chlorides present in the brackish water.

The SUL-bi SUL process, developed by the NALCO Chemical Company, has been used in the desalination process and in the treatment of acid mine drainage. The process is described in two papers [5,6] where an anion-exchange resin in sulfate form removes the acid from the effluent of the cation exchanger and is hence converted to the bisulfate form. Equation (2.1) describes the sulfate-bisulfate cycle of the process.



where R represents the complex cation groups present in the resin and A represents anions like chlorides and nitrates. The anion-exchanger, however, is not regenerated with the expensive caustic soda normally used, but with raw water containing adequate alkalinity, as shown in equation (2.2).



The substitution of water for expensive caustic soda constitutes the major saving in operating cost accomplished by the SUL-bi SUL process. The process is controlled by the equilibrium reaction between bisulfate and sulfate ions as

described by equation (2.3).



Only a very few researchers [7,8] have investigated the possible use of ion-exchange resins in the regeneration of spent seed material from the MHD-based systems. At the University of Tennessee Space Institute, (UTSI), Sheth [7] and his co-workers have successfully demonstrated the simultaneous removal of sulfates and chlorides from the MHD spent seed using weak-base anion-exchange resins. This ion-exchange resin-based concept, can also be applied to simultaneously desulfurize and dechlorinate the spent sorbents (alkali metal compounds) used in the conventional power plants and waste incinerators.

NaHCO_3 , Na_2CO_3 , and Trona type sorbents when injected after the air heater in the duct work of conventional power plants, can remove SO_2 efficiently with high sorbent utilization. The spent sorbent materials in such a case contain mostly Na_2SO_4 and Na_2SO_3 . UTSI's resin-based scheme can be applied to desulfurize this spent sorbent material for recycle and reuse rather than dispose them in a landfill. Similarly, scrubber liquors in lime/limestone based flue gas desulfurization (FGD) systems, can be processed using the ion-exchange resin-based concept to simultaneously remove sulfates and chlorides.

Other applications of ion-exchange concepts include, removal of

organic acids from water [9,10], removal of nitrates from water [11,12], silica removal from boiler feed water [13], removal of heavy metals from water and waste water [14], condensate polishing [15], desalination of brackish waters [6], potassium recovery from potash [16], pretreatment to prevent scale formation in desalting systems [17], and treatment of acid mine drainage [18].

MATHEMATICAL MODELS

Several mathematical models, with different descriptive capabilities, have been developed. In general, models for fixed-bed systems consist of mathematical equations that describe the mass transfer of adsorbate from the solution or bulk phase to the interior of the resin particle. Usually, the models are derived from material balances and equations of continuity and motion. These models usually require numerical methods to solve the complicated differential equations that are encountered.

Models describing the ion-exchange process differ from each other depending on the assumptions made and the equations chosen to relate the concentration of the adsorbate in the solution, C_0 , to the concentration of the adsorbate in the resin, q . The mathematical model developed by Rosen [19], assumes a linear equilibrium of the form:

$$q_s = KC_0 \quad (2.4)$$

where K is the equilibrium constant for the exchange reaction and q_s is the

concentration of the exchanged ion on the resin surface in equilibrium with C_0 , the concentration of the ion in bulk phase. The assumption that exchange system exhibits a linear equilibrium is valid for exchange systems where the equilibrium is governed by monovalent-monovalent exchanges and when the solution concentration is very low. For the situations where the exchanging ions are transferred by divalent-monovalent exchanges as in the present case, Selke and Bliss [20], have concluded that such systems tend to follow a non-linear equilibrium isotherm.

Butler [1], applied the model developed by Selke and Bliss [20], for a non-equilibrium relationship between the concentration of the exchanging ions in the resin and bulk phase in the exchange zone of the resin bed that is given by:

$$\frac{C}{C_0} = \frac{q}{q_{\infty}} \quad (2.5)$$

Butler assumed that the liquid film diffusion controlled the overall mass transfer rate. A more extensive study based on a Langmuir-type non-linear equilibrium was carried out by Antonson [21], for the sorption rate of ethane in a fixed-bed system employing type 4A molecular sieves. His study concluded that the intraparticle diffusion controlled the overall mass transfer rate rather than external film diffusion for that system.

Thomas [22], has developed analytical results for an ion-exchange

system, assuming a reaction rate-controlled mass transfer mechanism and a linear equilibrium relationship. Heister and Vermeulen [23], extended his model by including a non-linear equilibrium relationship between the adsorbate concentration in the resin and the bulk phase.

Other models found in the literature are listed below:

- Klein et.al., [24], developed a mathematical model for multi-component operation based on the equilibrium theory.
- The model developed by Evangelista et.al., [25], for multicomponent fixed-bed ion-exchange, takes in to account the liquid phase resistance by the film model and the solid phase resistance is accounted for by the effective concentration profile inside the resin bed.
- A mathematical model for estimating the distribution of cations in multicomponent ion-exchange reactions was developed by Sallach. [26]
- A mathematical model of ion-exchange equilibria that establishes a relationship between the selectivity, structure and ionic composition of an ion exchanger was presented by Soldatov. [27]
- A simplified mathematical model of the ion-exchange process that relates the non-dimensional rate factor coefficient to the fractional saturation of the cation-exchanger was developed by Datta. [28]
- A mathematical model of the process of rinsing of ion-exchange resins has been reported by Gromoglasov. [29]
- A model for multicomponent heterovalent ion-exchange systems governed

by the mass action equilibria that discusses inversion of resin affinities was developed by Tondeur. [30]

- A complex model for the simulation of ion-exchange that describes the dependence of ion-exchange and moisture content on the exchange capacity of the resin, ionic composition, solution concentration, temperature, pressure and other factors was developed by Gantman. [31]

Extensive literature is available on the kinetics of ion-exchange in weak-base anion-exchange resins [32,34] and exchange equilibria in anion-exchange resins [33,35,36]. Gopala Rao [32], described in his investigation on the kinetics of ion-exchange in weak-base anion-exchange resins that in very dilute solutions resin phase or pore diffusion controlled the sorption rate of anions. Boari, et. al., [33], in their investigation on the exchange equilibria on anion-exchange resins, showed that the selectivity of the resin for the bivalent ion depended strongly on the basicity of the resin.

The mathematical models found in the literature were either too complex or were specific for certain type of exchange reactions, and involved computer programs that were not easily available. Thus, in the present study, the mathematical model developed by Antonson [21] , and successfully utilized for the ion-exchange process by previous investigators at UTSI [2,3] was selected to describe the bicarbonate-sulfate and bicarbonate-chloride ion-exchange.

CHAPTER III

THEORY

In the fixed-bed ion-exchange process, continuous exchange of ions take place between the liquid phase, usually termed as adsorbate phase and the solid or resin phase, referred to as the adsorbent phase. The liquid phase of known concentration is brought in to contact with the stationary resin phase at a constant flow rate. As the liquid front moves through the bed, the concentration in the resin phase increases until it is in equilibrium with the surrounding fluid. The concentration of the ions in the resin and in the effluent liquid increases with time. The change in the concentration of the effluent plotted as a function of time or volume of liquid passed through the fixed-bed is called the "breakthrough curve". A typical breakthrough curve for a fixed-bed system is shown in Figure 1. The breakthrough curve is affected by various parameters such as the inlet liquid phase concentration, height of the bed, and the exchange kinetics. The "breakthrough point" is described as the point when concentration of the adsorbate in the effluent is about 5 % of the inlet adsorbate concentration. A quantitative description of the ion-exchange resin-based process can be obtained by doing a differential material balance over a slice of the bed. If the resin particles are assumed to be spherical in

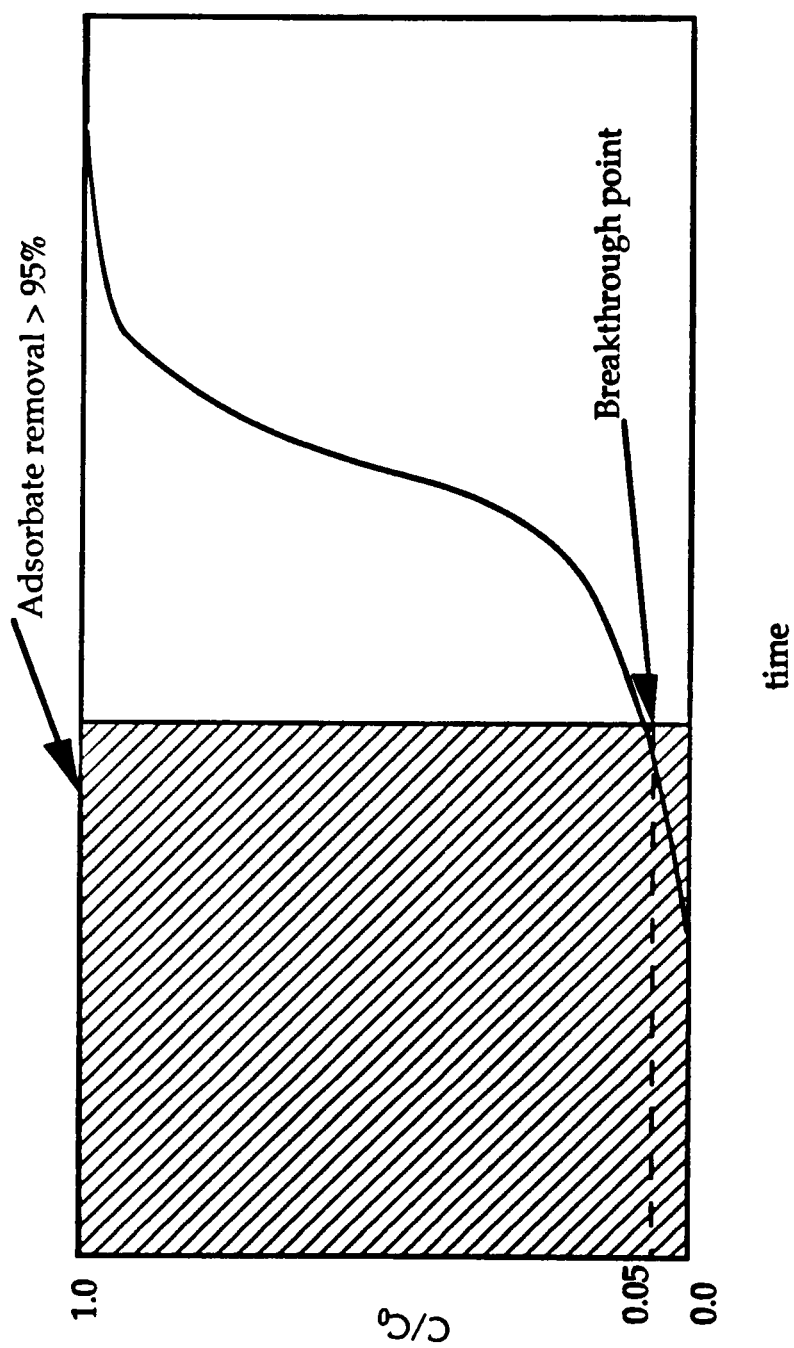


Figure 1: Typical breakthrough curve for a fixed-bed system.

shape, and flow rate is considered constant across the bed (plug flow assumption), a differential material balance around the cross-section of the bed shown in Figure 2 would yield the following equation:

$$\left(\frac{\partial C}{\partial t}\right)_z + v \left(\frac{\partial C}{\partial z}\right)_t + \frac{1}{m} \left(\frac{\partial q}{\partial t}\right)_t = 0 \quad (3.1)$$

where, C is the concentration of the ions in the liquid phase, v is superficial velocity in the bed, t is time, q is concentration of the ions on the resin at time t , m is ratio of the void fraction-to-the particle fraction, and z is axial position in bed. Applying proper equilibrium and mass transfer constraints, a solution to equation (3.1) can be obtained, which can predict the behavior of the fixed-bed system.

EQUILIBRIUM RELATIONSHIPS

The behavior of the fixed-bed ion-exchange system is affected by the nature of the equilibrium that exists between the resin phase concentration of the ion, q_∞ , and the initial ion concentration in the bulk phase, C_0 . For the case of favorable equilibrium, the resin phase concentration, q_∞ is a non-

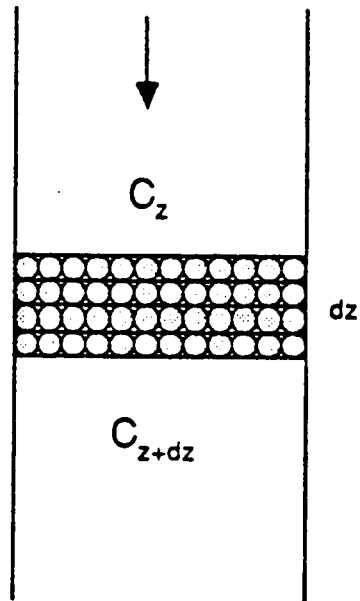


Figure 2 : Mass balance over a cross section of fixed-bed.

linear function of the adsorbate concentration, C_0 . A plot of q_∞ versus C_0 is usually concave upward in shape. Two isotherms, Langmuir and Freundlich type describe a non-linear equilibrium between the resin phase and liquid phase concentration and are expressed respectively as:

$$q_\infty = \frac{a_1 C_0}{1 + a_2 C_0} \quad \text{Langmuir} \quad (3.2)$$

$$q_\infty = AC_0^\alpha \quad \text{Freundlich} \quad (3.3)$$

In this investigation the Langmuir isotherm as given above is used extensively.

MASS TRANSFER MECHANISMS AND MATHEMATICAL MODELS

The study of the behavior of a fixed-bed ion-exchange system should not only include the ionic equilibrium in the system, but also the mechanisms that control the overall rate of mass transfer. Overall process of ion exchange between the adsorbate (the exchangeable ion in the liquid phase) and the exchange site in the adsorbent (resin phase) involve the following three steps:

1. Diffusion through the liquid film surrounding the resin particle

2. Diffusion through the pores inside the resin particle, and
3. Reaction or ion-exchange at the resin active site

It has been postulated [37] in the past that the mass transfer of the adsorbate to the adsorbent can be controlled by one or a combination of the following mechanisms:

1. Liquid film external mass transfer
2. Intraparticle diffusion
3. Reaction or sorption at active site of the adsorbent

Mass transfer in the fluid film within the pores of the adsorbent can be neglected if it is assumed that the amount of sorbate held by the fluid in the pores is small compared to the amount adsorbed by the solid phase. Mathematical models have been developed that have only one mechanism as the rate controlling step. In developing a mathematical model for series type mass transfer steps, the slowest step is the step that controls the rate of overall mass transfer and the other mass transfer steps are assumed to be relatively fast. For example in the Antonson's model [4], the intraparticle diffusion is assumed to be the overall mass transfer controlling step and the other two steps of liquid film external mass transfer and the reaction or sorption are assumed to be relatively fast. The Selke and Bliss' model [20] , assumes that the liquid film diffusion step controls the rate of overall mass transfer assuming the other two steps to be occurring relatively fast.

In general, the search for a mathematical model has two objectives.

1. To simulate, as accurately as possible, the real physical phenomenon/chemistry of the ion-exchange process, and
2. To get empirical or semi-empirical equations for the design of the large scale equipment.

The best model would incorporate all the important phenomena that take place in the overall process, would fit the real physical chemistry well and at the same time would imply a simple mathematical treatment suitable for design of the ion-exchange equipment. It must also reasonably predict the breakthrough curve, i.e. the time at which the breakthrough would occur, and its shape from the given input conditions of the system. The model must also describe the concentration of the solute i.e, the ionic concentration on the resin at equilibrium, and give useful results such as the amount of resin required for scale-up operations.

The Selke and Bliss' model [20], that assumes the liquid film diffusion to be the mass transfer controlling step was used by Butler [1] in his investigation. Using the equilibrium relationship given in equation (3.4) and integrating the material balance equation over the mass transfer zone, the final form of the mathematical model given by equation (3.5) was derived. Equations (3.4) and (3.5) are given in the next page. A more detailed treatment of this derivation can be found in Butler [1].

$$\frac{C}{C_0} = \frac{q}{q_\infty} \quad (3.4)$$

$$\ln \frac{C}{C_0} = \frac{k_L s C_0}{q_\infty V} y - \frac{k_L s x}{V} - 1 \quad (3.5)$$

In equation (3.5) k_L is the liquid film mass transfer coefficient, V is volumetric flow rate of the solution, s is effective surface area of the resin, x is weight of resin traversed in the bed, and y is volume of effluent from the bed. If the experimental data conform to this model, then a semi-logarithmic plot of $\ln(C/C_0)$ versus y , the volume of effluent from the bed, would yield a straight line. From the slope of this line equal to $(k_L s C_0 / q_\infty V)$, and the intercept equal to $\{(k_L s x / V) + 1\}$, the $k_L s$ parameter can be determined. Butler [1] found that at low superficial velocities (~ 0.009 cm/sec) the model predicted the breakthrough curves for a sulfate-bicarbonate exchange system reasonably well. He found that for superficial velocities above 0.02 cm/sec, the film side mass transfer parameter $k_L s$ approached a constant value. He also found that C/C_0 values predicted by the model for the tail end portion of the breakthrough curves i.e., when $C/C_0 > 0.8$, diverged from the actual data. He attributed it to the fact that the intraparticle diffusion probably became more significant during the later portion of the experimental runs.

ANTONSON'S MODEL

Modeste [2], and Strevel [3], in their investigations used the Antonson's model that assumes intraparticle diffusion as the overall mass transfer controlling step. In the present study, the Antonson's model was applied for fixed-bed experiments carried out with precarbonated resin. The assumptions used in the development of this model are the non-linear Langmuir type equilibrium, and intraparticle diffusion control. For intraparticle diffusion, the expression for the concentration of ions in the resin particle is given by:

$$\frac{\partial q_i}{\partial t} = \frac{D}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial q_i}{\partial r} \right) \quad (3.6)$$

where D is the effective diffusivity q_i is the local resin phase concentration, and r is the radial coordinate in spherical particle. The average concentration of the particle is then given by equation (3.7) in the next page.

$$q(z,t) = \frac{3}{R^3} \int_0^R q_i(r,z,t) r^2 dr \quad (3.7)$$

where $q(z,t)$ is the volume averaged value of the concentration in the resin particles at time t , for bed cross section at height z . The surface concentration $q_i(R,z,t)$ is described by the Langmuir type isotherm as:

$$q_i(R,z,t) = \frac{a_1 C_s}{1 + a_2 C_s} \quad (3.8)$$

where C_s is the concentration of anions in the liquid-solid interface. The equilibrium and the mass transfer relationships given by equations (3.6) through (3.8) along with the mass balance expression given by equation (3.1) are the key elements in the development of the Antonson's model.

Equations (3.1), (3.6), (3.7) and (3.8) can be simplified by a change of variables given by:

$$X^* = \frac{z}{m v} \quad \text{and} \quad \theta^* = t - \frac{z}{v}$$

where X^* is the column length parameter and θ^* is the time parameter.

This converts equation (3.1) to :

$$\frac{\partial C}{\partial X^*} + \frac{1}{m} \frac{\partial q}{\partial \theta^*} = 0 \quad (3.9)$$

where m is the ratio of the void fraction-to-particle fraction. The rate expression given in equation (3.6) will result in the following expression after the change of variables.

$$\frac{\partial q_i}{\partial \theta^*} = \frac{D}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial q_i}{\partial r} \right) \quad (3.10)$$

The average concentration in the resin particles is now given by:

$$q(X^*, \theta^*) = \frac{3}{R^3} \int_0^R q_i(r, X^*, \theta^*) r^2 dr \quad (3.11)$$

and the resin phase surface concentration described by equation (3.8) becomes:

$$q_i(R, X^*, \theta^*) = \frac{a_1 C_s}{1 + a_2 C_s} \quad (3.12)$$

Since the above system of equations is non-linear, an exact solution cannot be obtained analytically; however, by applying proper initial and boundary

conditions, the system of equations can be reduced to a partial integro-differential equation that can be solved by numerical methods. The initial and boundary conditions which apply to this system are equation (3.12) and

$$\begin{aligned} q(\theta^* = 0) &= 0 \\ C(X^* = 0) &= C_0 \\ \frac{\partial q_i}{\partial r}(r = 0) &= 0 \end{aligned}$$

The resulting partial integro-differential equation is given by:

$$\frac{\partial C}{\partial X^*} = -\frac{6 D a_1}{m R^2} \sum_{n=1}^{\infty} \int_0^{\theta^*} \frac{\partial \left(\frac{C}{1 + a_2 C} \right)}{\partial \lambda} \exp \left(-\frac{D}{R^2} n^2 \pi^2 (\theta^* - \lambda) \right) d\lambda \quad (3.13)$$

where λ is a dummy variable of integration.

Equation (3.13) can be generalized by making the concentration variable dimensionless. Hence we get:

$$\frac{\partial \phi}{\partial X} = -2 \sum_{n=1}^{\infty} \int_0^{\theta} \frac{\partial \left(\frac{\phi}{1 + a_2 C_0 \phi} \right)}{\partial \lambda} \exp \left(-\frac{1}{2} n^2 \pi^2 (\theta - \lambda) \right) d\lambda \quad (3.14)$$

where,

$$\phi = \frac{C}{C_0}$$

$$\theta = \frac{2D}{R^2} \left(t - \frac{z_T}{v} \right)$$

$$X = \frac{3D a_1 z_T}{m R^2 v}$$

The boundary condition for the equation (3.14) is then:

$$\phi (X = 0) = 1$$

The initial conditions are :

$$\phi (\theta < 0) = 0$$

$$q_i (\theta = 0) = 0$$

a_1 and a_2 are the first and second Langmuir constants from the Langmuir non-linear equilibrium relationship defined by:

$$q_{\infty} = \frac{a_1 C_0}{1 + a_2 C_0}$$

The other variables are:

D = effective intraparticle diffusion coefficient,

R = characteristic length of the resin particle,

X = dimensionless column length parameter,

z_T = bed height,

v = superficial velocity in the resin bed,

m = ratio of void fraction-to-the particle fraction,

C_0 = inlet concentration of the bulk phase,

t = time,

q_{∞} = resin phase equilibrium concentration, and

C_0 = concentration in bulk phase.

By solving this partial integro-differential equation (3.14), a solution is obtained that can predict the breakthrough curve at a given inlet ion concentration as a function of dimensionless time. A finite difference method is used to solve the partial integro-differential equation (3.14), by dividing the equation in to a large number of intervals. This equation is the starting point

for the numerical solution developed by Antonson. The details of Antonson's formulation of the numerical solution are described in detail by Modeste [2] and Strevel [3]. The actual computer code modified by Strevel for the use in UTSI's computer system is given in the Appendix-A, along with an example of a typical input and output.

REACTION KINETICS MODEL FOR EXPERIMENTS CARRIED OUT WITH SIMULTANEOUS EXHAUSTION AND CARBONATION

In this investigation, a mathematical model for predicting the breakthrough curve was developed for an ion-exchange system by assuming that the rate of the ion-exchange step controls the overall mass transfer between the liquid and the resin phase. An attempt was made to apply this reaction-control model to satisfy the experiments where the resin was exhausted and carbonated simultaneously. In developing this model, the following assumptions were made:

1. All exchanges between the ions and the resin are irreversible.
2. By considering the fixed-bed to be a small isothermal differential bed, the radial and axial variations in the resin phase concentration are neglected.
3. The resin phase ion concentration and the liquid phase concentration at any time is assumed to follow a Langmuir-type

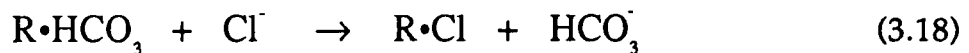
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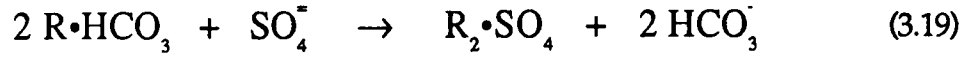
A material balance over a given volume of resin under the conditions of simultaneous exhaustion and carbonation was performed with the above assumptions. The respective sulfate and chloride ion mass balance equations derived are:

$$F C_{os} - F C_s = V_R \left[\frac{dq_s}{dt} + m \frac{dC_s}{dt} \right] \quad (3.15)$$

$$F C_{oc} - F C_c = V_R \left[\frac{dq_c}{dt} + m \frac{dC_c}{dt} \right] \quad (3.16)$$

where, F is flow rate of the liquid phase through the ion-exchange column, V_R is resin volume, t is time variable; C_0 , q , and C are inlet ion concentration, resin phase concentration, and outlet ion concentrations respectively. Subscripts 'S' and 'C' are for sulfate and chloride ion respectively. The following exchange reactions were assumed to be taking place during the process of simultaneous exhaustion and carbonation.





If K_1 , K_2 , and K_3 are the reaction constants for the above reactions in the same order, then from reaction kinetics the following rate equations were derived.

$$\frac{dq_{OH}}{dt} = -K_1 q_{OH} P \quad (3.20)$$

$$\frac{dq_c}{dt} = K_2 q_{HCO_3} C_c \quad (3.21)$$

$$\frac{dq_s}{dt} = K_3 q_{HCO_3}^2 C_s \quad (3.22)$$

$$\frac{dq_{HCO_3}}{dt} = K_1 q_{OH} P - K_2 q_{HCO_3} C_c - K_3 q_{HCO_3}^2 C_s \quad (3.23)$$

where q_{OH} , q_s , q_c , and q_{HCO_3} are the resin phase concentrations of the hydroxide, sulfate, chloride and bicarbonate ions and P is the static CO_2 pressure.

Equation (3.20) on integration gave q_{OH} as a function of time by :

$$q_{OH} = C_T \exp (-K_1 P t) \quad (3.24)$$

where, C_T is the total concentration of exchangeable sites in the resin.

At any time t , the concentration of ion-exchange sites in the resin was assumed to be constant and equal to the sum of the individual ionic concentrations. Hence,

$$C_T = q_{OH} + q_s + q_c + q_{HCO_3} \quad (3.25)$$

Since, the concentration of the bicarbonate sites on the resin was unknown, substitution of equation (3.24) in equation (3.25) gave,

$$q_{HCO_3} = C_T \{1 - \exp(-K_1 Pt)\} - q_s - q_c \quad (3.26)$$

By assuming a Langmuir type equilibrium non-equilibrium relationship existing at all the time between the resin phase ion concentration and the solution phase concentration, the following equations were derived.

$$q_s = \frac{A_{1s} C_s}{1 + A_{2s} C_s} \quad (3.27)$$

$$q_c = \frac{A_{1c} C_c}{1 + A_{2c} C_c} \quad (3.28)$$

From the fixed-bed experimental data, the concentrations of sulfate and chloride ions in the solution phase as a function of time were available. To fit the Langmuir type relationship between the resin phase ion concentration

and the solution phase concentration and to calculate the values of A_1 and A_2 equations (3.15) and (3.16) were solved numerically to find out the values of q_s and q_c at different values of time. In doing so the $m(dc/dt)$ term was neglected. With the values of q_s and q_c known, the constants A_1 and A_2 for sulfate and chloride ions were obtained by employing appropriate regression technique. Equations (3.27) and (3.28) were linearized to give the following form:

$$\frac{C}{q} = \frac{1}{A_1} + \frac{A_2}{A_1} C \quad (3.29)$$

A plot of C/q versus C would be linear with a slope equal to A_2/A_1 and an intercept equal to $1/A_1$. The regression technique can be applied to both the sulfate and chloride ions separately to find out the constants A_1 and A_2 . The values of these constants would be run specific, and would be functions of the specific ion concentration and the sulfate-to-chloride equivalent ratio used in that run. Hence, from the available experimental data, a relationship between the Langmuir constants, the ionic concentration and sulfate-to-chloride equivalent ratio was derived using this linear regression technique.

In order to predict the breakthrough curve of the sulfate and chloride ions, Equation (3.26) was substituted in equations (3.21) and (3.22) to eliminate q_{HCO_3} as shown in the next page:

$$\frac{dq_c}{dt} = K_2 C_c [C_T \{1 - \exp(-K_1 Pt)\} - q_c - q_s] \quad (3.30)$$

$$\frac{dq_s}{dt} = K_3 C_s [C_T \{1 - \exp(-K_1 Pt)\} - q_c - q_s]^2 \quad (3.31)$$

By substituting the expressions for (dq_c/dt) and (dq_s/dt) in equations (3.15) and (3.16) respectively and rearranging, the following expressions were obtained.

$$\frac{d\left(\frac{C_c}{C_{oc}}\right)}{dt} = \frac{F}{m V_R} \left[1 - \frac{C_c}{C_{oc}}\right] - \frac{K_2 C_c}{m C_{oc}} [C_T \{1 - \exp(-K_1 Pt)\} - q_c - q_s] \quad (3.32)$$

$$\frac{d\left(\frac{C_s}{C_{os}}\right)}{dt} = \frac{F}{m V_R} \left[1 - \frac{C_s}{C_{os}}\right] - \frac{K_3 C_s}{m C_{os}} [C_T \{1 - \exp(-K_1 Pt)\} - q_c - q_s]^2 \quad (3.33)$$

The initial and boundary conditions applied to this system are:

$$\text{At } t = 0, \quad C_s = 0; C_c = 0.$$

$$\text{At any time } t, \quad q = A_1 C / (1 + A_2 C)$$

Since the differential equations in equations (3.32) and (3.33) were coupled and non-linear, an exact analytical solution could not be obtained. However, by applying the initial and boundary conditions, and in conjunction with

equations (3.27) and (3.28), they could be solved simultaneously by available numerical methods. The values of the reaction rate constants for sulfate ion and chloride ion (K_2 and K_3) were calculated from the experimental run data at shorter times by assuming irreversible reactions. Here again, the values of the rate constants would be run specific, and would be functions of the specific ion concentration and the sulfate-to-chloride equivalent ratio used in that run. Hence, from the available experimental data a relationship between the reaction rate constants and the ionic concentration and sulfate-to-chloride equivalent ratio was derived using linear regression technique. A computer program was then developed to solve the coupled differential equations (3.32) and (3.33) by the Euler's method. By choosing different values of the carbonation rate constant K_1 , this program was run to obtain the values of (C/C_0) for sulfate and chloride as a function of time. The results of the program are discussed later in this thesis and the actual computer code is given in Appendix A.

CHAPTER IV

BATCH MODE EXPERIMENTAL PROCEDURE

Bench scale batch mode experiments were performed to evaluate the anion-exchange resins' capability to simultaneously remove sulfate and chloride ions and to study the effect of process variables. In these experiments, three candidate resins, IRA-35, IRA-68, and IRA-93 that were previously identified by Strevel [3] were utilized. In these experiments, reagent grade chemicals were used to make solutions of K_2SO_4 , KCl and K_2CO_3 . The concentration of the anions in the feed solution and in the effluent solution were analyzed by ion-chromatograph, available in UTSI's chemistry laboratory.

Before going to the actual experimental procedure, it is essential to define exhaustion and regeneration. "Exhaustion" is the step in which the resin in its active form (bicarbonate form in our case) is brought in to contact with the feed solution containing sulfate and chloride ions. Due to the chemical properties of the resin, it exchanges bicarbonate ions for the sulfate and chloride ions in the solution. Since the number of active sites i.e., the amount of exchangeable bicarbonate ions in the resin is limited, a stage is reached when there are no more active sites available on the resin for ion

exchange. At this point an equilibrium is reached between the concentration of ions in the resin phase and the liquid phase. Now the resin is said to be "exhausted" or "saturated" and has to be regenerated to restore it to the active form. "Regeneration" is the step in which the exchanged ions (sulfate and chloride ions) are removed from the functional groups on the resin by bringing it into contact with a suitable regenerant such as, ammonium hydroxide solution.

In the batch mode experiments, samples of the candidate resins were regenerated by taking a known quantity of resin and 4 weight % ammonia solution in the volumetric ratio of 1 : 2 in a beaker. Using a magnetic stirrer, the resulting slurry was constantly mixed and left sealed overnight to ensure complete regeneration. After about 24 hours, the mixing was stopped and the resin was rinsed free of ammonia with deionized water. The resin on regeneration with ammonia is converted to the OH⁻ form. The resin was then carbonated by contacting it with CO₂ gas to convert it to the active bicarbonate form.

The carbonation apparatus consisted of a CO₂ cylinder with a pressure regulator, a plastic sample jar for holding the resin and a flow meter with associated connecting tubing. Carbonation was carried out at a CO₂ flow rate of about 2 SCFM for 30 minutes. Before starting an exhaustion experiment, a known volume of resin was measured in a graduated cylinder and was tapped frequently to ensure that the resin was fully settled and compact. It was

then slowly transferred to a beaker with deionized water. This water was then removed by using a small tube with a screen at the inlet connected to a vacuum pump. The water-free resin was then mixed with the appropriate solution in a pre-determined solution-to-resin volumetric ratio using a magnetic stirrer. After the desired mixing time, the slurry of resin and the solution was transferred to a filtering apparatus. The filtering apparatus consisted of a funnel with a filter paper, and a side armed Erlenmeyer flask connected to a vacuum pump. The volume of the filtered solution was recorded and a small aliquot was analyzed for the concentration of sulfate and chloride ions. From the laboratory analyses of the feed and the effluent solution samples, the removal efficiencies of the candidate resins were calculated. The batch mode experimental setup is shown in Figure 3.

The parameters affecting the sulfate and chloride removal efficiency tested in the batch mode experiments include:

- Effect of concentration of sulfates and chlorides in the feed solution
- Effect of solution-to-resin ratio
- Effect of multi-stage operation
- Effect of presence of carbonate ions on the sulfate and chloride removal efficiency of the resin
- Effect of temperature

Results from the batch mode experiments and the process variables that affect the anion removal efficiency are discussed in the next chapter.

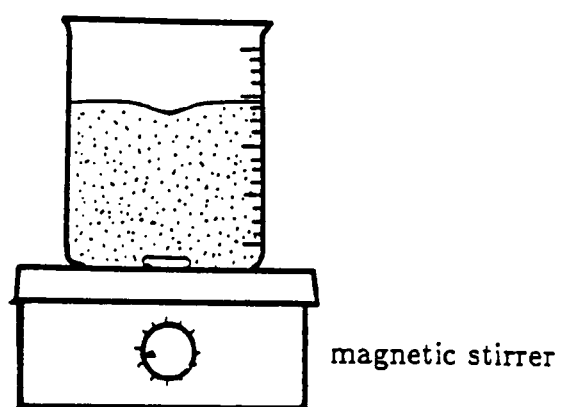


Figure 3 : Batch experimental setup.

CHAPTER V

BATCH MODE EXPERIMENTAL RESULTS AND ANALYSIS

In this chapter, results from the batch mode experiments are analyzed and the performance of the three candidate resins under different process conditions are evaluated.

EFFECT OF SOLUTION CONCENTRATION ON SULFATE AND CHLORIDE ION REMOVAL

To evaluate the potential of simultaneous sulfate and chloride removal at different solution concentration, three runs were conducted at different sulfate and chloride concentrations. The basis for the chloride concentration in the feed solution was the average chloride content expected in the spent seed from firing Illinois # 6 coal in the MHD system, which is about 0.1 weight % (1000 ppm).

In this series of experimental runs, a mixing time of 45 minutes and a solution-to-resin volumetric ratio of 2 were chosen. For the bench scale experiments, Strevel [3], in his master's thesis concluded that a mixing time between 15 to 60 minutes was sufficient, since, there was very little improvement in the ion removal efficiency of the resin beyond 60 minutes.

The experimental procedure as described in the last chapter was used for all the batch mode runs. The results from these experiments are given in Table 1.

From these results the following observations were made:

- At any given sulfate and chloride concentration, the IRA-35 and IRA-68 resins seem to perform better than the IRA-93 resin in terms of the removal efficiency.
- The efficiency of sulfate and chloride removal for each of the candidate resins improves as the solution concentration is reduced.

EFFECT OF SOLUTION-TO-RESIN RATIO ON SULFATE AND CHLORIDE ION REMOVAL

The effect of solution-to-resin volumetric ratio on the sulfate and chloride removal was studied by conducting three runs at different solution-to-resin ratios with a feed solution containing about 1000 ppm of chloride and 9500 ppm of sulfate ions. A solution-to-resin volumetric ratio of 2 means, 2 volumes of solution are mixed with one volume of resin in active form. A constant mixing time of 30 minutes was chosen. The results from these experiments are given in Table 2.

From the results it was observed that:

Table 1 : Effect of Solution Concentration on Sulfate and Chloride Ion Removal

Basis:

- Mixing time = 45 minutes.
- Solution-to-resin volume ratio = 2.

Initial concentration (ppm)		Percentage chloride removed			Percentage sulfate removed		
Chlorides	Sulfates	IRA-35	IRA-68	IRA-93	IRA-35	IRA-68	IRA93
1,200	9,600	59	60	14	76	67	62
2,400	50,000	45	47	30	37	37	30
4,800	50,000	47	49	34	41	32	36

Table 2 : Effect of Solution-to-Resin Ratio on Sulfate and Chloride Ion Removal

Basis:

- Mixing time = 30 minutes.
- Feed sulfate concentration = 9,500 ppm
- Feed chloride concentration = 1,000 ppm

Solution-to-resin volume ratio	Percentage chlorides removed			Percentage sulfates removed		
	IRA -35	IRA-68	IRA-93	IRA-35	IRA-68	IRA-93
0.66	83	86	74	96	96	88
1.00	74	73	54	90	82	63
1.50	68	73	21	87	87	71

- For a given solution-to-resin ratio, the IRA-35 and IRA-68 resins provided a significantly better ion removal efficiency than the IRA-93 resin.
- With the increase in the ratio of the solution-to-resin, the removal efficiency starts decreasing , indicating that the resin's active sites are getting completely occupied.
- At a given ratio, the sulfate removal efficiency for each of the candidate resins is slightly higher than the chloride removal efficiency.
- By employing suitable solution concentration and solution-to-resin volumetric ratio, sulfate and chloride removal efficiencies approaching 100 % are possible.

EFFECT OF MULTI-STAGE OPERATION

In these experiments, the possible advantage of using a multi-stage contact between the resin and the feed solution was evaluated. The feed solution was contacted with the resin in a single stage operation in one run and in three separate stages in another run. In the three stage operation, the feed solution was mixed with fresh batch of resin in the 1st stage and after a mixing time of 15 minutes, the solution was filtered and mixed with another fresh batch of resin in the 2nd stage and so on. In each stage a solution-to-resin volumetric ratio of 2 was maintained. The other parameters that were kept constant were, the feed solution concentration (46,500 ppm sulfate and 2,200

ppm chloride ion) and the mixing time (45 minutes for single stage operation and 15 minutes per stage for multi-stage operation).

The results from these experiments are given in Table 3, and the following observations were drawn from it.

- Sulfate and chloride ion removal efficiencies are significantly higher in a three stage operation than the single stage operation for each of the candidate resins. This indicates that to achieve desired removal efficiency in a fixed-bed mode, a series operation is preferable than one large stage operation.
- IRA-35 and IRA-68 resins demonstrated a slightly better performance than the IRA-93 resin.

EFFECT OF PRESENCE OF CARBONATE IONS ON SULFATE AND CHLORIDE ION REMOVAL

In this series of experiments, the possible effect of the presence of carbonate ions on the sulfate and chloride ion removal was studied. The solution concentration in these runs were chosen in such a manner as to closely simulate the concentrations that would be expected in the wet cake obtained from the UTSI's wet electrostatic precipitator (WESP) and rotary drum vacuum filter setup for a high K_2/S ratio operation. The weight ratio of $KCl : K_2CO_3 : K_2SO_4$ in the wet cake from such a setup was estimated as approximately equal to 3 : 19 : 78. The other process parameters maintained

Table 3 : Effect of Multi-stage Operation on Sulfate and Chloride Ion removal

Basis:

- Mixing time = 45 minutes
- Feed sulfate concentration = 46,500 ppm
- Feed chloride concentration = 2,200 ppm
- Solution-to-resin volume ratio = 2

Mode of operation	Percentage chloride removed.				Percentage sulfate removed.			
	IRA-35	IRA-68	IRA-93	IRA-93	IRA-35	IRA-68	IRA-93	IRA-93
Single stage	42	52	27		45	45	39	
Three stages	84	86	81		82	84	74	

constant were, mixing time of 30 minutes and solution-to-resin volumetric ratio of 2. The results from these bench scale experiments are given in Table 4.

From these results the following observations were drawn:

- Presence of small levels of carbonate does not affect the removal of sulfate and chloride ions significantly. A comparison was made between two experiments, one with carbonate ion, and the other without. From Table 4 we can see that the anion removal efficiencies of the resins dropped only by about 5-10 %. Although, only up to 55-60 % removal of chloride and sulfate ions were achieved by IRA-68 under the conditions employed in the experimental runs, by suitable optimization (i.e. reducing solution-to-resin ratio, as well as carrying out a multi-stage operation), removal efficiencies exceeding 90 % can be easily achieved.
- In the presence of very high carbonate ion concentration, some (20 to 30 %) of chloride can still be removed.
- At any given solution concentration, IRA-35 and IRA-68 resins performed slightly better than the IRA-93 resin.

Table 4 : Effect of Presence of Carbonate Ions on Sulfate and Chloride Ion Removal

Basis:

- Mixing time = 30 minutes.
- Solution-to-resin volume ratio = 2.

Initial concentration (ppm)		Percentage chloride removed.				Percentage sulfate removed.			
Carbonate	Chloride	Sulfate	IRA-35	IRA-68	IRA-93	IRA-35	IRA-68	IRA-93	IRA-93
4,000	700	21,700	45	56	26	49	58	37	37
8,300	1,400	44,600	39	47	32	29	33	24	24
0	2,400	50,000	45	47	30	37	37	30	30
151,400	700	—	30	24	—	—	—	—	—

EFFECT OF TEMPERATURE ON THE SULFATE AND CHLORIDE REMOVAL EFFICIENCIES

To study the effect of temperature on the sulfate ion removal efficiency, experiments were performed with IRA-35 and IRA-68 resins at four different temperatures. The temperatures chosen were below 70°C, the maximum allowable temperature to which the resin can be exposed. Batch mode experiments were performed at two different concentration levels of sulfate with a constant mixing time of 30 minutes and a solution-to-resin volumetric ratio of 2. The results from these experiments are tabulated in Table 5.

From the results the following observations were made:

- As the temperature increases, the percentage removal of sulfates drops drastically for both the resins.
- The IRA-68 resin performed better than the IRA-35 resin in removal efficiency at all temperatures.

The first result is particularly interesting, since normally one would expect the performance of the resin to go up with a rise in temperature due to relatively faster diffusion of the ions into the molecular network of the exchanger at a higher temperature. One possible reason that could explain the observed drop in the performance of the resin at elevated temperatures, is that some of the bicarbonate sites on the resin may be converted back to the

Table 5 : Effect of Temperature on Sulfate Ion Removal

Basis:

- Mixing time = 30 minutes.
- Solution-to-resin volumetric ratio = 2

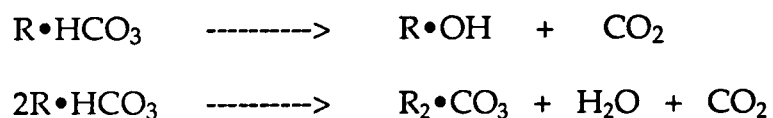
* Feed sulfate concentration = 56,700 ppm.

Temperature (°C)	Percentage sulfate removed.	
	IRA-35	IRA-68
28	34	34
45	19	31
55	20	27
65	16	20

* Feed sulfate concentration = 27,200 ppm.

Temperature (°C)	Percentage sulfate removed.	
	IRA-35	IRA-68
28	33	56
45	31	45
55	30	46
65	24	37

OH⁻ or (CO₃)²⁻ sites. It is possible that a higher temperature would enhance the following reactions:



Since OH⁻ ions are strongly attached to the resin's active sites and the (CO₃)²⁻ are located to the left of the (SO₄)²⁻ ions in the affinity chart (reported by Dharmapurikar [39]), the sulfate removal efficiency of the resin would decrease significantly as the temperature is increased.

CHAPTER VI

FIXED-BED EXPERIMENTAL SET UP & PROCEDURE

The fixed-bed mode of experiments were carried out in the setup whose schematic is shown in Figure 4.

This experimental apparatus consists of :

- a) 2 - glass columns (one column of I.D. = 1" and the other column of I.D. = 2" ; and height of both = 2 ft)
- b) 3 - stainless steel tanks for feed solution, deionized water and ammonia solution. (capacity of each tank $\approx$ 6 liters)
- c) CO₂ cylinder for pressure runs and carbonation
- d) N₂ cylinder for maintaining positive pressure in the feed tank during exhaustion run.
- e) Solenoid valves at column outlet, and CO₂ cylinder outlet.

The fixed-bed system also included manually operated valves and associated tubing, rotameter, pressure regulators on gas cylinders, a pressure gauge on the column and an auto sampler. In this investigation only the 1" I.D. column was used. The system was supposed to operate in a semi-automatic fashion, but due to unstable system flow rates, constant monitoring and manual regulation were necessary to keep the flow rate nearly constant. Other problems such as air entrainment and rotameter fouling by resin

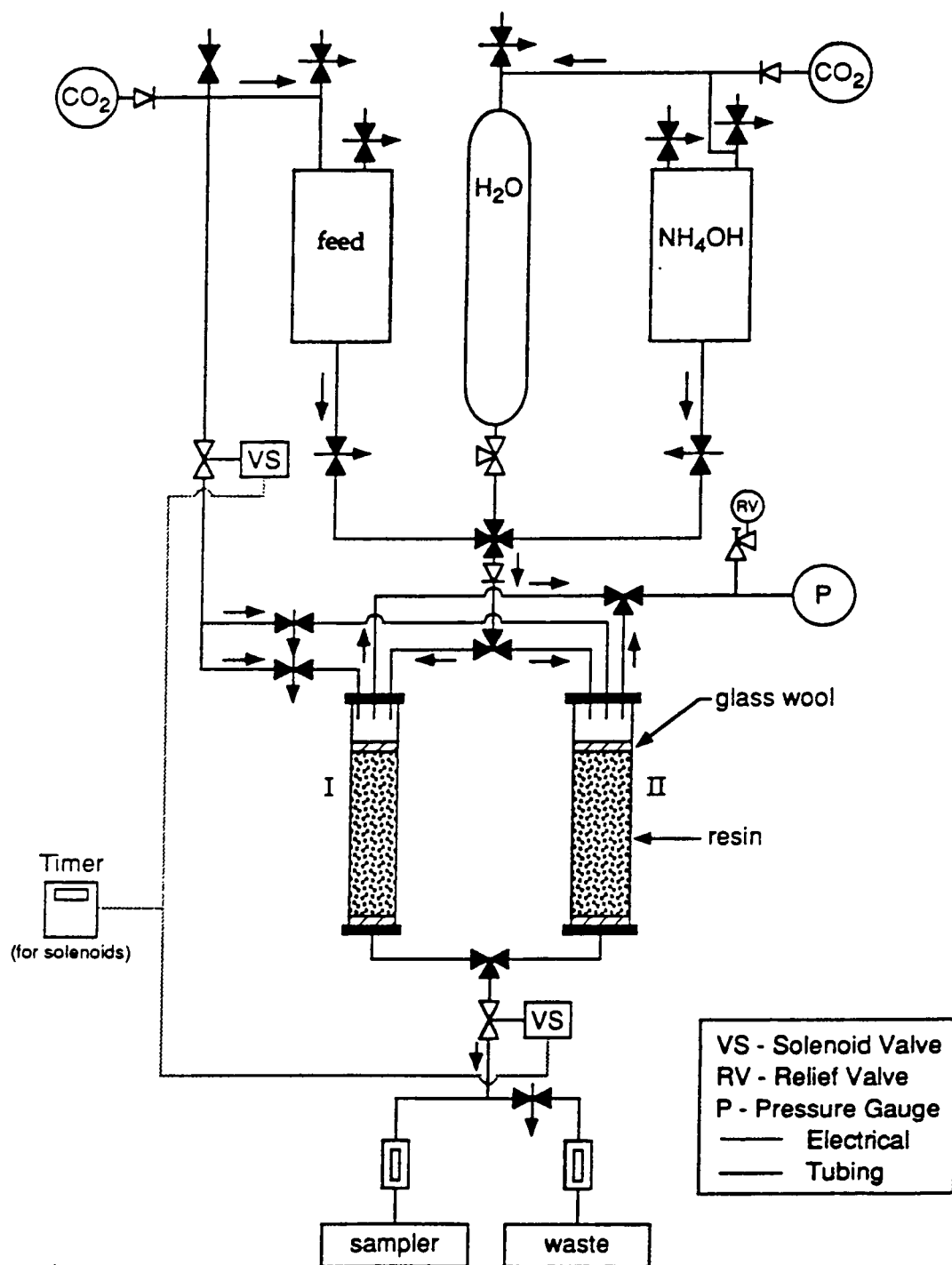


Figure 4 : Fixed-bed experimental setup.

particles were encountered, but they were rectified with proper care.

EXPERIMENTAL PROCEDURE

Results from the batch mode experiments indicated that the IRA-68 resin outperformed the other two resins, IRA-35 and IRA-93 in terms of ion removal efficiency. As a result, in the fixed-bed experiments, the performance of only the IRA-68 resin to simultaneously remove sulfate and chloride was studied. Initially, the resin was regenerated by taking a known quantity of resin and 4 weight % ammonia solution (volumetric ratio 1:2) in a beaker. Using a magnetic stirrer, the slurry was constantly mixed and left overnight to ensure complete regeneration. After about 24 hours, the mixing was stopped and the resin was rinsed free of ammonia with deionized water.

The feed solution tank was first filled with hot water and flushed using nitrogen pressure to clean the tank. The feed tank was then filled again with deionized water, and flushed empty. The tank was depressurized and then the feed solution was filled in manually.

Before starting an experimental run, the column was dismounted and the top flange was removed. The exhausted resin in the column from the previous run was displaced by running deionized water through the column. The column was then rinsed twice with the deionized water to remove all the resin and any traces of solution from the previous run. A fresh plug of

glass wool was placed on the mesh at the bottom of the column to ensure that the resin did not carry over to the outlet. About 150 ml. of resin by volume (OH or HCO_3 form) was measured in graduated cylinder. The measuring cylinder was tapped frequently to ensure that the resin was fully settled to occupy 150 ml by volume. The fresh settled resin was transferred to the column with deionized water and a glass wool plug was placed on the top of the resin. The column top flange was then replaced and the column was remounted. The column tubings were then connected to the feed solution tank, CO_2 cylinder and the outlet valve.

Before the start of the run, the resin in the column was ensured to be in wet condition by keeping the water level up to the top of the resin. Deionized water was then introduced in to the column (approximately 4 bed volumes) to flush the outlet tubing of any remaining feed solution from the previous run. The water level was then brought down up to about one inch above the top of the resin. The feed solution was then introduced in to the column by creating a positive pressure differential between the column and the feed tank using N_2 pressure. During the exhaustion step, flow rate was measured and adjusted as required, both manually and by the rotameter. Samples were collected at appropriate time intervals and analyzed in the laboratory for sulfate and chloride concentration.

Three different experimental procedures were used to study the procedural effects on the performance of the resin. These procedures were:

1. Fixed-bed exhaustion runs with precarbonated resin under atmospheric pressure,
2. Fixed-bed exhaustion runs with precarbonated resin under 50 psig CO₂ pressure, and
3. Simultaneous exhaustion and carbonation runs with OH form of resin under 50 psig CO₂ pressure with precarbonation at 50 psig for 20 minutes.

PROCEDURE # 1 (RUNS WITH PRECARBONATED RESIN UNDER
ATMOSPHERIC AIR PRESSURE)

In these experiments, the carbonation of the regenerated resin was carried out separately by taking a known volume of resin in a beaker and bubbling CO₂ gas through it at a flow rate of 2 SCFM for 30 minutes. The carbonated resin was then loaded in to the column as described earlier and the experiment was carried out at atmospheric air pressure.

PROCEDURE: # 2 (RUNS UNDER ELEVATED PRESSURE WITH PRECARBONATED RESIN)

In these experiments, the resin before being loaded into the column, was carbonated separately to ensure it was in the active HCO_3^- form. This was done by taking 150 ml of regenerated settled resin in a beaker and then bubbling CO_2 through the slurry of deionized water and resin for about 2 hours. In order to increase the interfacial area of contact between the CO_2 gas phase and the resin phase, a porous ceramic frit was used at the end of the tubing from the CO_2 cylinder. The carbonated resin was then loaded into the column as described earlier. The column was then pressurized to 50 psig using CO_2 gas. After about 15 minutes, the outlet tube at the bottom of the column was removed from its connection to let the CO_2 gas come in contact with the bottom portion of the resin. After about a minute, the outlet tube was connected back and the column was again pressurized to 50 psig. This pressure was maintained for about 45 minutes and then the exhaustion cycle was started as described earlier.

PROCEDURE # 3 (RUNS WITH SIMULTANEOUS EXHAUSTION AND CARBONATION)

The regenerated resin in OH form was used in these experiments and the exhaustion cycle was carried out under CO₂ pressure. Initially the resin was loaded into the column and filled with water up to the top of the resin. The column was then placed under 50 psig CO₂ pressure for approximately 25 minutes, to enable the formation of bicarbonate ions on the active sites of the resin. After this pre-run carbonation time, the exhaustion cycle was started and the experiment was carried out under 50 psig CO₂ pressure. This procedure was utilized in the initial part of this investigation and was also used by Modeste [2], and Strevel [3] in their investigations.

EXPERIMENTAL PLAN

A wide variety of fixed-bed experiments were performed with potassium sulfate solution, potassium chloride solution and a mixture of both under CO₂ pressure and at atmospheric pressure. As described earlier three different procedures were used in the experimental runs. A “base case” run was selected so that the effect of the variables like the sulfate-to-chloride equivalents ratio, ionic concentration and degree of resin carbonation on the process performance could be studied. Experiments were performed at three

different overall ionic concentrations and five different sulfate-to-chloride equivalents ratios were used. The unit of "equivalents" was used to measure the concentration because of the fact that this investigation dealt with two different anions, one being bivalent and the other being monovalent. CO₂ pressure was maintained constant at 50 psig for the runs that were conducted at high pressures (procedure # 2 and 3).

Experiments with solutions of high ionic concentration of sulfate combined with varying amounts of chloride ions were conducted to study the process performance under simulated MHD spent seed conditions. An experimental run was also conducted with base case conditions at elevated temperature. The experimental matrix used in planning the fixed-bed experiments is shown in Table 6.

In order to verify the reproducibility of the fixed-bed experiments, an experiment was conducted at the same conditions as used by Strevel [3]. The breakthrough curve obtained from this run is compared with that obtained by Strevel in Figure 5. The conditions used in this run were: feed solution concentration: $C_0 = 25,000$ ppm sulfates, CO₂ pressure : 10 psig, and flow rate = 11 ml/min. From the figure one can see that the fixed-bed system and procedure adopted in the present study provided the necessary stability to ensure run reproducibility.

Table 6 : Experimental Matrix

CO ₂ PRESSURE = 50 psig				
TOTAL IONIC CONCENTRATION (meq /liter)				
SO ₄ -to-Cl ratio†	208	416	624	1140
0	✓	✓	✓	X
0.67	✓	✓	✓	X
1.0	X	✓	X	X
1.5	✓	✓*	✓	X
24	X	✓	X	✓
30	X	X	X	✓
∞	✓	✓	✓	X

Legend: ✓ = Experiment done.
X = Experiment not done.
* = Base case.
† = equivalents ratio.

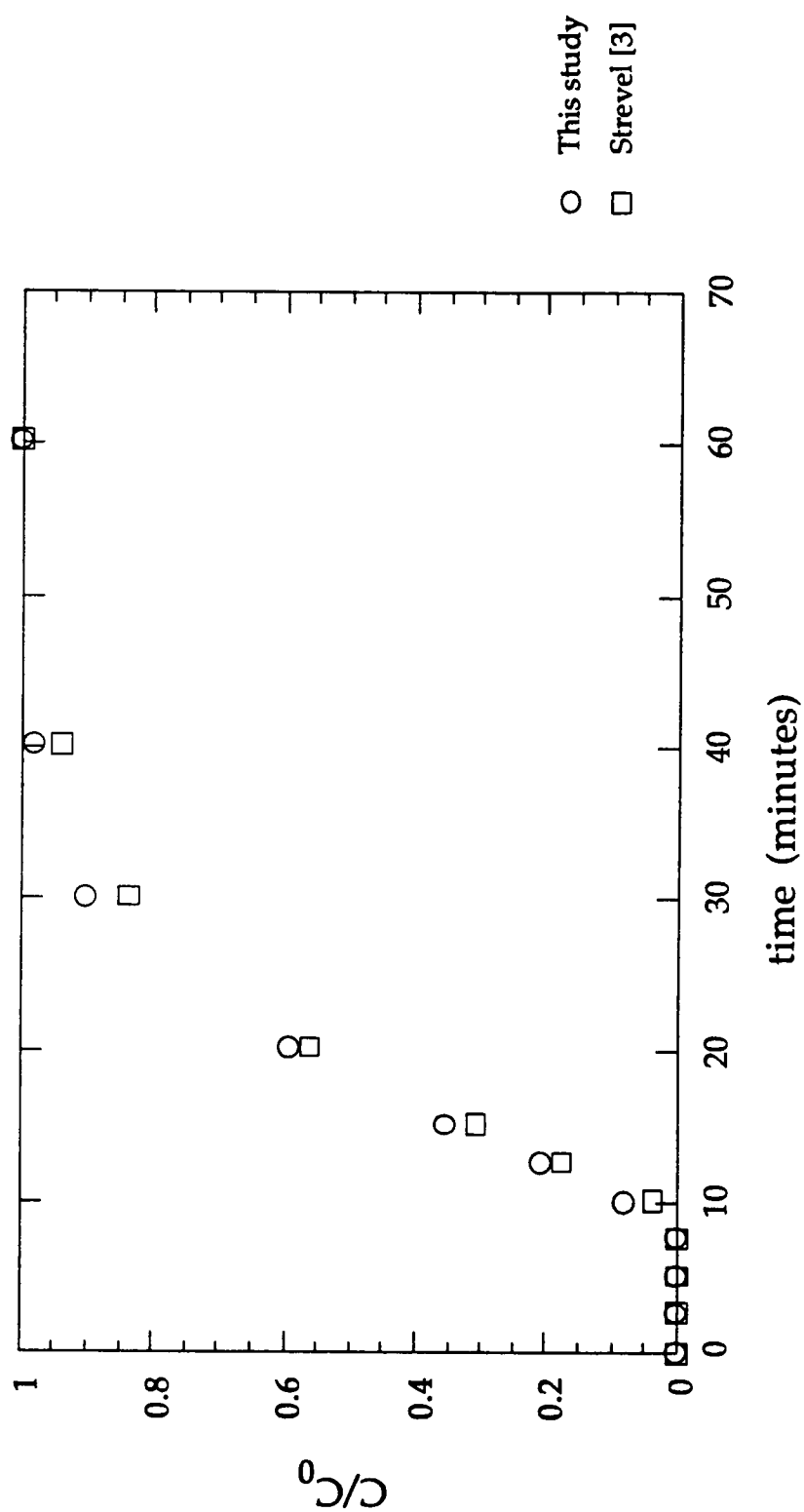


Figure 5: Reproducibility check for fixed-bed setup. Conditions: Feed sulfate = 25,000 ppm; CO₂ pressure = 10 psig; Flow rate = 11 ml/min; Volume of resin = 100 ml.

CHAPTER VII

FIXED-BED EXPERIMENTAL RESULTS AND DATA ANALYSIS

In this chapter, the fixed-bed experimental results along with the data analysis are presented. The fixed-bed runs were performed at various solution concentrations, flow rates, ionic equivalent ratios and carbonation procedures. The summary of the experiments along with the process conditions used are given in Appendix B.

DETERMINATION OF RESIN CAPACITY

Laboratory analysis of the samples from the experimental run gave information on the amount of anion in the fixed-bed effluent as a function of time. By performing a material balance for the fixed-bed system, we get the following equation:

$$F C_0 - F C = V_R \frac{dq}{dt} \quad (7.1)$$

where C_0 is inlet ionic concentration; C is ionic concentration in the effluent; q is the concentration of ions in the resin at any time t ; F is solution flow rate and V_R is volume of resin. Equation (7.1) can be solved by applying the

separation of variables technique as follows:

$$F C_0 \left(1 - \frac{C}{C_0}\right) = V_R \frac{dq}{dt} \quad (7.2)$$

Separating and integrating under appropriate limits of integration would then yield:

$$F C_0 \int_0^{t_\infty} \left(1 - \frac{C}{C_0}\right) dt = V_R \int_0^{q_\infty} dq \quad (7.3)$$

where t_∞ is the time at which $C/C_0 \approx 1.0$ and q_∞ is the equilibrium capacity of the resin. The area A , under the plot of $(1 - C/C_0)$ versus t would yield the value of the specific integral in the left hand side of equation (7.3). The equilibrium capacity is then given as:

$$q_\infty = \frac{A F C_0}{V_R} \quad (7.4)$$

The area (A) under the plot of $(1 - C/C_0)$ versus t , was determined by using a computer program developed by Modeste [2] that uses the trapezoidal method of numerical integration. For the cases when two anions are involved, area

under the breakthrough curves of both the anions were calculated separately by using the above mentioned technique for each anion. The sample program and examples of typical input and output are given in Appendix-A. The equilibrium capacity of the resin is sometimes called the total exchange capacity of the resin. Another means of expressing the capacity of the resin is the operating exchange capacity. In ion exchange applications, only a certain fraction of the influent ions is tolerated in the product. This limit was assumed to be about 5 % for the MHD seed regeneration option. In other words, if C/C_0 reaches a value of 0.05 the exhaustion step would be stopped and the resin would be regenerated. The operating exchange capacity of the resin would then be the amount of anions that are retained in the resin at this limit. Thus the calculation of the operating exchange capacity is very important since it gives an idea of the amount of anions the resin can take before it is ready for regeneration. The equilibrium capacities and the operating capacities of the resin for various experimental runs are given in Appendix B.

COMPARISON OF RESIN CAPACITIES FOR SULFATE AND CHLORIDE IONS

To study the effect of anions on the resin capacity, fixed-bed experiments were conducted at different concentrations of sulfate-only and chloride-only solutions with precarbonated resin under 50 psig CO₂ pressure. Table 7, gives the values of the equilibrium capacity and operating capacity for the sulfate and chloride ions. All the units involved are in milliequivalent instead of grams of anions, since the chloride is a monovalent ion and the sulfate ion is bivalent. From the results, it is clear that within the experimental scatter, the resin capacity remains constant irrespective of the anion. However, the operating exchange capacity of the sulfate ion seems to be slightly higher than that of the chloride ion at a concentration of 210 meq/l. This result at low ionic concentration seems to be different from the other results and could be attributed to experimental scatter, and needs to be verified in future study.

Table 7 : Comparison of Resin Capacities for Sulfate and Chloride Ions
(for runs carried out with sulfate-only and chloride-only solutions)

Solution concentration (meq/l)	Equilibrium capacity (meq/l)		Operating capacity (meq/l)	
	Sulfate	Chloride	Sulfate	Chloride
210	2.33	1.95	1.86	1.49
375	1.82	1.85	1.25	1.18
575	2.20	2.17	1.34	1.41

APPLICATION OF LANGMUIR EQUILIBRIUM RELATIONSHIP TO FIXED BED DATA

The Langmuir equilibrium relationship is derived from the rate equation for a reversible adsorption or ion-exchange process assuming that all the sites on the resin have the same activity for ion-exchange. It can be carried out by separately writing the rate of adsorption (forward exchange) and desorption (reverse exchange) of the adsorbate (anions in our case) on the resin.

$$\text{Rate of adsorption} = K_a C_0 (C_T - q)$$

$$\text{Rate of desorption} = K_d q$$

where, q is concentration of adsorbate on the resin, C_0 is initial concentration of the adsorbate, C_T is total available ion-exchange sites, and K_a , K_d are the forward and reverse exchange reaction constants respectively. The net kinetic rate of reversible adsorption or ion-exchange can then be written as:

$$\frac{dq}{dt} = K_a C_0 (C_T - q) - K_d q \quad (7.5)$$

When the ion exchange system is at equilibrium, equation (7.5) is equal to zero and the value of q is at its maximum equal to q_∞ . After performing the mathematical simplification we get the following equation:

$$q_{\infty} = \frac{K_d C_T C_0}{K_d + K_d C_0} \quad (7.6)$$

By dividing the numerator and denominator of equation (7.6) by K_d and setting,

$$a_1 = \frac{K_d}{K_d} C_T ; a_2 = \frac{K_d}{K_d} \quad (7.7)$$

we get the familiar form of Langmuir isotherm as:

$$q_{\infty} = \frac{a_1 C_0}{1 + a_2 C_0} \quad (7.8)$$

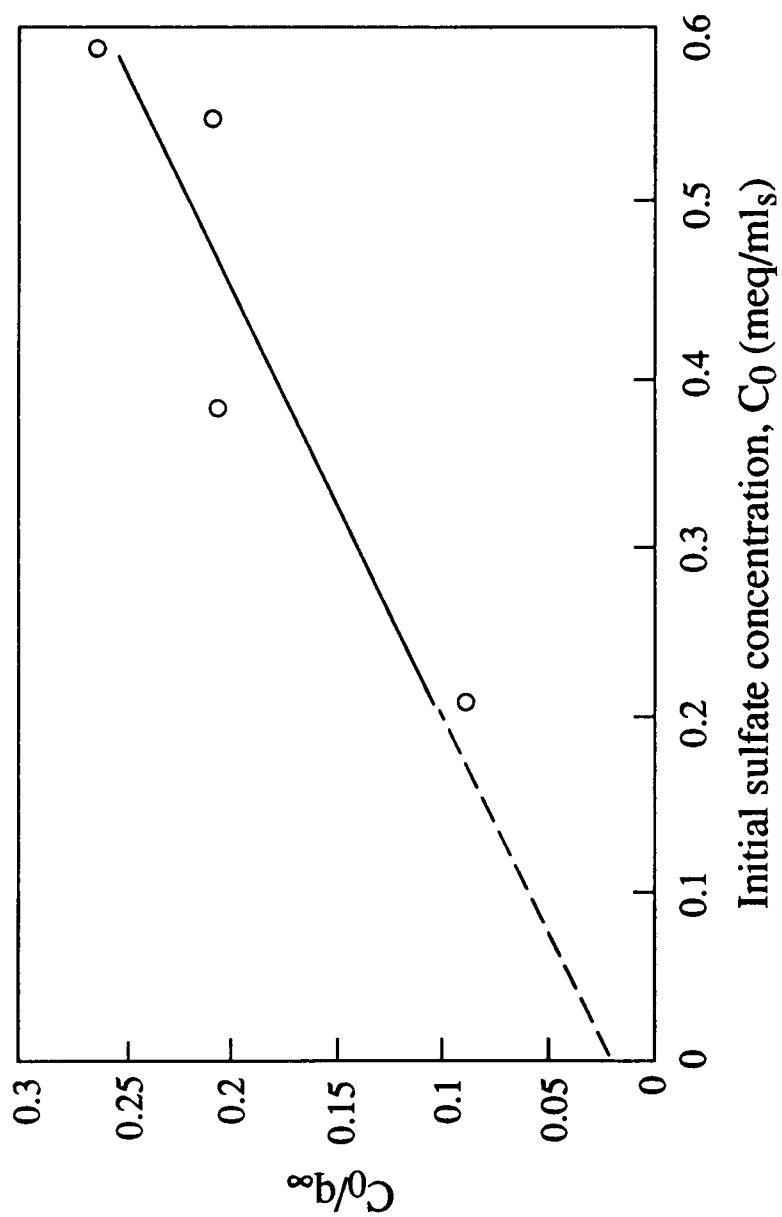
where a_1 and a_2 are the Langmuir constants. With q_{∞} and C_0 known from the experimental data, the Langmuir constants can be calculated by regression technique. To accomplish this task, equation (7.8) is linearized to obtain the following expression:

$$\frac{C_0}{q_{\infty}} = \frac{1}{a_1} + \frac{a_2}{a_1} C_0 \quad (7.9)$$

A plot of C_0/q_{∞} versus C_0 should be linear, with a slope equal to a_2/a_1 and an

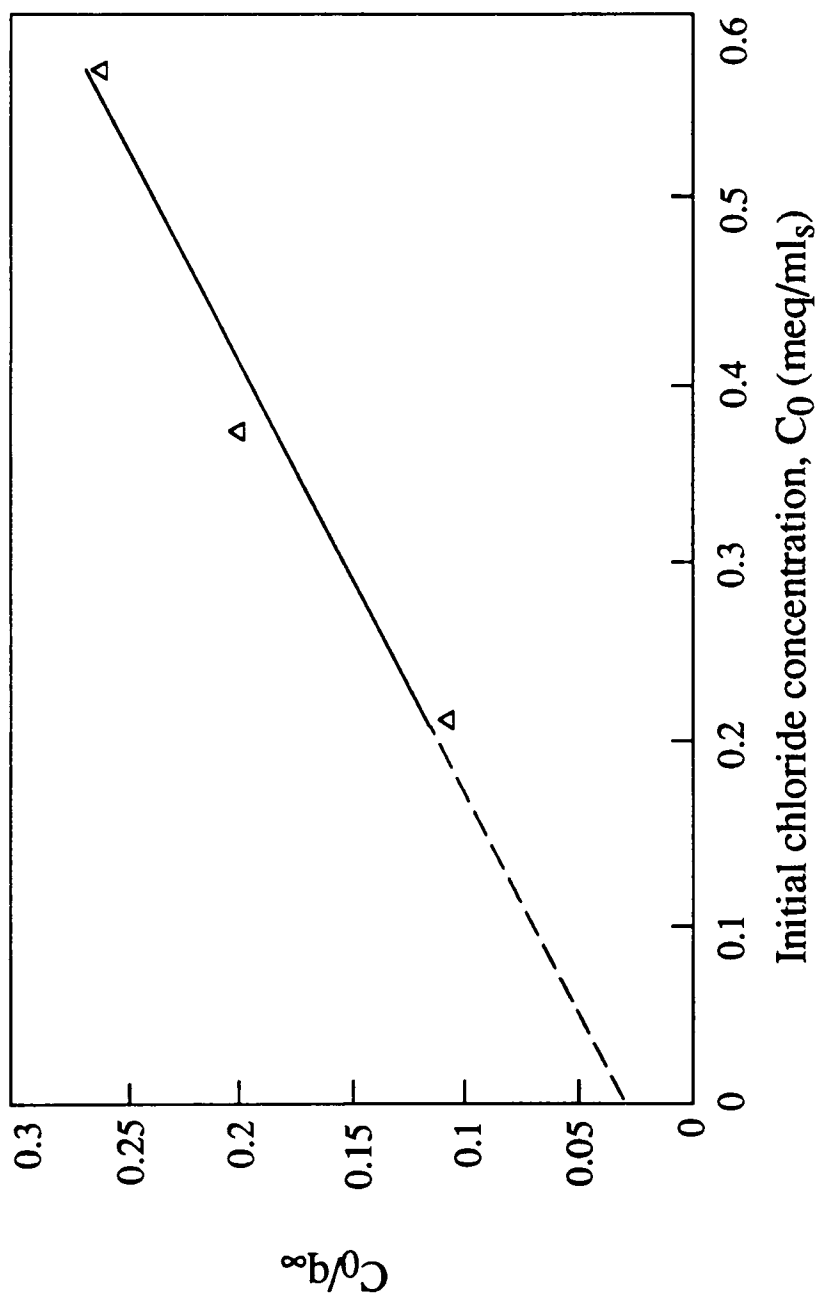
intercept of $1/a_1$. From the values of the intercept and the slope, the Langmuir constants and C_T , the total available ion-exchange sites can be calculated. The linearized Langmuir isotherm (equation 7.9) for experiments carried out with 2 hour precarbonation (procedure # 2) is plotted for sulfate-only runs, chloride-only runs, and a mixture of sulfate and chloride runs in Figure 6 - 9. In Table 8, the values of Langmuir constants and C_T obtained for various types of runs performed under procedure # 2 are given. For experiments involving simultaneous sulfate and chloride ion removal, the linearized Langmuir isotherm is plotted separately for the individual ions. All the concentration related values are expressed in milliequivalent.

From Table 8, we one see that the C_T values for sulfate-only and chloride-only runs are approximately equal. This suggests that the resin's exchange capacity remains same irrespective of the anion. In Figure 10 the breakthrough curves for two separate runs, one with sulfate-only solution and the other with chloride-only solution are plotted. Same experimental conditions were maintained for both the runs. As one can see from the figure, the breakthrough curves for both the sulfate and chloride ions are very similar implying that the resin's performance is probably not affected by the type of anion.



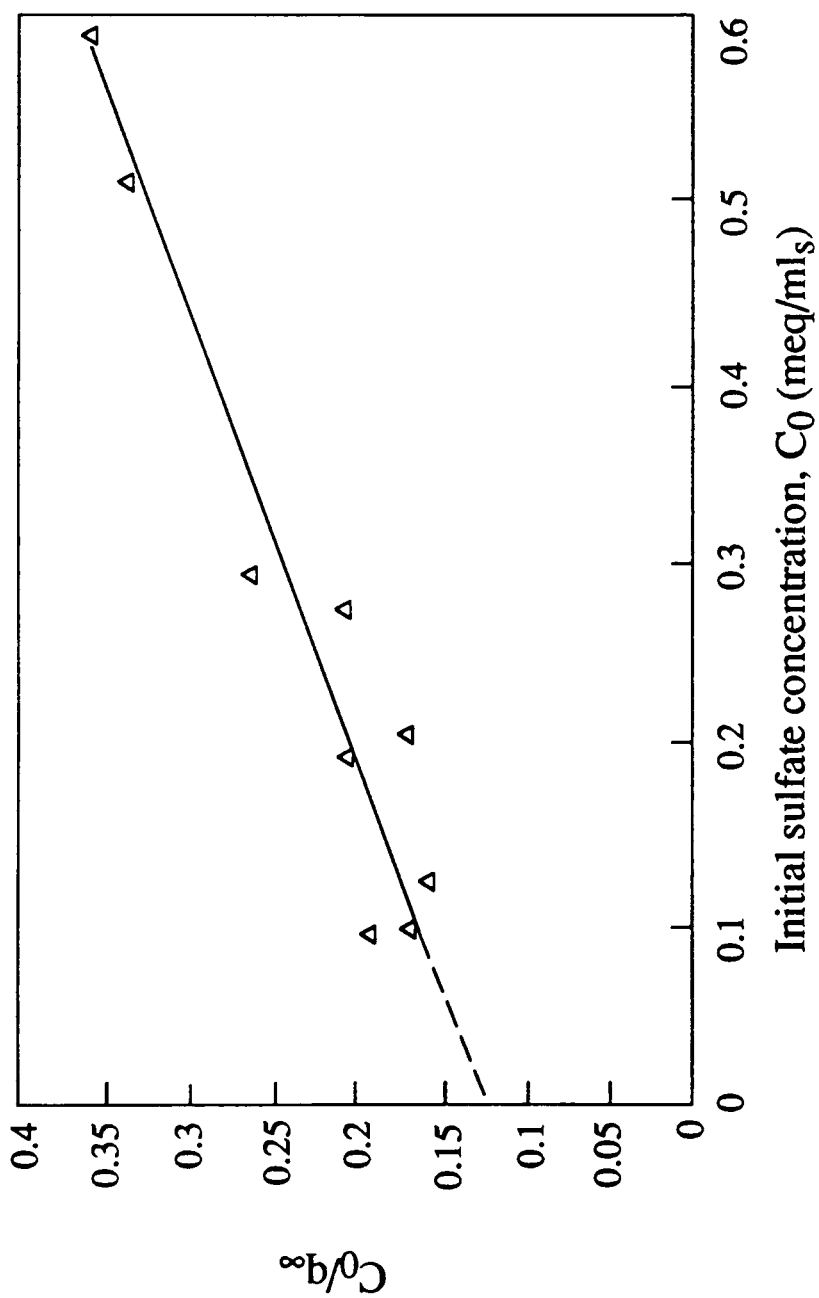
CG-3153

Figure 6: Plot of linearized Langmuir isotherm for sulfate-only experiments carried out with precarbonated resin.



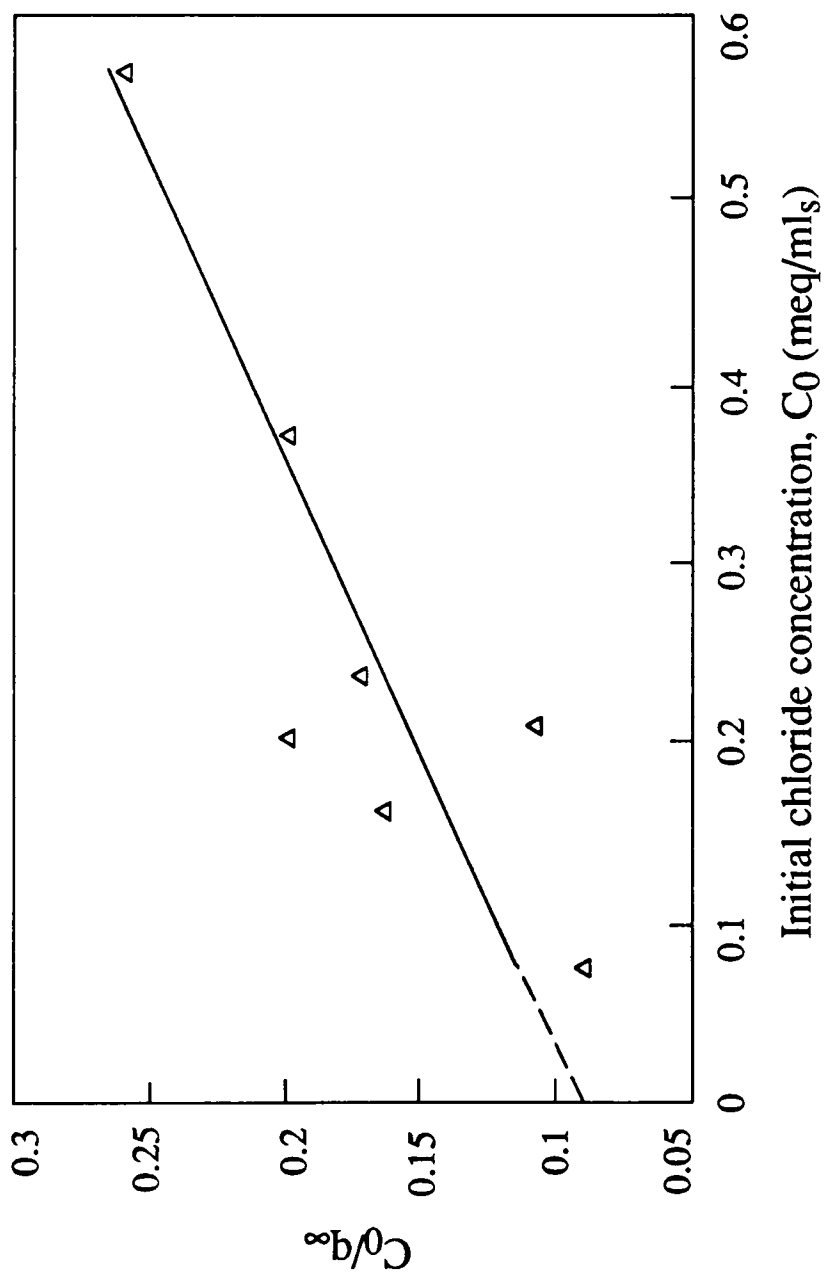
CG-3154

Figure 7: Plot of linearized Langmuir isotherm for chloride-only experiments carried out with precarbonated resin.



CG-3155

Figure 8: Plot of linearized Langmuir isotherm for sulfate part experiments carried out with precarbonated resin and a mixture of sulfate and chloride ions.



CG-3156

Figure 9: Plot of linearized Langmuir isotherm for chloride experiments carried out with precarbonated resin a mixture of sulfate and chloride ion.

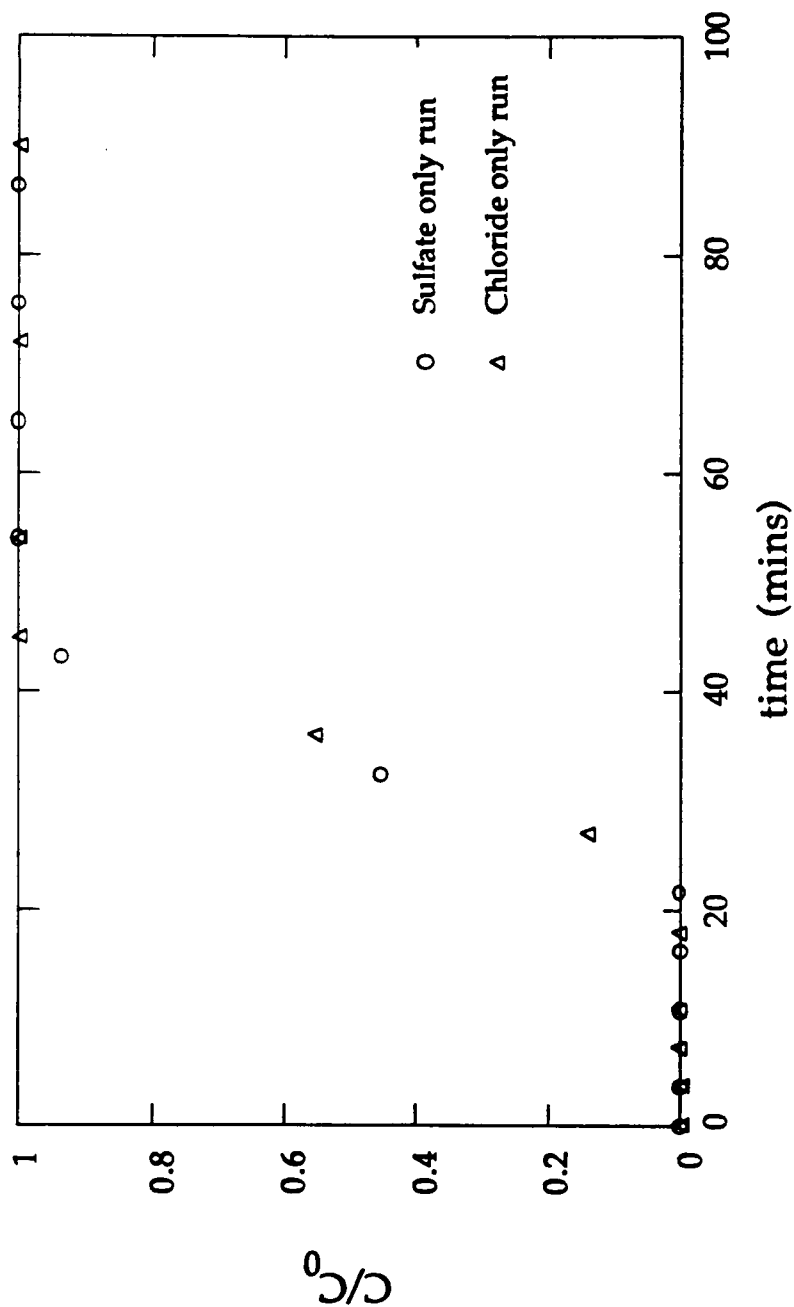


Figure 10: Effect of anion on breakthrough curves. Conditions : Feed solution concentration = 416 meq/l; Flow rate = 16 ml/min; CO₂ pressure = 50 psig; Resin volume = 150 ml; Precarbonated resin.

Table 8 : Values of Langmuir Constants and C_T for Experiments Carried out with Precarbonated Resin

Run type	a ₁		a ₂		C _T	
	(Dimensionless)		(meq/ml)		(meq/ml _{resin})	
	Sulfate	Chloride	Sulfate	Chloride	Sulfate	Chloride
Only sulfate	47.12	—	18.89	—	2.49	—
Only chloride	—	37.37	—	15.91	—	2.35
Mixture of sulfate and chloride	9.20	8.95	2.00	2.60	4.60	3.42

From the mixed-run results, where sulfate and chloride are simultaneously removed by the resin, the C_T value of the resin for sulfate is higher than that of the chloride. The C_T values of the sulfate and chloride in a mixture seems to be much higher than the sulfate-only and the chloride-only cases respectively. This particular result needs to be validated by further study, since the total amount of exchangeable sites, C_T , in the resin should be a constant and may not vary significantly.

In Table 9, the values of the Langmuir constants and C_T for the experiments performed by the simultaneous exhaustion and carbonation procedure are presented along with the values obtained by other investigators. The linearized Langmuir isotherm for the sulfate and chloride part of the mixed-runs are plotted separately in Figure 11 and 12.

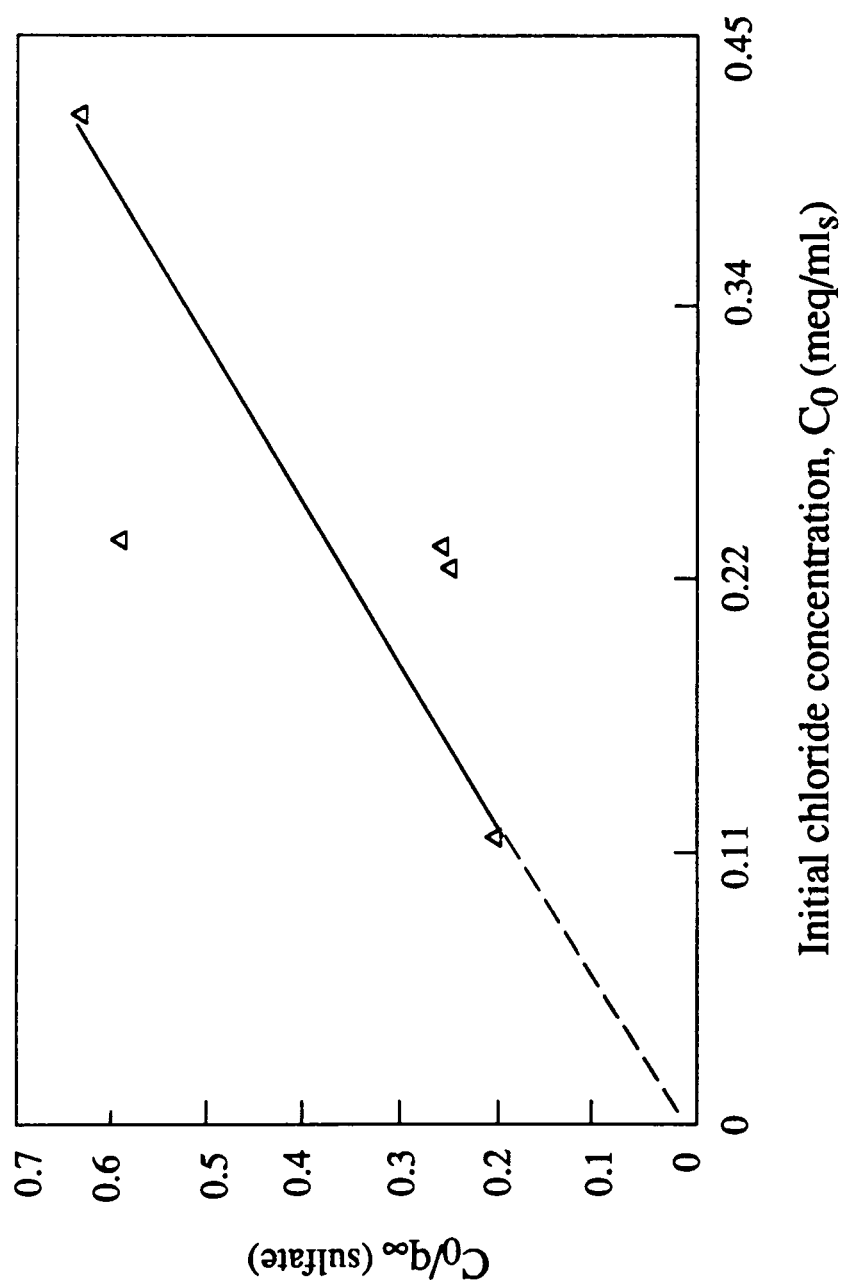
Table 9 : Langmuir Constants and C_T for Runs Performed Using Simultaneous Exhaustion and Carbonation Procedure

	a_1	a_2	C_T
	(Dimensionless)	(meq/ml)	(meq/ml _r)
Chloride-part†	7.95	7.03	1.13
Sulfate-part†	86.6	129.4	0.67
Sulfate only*	42.7	15.46	2.76
Sulfate only†	3.13	0.91	3.44

* Modeste's values @ 40 psig CO₂ pressure.

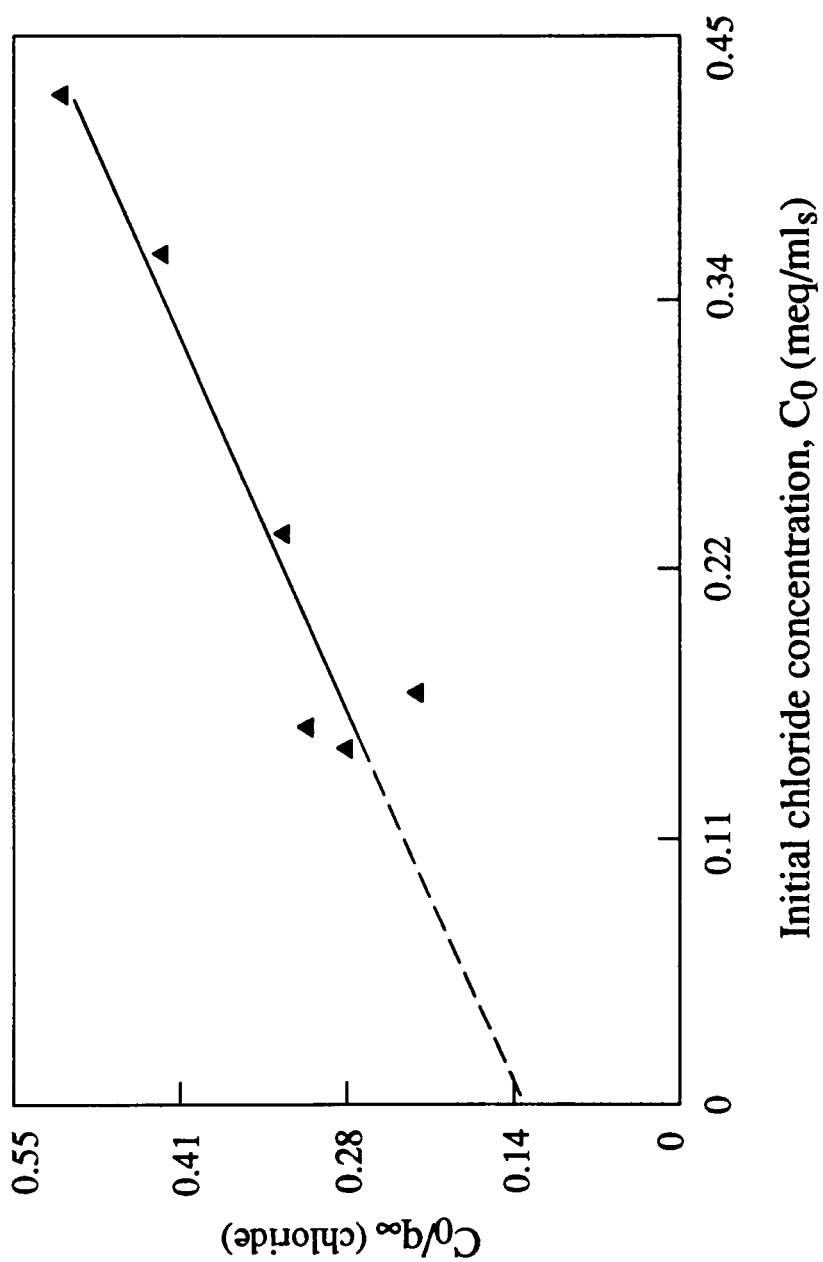
† Strevel's values @ 50 psig CO₂ pressure.

‡ Values from this study @ 50 psig CO₂ pressure.



CG-3157

Figure 11: Plot of linearized Langmuir isotherm for sulfate experiments carried out with simultaneous carbonate and a mixture of sulfate and chloride ion.



CG-3158

Figure 12: Plot of linearized Langmuir isotherm for sulfate experiments carried out with simultaneous carbonated and a mixture of sulfate and chloride ion.

From Table 9 one can see that the C_T values obtained in the present study are lower than the values obtained by Modeste and Strevel. One possible cause may be due to the presence of two anions encountered in this investigation compared to one anion in their studies. The effect of the presence of the chloride ion on the carbonation of the resin and the uptake of sulfate ions by the resin are discussed in the later sections of this chapter.

ANALYSIS OF ANION BREAKTHROUGH POINT

When a solution containing a mixture of anions like sulfate and chloride is treated in the fixed-bed, the ion to breakthrough first depends on the concentration of the various anions present in the solution. In this section, the breakthrough points of the anions in eight different experiments carried out using procedure # 2 are analyzed. The "breakthrough point" is described as the point when the concentration of the adsorbate in the effluent is about 5 % of the inlet concentration. The definition of the terms used in Table 10 are:

- J_s = C/C_0 value of sulfate ion at $C/C_0 = 0.05$ for chloride ion
- J_c = C/C_0 value of chloride ion at $C/C_0 = 0.05$ for sulfate ion
- t_1 = time required to reach the breakthrough point for sulfate ion,
(minutes)

Table 10: Experimental Data Used in Anion Breakthrough Point Analysis

When $J_s > 0.05$, then $t_1 < t_2$

Obs. #	Inlet concentration (meq/l)		Time at breakthrough point (min.)		J_s
	sulfate	chloride	sulfate (t_1)	chloride (t_2)	
1	189	239	25	29	0.18
2	352	237	11	15	0.13
3	1180	39	11	13	0.20

When $J_c > 0.05$, then $t_1 > t_2$

Obs. #	Inlet concentration (meq/l)		Time at breakthrough point (min.)		J_c
	sulfate	chloride	sulfate (t_1)	chloride (t_2)	
4	192	203	31	25	0.25
5	245	162	30	20	0.20
6	123	77	72	49	0.38
7	1017	42	11	9	0.09
8	406	17	30	17	0.35

t_2 = time required to reach the breakthrough point for chloride ion,
(minutes)

In the first three observations of Table 10 the sulfate ion breaks through earlier and hence the value of t_1 is less than t_2 . The value of J_s for observation # 1 - 3 being greater than 0.05 indicates that the sulfate ion has broken through earlier than the chloride ion. In observation # 2 and 3 the concentration of sulfate ion is higher than that of chloride ion and hence the sulfate ion breaks through earlier since more sulfate ions are present in the bulk phase. But in observation # 1, though the sulfate concentration is slightly less than that of chloride, the sulfate ion breaks through earlier than the chloride ion. Hence from the available experimental data there seems to be no particular trend in the breakthrough of sulfate ion.

Observations 4 - 8 relate to experiments in which the chloride ion breaks through before the sulfate ion and hence the values of t_1 are greater than t_2 . The value of J_c for observation # 4 - 8 being greater than 0.05 indicates that the chloride ion has broken through earlier than the sulfate ion. Though the concentration of the chloride ion is either equal to or less than that of the sulfate ion, the chloride ion seems to break through earlier than the sulfate ion. This behavior is contrary to the trend seen in observation # 2 and 3 where the ion that is present in greater concentration in the bulk phase broke through first. Here too, from the available experimental data there seems to be no particular trend in the breakthrough of chloride ion. Hence, further

study is required to collect additional data so that one can reasonably predict which anion would breakthrough first.

EFFECT OF CARBONATION PROCEDURE ON RESIN PERFORMANCE

To study the procedural effect on the performance of the resin, experiments were carried out using different procedures for carbonating the resin.

The three methods used to precarbonate the resin were:

- a) Bubbling CO₂ gas through the resin in a beaker for 2 hours and then keeping it under a static CO₂ pressure for 1 hour in the fixed-bed setup. The exhaustion step was then carried out under 50 psig CO₂ pressure.
- b) Hydroxide form of resin kept for 20 minutes under static CO₂ pressure in the fixed-bed setup. The exhaustion step was then carried out under 50 psig CO₂ pressure and
- c) Hydroxide form of resin kept under no static CO₂ pressure prior to the start of the exhaustion run and exhaustion step carried out under 50 psig CO₂ pressure.

Methods (a) and (b) respectively are Procedure # 2 and Procedure # 3 described earlier in Chapter VI. The term "static CO₂ pressure" means that the fixed-bed system is kept idly under CO₂ pressure for a predetermined length of time before introducing the feed solution. This helps in converting the hydroxide

sites on the resin to bicarbonate sites. The equilibrium resin capacities of the resin for sulfate and chloride ion are compared in Table 11 for the "Base case" experiments (defined previously in Chapter VI) that were carried out using different carbonating procedures.

Table 11: Effect of Carbonation Procedure on Resin Performance

Base case: Feed solution = 250 meq/l sulfate, 166 meq/l chloride, Flow = 16 ml/min., 50 psig CO₂ pressure and (SO₄)²⁻/Cl ratio = 1.5

Carbonation Procedure	Equilibrium Capacity of Resin (meq/ml _{resin})	
	Sulfate	Chloride
2 hrs CO ₂ Bubbling and 1 hr Static CO ₂ Pressure.	1.53	1.00
20 minutes Static CO ₂ pressure	0.93	0.54
0 minutes Static CO ₂ pressure	0.93	0.50

As we can see from the results, the resin when carbonated under a procedure that involves two hours of CO₂ bubbling prior to the exhaustion step, gives a higher resin capacity than the other two procedures. Since two hours is a long time to be spent on carbonating the resin, a trade-off is needed between the carbonation time and the resin's useful capacity that is desired.

EFFECT OF TEMPERATURE ON RESIN'S PERFORMANCE

The effect of temperature on the resin's performance was studied by conducting an experiment at a higher temperature under the "base case" conditions. The high temperature experiment was conducted with precarbonated resin at 50 psig CO₂ pressure by heating the feed solution to 45° C and then introducing it in to the fixed-bed system. The resin capacity realized from this experiment is compared with the "base case" resin capacity in Table 12.

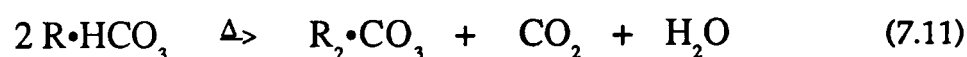
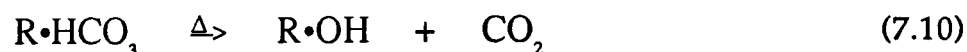
Table 12 : Effect of Temperature on Resin Capacity

Basis : "Base case" conditions

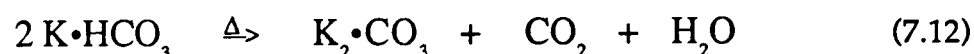
Temperature (° C)	Resin Capacity (meq/ml _{resin})	
	Sulfate	Chloride
21	1.53	1.00
45	1.37	0.80

From the results it is evident that increasing the temperature does not improve the resin's capacity. This result is interesting since a rise in temperature is expected to favor the mass transfer and kinetic rates. The reasoning is that at higher temperature some of the bicarbonate sites on the

resin may be converted back to hydroxide sites or carbonate sites according to the following reactions:



Equation (7.11) is similar to the reaction shown in (7.12) that occurs when potassium bicarbonate solution is heated to give potassium carbonate solution, carbon-dioxide and water vapor.



Since the OH^- ion and the $(CO_3)^{2-}$ ion are to the left of sulfate and chloride ions on the resin affinity chart revised by Dharmapurikar [39], they are not easily converted to the $R_2 \cdot SO_4$ or $R \cdot Cl$ form. Hence, with a rise in temperature the resin's preference for sulfate and chloride ion would be expected to decrease resulting in a lower capacity.

DETERMINATION OF DIFFUSION PARAMETER USING ANTONSON'S MODEL

The Antonson's model can be used to estimate the breakthrough curve, i.e. the values of C/C_0 for the fixed-bed ion-exchange system as a function of dimensionless time. The model assumes that the intraparticle diffusion is the overall rate-controlling mass transfer step. This model was successfully used by previous investigators [2,3] to fit the experimental breakthrough curves for their fixed-bed experiments involving single anion. In this study, since two anions, sulfate and chloride are involved, the Antonson's model is applied to sulfate and chloride ions separately assuming no interference between the ions.

The computer program for the Antonson's model requires two input values, X , the dimensionless column length parameter and the non-linear equilibrium parameter a_2C_0 . The parameter a_2C_0 is obtained from the experimental data and is a constant for a particular fixed-bed experiment. It is used to generate a set of theoretical breakthrough curves at various values of X . The theoretical curves obtained for different values of X are then plotted on a semi-log graph paper and are visually matched with the experimental breakthrough curve by sliding along the time axis. The X value of the theoretical curve that best matches the experimental curve is then used to determine the diffusion parameter. The procedure involved in the curve

matching technique is simple. First, the experimental breakthrough data is plotted in a semi-log graph sheet with C/C_0 in the y-axis and θ^* , the time parameter, plotted on the x-axis. The time parameter θ^* , is given by the following equation:

$$\theta^* = (t - z_T/v) \quad (7.13)$$

Then a semi-log plot of the model estimated C/C_0 versus θ for different values of X is plotted using Antonson's model program. The dimensionless time (theoretical time), θ is expressed as:

$$\theta = \{2 D (t - z_T/v)\}/R^2 \quad (7.14)$$

The two semi-log plots are then compared by placing the experimental plot on the top of the theoretical plot and then sliding it along the x-axis until the experimental curve matches with the theoretical curve. The relationship between θ and θ^* can be expressed as:

$$\ln (\theta) = \ln (\theta^*) + \ln (2 D/R^2) \quad (7.15)$$

The semi-log plots were plotted on transparent graph papers and were matched by placing them on an illuminated glass plate. Examples of typical best fit curves for sulfate ion and chloride ion are shown in Figure 13 & 14. The value of X of the best matching curve is used to calculate the diffusion parameter, D/R^2 . It is calculated from the following expression:

$$X = \frac{3 D a_1 z_T}{m R^2 v} \quad (7.16)$$

where ' a_1 ' is the first Langmuir constant, ' z_T ' is the height of the resin bed, ' v ' is the superficial velocity and ' m ' is the ratio of the void fraction-to-the particle fraction in the bed. In Figure 15, the theoretical breakthrough curves obtained by using the Antonson's model are plotted for various values of X . As the value of X increases the breakthrough curve becomes much steeper, hence the curve's slope changes from small positive to very large values.

The calculated diffusion parameter, D/R^2 , and the corresponding X values for fixed-bed experiments performed with sulfate-only and chloride-only solutions are given in Table 13. The diffusion coefficient is presented as a diffusion parameter D/R^2 where, R is the characteristic length of the resin particle and D is the effective diffusion coefficient. Since the occurrence of micropore or macropore diffusion would be dependent on the pore size and they were not differentiated in the present study, the characteristic length (R)

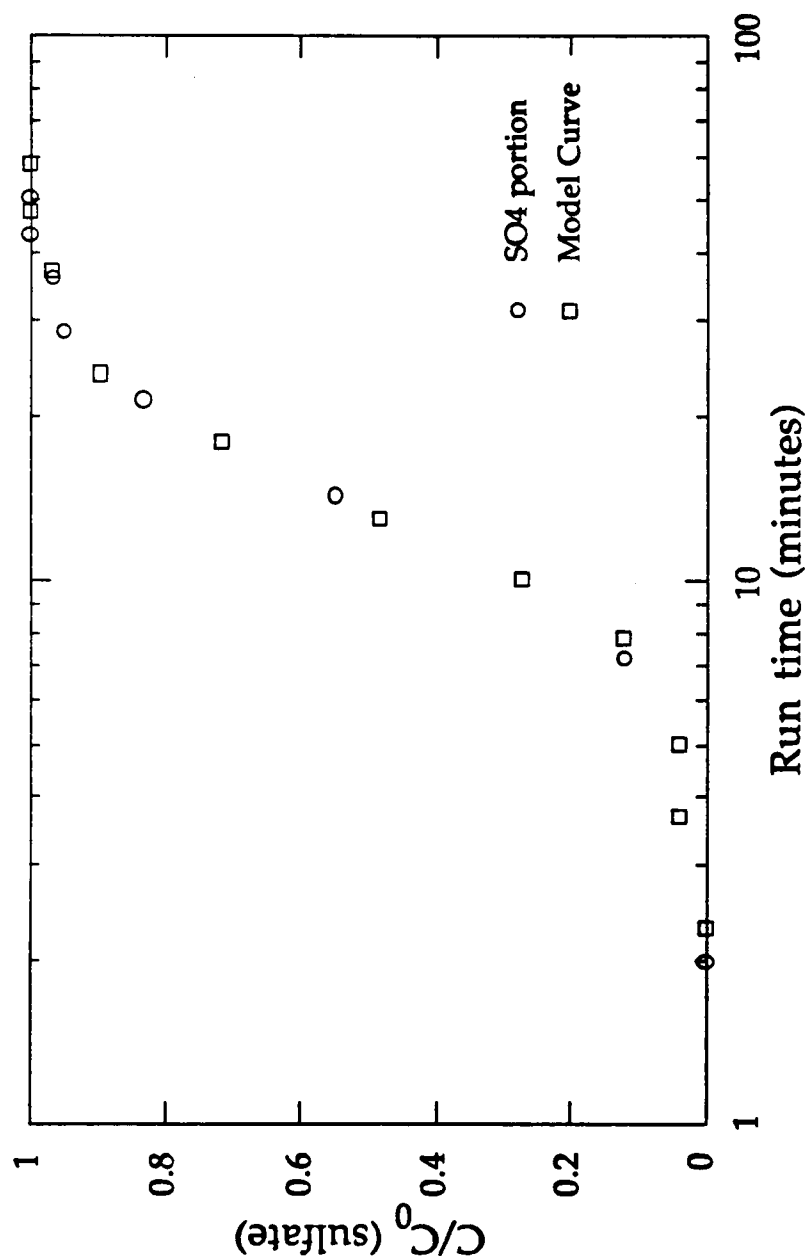


Figure 13: Typical best fit for sulfate ion by Antonson's model. Conditions: Feed sulfate concentration = 352 meq/l; chloride = 237 meq/l; Flow rate = 16 ml/min; CO₂ pressure = 50 psig.

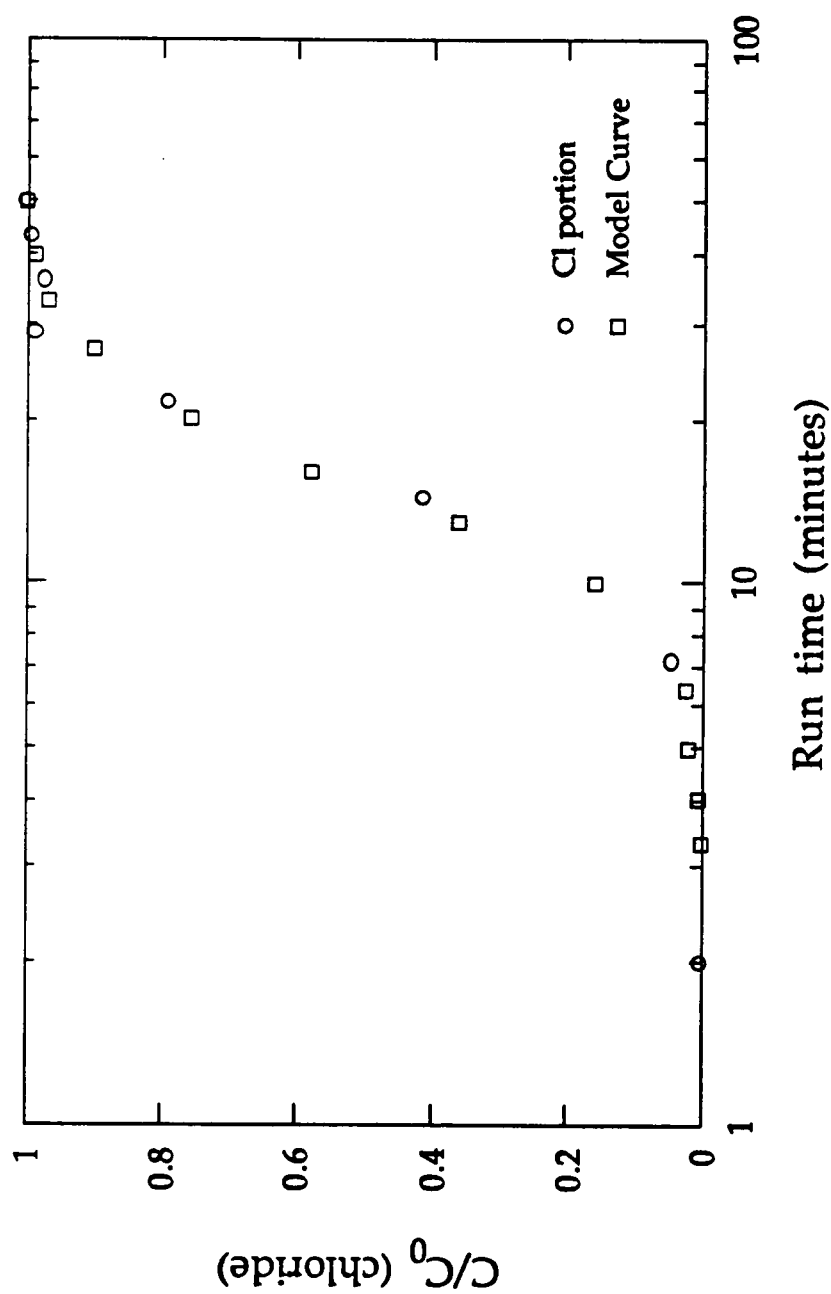


Figure 14: Typical best fit for chloride ion by Antonson's model. Conditions: Feed sulfate concentration = 352 meq/l; chloride = 237 meq/l; Flow rate = 16 ml/min; CO_2 pressure = 50 psig.

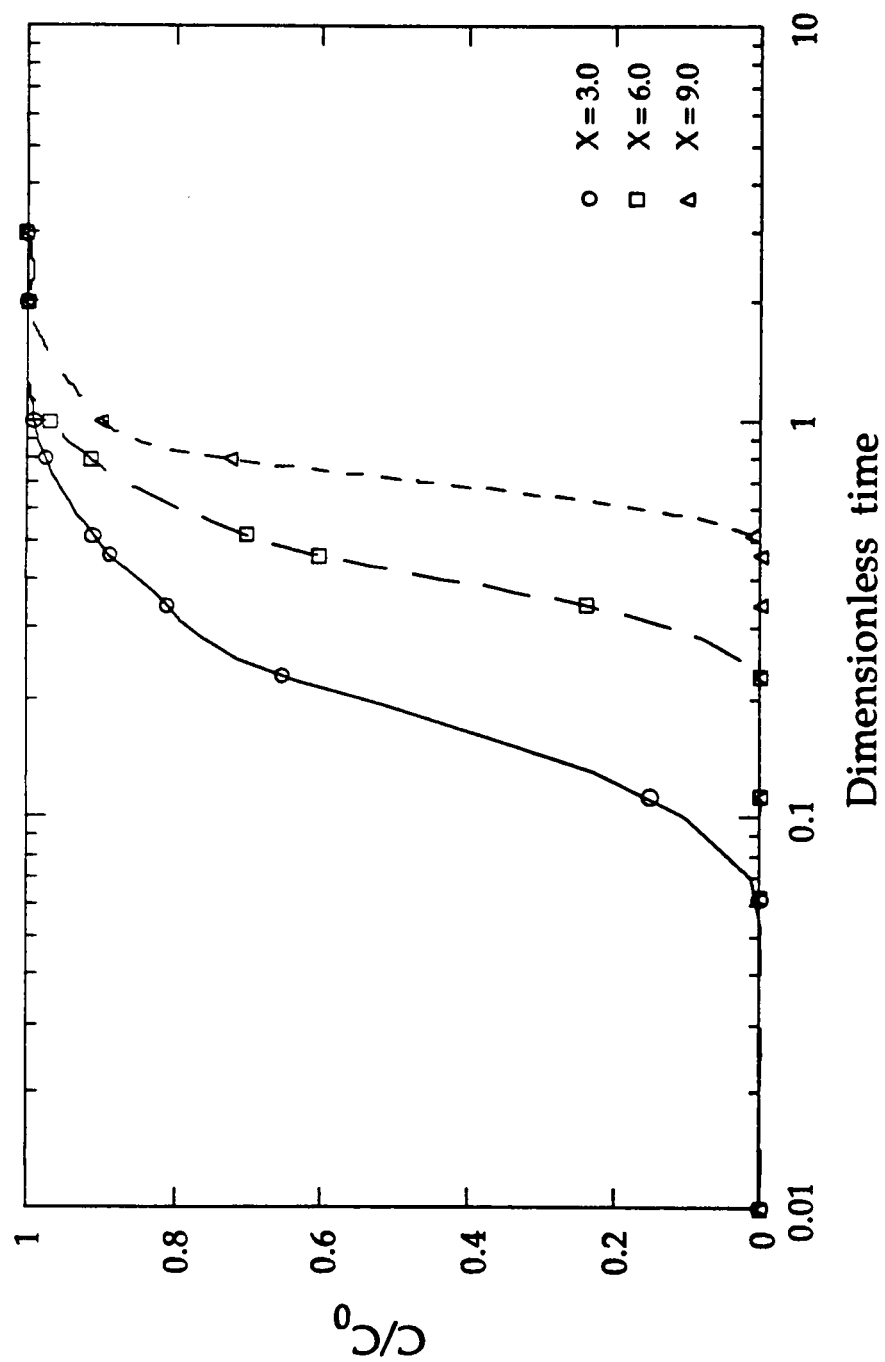


Figure 15: Antonson's model curves for different values of X . Conditions: Feed concentration = 381 meq/l; Flow rate = 16 ml/min; CO_2 pressure = 50 psig; $a_2 C_0 = 7.20$

Table 13 : D/R² Values for Single Anion Exhaustion Runs

Only sulfate runs:

Solution concentration	X	(D/R ² x 1000)
C ₀ , (meq/l)	(Dimensionless)	(1/sec)
208	9.0	0.036
381	8.0	0.032
545	7.0	0.028
586	6.5	0.026

Only chloride runs:

Solution concentration	X	(D/R ² x 1000)
C ₀ , (meq/l)	(Dimensionless)	(1/sec)
211	8.5	0.043
372	7.5	0.038
569	6.5	0.033

of the resin particle was coupled with the diffusion coefficient and presented as the diffusion parameter D/R^2 . In Table 14 the diffusion parameter values obtained from this study for sulfate-only runs are compared with those found in the literature. The D/R^2 values found by other investigators for IRA-68 seem to be slightly higher than the values found in this study. This may be attributed to the different type of carbonation procedure used in this study. However, the magnitude of the diffusion parameter obtained in this study is of the same order as the Literature values.

For experiments involving mixtures of sulfate and chloride ions, the Antonson's model program was run separately for each ion and the curve matching procedure was also carried out separately. Table 15 gives the values of the diffusion parameter, D/R^2 , and corresponding X for experiments performed with mixtures of sulfate and chloride ions.

EFFECT OF IONIC CONCENTRATION ON SULFATE ION'S DIFFUSION PARAMETER

The calculated diffusion parameters for various fixed-bed experiments were plotted as a function of sulfate ion concentration in Figure 16 for the sulfate-only runs. The diffusion parameter shows a decreasing trend as the solution concentration increases. But Strevel [3], in his investigation reported an increase in the diffusion parameter with the increase in the sulfate ion

Table 14 : Comparison of D/R^2 values with the Literature

Reference	Sulfate Concentration (meq/l)	($D/R^2 \times 1000$) (1/sec)
Present	208	0.036
Present	545	0.028
Strevel [†] [3]	250	0.043
Strevel [†] [3]	562	0.034
Modeste* [2]	83	0.050
Modeste* [2]	333	0.183
Dharmapurikar [†] [39]	574	0.201

[†] Experiment performed @ 10 psig

* Experiment performed @ 20 psig

Table 15: D/R² Values for Sulfate and Chloride Ions

Inlet concentration (C ₀)		SO ₄ /Cl	X		(D/R ² x 1000)	
(meq/l)		(Ratio)	(Dimensionless)		(1/sec)	
Sulfate	Chloride		Sulfate	Chloride	Sulfate	Chloride
189	239	0.8	3.0	3.0	0.061	0.063
192	203	0.9	5.0	4.5	0.102	0.094
246	163	1.5	5.0	3.0	0.102	0.063
352	237	1.5	2.0	2.5	0.040	0.052
123	77	1.6	9.0	5.0	0.183	0.105
1017	42	24	3.0	4.5	0.061	0.094
406	17	24	4.0	7.5	0.081	0.157
1177	39	30	3.0	7.0	0.061	0.147

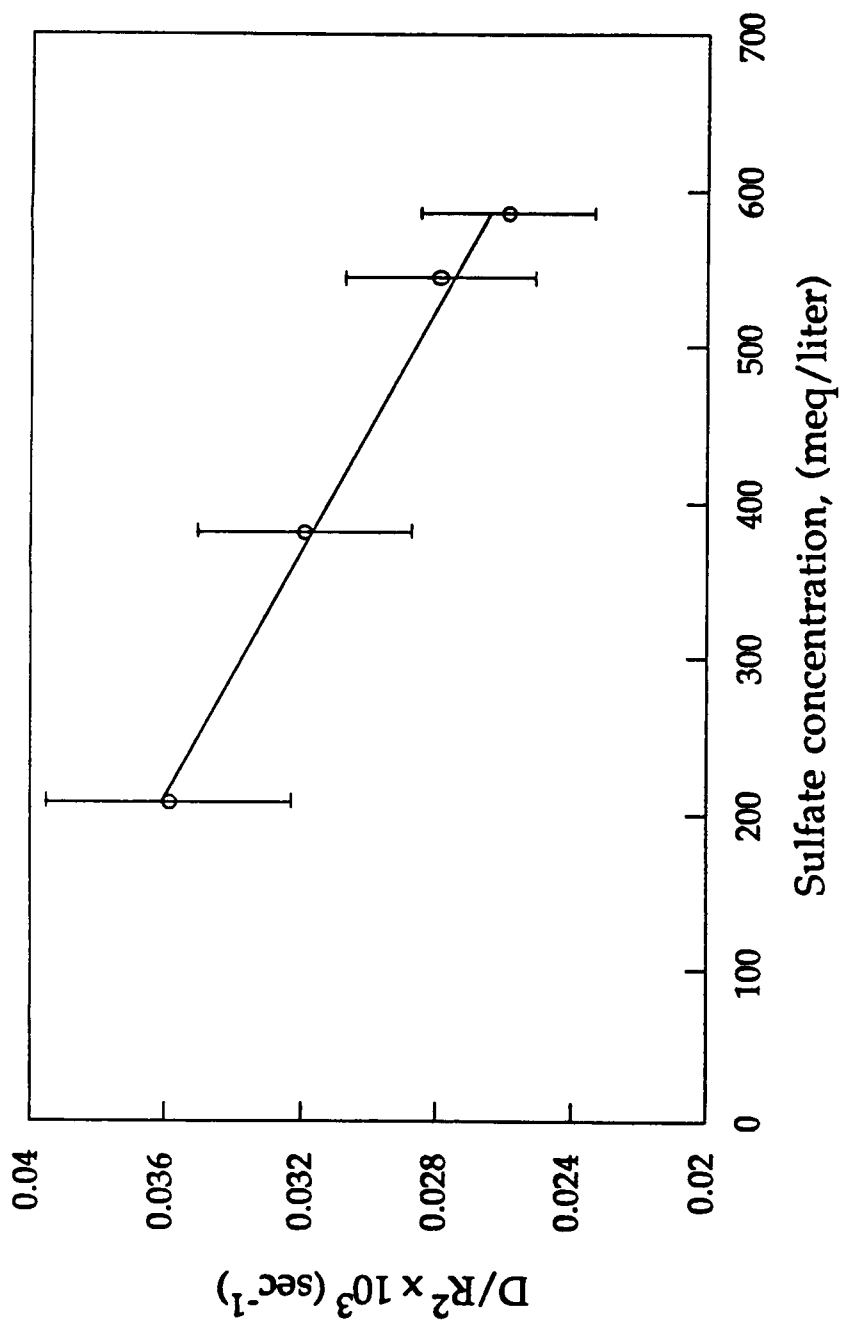
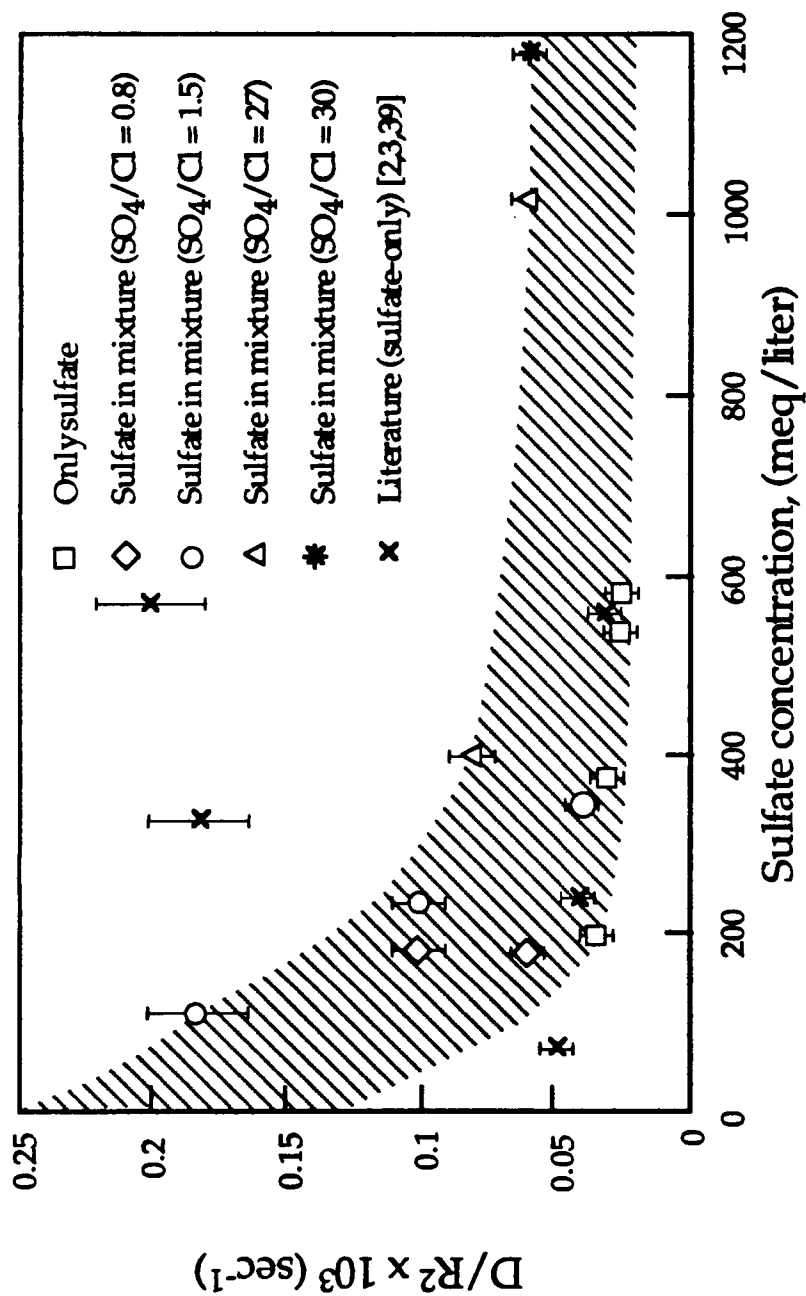


Figure 16: Plot of diffusion parameter versus sulfate concentration for sulfate-only runs.

concentration for IRA-68. For IRA-35 and IRA-93 resins, however this parameter did not change much in his study. This contradicting behavior for IRA-68 resin can probably be attributed to the different carbonation procedure used in this study versus that used by Strevel. Modeste [2], working with IRA-68 resin used the same experimental procedure as Strevel [3] in his investigation and also reported an increase in the diffusion parameter with the increase in the inlet concentration of the sulfate ions. Hence the effect of concentration on the diffusion parameter needs to be verified by carrying out additional experiments under different carbonation procedures.

For the experiments involving both sulfate and chloride ions, their concentration ratio becomes another major parameter. Figure 17 shows a plot of sulfate concentration versus diffusion parameter for all the experiments carried out with a mixture of sulfate and chloride ions with sulfate-to-chloride ratio as parameter. In plotting the experimental points, an error band of $\pm 10\%$ as theoretical breakthrough curves were available only for finite values of X , and the curve matching procedure may introduce some error. In the same plot additional values of the sulfate ion diffusion parameter found by other investigators [2,3,39] for single ion study with IRA-68 resin are also included for comparison. From Figure 17 one can see that most of the diffusion parameter values seem to fall in a narrow band. The diffusion parameter for sulfate ion seems to decrease with the increase in



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Figure 17: Plot of diffusion parameter for sulfate versus sulfate concentration for experiments conducted with a mixture of sulfate and chloride ions

the sulfate concentration at low concentrations. But, at higher concentrations and higher sulfate-to-chloride ratios the diffusion parameter seems to level off. In the same plot, the diffusion parameter values obtained from the sulfate-only experiments from this study are also included for comparison. The diffusion parameter of sulfate ion in a mixture with chloride ion appears to be slightly higher than that for the sulfate-only case. Any possible effect of the other anion (Cl^- ion in this case) on the diffusion parameter of the $(\text{SO}_4)^{2-}$ ion needs to be determined in future study.

EFFECT OF IONIC CONCENTRATION ON CHLORIDE ION'S DIFFUSION PARAMETER

The diffusion parameters for the fixed-bed experiments were plotted as a function of chloride ion concentration in Figure 18 for the chloride-only runs. The diffusion parameter shows a decreasing trend with increase in chloride ion concentration. Thus, a decrease in diffusion parameter with increase in solution concentration may mean that the diffusion of the ions in the resin proceeds slower with increased concentration. As a result one would believe that the intraparticle diffusion will most likely control the overall mass transfer rate at still higher concentrations of anions.

In Figure 19, the chloride concentration in mixture with sulfate in feed

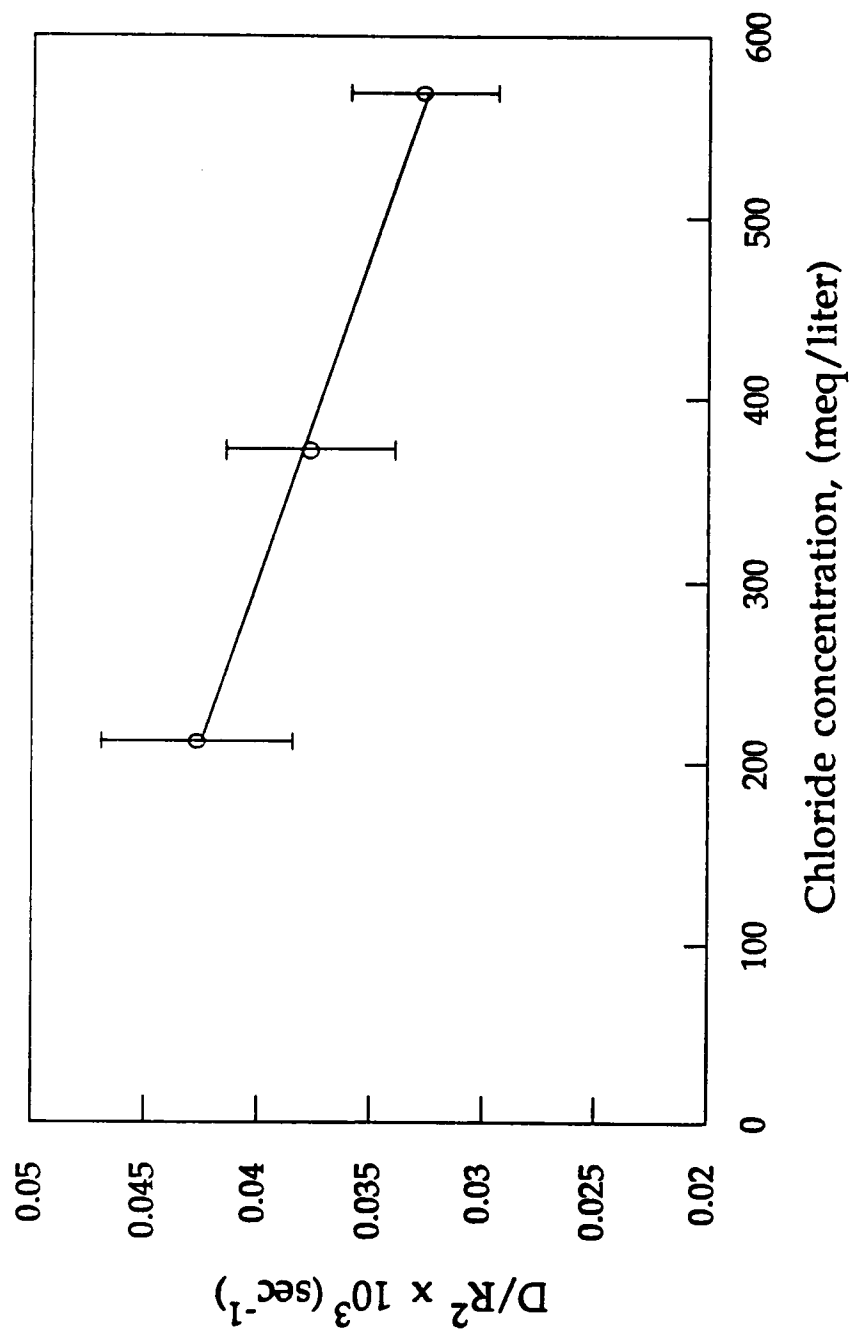
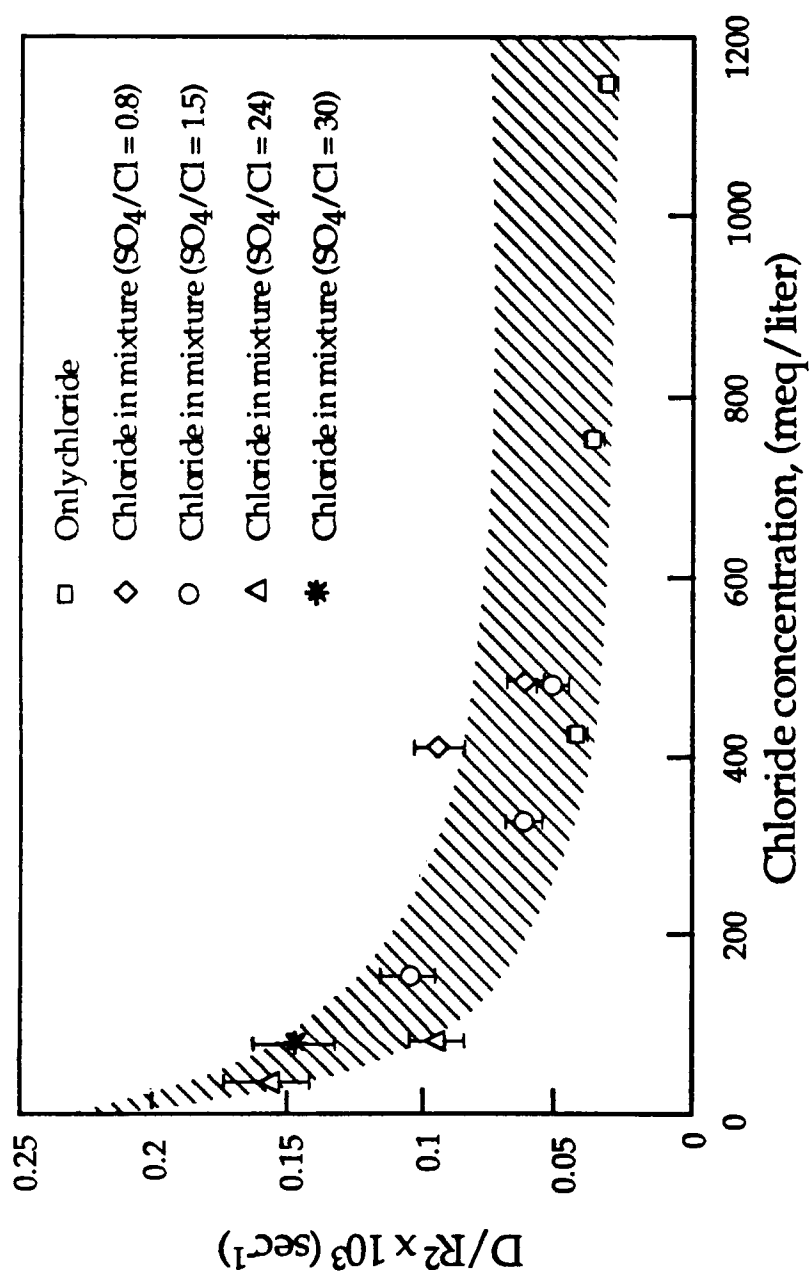


Figure 18: Plot of diffusion parameter versus chloride concentration for chloride-only runs.



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Figure 19: Plot of diffusion parameter for chloride versus chloride concentration for experiments conducted with a mixture of sulfate and chloride ions

solution is plotted versus the diffusion parameter for chloride ions for different sulfate-to-chloride ratios. An error band of $\pm 10\%$ in the calculated values was assumed because of the availability of model predicted curves for only a finite number of X , the dimensionless column length and the built-in error in the curve matching procedure. From Figure 19 one can see that most of the diffusion parameter values seem to fall in a narrow band. Also there is a decrease in the diffusion parameter with increase in chloride concentration at low concentration of chlorides. This behavior is similar to that of the sulfate ion in a mixture with chloride ion shown in Figure 17. However, additional experiments need to be carried out at low sulfate-to-chloride ratios to study the behavior of diffusion parameter of chloride ion at high chloride concentrations in a mixture with sulfate ions.

The values of diffusion parameter for chloride-only runs were also plotted in the same figure for comparison. The diffusion parameter for the chloride-only runs seems to be slightly lower than that of the chloride in mixture with the sulfate ions. Similar behavior was also seen for the diffusion parameter for the sulfate ions.

REACTION KINETICS MODEL FOR EXPERIMENTS CARRIED OUT WITH SIMULTANEOUS CARBONATION/EXHAUSTION PROCEDURE

As mentioned earlier, fixed-bed experiments were performed using three different carbonation procedures. The results obtained from experiments conducted with precarbonated resin were analyzed using the Antonson's model. All these results have been discussed in the earlier sections. Experiments were also performed in this study using the simultaneous exhaustion and carbonation procedure developed by Modeste [2]. The experiments carried out by Modeste involved only the sulfate ion as compared to two anions (sulfate and chloride) in this work.

Breakthrough curves obtained from experiments conducted with the simultaneous carbonation/exhaustion procedure showed an unique behavior. For experiments conducted with both sulfate and chloride ions, the C/C_0 values did not reach the limiting value of 1.0, but instead, leveled off at a value of about 0.8 for the sulfate ion and about 0.95 for the chloride ion. Figure 20, shows such a behavior encountered in this study. Experiments conducted by Modeste and Strevel [3], used only sulfate ion following the same procedure and they did not observe such behavior in their C/C_0 values. It was believed that probably the presence of another exchangeable anion, the chloride ion, in this work may have had some effect on the simultaneous carbonation of the resin sites. An attempt was made in this study to explain

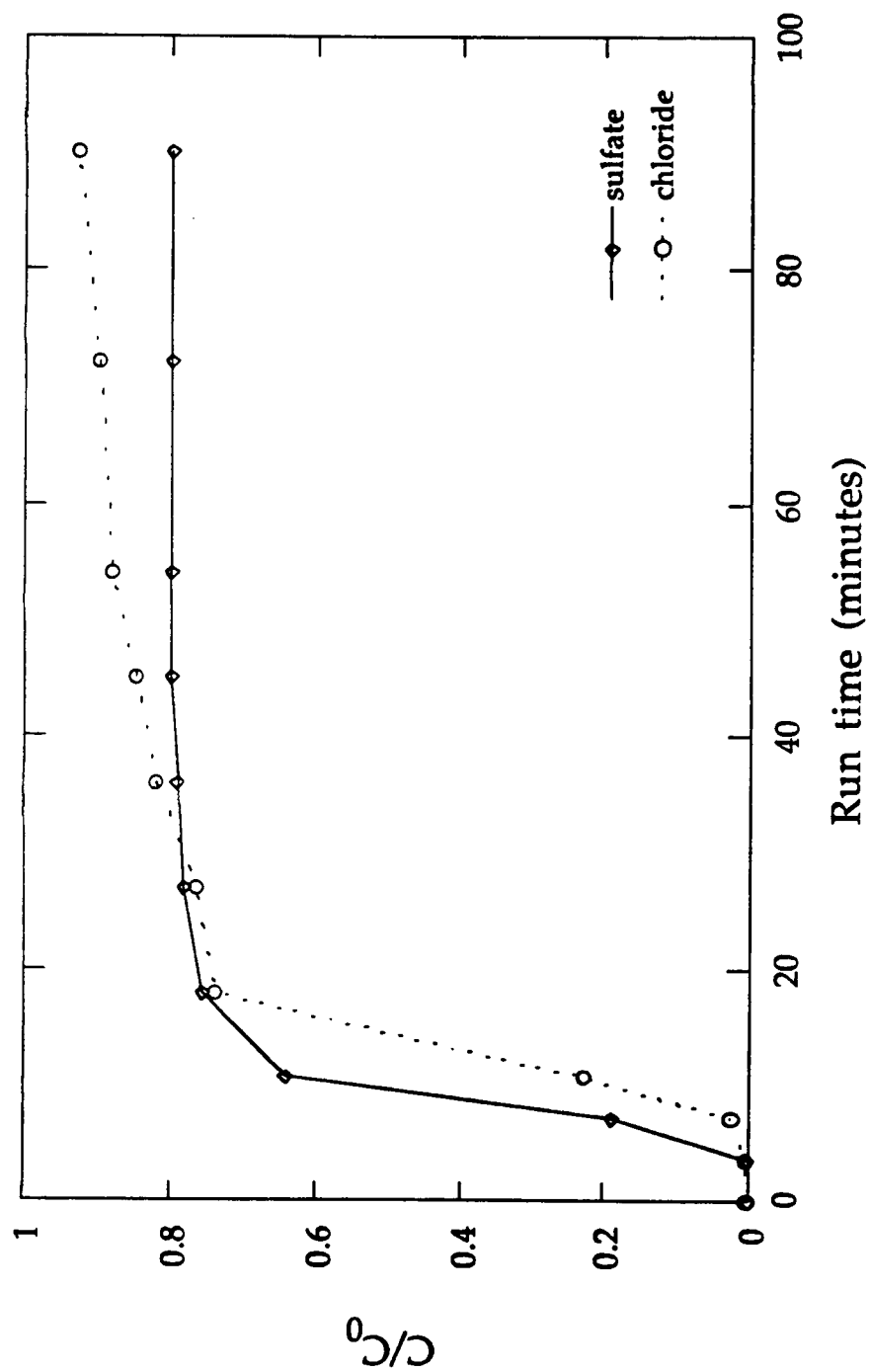


Figure 20: Breakthrough curve for an experiment conducted with simultaneous carbonation and exhaustion in which C/C_0 values did not reach 1.0

this observed behavior of the breakthrough curves on the basis of a kinetic model that assumes reaction rate as the overall rate controlling step and incorporates reaction kinetics for carbonation, dechlorination and desulfurization as simultaneously occurring parallel steps.

After performing the material balance calculations and assuming a Langmuir type non-equilibrium relationship between the resin phase concentration and the solution phase concentration, the following equations were derived in Chapter III.

$$\frac{d\left(\frac{C_c}{C_{oc}}\right)}{dt} = \frac{F}{m V_R} \left[1 - \frac{C_c}{C_{oc}} \right] - \frac{K_2 C_c}{m C_{oc}} [C_T \{1 - \exp(-K_1 P t)\} - q_c - q_s] \quad (7.17)$$

$$\frac{d\left(\frac{C_s}{C_{os}}\right)}{dt} = \frac{F}{m V_R} \left[1 - \frac{C_s}{C_{os}} \right] - \frac{K_3 C_s}{m C_{os}} [C_T \{1 - \exp(-K_1 P t)\} - q_c - q_s]^2 \quad (7.18)$$

The initial and boundary conditions that apply to this system of equations are:

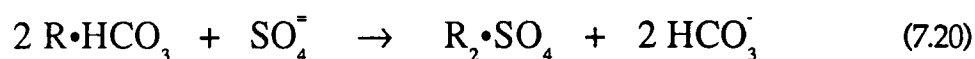
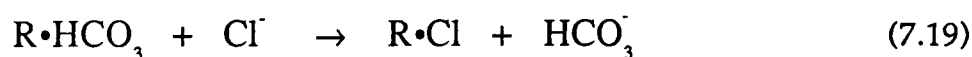
$$\text{At } t = 0, \quad C_s = 0 ; C_c = 0.$$

$$\text{At any time } t, \quad q = A_1 C / (1 + A_2 C) \quad (\text{non-linear Langmuir Equilibrium relationship})$$

where C is the solution phase concentration of the anion and q is the resin phase concentration. The values of F , m , V_R , C_T , P , C_{0s} and C_{0c} are all known quantities from the experimental conditions. The values of the reaction rate constants K_2 and K_3 for the chloride and the sulfate ion respectively, can be approximated from the experimental run data by assuming irreversible reactions at shorter time periods for example $t \leq 10$ minutes.

CALCULATION OF REACTION CONSTANTS

The reaction constants K_2 and K_3 for the two reactions given earlier in Chapter III and below are calculated from their respective kinetic rate expressions for irreversible ion-exchange.



By assuming irreversible reactions, the kinetic rate of irreversible ion-exchange can be written as:

$$\frac{dq}{dt} = K C_0 (C_T - q) \quad (7.21)$$

The K in equation (7.21) may be either K_2 or K_3 depending on whether the

calculation pertains to chloride or sulfate ion removal. Equation (7.21) is a first order differential equation that can be easily solved by applying the initial condition:

$$q = 0 \quad \text{at} \quad t = 0$$

Solving the differential equation we get the following expression:

$$q = K^2 C_0^2 C_T (1 - \exp(-K C_0 t)) \quad (7.22)$$

From the experimental data and from a material balance for the fixed-bed setup, the resin phase concentration q , can be calculated for different values of time t . To calculate the forward reaction rate constants for the reactions in equation (7.19) and (7.20), the values for ' q ' at small time (e.g. $t \leq 10$ minutes) were considered. This is due to the fact that during the initial period of the experiment, the forward reaction will be more dominant. Taking two values of ' q ' at two different times (say at $t = 5$ and $t = 10$ minutes), two equations were obtained and were solved to obtain the values of the reaction constants for chloride and sulfate ions. Similarly calculated reaction constants for chloride and sulfate for different experimental runs are given in Table 16.

The next step is to obtain the values of A_1 and A_2 the Langmuir constants for both sulfate and chloride ions for these experiments. The A_1 and A_2 values for sulfate and chloride are distinguished by adding an additional subscripts ' S ' and ' C ' respectively. Using the linearization method described in Chapter III by equation (3.29), the values of A_1 and A_2 were calculated and are

Table 16 : Reaction Constants for Sulfate and Chloride Ions in Simultaneously Carbonated Case

Solution concentration (meq/l)		SO ₄ /Cl (Equivalents ratio)	K ₂ [ml _s /(meq • min)]	K ₃ [(ml _s • ml _p)/meq ²]
Sulfate	Chloride	(Chloride) (Sulfate)		
119	172	0.7	0.001	0.008
242	358	0.7	0.007	0.023
229	150	1.5	0.013	0.080
382	249	1.5	0.019	0.150

given in Table 17. The plots of C/q versus C used to calculate these values are shown in Figure 21 and 22.

The values of the reaction constants K_2 and K_3 , and the Langmuir constants A_1 and A_2 are run specific, and are functions of the specific ion concentration and the sulfate-to-chloride ratio used in that run.

$$K_2 \text{ and } A_{1C} \text{ } A_{2C} = f(\text{chloride ion concentration, and } SO_4/Cl \text{ ratio})$$

$$K_3 \text{ and } A_{1S} \text{ \& } A_{2S} = f(\text{sulfate ion concentration, and } SO_4/Cl \text{ ratio})$$

Hence from values used for these parameters, a relationship between these parameters and the ionic concentration and sulfate-to-chloride ratio was derived by a linear regression technique. The linear regression technique used to find the regression coefficients is as follows:

- a) The data were arranged in a matrix form with the "X" matrix containing the values of the variables; the ionic concentration, the sulfate-to-chloride equivalents ratio, and an intercept in that order. The intercept is nothing but a constant used in linear regression technique.
- b) The values of the dependent variable, (K_2 or K_3 or A_1 or A_2) were arranged as one column in the "Y" matrix.
- c) The regression coefficients to be calculated, were arranged as column matrix "G".

After the matrix arrangement one gets the following expression:

Table 17 : Calculated Values of A_1 and A_2 (Langmuir Constants) for Simultaneously Carbonated Case

Concentration (meq/l)		SO_4/Cl	A_{1s}	A_{1c}	A_{2s}	A_{2c}
Sulfate	Chloride	Equivalents ratio	(Dimensionless)		(ml_{resin}/meq)	
119	172	0.7	113	253	212	360
242	358	0.7	22	22	46	23
382	249	1.5	14	40	13	54

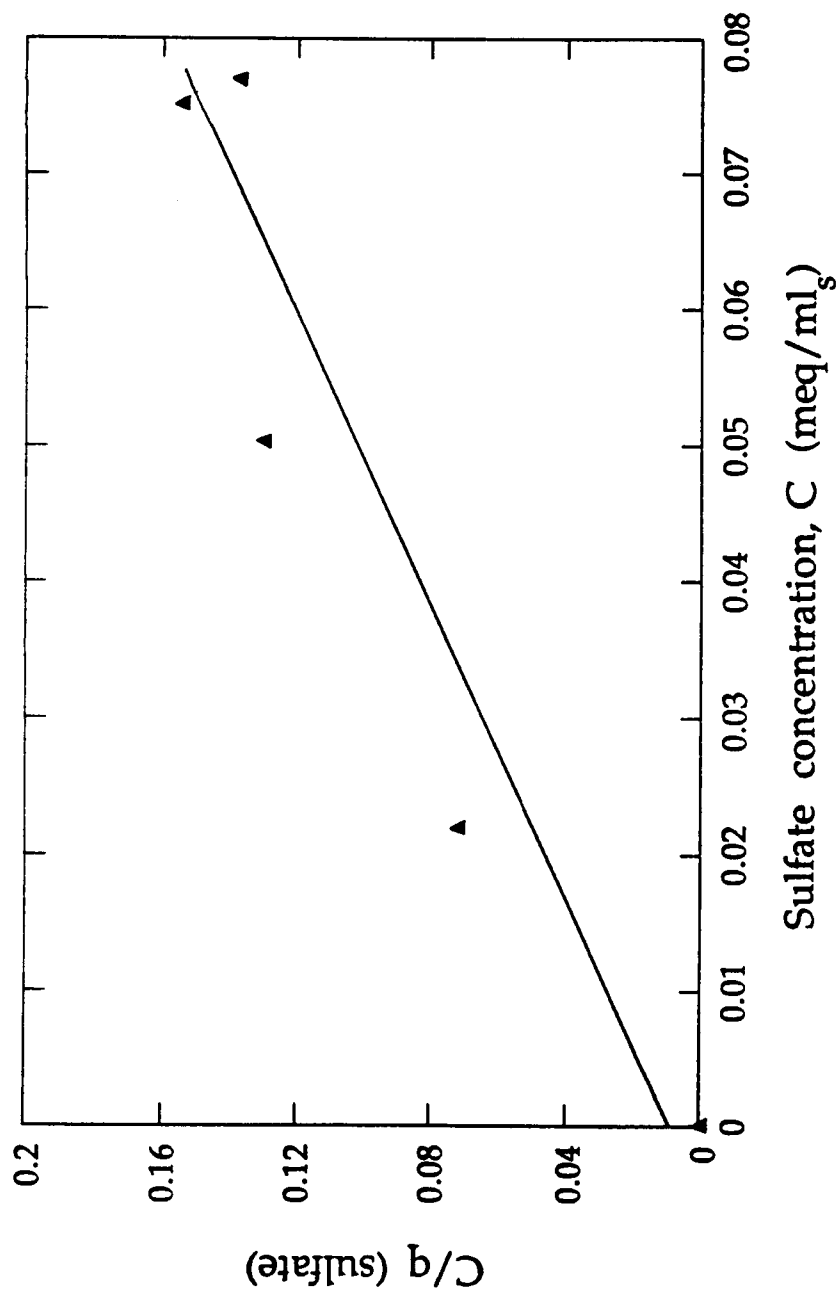


Figure 21: Plot of C/q versus concentration for sulfate portion of an experimental run to calculate Langmuir constants A_1 and A_2 for simultaneously carbonated case.

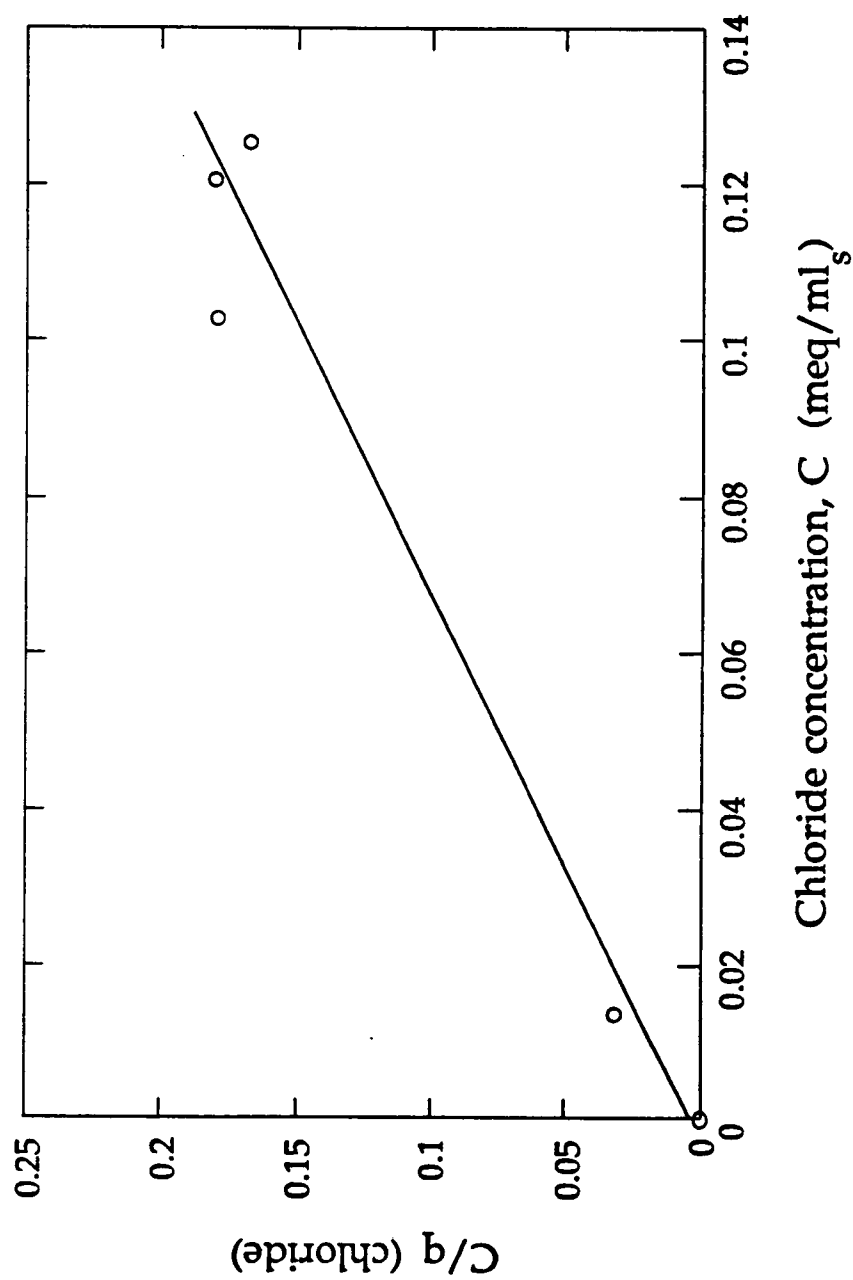


Figure 22: Plot of C/q versus concentration for chloride portion of an experimental run to calculate Langmuir constants A_1 and A_2 for simultaneously carbonated case.

$$X \cdot G = Y. \quad (7.23)$$

By multiplying both sides by the transpose matrix of X , we get

$$[X^T \cdot X] \cdot G = X^T \cdot Y \quad (7.24)$$

$$G = [X^T \cdot X]^{-1} \cdot [X^T \cdot Y] \quad (7.25)$$

A computer program was written to perform the calculations involved in the above equations and is presented in Appendix A. Subroutines from the International Mathematical Subroutine Library [IMSL] were utilized in the program to perform operations like matrix inversion and matrix multiplication. Computer programs were written to evaluate the regression coefficients and as a result the following relationships were developed:

$$K_2 [\text{ml}_s / (\text{meq} \cdot \text{min})] = 0.00004 \times (h_3) + 0.01744 \times (h_1) - 0.0184 \quad (7.26)$$

$$K_3 [(\text{ml}_s \cdot \text{ml}_r) / \text{meq}^2] = 0.00032 \times (h_2) + 0.07 \times (h_1) - 0.09188 \quad (7.27)$$

$$A_{1S} [\text{dimensionless}] = -0.748 \times (h_2) + 115.8 \times (h_1) + 122.8 \quad (7.28)$$

$$A_{2S} [\text{ml}_r / \text{meq}] = -1.357 \times (h_2) + 187.7 \times (h_1) + 244.5 \quad (7.29)$$

$$A_{1C} [\text{dimensionless}] = -1.240 \times (h_3) - 139.3 \times (h_1) + 562.5 \quad (7.30)$$

$$A_{1C} [\text{ml}_r / \text{meq}] = -1.815 \times (h_3) - 198.9 \times (h_1) + 809.9 \quad (7.31)$$

where, h_1 is sulfate-to-chloride equivalents ratio, h_2 is sulfate ion concentration in milliequivalent/liter, and h_3 is chloride ion concentration in milliequivalent/liter. The computer programs for calculating these regression coefficients are presented in Appendix A. These relationships, although empirical, were used to calculate the values of the parameters for the "base case" conditions of :

Feed solution = 250 meq/l of sulfate ions and 166 meq/l of chloride ions,

Flow rate = 16 ml/min; CO₂ pressure = 50 psig ; SO₄/Cl Equivalents ratio = 1.5.

$$K_2 = 0.0137 \text{ [ml}_s\text{/(meq} \cdot \text{min)]}$$

$$K_3 = 0.0960 \text{ [(ml}_s\text{} \cdot \text{ml}_r\text{)/meq}^2\text{]}$$

$$A_{1S} = 109.6 \text{ [dimensionless]}$$

$$A_{2S} = 188.6 \text{ [ml}_r\text{/meq]}$$

$$A_{1C} = 147.7 \text{ [dimensionless]}$$

$$A_{2C} = 210.2 \text{ [ml}_r\text{/meq]}$$

After obtaining all the values of unknowns, a computer program was prepared to solve the coupled differential equations (7.17) and (7.18) by Euler's method. By choosing different values of the constant K_1 , this program was run to calculate the values of C/C_0 for sulfate and chloride as a function of time. The input variables for the computer program such as the sulfate concentration, (SO₄)²⁻/Cl ratio and the flow rate were taken for the "base case" run. Figure 23 and 24 show the calculated breakthrough curves for sulfate and chloride ions as a function of time for different assumed values of

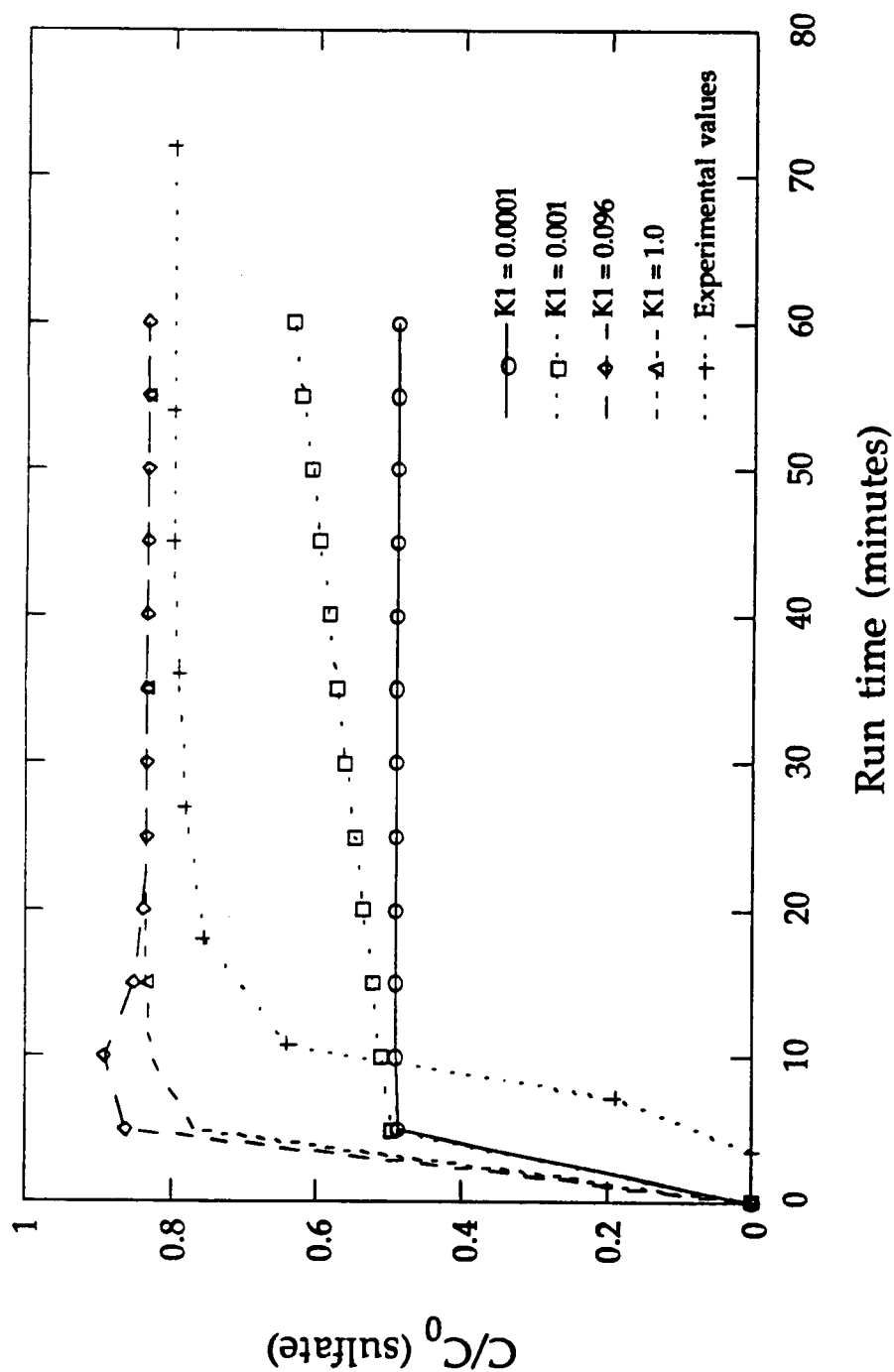


Figure 23: Breakthrough curves for simultaneously carbonated case predicted by the reaction kinetics model for sulfate ion at different values of K_1 . ($K_2 = 0.013$; $K_3 = 0.096$)

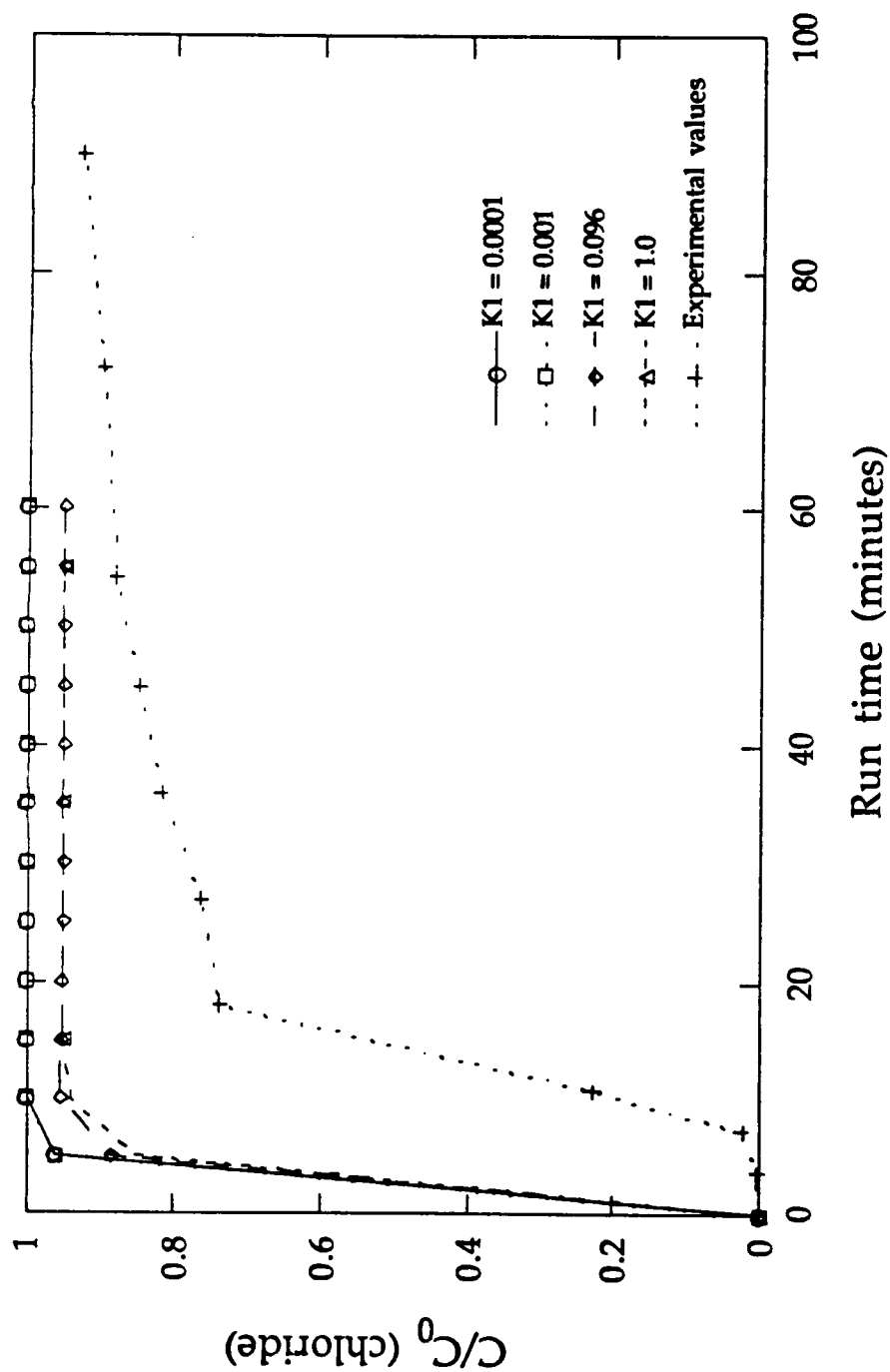


Figure 24: Breakthrough curves for simultaneously carbonated case predicted by the reaction kinetics model for chloride ion at different values of K_1 . ($K_2 = 0.013$; $K_3 = 0.096$)

K_1 , the carbonation reaction constant.

For comparison, model breakthrough curves were also similarly obtained for an sulfate-only case. Strevel's [3] experimental run with an initial concentration of 288 meq/l (about 13,800 ppm) of sulfate ions at 10 psig CO_2 pressure, using simultaneous carbonation procedure was used for such an analysis. The procedure used in calculating the reaction constant for sulfate exchange K_3 , for this case was same as one mentioned earlier. The value of K_3 obtained for the sulfate-only case was 0.001 $[(\text{ml}_s \bullet \text{ml}_r)/\text{meq}^2]$ and is lower than the value of K_3 obtained for the "base case" condition involving both sulfate and chloride ions. This lower value of K_3 may be due to the lower static CO_2 pressure used by Strevel [3]. The Langmuir equilibrium constants A_1 and A_2 for this specific case were similarly calculated from the plot of C/q versus C for sulfate ion. With values of necessary parameters calculated, the computer program used earlier was modified slightly to handle the sulfate-only case. The modified computer program involved only one differential equation (7.18) as this being a sulfate-only case. This modified program is also presented in Appendix A.

ANALYSIS OF RESULTS FROM THE REACTION KINETICS MODEL FOR SIMULTANEOUSLY CARBONATED CASE

In Table 18 the effect of various possible values of the carbonation reaction constant K_1 , on the C/C_0 values is presented for experiments conducted with sulfate and chloride ions and for the sulfate-only cases. For the experiments involving only sulfate ion, we can see from the table that when the value of the carbonation reaction constant K_1 , is equal to or less than that of the sulfate exchange constant K_3 , the C/C_0 values approached a value of 1.0. This means that when the rate of conversion of the hydroxide sites on the resin to the bicarbonate form is equal to or lower than the rate of the sulfate exchange reaction, the resin is totally exhausted in a finite time, and therefore the C/C_0 values reached the limiting value of 1.0. Figure 25 shows the breakthrough curve obtained for the sulfate-only case as a function of time for different values of K_1 . In this figure one can see that when the value of K_1 is equal to K_3 , the reaction rate constant for sulfate at a value of 0.001, the breakthrough curves reached the limiting value of C/C_0 equal to 1.0. Such a behavior of the calculated breakthrough curves was found to be similar to the experimental curve. For the case when the carbonation reaction constant, K_1 was higher than that of the sulfate exchange reaction constant K_3 , (for example, $K_1 = 0.1$; $K_3 = 0.001$) the C/C_0 value leveled off at about 0.95. This could mean that bicarbonate sites were formed on the resin active sites at a

Table 18: Results From Reaction Kinetics Model for Simultaneously Carbonated Case

Conditions	K_1 (Carbonation) $\text{cm}^2/(\text{Kg} \cdot \text{min})$	K_2 (Dechlorination) $\text{ml}_s/(\text{meq} \cdot \text{min})$	K_3 (Desulfurization) $(\text{ml}_s \cdot \text{ml}_p)/\text{meq}^2$	Effect on C/C_0 values
				sulfate chloride
<u>For experiments with sulfate ion only:</u>				
$K_1 = K_3$	0.001	—	0.001	~ 1.00 —
$K_1 < K_3$	0.0005	—	0.001	~ 1.00 —
$K_1 > K_3$	0.1	—	0.001	~ 0.95 —
<u>For experiments with sulfate and chloride ions:</u>				
$K_1 = K_3$	0.096	0.013	0.096	~ 0.83 ~ 0.95
$K_1 < K_3$	0.05	0.013	0.096	~ 0.83 ~ 0.95
$K_1 > K_3$	10.0	0.013	0.096	~ 0.83 ~ 0.95

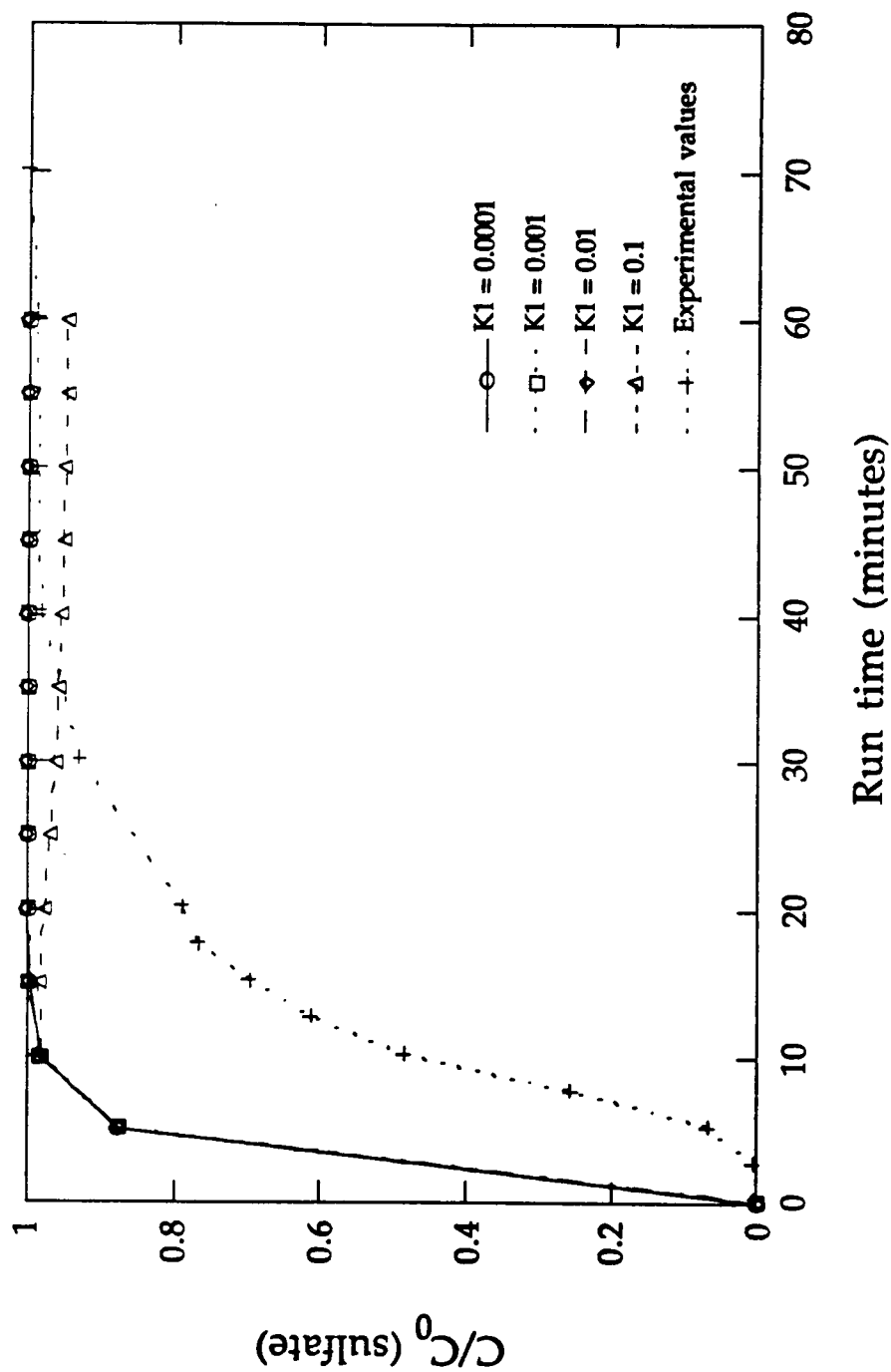
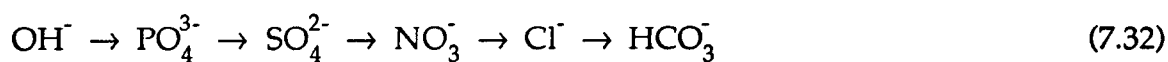


Figure 25: Breakthrough curves for simultaneously carbonated case predicted by the reaction kinetics model for a sulfate-only experimental run at different values of K_1 . ($K_3 = 0.001$)

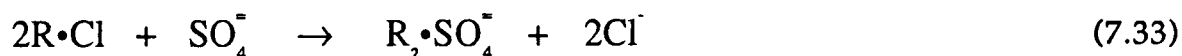
slightly higher rate than the rate at which the sulfate ion would have been exchanged. Hence after a similar amount of time (as in $K_1 \leq K_3$ case) the resin would not be completely exhausted and so the C/C_0 values would not approach 1.0 but instead level off at about 0.95.

For the experiments carried out with a mixture of sulfate and chloride ions, irrespective of the value of K_1 , being equal to or lower or higher as compared to K_3 , the C/C_0 values for sulfate and chloride ions both did not reach a value of 1.0 in finite amount of time. From Figure 23 and 24 for the sulfate and chloride part respectively of the combined sulfate and chloride run, one can see that the breakthrough curve did not approach a C/C_0 value of 1.0 for the range of K_1 values studied. This behavior is similar to that of the experimental results obtained at similar conditions. One possible reason for this kind of behavior could be the influence of chloride ion the sulfate-bicarbonate ion-exchange. Since the chloride ion is present in the affinity chart to the right of the sulfate ion as shown in equation (7.32), the resin has higher affinity for the sulfate ions in comparison to the chloride ions and therefore, would hold more sulfate than chloride ions.



This is reflected in the C/C_0 values for sulfate ion being lower at 0.83 in comparison with the C/C_0 value of 0.95 for the chloride ion in a similar time interval. Because of the resin's preference for the sulfate ions over the

chloride ions in a mixture of both, it is also possible that the chloride sites on the resin would be exchanged for the sulfate ion in the bulk phase as described by the following equation.



As a result, after a finite amount of time, the resin may not be completely exhausted and can still exchange the chloride ions on the resin for the sulfate ions in the bulk phase. Hence the C/C_0 values of the sulfate ion would not reach the limiting value of 1.0 and instead level off at about 0.83. Thus the presence of chloride ion seems to have some kind of influence on the bicarbonate-sulfate exchange for experiments carried out with a mixture of sulfate and chloride ions under the conditions of simultaneous carbonation. Such a behavior was not seen in the precarbonated case due to absence of competition between the carbonation reaction (i.e, the formation of the resin active sites) and the desulfurization/dechlorination (i.e., the consumption of the active sites) reactions.

The kinetic model however, was not able to predict the shape of the breakthrough curve during the early stages of the experiments because of neglecting the axial and radial variations and treating the entire bed as a small differential fixed-bed.

CHAPTER VIII

CONCLUSIONS AND RECOMMENDATIONS

The study of the UTSI's ion-exchange resin-based process for the simultaneous removal of sulfate and chloride from the MHD spent seed in this work yielded information about the behavior of the bicarbonate-sulfate-chloride system. Based on the batch mode experiments, it was concluded that the IRA-68 resin performed better than the other two resins in all aspects. Increasing the temperature had a negative effect on the removal efficiency, since the bicarbonate sites on the resin may be partially converted to hydroxide or carbonate form. A low solution-to-resin volumetric ratio and a multi-stage operation seemed to improve the desired ion removal efficiency. The ion-exchange resin IRA-68 was also found to be capable of removing sulfate and chloride in the presence of carbonate ions. This result will be particularly useful in the MHD system while operating under a high potassium-to-sulfur ratio.

From the fixed-bed experiments the following conclusions were drawn:

- Both the total exchange capacity and the operating exchange capacity of the resin remains approximately the same, irrespective of the anion.
- The total available ion-exchange sites, C_T remained fairly constant for the sulfate-only and chloride-only experiments. For experiments involving both

sulfate and chloride ions, the C_T values were calculated separately for each anion and it was found that their total value was much higher than the experiments involving only one anion. This results needs to be verified by conducting additional experiments with a mixture of sulfate and chloride ions since the value of C_T should be a constant for a particular type of resin.

- Extended precarbonation of the resin gives a higher resin capacity than that achieved with simultaneous carbonation and exhaustion.
- The fixed-bed experiment performed at a higher temperature (45° C) resulted in a lower resin capacity, compared to experiments performed at room temperature.
- The Antonson's fixed-bed model when applied separately to the sulfate and chloride parts of a run with the mixture of sulfate and chloride ions satisfies the experimental data reasonably well.
- Diffusion parameters calculated by applying the Antonson's fixed-bed model for sulfate-only and chloride-only runs decrease with the increase in the respective ionic concentration.
- The diffusion parameter of sulfate-only and chloride-only experiments seem to be slightly lower than when they are in a mixture.
- The diffusion parameter for the sulfate in a mixture with chloride seems to level off at high sulfate-to-chloride equivalent ratios.
- The diffusion parameter for the chloride in a mixture with sulfate seems to decrease with increase in chloride concentration up to a chloride

concentration of 200 meq/l.

- The magnitude of the diffusion parameters calculated in this study are of the same order as reported in previous investigations [2,3].
- For values of carbonation reaction rate constant K_1 , equal to or lower than that of the sulfate reaction constant K_3 , the behavior of the experimental breakthrough curves using the simultaneous exhaustion and carbonation procedure for the sulfate-only case is predicted fairly well by the kinetic model.
- The presence of chloride ion seems to have an influence on the sulfate-bicarbonate exchange for experiments carried out with simultaneous carbonation. This is believed to be due to the resin's preference for the sulfate ions over the chloride ions causing chloride sites on the resin to be exchanged with the sulfate ions in the bulk phase during the intermediate and later portion of an experimental run resulting in the C/C_0 values for sulfate ion not reaching the limiting value of 1.0 in finite time.

For future work the following should be considered:

- Ways and means to speed up the in-situ carbonation of the resin needs to be explored.
- Experiments should be carried out with low sulfate-to-chloride ratios to find out whether the diffusion parameter for the chloride ion would level off at

high chloride concentrations.

- With the available experimental data, no particular trend was observed as to which anion would breakthrough earlier in a mixture of sulfate and chloride ions. More experiments at different ionic concentrations of sulfate and chloride should be carried out to reasonably predict the anion that would breakthrough first.
- The reaction kinetics model considered in this study needs to be combined with an appropriate fixed-bed model to accurately predict the breakthrough curves from experiments involving both sulfate and chloride ions in the integral fixed-bed setup.
- Additional experiments should be carried out to evaluate the effect of the chloride ion on the carbonation of the resin under representative conditions of simultaneous exhaustion and carbonation.

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LIST OF REFERENCES

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APPENDICES

APPENDIX A
COMPUTER PROGRAMS

Antonson's Model Computer Program

```

PROGRAM MATH_MODEL
  NAMELIST /CONTROL/ KK,N,M2,IH,EL,CUT,XZERO,I1,I2,K2,NJ,CON,
  *   /THETA/ EE,/XINC/ HINC
  DOUBLE PRECISION PHI(3,2000),TAU(2000),HINC(20),DE(20,170),
  *   EE(20),NN(20),S(170),EL1(20),E(20,170),prntit,
  *   x,h,psi,pi,sum,derv,xlang,xmuir,p,c,b,chk,con,
  *   cut,xzero,el,t
  OPEN(UNIT=8,STATUS='OLD')
  READ(8,CONTROL)
  READ(8,THETA)
  CLOSE(UNIT=8)
  OPEN(UNIT=10,STATUS='OLD')
  READ(10,XINC)
  CLOSE(UNIT=10)
C
C   *****
C   CALCULATION OF INITIAL AND BOUNDARY CONDITIONS FOR
PHI
C   *****
C
  PHI(2,1) = 0.0d+00
  PI = 3.14159265359
  PSI = PI * PI / 2.0
C
  DO K= 1, KK
    PHI(2,K) = 0.0d+00
  ENDDO
  IF (I2-1) 9,9,8
8   open(unit=25,status='old')
   read(25,*) k2
   do k= 2, kk, 4
     read(25,*) (phi(1,j), j= k,k+3)
   enddo
   close(unit=25)
  GO TO 11
9   DO K= 2, KK
    PHI(1,K) = 1.0d+00
  ENDDO
C
C   *****

```

```

C    CALCULATION OF PARAMETERS FOR USE IN THE FINITE
DIFFERENCE
C    SCHEME
C    *****
C
    sum = 0.0d+00
11 DO J= 1,N
    DE(1,J) = EXP(-PSI*(J**2)*EL)
    E(1,J) = (1.0 - DE(1,J)) / (EL * PSI * (J**2))
    sum = sum + e(1,j)
ENDDO
    OPEN(UNIT=15,STATUS='NEW')
    OPEN(UNIT=16,STATUS='NEW')
    write(15,*) 'l=',1,' nn(l)=' ,n
    do j= 1,n
        write(15,*) 'j=',j,' de(l,j)=' ,DE(1,J)
        write(15,*) 'e(l,j)=' ,E(1,J)
    enddo
    write(15,*) 'EE(l)=' ,ee(1),' sum=' ,sum
    NN(1) = N
    EL1(1) = EL
    DO L= 2,M2
        EL1(L) = EL1(L-1) * 2
        NN(L) = (NN(L-1) * 23) / 32
        N10 = NN(L-1)
        write(15,*) 'l=',L,' nn(l)=' ,nn(l)
        sum = 0.0d+00
        DO J= 1,N10
            DE(L,J) = DE(L-1,J)**2
            E(L,J) = (1.0 - DE(L,J)) / (PSI * EL1(L) * (J**2))
            sum = sum + e(l,j)
            write(15,*) 'j=',j,' de(l,j)=' ,DE(L,J)
            write(15,*) 'e(l,j)=' ,E(L,J)
        enddo
        write(15,*) 'ee(l)=' ,ee(l),' sum=' ,sum
    ENDDO
C
C    *****
C    CALCULATION OF THE TIMES AT WHICH PHI(2,I) IS WRITTEN OUT
C    *****
C
    TAU(1) = 0.0d+00
    DO K= 6,KK,5
        I = ((K - 6) / 30) + 1

```

```

        IF (I-M2) 15,15,14
14      I = M2
15      TAU(K) = TAU(K-5) + 5.0 * EL1(I)
        ENDDO
        NI = 1
        I = I1
        K1 = K2
        X = XZERO
        H = HINC(1)
        write(16,*) 'con =',con
        write(16,*) 'Increment in X=',H
C
C      *****
C      BEGINNING OF FINITE DIFFERENCE SCHEME
C      *****
C
        t = 1.0d+00
        ic = 1
18      DO J= 1,N
            S(J) = 0.0d+00
        ENDDO
        ik = i
        SUM = 0.0d+00
        X = X + H
        XLANG = 0.0d+00
C
        DO K= K1,KK
            C = (PHI(1,K) + 2.0 * H * EE(I) * XLANG - 2.0 * H * SUM) / CON
            B = -(C * CON) + ((1.0 + 2.0 * H * EE(I)) / CON)
            PHI(2,K) = (-B + SQRT((B**2) + 4.0 * C)) / 2.0
            IF (PHI(2,K)-1.0d-07) 20,21,21
20          PHI(2,K) = 0.0d+00
            K2 = K + 1
21          XMUIR = (PHI(2,K) / ( 1.0 + CON * PHI(2,K)))
            DERV = XMUIR - XLANG
            XLANG = XMUIR
            P = ((K -1.0) / 30.0) + 1.0
            IF (P-M2) 23,23,22
22          NK = M2
            I = NK
            GO TO 26
23          Q = INT(P)
            IF (P-Q) 24,24,25
24          NK = I - ik

```

```

        if (k.gt.k1) i = i + 1
        ik = i
        GO TO 26
25    NK = I
26    N10 = NN(NK)
        SUM = 0.0d+00
        DO J= 1,N10
            S(J) = (S(J) + DERV * E(NK,J)) * DE(I,J)
            SUM = SUM + S(J)
        ENDDO
    ENDDO
    prntit = t * (10.0**(ic-2))
    if (x.ge.prntit) then
        write(16,200)
200    format(1x,' X2 ',2X,' THETA2 ',2X,' C/C0 ')
        write(16,201) x,tau(1),phi(2,1),k2,t
201    format(1x,f10.6,2x,f10.5,2x,f12.8,2x,'k1=',i3,1x,'t=',f10.3)
        do j=6,kk,5
            if ((phi(2,j).gt.0.0d+00).and.(phi(2,j).le.0.99999999d+00))
                * WRITE(16,202) tau(j),phi(2,j)
            if (phi(2,j).ge.0.99999999d+00) phi(2,j+5) = phi(2,j+5) + 1.0
202    format(13x,f10.5,2x,f12.8)
        enddo
        t = t + 1.0d+00
        if (t.gt.20.0d+00) t = 1.5d+00
        chk = 10.0 * (2.0**(ic-2))
        if (prntit.ge.chk) ic = ic + 1
    endif
C
C          *****
C    PREPARATION FOR NEXT STEP IN THE X-2 DIRECTION
C          *****
C
    K1 = K2
    I = ((K2 - 2) / 30) + 1
    IF (I-M2) 32,32,29
29    I = M2
32    IF (NI-IH) 31,30,30
30    NI = IH
    GO TO 36
31    NI = (NJ / 30) + 1
    NJ = NJ + 1
36    H = HINC(NI)
    IF (X-CUT) 33,35,35

```

```
33  DO K= K1,KK
    PHI(1,K) = PHI(2,K)
ENDDO
GO TO 18
35  CONTINUE
    open(unit=25,status='new')
    write(25,*) k1
    do k= 2,kk,4
        WRITE(25,*) (PHI(2,j),j= k,k+3)
    enddo
    CLOSE(UNIT=15)
    CLOSE(UNIT=16)
    CLOSE(UNIT=25)
END
```

```
*****
Input for Antonson's Model Program (Data file name : for008.dat)
*****
```

\$CONTROL

KK=571,N= 160,M2=10,IH= 7,EL= 0.00009,CUT= 10.0,
XZERO= 0.0000000,I1= 1,I2= 1,K2= 1,NJ= 1,con=7.200

\$END

\$THETA

EE= 0.8360440826E+02, 0.5897080231E+02, 0.4155220413E+02,
0.2923540115E+02,

0.2052610207E+02, 0.1436770058E+02, 0.1001305103E+02, 0.6933850288E+01,
0.4756525517E+01, 0.3216925144E+01, 0.0000000000E+00, 0.0000000000E+00,
0.0000000000E+00, 0.0000000000E+00, 0.0000000000E+00, 0.0000000000E+00,
0.0000000000E+00, 0.0000000000E+00, 0.0000000000E+00, 0.0000000000

\$END

```
*****
Input for Antonson's Model Program (Data file name : for010.dat)
*****
```

```
$XINC
HINC=    0.125,      0.25      0.5,      1.000
        2.000,      4.000000,   8.000000,   0.00000,
        0.00000,      0.00000,   0.0000000,   0.0000,
        0.00000,      0.0000,    0.0000,     0.00000,
        0.0000000,    0.00000000,  0.0000000,   0.00000
$END
```

Output of Antonson's Model (Data file = for016.dat)

con = 7.2000000000000000

X2	THETA2	C/C0
3.000000	0.00000	0.00000000 k1=122 t= 4.500
0.04770	0.00000198	
0.05490	0.00001372	
0.06210	0.00006406	
0.06930	0.00024811	
0.07650	0.00087456	
0.08370	0.00288402	
0.09810	0.05203786	
0.11250	0.15093176	
0.12690	0.27028973	
0.14130	0.36680482	
0.15570	0.44169508	
0.17010	0.50154705	
0.19890	0.58968997	
0.22770	0.65136980	
0.25650	0.70365500	
0.28530	0.74616402	
0.31410	0.78129233	
0.34290	0.81078146	
0.40050	0.85173785	
0.45810	0.88652269	
0.51570	0.91360860	
0.57330	0.93423575	
0.63090	0.94993355	
0.68850	0.96188309	
0.80370	0.97570658	
0.91890	0.98583099	
1.03410	0.99178179	
1.14930	0.99523749	
1.26450	0.99724084	
1.37970	0.99840173	
1.61010	0.99934321	
1.84050	0.99977904	
2.07090	0.99992592	
2.30130	0.99997518	
2.53170	0.99999169	
2.76210	0.99999722	

2.99250	0.99999907
3.22290	0.99999969

```

*****
Program to calculate resin capacities from sulfate and chloride
breakthrough curves.
*****

```

```

implicit real*8 (a-h,o-z)
dimension x(50),y(50),y1(50)
open (unit=21,file='2ion.inp',status='old')
open (unit=20,file='2ion.dat',status='new')
read(21,*) n,c,c1,flow,rv
do i= 1,n
read (21,*) x(i),y(i),y1(i)
temp = y(i)/c
temp1= y1(i)/c1
y(i)=1.0-temp
y1(i)=1.0-temp1
write(20,*) x(i),temp,temp1
enddo
close (unit=21)
nint=n-1
area=0.0
area1=0.0
do i = 1,nint
area=area + (y(i)+y(i+1))*(x(i+1)-x(i))/2.0
area1=area1+(y1(i)+y1(i+1))*(x(i+1)-x(i))/2.0
enddo
write(20,*) 'the area under sulfate bt curve is',area
write(20,*) 'the area under chloride bt curve is',area1
cap=flow*area*c/(rv*0.746*1.0e+06)
cap1=flow*area1*c1/(rv*0.746*1.0e+06)
write(20,*) 'the sulfate resin capacity is',cap
write(20,*) 'the chloride resin capacity is',cap1
close(unit=20)
stop
end

```

Input for program that calculates equilibrium
resin capacities.

11,56570,1390,16,150

0,0,0

1.3,8,8

3.3,3,3

6.7,79,35

10,1060,65

13.4,11130,72

20,40900,198

26.8,47630,595

33.5,51870,1350

40,54280,1370

47,56570,1390

Output for program that calculates equilibrium resin capacities.

0.0000000000000000E+00	0.0000000000000000E+00	0.0000000000000000E+00
1.3000000000000000	1.4141771256849921E-04	5.7553956834532374E-03
3.3000000000000000	5.3031642213187201E-05	2.1582733812949640E-03
6.7000000000000000	1.3964999116139297E-03	2.5179856115107914E-02
10.0000000000000000	1.8737846915326145E-02	4.6762589928057554E-02
13.4000000000000000	0.1967473926109245	5.1798561151079137E-02
20.0000000000000000	0.7229980555064522	0.1424460431654676
26.8000000000000000	0.8419657062047021	0.4280575539568345
33.5000000000000000	0.9169170938660067	0.9712230215827338
40.0000000000000000	0.9595191797772671	0.9856115107913669
47.0000000000000000	1.0000000000000000	1.0000000000000000

the area under sulfate bt curve is 19.39267367862825
the area under chloride bt curve is 26.07794964028777

the sulfate resin capacity is 0.1568605612153709
the chloride resin capacity is 5.1829633601429848E-03

```

*****
Program to calculate regression coefficients for reaction constants
and Langmuir constants for the reaction kinetics model.
*****
implicit real*8(a-h,o-z)
parameter(nrow=3,ncol=4)
dimension a(3),x(3,4),xt(3,3),y(3),x1(3,3),x1inv(3,3)
dimension y1(3),wkarea(18)
open (unit=5,file='thes2c.inp',status='old')
open (unit=10,file='thes2c.out',status='new')
  do i = 1,nrow
    read(5,*) (x(i,j),j=1,ncol)
    y(i)=x(i,4)
  enddo
write(10,*) 'The x-matrix'
write(10,*)
write(10,1) ((x(i,j),j=1,4),i=1,nrow)
write(10,*)
write(10,*)
write(10,2) (y(i),i=1,nrow)
! ** x transpose formation *****
do i = 1,nrow
  do j = 1,3
    xt(j,i)=x(i,j)
  enddo
enddo
! *** x transpose * x matrix****
do i= 1,3
  do j = 1,3
    c1=0.0
    do k = 1,3
      c1=c1+xt(i,k)*x(k,j)
    enddo
    x1(i,j)=c1
  enddo
enddo
! ** x transpose * Y matrix ***
l1=3
m1=3
n1=1
ixt=3
iy=3
iy1=3
call vmulff(xt,y,l1,m1,n1,ixt,iy,y1,iy1,ier)

```

```

! *****
! ** Inverse of xt*x=x1 matrix*****
n2=3
ix1=3
idgt=5
Call linv2f(x1,n2,ix1,x1inv,idgt,wkarea,ier)
! ** Calculation of regression constants***
l2=3
m2=3
n3=1
ix1inv=3
ia=3
call vmulff(x1inv,y1,l2,m2,n3,ix1inv,iy1,a,ia,ier)
! *****
write(10,*)
write(*,3) ((xt(i,j),j=1,nrow),i=1,3)
write(*,4) ((x1(i,j),j=1,3),i=1,3)
write(*,*) ' The xt * Y matrix'
write(*,6) (y1(i),i=1,3)
write(*,7) ((x1inv(i,j),j=1,3),i=1,3)
write(10,*)
write(10,*) ' The Regression constants are'
do i = 1,3
write(10,8) i,a(i)
enddo
1 format(/4(1x,f15.6))
2 format(1x,f15.6)
3 format(/3(1x,f15.6))
4 format(/3(1x,f15.6))
6 format(1x,f15.6)
7 format(/3(1x,f14.5))
8 format(/1x,'a('i3,')=',f15.6)
end

```

```

*****
Program to calculate theoretical breakthrough curves for sulfate and
chloride ions using the reaction kinetics model.
*****

```

```

implicit real*8(a-h,k,m,o-z)
dimension x(0:720),y(0:720),cs(0:720),cc(0:720),gs(0:720),gc(0:720)
dimension q(0:720),t(0:720)
open(unit=6,file='thes3.out',status='new')
k2=0.0137
k1=0.096
k3=0.096
m=0.34
cs(0)=0.0
cc(0)=0.0
c0s=0.250
c0c=0.166
! x(i)=cs(i)/c0s
! y(i)=cc(i)/c0c
f=16
vr=112
dt=0.1
! pco2 is CO2 pressure in kg/cm2
pco2=3.402
a1s=109.6
a2s=188.6
a1c=147.7
a2c=210.2
ct=1.793
x(0)=0.0
y(0)=0.0
! *** Start Euler method*****
do i = 0,600
t(i)=(i)*dt
q(i)=(a1s*cs(i)/(1+a2s*cs(i)))+(a1c*cc(i)/(1+a2c*cc(i)))
gs(i)=(f/(m*vr))*(1.0-x(i)) - (k3*x(i)/m)*((ct*(1.0-exp(-k1*pco2*t(i)))
$-q(i)**2)
gc(i)=(f/(m*vr))*(1.0-y(i)) - (k2*y(i)/m)*(ct*(1.0-exp(-k1*pco2*t(i)))
$-q(i))
x(i+1)= x(i)+dt*gs(i)
y(i+1)= y(i)+dt*gc(i)
cs(i+1)=c0s*x(i+1)
cc(i+1)=c0c*y(i+1)
enddo

```

```

do i = 0,600,50
write(*,1) i,x(i),i,y(i)
write(6,1) i,x(i),i,y(i)
write(6,2) i,t(i)
write(*,2) i,t(i)
enddo
write(6,3) k1,k2,k3
write(*,3) k1,k2,k3
1  format(/1x,'x(',i4,')=' ,f14.6,2x,'y(',i4,')=' ,f14.6)
2  format(/1x,'t(',i4,')=' ,f14.6)
3  format(1x,'K1=' , f14.6,2x,'K2=' ,f14.6,2x,'K3=' ,f14.6)
end

```

Output of reaction kinetics model for the case of two anions.

K1= 0.096000 K2= 0.013700 K3= 0.096000

x(0)= 0.0000 y(0)= 0.0000 t(0)= 0.0000

x(50)= 0.8629 y(50)= 0.8851 t(50)= 5.0000

x(100)= 0.8913 y(100)= 0.9536 t(100)= 10.0000

x(150)= 0.8502 y(150)= 0.9528 t(150)= 15.0000

x(200)= 0.8376 y(200)= 0.9510 t(200)= 20.0000

x(250)= 0.8347 y(250)= 0.9505 t(250)= 25.0000

x(300)= 0.8342 y(300)= 0.9504 t(300)= 30.0000

x(350)= 0.8341 y(350)= 0.9504 t(350)= 35.0000

x(400)= 0.8340 y(400)= 0.9504 t(400)= 40.0000

x(450)= 0.8340 y(450)= 0.9504 t(450)= 45.0000

x(500)= 0.8340 y(500)= 0.9504 t(500)= 50.0000

x(550)= 0.8340 y(550)= 0.9504 t(550)= 55.0000

x(600)= 0.8340 y(600)= 0.9504 t(600)= 60.0000

```

*****
Program to calculate theoretical breakthrough curve
for sulfate-only case using the reaction kinetics model.
*****

implicit real*8(a-h,k,m,o-z)
dimension x(0:720),cs(0:720),gs(0:720)
dimension q(0:720),t(0:720)
open(unit=6,file='thes3d.out',status='new')
k1=0.1
k3=0.001079
m=0.369
cs(0)=0.0
c0s=0.2875
! x(i)=cs(i)/c0s
f=11
vr=73
dt=0.1
! pco2 is CO2 pressure in kg/cm2
pco2=0.68
a1s=11.88
a2s=17.00
ct=3.4375
x(0)=0.0
! *** Start Euler method*****
do i = 0,600
t(i)=(i)*dt
q(i)=(a1s*cs(i)/(1+a2s*cs(i)))
gs(i)=(f/(m*vr))*(1.0-x(i)) - (k3*x(i)/m)*((ct*(1.0-exp(-k1*pco2*t(i)))
$-q(i))*2)
x(i+1)= x(i)+dt*gs(i)
cs(i+1)=c0s*x(i+1)
enddo
do i = 0,600,50
write(*,1) i,x(i),i,t(i)
write(6,1) i,x(i),i,t(i)
enddo
write(6,3) k1,k3
write(*,3) k1,k3
1 format(1x,'x(' ,i4,')=' ,f14.6,1x,'t(' ,i4,')=' ,f14.6)
3 format(1x,'K1=' ,f14.6,2x,'K3=' ,f14.6)
end

```

Output of reaction kinetics model for sulfate-only case.

K1 = 0.001 ; K3 = 0.001079

x(0)=	0.0000	t(0)=	0.0000
x(50)=	0.8744	t(50)=	5.0000
x(100)=	0.9825	t(100)=	10.0000
x(150)=	0.9960	t(150)=	15.0000
x(200)=	0.9977	t(200)=	20.0000
x(250)=	0.9980	t(250)=	25.0000
x(300)=	0.9981	t(300)=	30.0000
x(350)=	0.9982	t(350)=	35.0000
x(400)=	0.9983	t(400)=	40.0000
x(450)=	0.9983	t(450)=	45.0000
x(500)=	0.9984	t(500)=	50.0000
x(550)=	0.9985	t(550)=	55.0000
x(600)=	0.9986	t(600)=	60.0000

APPENDIX B
FIXED-BED EXPERIMENTAL DATA

Summary of fixed-bed experimental conditions and results

Run	Solution conc. (meq/lit)		Eq. ratio SO ₄ /Cl	Resin vol. (ml)	Flow (ml/min)	CO ₂ Pr. (psig)	Total capacity (meq/ml _{resin})		Optg. capacity (meq/ml _{resin})		Procedure
	SO ₄	Cl					SO ₄	Cl	SO ₄	Cl	
001	242	32	7.5	150	30	0	1.51	0.17	1.10	0.11	1
002	963	121	8.0	150	20	0	1.41	0.27	0.20	0.13	1
003	208	28	7.5	150	18	0	1.37	0.12	0.93	0.07	1
004	417	56	7.5	150	18	0	1.40	0.17	0.66	0.04	1
005	435	0	∞	150	25	50	1.38	0.00	0.06	0.00	3
006	382	249	1.5	150	23	50	0.92	0.72	0.15	0.27	3
007	242	358	0.7	150	13	50	0.41	0.83	0.15	0.45	3
008	246	163	1.5	150	16	50	1.53	1.00	1.02	0.58	2
009	513	0	∞	100	11	10	1.53	0.00	0.67	0.00	3
010	0	372	0	150	16	50	0.00	1.85	0.00	1.18	2
011	229	150	1.5	150	16	50	0.93	0.54	0.17	0.16	3
012	381	0	∞	150	16	50	1.82	0.00	1.25	0.00	2
013	586	0	∞	150	16	50	2.20	0.00	1.34	0.00	2
014	0	569	0	150	16	50	0.00	2.17	0.00	1.41	2
015	352	237	1.5	150	16	50	1.11	0.80	0.53	0.48	2
016	123	77	1.6	150	16	50	1.56	0.86	1.25	0.53	2
017	0	211	0	150	16	50	0.00	1.95	0.00	1.47	2
018	208	0	∞	150	16	50	2.33	0.00	1.86	0.00	2

Run	Solution conc.		Eq. ratio	Resin vol. (ml)	Flow (ml/min)	CO ₂ Pr. (psig)	Total capacity (meq/ml _{resin})		Optg. capacity (meq/ml _{resin})	Procedure
	SO ₄	Cl					SO ₄	Cl		
	SO ₄	Cl	SO ₄ /Cl				SO ₄	Cl		
019	192	203	0.9	150	16	50	1.12	1.01	0.83	2
020	1017	42	24	150	16	50	3.00	0.11	1.54	2
021	406	17	24	150	16	50	2.34	0.07	1.72	2
022	244	161	1.5	150	16	50	1.37	0.80	1.03	2†
023	189	239	0.8	150	16	50	0.97	1.37	0.68	2
024	1179	39	30	150	16	50	3.26	0.14	1.85	2

† High temperature run (45° C)

Fixed-bed experimental run data

Run 1:

Time (min)	C/C_0 (sulfate)	C/C_0 (chloride)
0.0	0.000	0.000
6.0	0.020	0.010
12.0	0.025	0.010
18.0	0.034	0.217
24.0	0.370	0.791
30.0	0.862	0.886
36.0	1.000	0.940
42.0	1.000	1.000

Run 2:

Time (min)	C/C_0 (sulfate)	C/C_0 (chloride)
0.0	0.000	0.000
4.0	0.245	0.003
8.0	0.533	0.136
12.0	0.815	0.480
16.0	0.924	0.774
20.0	0.954	0.924
24.0	0.980	0.964
28.0	1.000	1.000

Run 3:

Time (min)	C/C_0 (sulfate)	C/C_0 (chloride)
0.0	0.000	0.000
8.0	0.000	0.000
16.0	0.000	0.025
24.0	0.000	0.350
32.0	0.120	0.650
40.0	0.380	1.000

Run 3: (continued)

Time (min)	C/C_0 (sulfate)	C/C_0 (chloride)
48.0	0.900	1.000
56.0	0.980	1.000
64.0	1.000	1.000

Run 4:

Time (min)	C/C_0 (sulfate)	C/C_0 (chloride)
0.0	0.000	0.000
8.0	0.003	0.090
16.0	0.254	0.195
24.0	0.735	0.782
32.0	0.917	0.976
40.0	0.981	1.000
48.0	1.000	1.000

Run 5:

Time (min)	C/C_0 (sulfate)
0.0	0.000
7.0	0.740
14.0	0.813
21.0	0.816
28.0	0.796
35.0	0.761
42.0	0.777
49.0	0.851
56.0	0.794

Run 6:

Time (min)	C/C ₀ (sulfate)	C/C ₀ (chloride)
0.0	0.000	0.000
5.0	0.238	0.028
10.0	0.746	0.540
15.0	0.835	0.783
20.0	0.864	0.850
25.0	0.833	0.819
30.0	0.857	0.862
35.0	0.841	0.852
40.0	0.870	0.893

Run 7:

Time (min)	C/C ₀ (sulfate)	C/C ₀ (chloride)
0.0	0.000	0.000
5.0	0.029	0.006
10.0	0.306	0.033
15.0	0.754	0.267
20.0	0.838	0.596
25.0	0.854	0.825
30.0	0.875	0.875
35.0	0.945	0.959
40.0	0.861	0.869

Run 8:

Time (min)	C/C ₀ (sulfate)	C/C ₀ (chloride)
0.0	0.000	0.000
3.6	0.000	0.000
7.2	0.000	0.000
10.8	0.000	0.005
18.0	0.000	0.005
27.0	0.015	0.071

Run 8: (continued)

Time (min)	C/C ₀ (sulfate)	C/C ₀ (chloride)
36.0	0.278	0.497
54.0	0.939	0.745
72.0	0.966	0.969
90.0	1.000	1.000

Run 9:

Time (min)	C/C ₀ (sulfate)
0.0	0.000
2.7	0.000
5.2	0.003
7.7	0.006
10.2	0.081
12.7	0.206
15.2	0.353
20.2	0.593
30.2	0.902
40.2	0.980
60.2	1.000

Run 10:

Time (min)	C/C ₀ (chloride)
0.0	0.000
3.6	0.000
7.2	0.002
10.8	0.002
18.0	0.003
27.0	0.142
36.0	0.553
45.0	1.000
54.0	1.000
72.0	1.000

Run 11:

Time (min)	C/C ₀ (sulfate)	C/C ₀ (chloride)
0.0	0.000	0.000
3.6	0.001	0.003
7.2	0.189	0.024
10.8	0.640	0.226
18.0	0.755	0.737
27.0	0.780	0.764
36.0	0.791	0.817
45.0	0.800	0.848
54.0	0.800	0.880
72.0	0.800	0.898
90.0	0.800	0.930

Run 12:

Time (min)	C/C ₀ (sulfate)
0.0	0.000
3.6	0.000
10.8	0.001
16.2	0.001
21.6	0.005
32.4	0.456
43.2	0.938
54.0	1.000
64.8	1.000
75.6	1.000
86.4	1.000

Run 13:

Time (min)	C/C ₀ (sulfate)
0.0	0.000
2.4	0.000
7.2	0.001

Run 13: (continued)

Time (min)	C/C_0 (sulfate)
14.4	0.020
21.6	0.258
28.8	0.693
36.0	0.908
43.2	0.980
50.4	0.988
57.6	1.000

Run 14:

Time (min)	C/C_0 (chloride)
0.0	0.000
2.4	0.000
7.2	0.001
14.4	0.003
21.6	0.188
28.8	0.668
36.0	0.955
43.2	0.980
50.4	0.995
57.6	1.000

Run 15:

Time (min)	C/C_0 (sulfate)	C/C_0 (chloride)
0.0	0.000	0.001
2.4	0.000	0.001
7.2	0.002	0.005
14.4	0.121	0.046
21.6	0.550	0.414
28.8	0.834	0.791
36.0	0.951	0.988

Run 15: (continued)

Time (min)	C/C ₀ (sulfate)	C/C ₀ (chloride)
43.2	0.965	0.973
50.4	1.000	0.993
57.6	1.000	1.000

Run 16:

Time (min)	C/C ₀ (sulfate)	C/C ₀ (chloride)
0.0	0.000	0.000
7.2	0.001	0.002
14.4	0.002	0.003
28.8	0.002	0.003
43.2	0.005	0.011
57.6	0.009	0.231
72.0	0.054	0.378
86.4	0.364	0.396
100.8	0.836	0.880
115.2	0.847	0.949

Run 17:

Time (min)	C/C ₀ (chloride)
0.0	0.000
7.2	0.001
14.4	0.001
28.8	0.001
43.2	0.011
57.6	0.275
72.0	0.839
86.4	0.886
100.8	0.958
115.2	1.000
130.0	1.000

Run 18:

Time (min)	C/C ₀ (sulfate)
0.0	0.000
7.2	0.000
14.4	0.000
28.8	0.000
43.2	0.000
57.6	0.001
72.0	0.190
86.4	0.917
100.8	0.970
115.2	0.980
130.0	1.000

Run 19:

Time (min)	C/C ₀ (sulfate)	C/C ₀ (chloride)
0.0	0.000	0.000
3.6	0.000	0.000
7.2	0.002	0.000
18.0	0.003	0.005
27.0	0.017	0.093
36.0	0.233	0.588
45.0	0.739	0.934
54.0	0.967	0.992
72.0	1.000	1.000
90.0	1.000	1.000

Run 20:

Time (min)	C/C ₀ (sulfate)	C/C ₀ (chloride)
0.0	0.000	0.000
1.4	0.000	0.001
3.5	0.000	0.001
7.0	0.002	0.020

Run 20: (continued)

Time (min)	C/C ₀ (sulfate)	C/C ₀ (chloride)
10.5	0.047	0.076
14.0	0.224	0.368
21.0	0.575	0.596
28.0	0.879	0.967
35.0	0.953	0.960
42.0	0.953	0.987
49.0	0.977	1.000

Run 21:

Time (min)	C/C ₀ (sulfate)	C/C ₀ (chloride)
0.0	0.000	0.000
3.6	0.000	0.002
7.2	0.004	0.012
18.0	0.002	0.053
27.0	0.011	0.100
36.0	0.401	0.542
45.0	0.826	1.000
54.0	0.933	1.000
72.0	0.935	1.000
90.0	1.000	1.000

Run 22:

Time (min)	C/C ₀ (sulfate)	C/C ₀ (chloride)
0.0	0.000	0.000
3.6	0.000	0.000
7.2	0.000	0.001
18.0	0.001	0.002
27.0	0.023	0.123
36.0	0.350	0.467
45.0	0.799	1.000
54.0	0.955	1.000
72.0	0.999	1.000
90.0	1.000	1.000

Run 23:

Time (min)	C/C ₀ (sulfate)	C/C ₀ (chloride)
0.0	0.000	0.000
3.6	0.001	0.001
7.2	0.002	0.002
18.0	0.002	0.007
27.0	0.115	0.032
36.0	0.544	0.318
45.0	0.843	0.754
54.0	1.000	0.955
72.0	1.000	0.986
90.0	1.000	1.000

Run 24:

Time (min)	C/C ₀ (sulfate)	C/C ₀ (chloride)
0.0	0.000	0.000
1.3	0.000	0.006
3.3	0.000	0.002
6.7	0.001	0.025
10.0	0.019	0.047
13.4	0.197	0.052
20.0	0.723	0.142
26.8	0.842	0.428
33.5	0.917	0.971
40.0	0.960	0.986
47.0	1.000	1.000

VITA

Santhanam Parthasarathy was born in Madras, India on October 28th 1968. From 1978 to 1985 he attended Sri Ramakrishna Mission Higher Secondary School at Madras. After finishing his high school, he entered the Regional Engineering College at Rourkela, and graduated with a Bachelor of Science Degree in Chemical Engineering. In October 1989, he joined Hindustan Petroleum Corporation at Visakhapatnam, India and worked as a Process Engineer for two and a half years. In August 1992, he entered the University of Tennessee Space Institute at Tullahoma, for a Master of Science Degree in Chemical Engineering.