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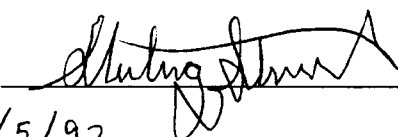
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THE ANION-EXCHANGE RESIN BASED DESULFURIZATION CONCEPT

A Thesis

Presented for the

Master of Science

Degree

The University of Tennessee, Knoxville

Sterling D. Strevel

December 1992

To My Mother
Vera G. Strevel
(Talks of Life)
and
My Father
Tedford M. Strevel
(Source of Pride)

ACKNOWLEDGEMENTS

I would like to thank my major professor, Dr. Atul C. Sheth, and the other members of my committee, Dr. Lloyed W. Crawford and Dr. Narendra B. Dahotre, for their guidance and comments on my thesis. I would also like to thank my parents, siblings, and friends for their infinite understanding and patience during this educational nightmare of mine. Special thanks should also be given to Norbert M. Ulbrich who provided an understanding ear for my problems of the past two years. I would like to express my thanks to the faculty and staff of The University of Tennessee Space Institute for providing me with a place conducive to learning. In closing I would also like to thank the Department of Energy for providing me with the means to my graduate degree.

ABSTRACT

Since SO_2 -emission from conventional power plants, the paper industry, and future coal-fired Magnetohydrodynamic (MHD) based power plants can be controlled with the injection of alkali metals or alkaline earth metal compounds, a cost-efficient and reliable method of desulfurization is needed. This thesis will further develop the anion-exchange resin-based desulfurization concept put forth by Butler (UTSI 1986) and Modeste (UTSI 1988). This thesis covers the following: screening of commercially available resins, developing a batch procedure to choose the three best candidate resins, designing the bench-scale fixed-bed system, developing the fixed-bed experimental procedure, carrying out process variable study, converting Antonson's computer program for use on the UTSI computer system (Northwestern 1968), analyzing the fixed-bed experimental runs using Antonson's model, and choosing the best resin(s) for future study. After the analysis of the fixed-bed data, no resin out-performed the others for all of the process variables. The final determination as to the best resin must wait until the cyclic operations and the regeneration optimization investigations are complete.

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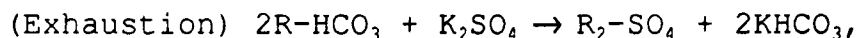
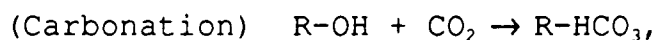
LIST OF SYMBOLS

- A: area under the $(1 - C/C_0)$ vs. time curve (min)
- a_1 : first Langmuir constant (dimensionless)
- a_2 : second Langmuir constant (ml/gm)
- C: concentration of sulfate (gm/ml solution)
- C_0 : bulk sulfate concentration (gm/ml solution)
- C_T : effective concentration of adsorption sites (gm/ml resin)
- $\bar{C}_T$: total concentration of adsorption sites (gm/ml resin)
- D: intraparticle diffusion coefficient (cm^2/s)
- k_1 : forward reaction rate
- k_2 : backward reaction rate
- l: step-size of θ
- m: ratio of void to resin fraction (dimensionless)
- ϕ : C/C_0 (dimensionless)
- q: average sulfate concentration on resin (gm/ml resin)
- q_∞ : capacity of resin (gm/ml resin)
- R: radius of resin bead (cm)
- θ : $2D\theta_A/R^2$ (dimensionless)
- θ_A : $t - z/v$ (s)
- t: time (s)
- v: linear (superficial) velocity (cm/s)
- V: volumetric flow-rate (cc/min)
- X: dimensionless column length ($3Da_1z/mvR^2$)
- z: resin height in column (cm)

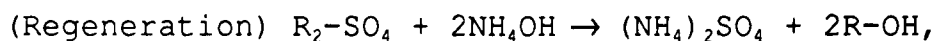
CHAPTER I

INTRODUCTION

In a coal-fired magnetohydrodynamic (MHD) power system, the power is produced primarily by passing a conductive plasma through a magnetic field and secondarily by producing high pressure steam from the residual heat downstream of the secondary combustor. In a coal-fired MHD system potassium seed is injected in carbonate form upstream of the magnetic field to increase the conductivity of the plasma and to act as a sulfur scavenger. Therefore, the recycling of the potassium is necessary to reduce the operational costs. These costs include both the purchase of new potassium carbonate (seed) and the disposal of the potassium sulfate (spent seed). In previous studies [1,2], a low-cost and efficient method of seed regeneration was developed. The proof of concept was performed by Butler [1], wherein both batch and fixed-bed studies were carried out using IRA-68, a weak-base anion exchange resin. The three-step process studied by Butler consisted of regeneration, carbonation, and exhaustion. The reactions are



and



where R is the complex cation group present in the resin.

Modeste [2] modified the above process by combining the carbonation and exhaustion steps. The reactions are

(Carbonation-Exhaustion) $2R-OH + 2CO_2 + K_2SO_4 \rightarrow R_2-SO_4 + 2KHCO_3$
and

(Regeneration) $R_2-SO_4 + 2NH_4OH \rightarrow (NH_4)_2SO_4 + 2R-OH$.

The work of Modeste continued the exclusive use of IRA-68.

In the present investigation, which is supported by a Department of Energy (DOE) grant, an exhaustive literature search was performed to determine the best resin testing procedure, to find any model innovations, and to find ion-exchange resin applications where a high inlet solution concentrations were used.

The non-linear equilibrium model developed by Antonson [3] will be used in this study to determine the solid phase diffusion coefficients for the fixed-bed runs involving the evaluation of the effects of concentration, superficial velocity, CO_2 -pressure, and dissolved impurities. The program developed by Antonson was modified for use on the present computer system at the University of Tennessee Space Institute (UTSI). The modified program's results were compared to the model's results from Sheth [4] as a verification.

In this study the best of the commercially available resins will be chosen for further study. All of the candidate resins will be screened by a batch experimental procedure developed for the purpose. The parameters with which the

batch evaluation will determine the best three resins include cation (other alkali metals) effects, cycle efficiency, concentration effects and the effect of dissolved impurities (spent seed). The three resins will then be evaluated by a fixed-bed procedure. The process variables used in the fixed-bed evaluations include static CO_2 -pressure, solution concentration, product inhibition, resin bed height, dissolved impurities, and superficial velocity.

CHAPTER II

LITERATURE REVIEW

The literature surveyed covers ion-exchange models, resin testing, and applications. The kinetic theories of Fick and Nernst-Planck are models for ideal systems. These models use curve fitting to interpret the kinetics of an ion-exchange system. The resulting conclusions are sometimes misleading because the model is not case specific. These models should be considered only as approximations to the physico-chemical systems being investigated [5]. The Nernst-Planck model has been used to analyze intraparticle mass transfer in ternary systems with constant self-diffusivities and particle diameter [6]. The Nernst-Planck non-linear equations of ionic motion are used to calculate the ideal limiting laws for the kinetics of particle diffusion in batch experiments with uniform bead size and ions of different mobilities [7]. Other models found in the literature are listed below:

- multicomponent model of mass-action equilibria which discusses the inversion of resin affinities [8]
- thermodynamic model which defines surface excess as the separative characteristics of ion exchangers [9]
- dimensionless numerical model for the constant-pattern pore- and solid- diffusion mechanisms which includes external mass transfer for irreversible equilibrium [10]

- zone height model based on a counter-current system with infinite bed height [11]
- linear mass transfer model for cyclic operation and co-current regeneration [12]
- simple physical model of coherent waves that defines their interference on multicomponent adsorption [13]
- ideal solid-solution model which considers the ionic interaction in calculating the thermodynamic equilibrium constants for the batch experimental method [14]
- multicomponent model which predicts the ion exchange equilibria from binary data [15]
- Wilson model which is used to calculate the solid phase activity coefficients [15]
- pore diffusion model based on the orthogonal collocation method which utilizes both batch and fixed-bed data [16]
- shrinking core model for batch experiments with Ligand exchange [17]
- model for cyclic systems with concave Langmuir isotherms [18]
- shell progressive, shrinking core, model with changing concentration and column volume [19].

In the literature resin testing is exhaustively described. Resin is tested for quality and deterioration by analyzing for total chemical capacity and physical strength [20]. Tests of gel resins result in the conclusions that particle size affects uptake rate and electrolyte invasion

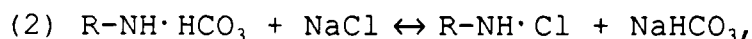
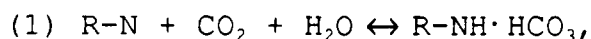
depends strongly on counter-ion valence and also governs the uptake rate [21]. Anion resin was tested for sulfate leakage by McNulty [22]. The leakage was directly related to the harmonic mean particle size of the anion resin in the mixed bed. Macroreticular resin structure with pore diameters between 10-100Å and 100-10000Å were shown to enhance chemical accessibility and mass transfer of ions and/or molecules by Lee [23]. The effect of cross-linking was evaluated by Glueckauf [24], and low cross-linking resulted in faster equilibrium. Equilibrium testing was performed for a porous exchanger batch system by Patell [25].

Anion-exchange resins were tested for stability and regenerant efficiency by Calmon [26]. These resins are distinguished by their functional groups: trimethyl groups (Type I) and dimethyl-ethanol groups (Type II). Type II resins were found to be less stable but they have higher regenerant efficiency than Type I resins. Tertiary amine oxide groups were found to give greater physical stability and to have less volume change during acid-base cycling than the aromatic tertiary amine group [26].

Glueckauf [24] found that ion-exchange operations can be optimized by using small particle size, large ratios of distribution coefficients, sufficiently small EHTP (Effective Height of the Theoretical Plate), a sufficiently large number of theoretical plates, the optimum solution concentration, and a displacing mixture with stronger ionic species. Some other

examples of related optimization work can be found in the references [27-36].

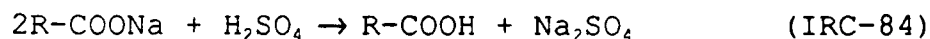
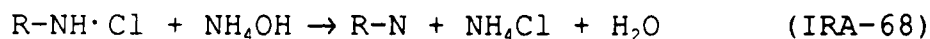
Some ion-exchange applications using weak electrolyte resin are the DESAL process or a modification of the DESAL process and SUL-BI-SUL processes. The DESAL process was created for use with 500-3000 ppm salinity brackish waters-- acid mine drainage and sewage plants. The DESAL process consist of an anion-, a cation- and an anion-exchange columns in series. The anion columns contain weak base resins (IRA-68). The cation column contains weak acid resin (IRC-84). The procedure is to (1) convert the weak base resin to a bicarbonate salt, (2) convert the bicarbonate salt to an alkali salt, and (3) convert the weak acid free base form to a sodium form. The chemical reactions involved are



and



where R is the resin's functional groups. The regeneration of the resins can be described by the following equations:



Modifications to the DESAL process consist of combining the carbonation and alkalization steps, increasing CO₂ pressure, and regeneration with lime instead of ammonia [37]. Additional modifications were implemented by Popper [38]. The

DESAL concept has also been used in the work of other investigators, including Wilmoth [39] and Popper [38] who used 2000-3000 ppm sulfate and which used 2000-10000 ppm salt concentrations, respectively.

The SUL-BI-SUL process consists of replacing the sulfate ion on an anion-exchange resin with a bisulfate ion and the anion to be removed. The advantage of this process is its use of a hydrated lime slurry for regeneration. The lime slurry is less expensive than sodium hydroxide. The SUL-BI-SUL process has also been used in the treatment of acid mine drainage [40].

Other applications of ion-exchange include scale prevention in process units [41,42], removal of organics [43-45], removal of nitrates [46], removal of ammonia [47], removal of sulfates [48], removal of decontamination solvents [49], potassium recovery from potash [50], removal of boron [51], and MHD seed regeneration [1,2,52].

CHAPTER III

THEORY

The fixed-bed ion-exchange process consists of an exchange of ions between a mobile (liquid) and stationary (solid) phase, where the mobile phase is of a known concentration and the stationary phase is subjected to the mobile phase concentration in a step-wise fashion. The mobile phase ideally will pass through the stationary phase with a constant flow-rate (plug flow). The mobile phase concentration of the effluent will increase with time. A plot of this increase in concentration over time is called a breakthrough curve. The differential material balance for a fixed-bed is given by:

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

Where C is the concentration of the mobile phase, V is the flow-rate, q is the concentration in the stationary phase, and m is the ratio of void to solid fraction in the stationary phase (fixed-bed), and z is the height of the stationary phase (fixed-bed). When the proper equilibrium and mass transfer constraints are applied to equation (1) a solution can be obtained that will predict the behavior of an ion-exchange system. The constraints used in the present study include the non-linear Langmuir equilibrium, the stationary phase

diffusion, and the external liquid film diffusion [2,3]. The resulting partial-integro differential equation is given by:

$$\frac{\partial \phi}{\partial X} = -2 \sum_{n=1}^{\infty} \int_0^{\theta} \frac{\partial (\phi / (1 + a_2 C_0 \phi))}{\partial \lambda} e^{-\frac{1}{2} n^2 \pi^2 (\theta - \lambda)} d\lambda, \quad (2)$$

where

$$X = \frac{3Da_1 z}{mR^2 v}$$

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

The ϕ stands for the concentration at any time divided by the initial concentration (C / C_0). a_1 and a_2 are the first and second Langmuir constants from the Langmuir Isotherm defined by

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

The D is the intraparticle diffusion coefficient. The R symbolizes the spherical radius of the particles. v stands for the linear velocity in the packed bed. t is the time, and λ is a dummy integration variable. The boundary condition for equation (2) is $\phi(X = 0) = 1$. The initial conditions are $\phi(\theta = 0) = 0$ and $q_1(\theta = 0) = 0$ [2,3]. A more detailed treatment of this derivation can be found in [2,3].

The finite difference method used to solve equation (2)

consists of dividing the equation into a large number intervals. Then the second mean value theorem of calculus is applied to the equation to yield:

$$\frac{\partial \phi}{\partial X} = -2 \sum_{n=1}^{\infty} \sum_{k=0}^M \left[\frac{\partial \phi}{\partial \lambda} \right]_{k+\alpha l} \int_{kl}^{(k+1)l} e^{-\frac{1}{2} n^2 \pi^2 (\theta - \lambda)} d\lambda, \quad (3)$$

where

$$0 < \alpha < 1$$

$$l = \Delta \theta$$

$$M = \frac{\theta - l}{l}.$$

Following the application of some additional substitutions and integrations and of the Colwell's recursive technique [53], a second order polynomial equation is obtained. The polynomial and the solution are given by:

$$\phi^2(i+1, M+1) + \beta \phi(i+1, M+1) - \gamma = 0 \quad (4)$$

$$\phi(i+1, M+1) = \frac{-\beta + \sqrt{\beta^2 + 4\gamma}}{2}, \quad (5)$$

where

$$\gamma = \frac{\phi(i, M+1) + 2hEE(l) \frac{\phi(i+1, M)}{1 + a_2 C_0 \phi(i+1, M)} - 2h \sum_{n=1}^N S_n(M-1)}{a_2 C_0} \quad (6)$$

$$\beta = \frac{-(\gamma a_2 C_0) + (1 + 2hEE(l))}{a_2 C_0}. \quad (7)$$

The term $EE(l)$ above is defined as follows:

$$EE(l) = \sum_{n=1}^{\infty} \frac{1 - e^{-\frac{1}{2}n^2\pi^2 l}}{n^2\pi^2 l}. \quad (8)$$

This infinite sum can be approximated with a formula derived by Paterson [54] as:

$$EE(l) \approx -\frac{1}{2} + \frac{\sqrt{2\pi l}}{\pi l}. \quad (9)$$

The $S_n(M-1)$ term can be defined as

$$S_n(M-1) = e^{-\frac{1}{2}n^2\pi^2 l} \left(S_n(m-2) + 2 \left[\frac{\phi(i+1, M)}{1 + a_2 C_0 \phi(i+1, M)} - \frac{\phi(i+1, M-1)}{1 + a_2 C_0 \phi(i+1, M-1)} \right] \frac{1 - e^{-\frac{1}{2}n^2\pi^2 l}}{n^2\pi^2 l} \right), \quad (10)$$

where

$$S_n(-1) = 0.$$

A more detailed treatment of the computer scheme's derivation is given by Antonson [3].

The actual computer code is given in Appendix A along with an example of its typical input and output. The program was modified to run on the UTSI computer system. To check the program after the modifications were made, the results for an $a_2 C_0$ of 4.2 and a X of 1.0 were compared with the same from

Sheth [4]. This value of a_2C_0 was chosen because it was mid-range of the experimental a_2C_0 -values. Figure 1 shows the results from the modified program and those obtained from Sheth's master's thesis. The differences are minor and probably caused by the use of the double precision representation used in the modified program.

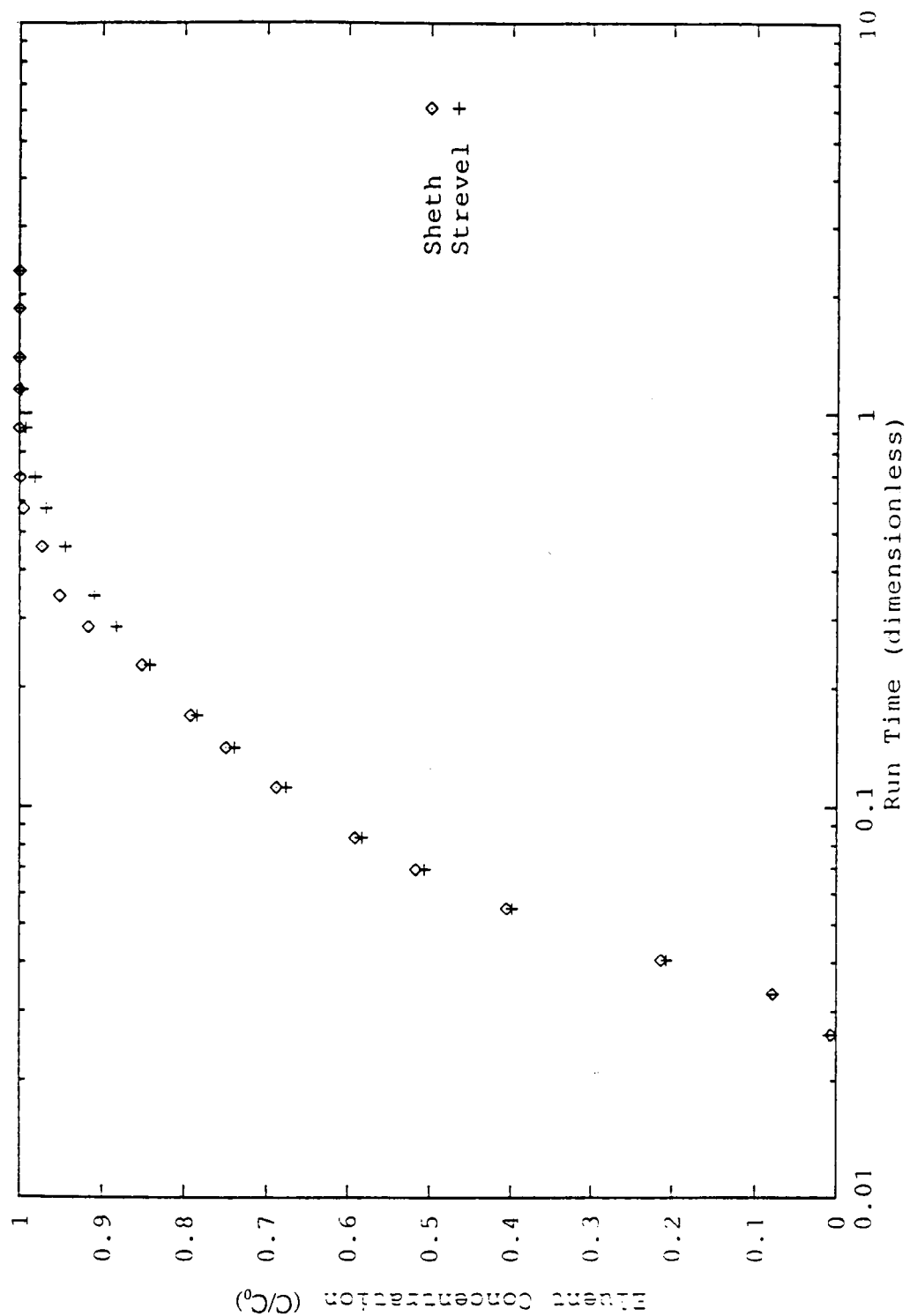


Figure 1: Reproducibility of Program Results for $a_2C_0 = 4.2$ and $X = 1.0$

CHAPTER IV

BATCH EXPERIMENTAL EQUIPMENT AND PROCEDURE

In this chapter the discussion on selecting the best three of the commercially available weak-base resins for further study is given. The testing parameters for the batch evaluation include cation (other alkali metals), cycle efficiency, solution concentration and dissolved impurities (spent seed). The resins, their manufactures and some of the manufacturer supplied properties are listed in Table 1.

Table 1: Candidate Resins and their Manufacturers and Properties.

Resin	Supplier	Properties			
		FG ¹	Mesh	Matrix ²	T(°C) ³
Unknown	Culligan	Unknown for all properties			
MWA-1	DOW Chemicals	TA	20-50	Styrene DVB	100
WGR-2	" "	TQA	20-40	Epoxy amine	93
Amberlite IRA-35	Rohm & Haas	TA	16-50	Acrylic	60
Amberlite IRA-68	" "	TA	16-50	Gel-Acrylic	60
Amberlite IRA-93	" "	TA	16-50	Styrene DVB	100
Amberlite IRA-94	" "	TA	16-50	Styrene DVB	100
Duolite A-7	" "	SA	16-50	Phenolic	40
Ionac A-305	Sybron	TQA	≈ 50	Poly-Amine	40
Ionac AFP-329	"	TA	16-50	Styrene DVB	60
Ionac A-365	"	TA	16-50	Poly-Acrylic	60

¹ Function group: T = tertiary, Q = quaternary, S = secondary, A = amine

² DVB = divinyl-benzene

³ Maximum operating temperature

These resins were screened by a batch experimental procedure

defined later in the chapter. The equipment used in the procedural development and subsequent analyses includes the standard laboratory equipment with the exception of the carbonation and resin de-watering apparatus. The carbonation apparatus consisted of a pressure regulator for the pressurized tank of CO₂, a 500 ml plastic sample jar with a approximately 1.6 mm diameter hole in the lid, a 1.6 mm stainless steel tube, a flowmeter and the associated connectors (see Figure 2). The de-watering apparatus consisted

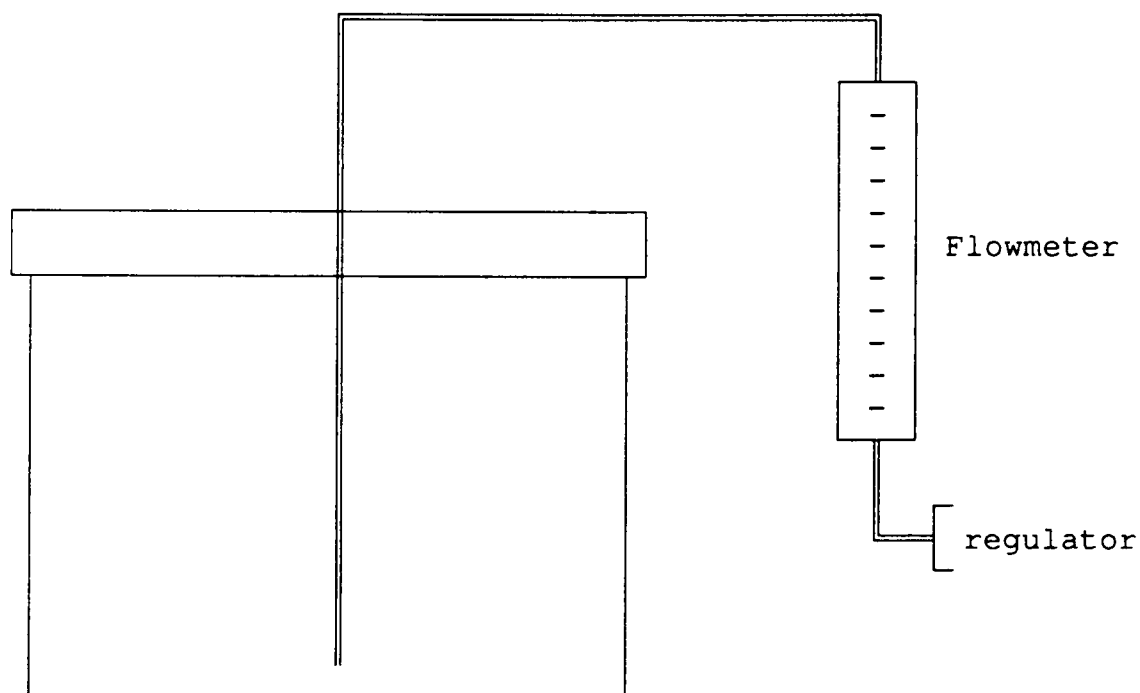


Figure 2: The Batch Carbonation Apparatus.

of the stem from a spray bottle, which had a small screen on the inlet, and a vacuum source. When a vacuum was applied to

the stem the standing water was removed from the resin. The chemicals used were all reagent grade. The water was obtained from the Barnstead water de-ionizing system installed in the chemistry lab. All the sulfate analyses were performed using a Dionex ion chromatograph.

The literature on resin testing discussed earlier was either too precise or too case specific to be of any help in this investigation. Therefore, an in-house batch procedure to evaluate the candidate resins was developed. The procedure was developed and optimized for IRA-68 because this resin was already on site and ready for use. Since the purpose of the batch evaluation was to choose, given our cost and performance criteria, the best performing resin, the batch procedure developed for IRA-68 did not bias the investigation in its favor. The cost criteria was to minimize, where possible, the use of chemicals and labor. The performance criteria was to choose a resin which would perform the best for the testing parameters given above.

Before going to the actual procedural development, it is necessary to define exhaustion and regeneration. Exhaustion is the part of the batch procedure where the resin removes the desired ions from the bulk phase solution (e.g. sulfate ions from the potassium sulfate solution). Regeneration is the part of the batch procedure where the exchanged ions are removed from the functional groups on the resin with a suitable regenerant (e.g. sulfate ions removed with ammonium

hydroxide).

The parameters optimized independently were regenerant concentration, mixing time, sample size, and carbonation time. Initially, the fresh resin was regenerated with a 1.20% by weight ammonia solution for one hour to ensure that the resin was in the free base form. For the regeneration optimization, only the ammonia concentration was varied. The other parameters such as solution-to-resin ratio (2:1), potassium sulfate concentration (25000 ppm), exhaustion mixing time (1.0 hr), regeneration mixing time (30 min), carbonation time (1.0 hr) and carbonation flow-rate (2.0 SCF/hr) were held constant. The results of these experiments are tabulated as percent retained (amount of SO_4^{2-} left on the resin after regeneration) versus ammonia percent in Table 2. The lower the percent sulfate ion retained on the resin the better is the regeneration efficiency. Therefore, considering the experimental errors, cost of ammonia and incremental

Table 2: Percent Ammonia Versus Percent Retained.

Ammonia (wt%)	Percent SO_4^{2-} Retained
0.58	77.7
1.16	44.4
1.74	29.2
2.90	13.4
3.84	11.2
4.35	11.6
4.64	8.5

improvement in the resin regeneration, the optimum ammonia percentage is considered to be approximately 4.0% by weight, which also agrees with the manufacture's suggested concentration.

To optimize the mixing time for both the regeneration and exhaustion steps, all the test conditions yet to be optimized were held constant except for the mixing time. The percentage of ammonia used was 4.0. The results are presented in Table 3. The mixing times used were 15, 30, and 60 minutes. Based on the results shown in Table 3 increasing the mixing time during the resin exhaustion step does not improve the percent removal (amount of sulfate removed from the potassium sulfate solution). Therefore, a mixing time of 15 minutes was utilized. Since the mass transfer rate and methodologies should be similar, the mixing time chosen for the exhaustion step was also used for the regeneration step.

Table 3: Mixing Time Versus Percent Removal

Mixing Time (min)	Percent SO_4^- Removal
15.0	88.0
30.0	85.4
60.0	85.8

To optimize the sample size, the optimum values for ammonia concentration and mixing time were used. The sample size was varied from 10 to 100 milliliters. Then the percent

removal and retained for each sample size were calculated. From Table 4 the sample size does not affect either percentage. Hence, a sample size of 25 ml was used for the batch resin evaluation.

Table 4: Sample Size Versus Percent Removal and Percent Retained.

Sample Size (ml)	Percent SO_4^- Removal	Percent SO_4^- Retained
10.0	88.0	9.6
50.0	85.4	10.0
100.0	85.8	9.7

In optimizing the carbonation time, the ammonia concentration, mixing time, and sample size determined above were used (even for the initial regeneration). The potassium sulfate concentration was also kept constant at 2.5% by weight. The carbonation time was varied from 15 to 60 minutes with a constant flow-rate of 2.0 SCF/hr. The results, percent sulfate removed versus carbonation time, are given in Table 5.

Table 5: Carbonation Time Versus Percent Removal

Carbonation Time (min)	Percent SO_4^- Removal
15.0	65.1
30.0	83.6
60.0	86.7

The carbonation time as can be seen from Table 5 affects the percent of sulfate removed. But beyond 30 minutes the increase in percent removal is very small. Therefore, the optimum carbonation time was chosen to be 30 minutes.

To summarize, the optimum batch mode screening conditions include a 15 minute mixing time, a 4.0 % by weight ammonia regenerant, a 30 minute carbonation time at a flow-rate of 2.0 SCF/hr, a 25 ml resin sample size, and a 2:1 solution-to-resin ratio.

CHAPTER V

BATCH RESULTS AND DATA ANALYSIS

In this chapter the results of the batch mode evaluation runs are analyzed with the analysis of variance, two-way fixed-effects model and a multiattribute technique.

Statistical Analysis

The analysis of variance, two-way fixed-effects model was used to determine the effects of resin type, solution concentration, cyclic operations, and cations on the resin's removal and regeneration efficiencies. The values used in these calculations were the first observations taken for each resin and test condition. The batch experimental procedure was developed before the first observation was made. Therefore, there was no learning curve associated with the results, which frees the data of any bias. Due to time constraints, only one observation was taken. This weakens the statistical results and combines the interaction (C-N-R) and error terms. Therefore, no interaction effect or error can be determined from the data. The test statistic is f_0 , which is the mean square (MS) resin and/or concentration divided by the mean square interaction. This test statistic follows the F distribution. The f_0 's are compared with the appropriate

values from a F distribution table for a 95% confidence that the null hypothesis is true, when it is true. In this analysis the null hypothesis is that none of the above factors affect the exhaustion or regeneration efficiency. When the f_0 and the F distribution table values are relatively close in magnitude, the conclusions drawn from the analysis are conditional [55]. In the tables that follow part (a) lists the percent removal or retained and part (b) gives the analysis of variance from which the effects are quantified. In part (b), SS and DF are the sum square and the degrees of freedom, respectively.

Tables 6 (a) and (b) details the data and calculations for the effects of solution concentration (1K, 25K, and 50K ppm K_2SO_4) and resin type on the exhaustion efficiency. In Table 6 (b) the comparison of the test statistic with the appropriate value from a F distribution table shows that the resin type and solution concentration definitely affect the removal efficiency. Based on non-linear Langmuir type equilibrium isotherm, increasing solution concentration should have an effect on the resin performance.

Table 7 (a) and (b) deals with the effect of resin type and solution concentration on the regeneration step of the batch procedure. The percent retained is 100 minus the regeneration efficiency. In Table 7 (b) the only effect on the regeneration efficiency was found to be due to the resin type. The amount of sulfate ion removed during the exhaustion

Table 6: Resin and Concentration Effects on Exhaustion Efficiency.

a) Percent Removal Data

RESIN	CONCENTRATION			
	ppm K ₂ SO ₄	1K	25K	50K
IRA-68		100.0	88.7	58.7
IRA-35		100.0	78.7	57.9
IRA-93		100.0	52.7	42.3
IRA-94		100.0	52.4	30.9
A-7		74.4	13.0	9.7
A-365		63.9	12.9	7.8
MWA-1		98.5	44.3	23.6
WGR-2		99.2	60.5	36.4
A-305		98.5	48.9	26.3
UNKNOWN		98.5	54.5	29.1

b) Analysis of Variance Table

Source	SS	DF	MS	f ₀	F _{0.05,9,18} F _{0.05,2,18}	Effect
Resin	8100.640	9	900.071	11.912	2.46	Yes
Conc.	19603.409	2	9801.704	129.717	3.55	Yes
C-N-R	1360.125	18	75.562	.000		
Error	.000	0	.000			
Total	29064.170	29				

Table 7: Resin and Concentration Effects on Regeneration Efficiency

a) Percent Retained Data

RESIN	CONCENTRATION			
	ppm K_2SO_4	1K	25K	50K
IRA-68		8.0	11.3	14.5
IRA-35		9.5	9.7	9.5
IRA-93		28.2	25.6	19.3
IRA-94		55.9	55.1	56.7
A-7		7.1	30.9	32.3
A-365		27.1	53.2	29.2
MWA-1		45.0	54.5	41.4
WGR-2		54.5	67.3	63.2
A-305		6.3	29.6	30.8
UNKNOWN		52.0	45.3	36.1

b) Analysis of Variance Table

Source	SS	DF	MS	f_0	$F_{0.05,9,18}$ $F_{0.05,2,18}$	Effect
Resin	8953.116	9	994.791	15.237	2.46	Yes
Conc	396.861	2	198.430	3.039	3.55	No
C-N-R	1175.173	18	65.287	.000		
Error	.000	0	.00			
Total	10525.150	29				

step (amount of sulfate on the resin) may have an effect on the regeneration efficiency. Theoretically, it is possible to see an effect of solution concentration on the regeneration efficiency. The observed uncertainty is believed to be due to the lack of multiple observations for each run.

Tables 8 and 9 deal with the effect of resin type and cyclic operations (4 cycles) on the exhaustion and regeneration efficiency. The solution concentration used was 25K ppm K_2SO_4 . As in Tables 6 and 7, Table 8 (a) contains the data for each run. Table 8 (b) shows that there is definitely an effect due to resin type on exhaustion efficiency. Also in Table 8 (b) the analysis leads to the conclusion that 4 consecutive cycles of exhaustion and regeneration do not affect the exhaustion efficiency. This is expected for a good commercial resin.

Table 9 (a) and (b) deal with the effect of resin type and cyclic operation on the regeneration efficiency. In Table 9 (b) the results from the fixed-effects calculations imply that both the resin type and exhaustion-regeneration cycles affect the regeneration efficiency. In some resins this means that the resin regeneration performance improves. In other cases the regeneration performance deteriorates or is erratic. Theoretically the regeneration efficiency for 4 consecutive cycles on a relatively new resin sample should either improve or remain constant. This inconsistent behavior is probably due to the lack of multiple observations.

Table 8: Resin and Cycle Effects on Exhaustion Efficiency

a) Percent Removal Data

RESIN	CYCLES	1	2	3	4
IRA-68		88.7	84.4	84.4	83.4
IRA-35		78.7	78.4	78.9	79.2
IRA-93		52.7	67.9	67.7	68.1
IRA-94		52.4	42.7	42.0	42.1
A-7		13.0	13.2	15.6	16.0
A-365		12.9	16.2	22.5	22.4
MWA-1		45.0	44.5	43.7	43.4
WGR-2		60.5	48.4	44.1	35.6
AFP-329		32.3	28.7	24.6	28.7
A-305		48.9	48.3	51.7	48.4
UNKNOWN		54.5	51.5	47.5	56.2

b) Analysis of Variance Table

Source	SS	DF	MS	f_0	$F_{0.05, 10, 30}$ $F_{0.05, 3, 30}$	Effect
Resin	20055.329	10	2005.533	82.377	2.16	Yes
Cycle	17.849	3	5.950	.244	2.92	No
C-N-R	730.371	30	24.346	.000		
Error	.000	0	.000			
Total	20803.550	43				

Table 9: Resin and Cycle Effects on Regeneration Efficiency

a) Percent Retained Data

RESIN	CYCLES	1	2	3	4
IRA-68		11.3	7.9	7.9	6.6
IRA-35		9.7	4.8	8.2	8.9
IRA-93		25.6	7.2	4.1	7.8
IRA-94		55.1	31.1	21.6	17.7
A-7		30.9	21.4	34.1	31.9
A-365		53.2	44.0	31.2	24.6
MWA-1		54.5	34.1	30.7	26.6
WGR-2		67.3	42.1	34.4	14.7
AFP-329		45.3	20.8	13.3	20.0
A-305		66.9	38.6	20.3	19.8
UNKNOWN		29.6	22.1	19.6	20.1

b) Analysis of Variance Table

Source	SS	DF	MS	f_0	$F_{0.05, 10, 30}$ $F_{0.05, 3, 30}$	Effect
Resin	5850.810	10	585.081	7.681	2.16	Yes
Cycle	3466.507	3	1155.502	15.170	2.92	Yes
C-N-R	2285.108	30	76.170	.000		
Error	.000	0	.000			
Total	11602.430	43				

Tables 10 and 11 deal with the effects of resin type and cation on the exhaustion and regeneration efficiency. The solutions used were 25K ppm K_2SO_4 and 20.4K ppm Na_2SO_4 . These solutions contain the same molar concentration of sulfate ion. Table 10 (a) gives the percent removal data. Table 10 (b) shows that there is definitely an effect of resin type on percent removal. The analysis also implies that there maybe an effect from different cations. However from

Table 10: Resin and Cation Effects on Exhaustion Efficiency

a) Percent Removal Data

RESIN	CONCENTRATION	
	ppm	
		K_2SO_4 25K Na_2SO_4 20.4K
IRA-68		88.7 83.7
IRA-35		78.7 75.6
IRA-93		52.7 53.6
A-305		48.9 45.9
UNKNOWN		54.5 51.8

b) Analysis of Variance Table

Source	SS	DF	MS	f_0	$F_{0.05,4,4}$ $F_{0.05,1,4}$	Effect
Resin	2350.054	4	587.514	255.053	6.39	Yes
Cation	16.641	1	16.641	7.224	7.71	No
C-N-R	9.214	4	2.303	.000		
Error	.000	0	.000			
Total	2375.909	9				

theoretical considerations, since no cation is involved in the anion-exchange chemistry, there should be no effect of the cation on the exhaustion efficiency of the anion-exchange resin.

In Table 11 part (a) lists the percent retained data and part (b) gives the analysis of variance results. In part (b) the resin type definitely has an effect on the regeneration

Table 11: Resin and Cation Effects on Regeneration Efficiency

a) Percent Retained Data

RESIN	CONCENTRATION		
	ppm	K ₂ SO ₄ 25K	Na ₂ SO ₄ 20.4K
IRA-68		11.3	8.6
IRA-35		9.7	10.1
IRA-93		25.6	29.2
A-305		29.6	39.3
UNKNOWN		45.3	44.7

b) Analysis of Variance Table

Source	SS	DF	MS	f ₀	F _{0.05,4,4} F _{0.05,1,4}	Effect
Resin	1897.994	4	474.499	40.717	6.39	Yes
Cation	10.816	1	10.816	.928	7.71	No
C-N-R	46.614	4	11.654	.000		
Error	.000	0	.000			
Total	1955.424	9				

efficiency. The cations, however, have no effect on the percent retained, because no cations are involved in the regeneration step.

In Tables 12 and 13, the effect of sulfate source (ie. pure reagent grade K_2SO_4 or spent seed extract from the MHD Baghouse/ESP material) and resin type on the exhaustion and regeneration efficiencies are determined. The seed extract for simplicity will be considered another cation. However the

Table 12: Resin and Seed Effect on Exhaustion Efficiency

a) Percent Removal Data

RESIN	CONCENTRATION		SEED
	ppm K_2SO_4	50K	48.1K
IRA-68		58.7	65.9
IRA-35		57.9	57.3
IRA-93		42.3	40.4
A-305		26.3	27.0
UNKNOWN		29.1	28.6

b) Analysis of Variance Table

Source	SS	DF	MS	f_0	$F_{0.05, 4, 4}$ $F_{0.05, 1, 4}$	Effect
Resin	2110.610	4	527.652	81.573	6.39	Yes
Seed	2.401	1	2.401	.371	7.71	No
C-N-R	25.874	4	6.469	.000		
Error	.000	0	.000			
Total	2138.885	9				

actual spent seed extract will also contain other dissolved impurities. Table 12 (b) shows that there is definitely an effect due to resin type. However there is no effect due to cation or seed.

In Table 13 the analysis of variance, fixed-effects calculation was performed for the 50K ppm K_2SO_4 solution, the spent seed extract, and resin type to determine the effect on

Table 13: Resin and Seed Effect on Regeneration Efficiency

a) Percent Retained Data

RESIN	CONCENTRATION		SEED
	ppm K_2SO_4	50K	48.1K
IRA-68		14.5	21.8
IRA-35		9.5	12.6
IRA-93		19.3	10.4
A-305		30.8	38.9
UNKNOWN		36.1	46.0

b) Analysis of Variance Table

Source	SS	DF	MS	f_0	$F_{0.05,4,4}$ $F_{0.05,1,4}$	Effect
Resin	1388.144	4	347.036	12.088	6.39	Yes
Seed	38.025	1	38.025	1.324	7.71	No
C-N-R	114.840	4	28.710	.000		
Error	.000	0	.00			
Total	1541.009	9				

the percent retained. Again the seed will be considered as another cation. In Table 13 (b) the effect of the resin type and the seed on the regeneration efficiency is determined. The only parameter that affects the percent retained is the resin type. The seed has no effect.

In summary the exhaustion and regeneration efficiencies are not affected by the same parameters. The only exception to this statement is resin type, which strongly affects both the exhaustion and regeneration efficiencies. The exhaustion efficiencies are affected by the resin type and the solution concentration. The regeneration efficiency is affected by the resin type and the cycling between the exhaustion and regeneration steps. Table 14 lists all the major parameters that affect the exhaustion and regeneration efficiencies.

Table 14: Parameter Effects on Exhaustion and Regeneration Efficiencies

Parameter	Efficiency	
	Exhaustion	Regeneration
Resin Type	*	*
Solution Concentration	*	-
Cyclic Operation	-	*
Cation (Na vs. K)	-	-
Dissolved Impurities (Spent Seed)	-	-

*: Effect; -: No Effect

Multiattribute Analysis

Multiattribute analysis involves the use of an importance rating and an utility scheme to determine the best of several alternatives [56]. For the data from the batch experiments, the scheme developed is one which considers the percent removal as the most important result. The importance of the resin's performance for each test condition has also been established. Table 15 lists the importance ratings in two columns. The first column lists the importance of each parameter. The second column lists the importance of the attributes contained within each parameter. These ratings

Table 15: Parameter Importance Ratings

Parameter Rating (k_p)		Attribute Rating (k_A)	
Concentration	0.3	Removal	0.6
Cycles	0.3	Retained	0.4
Cation	0.2		
Seed	0.2		
1.0		1.0	

were arbitrarily chosen to reflect the results of the previous section, which means that the high solution concentration and cyclic operations were given the most importance. The percent removal was given slightly more importance because it reflects the resin's capacity for spent seed regeneration.

The data presented in Tables 6 (a) through 13 (a) were

used in the weighting calculations. These calculations consisted of averaging the removal and retained percentages to reflect the resin's ability to handle concentration changes, repeated cycles of exhaustion and regeneration, and cation interference. The values associated with the spent seed solution were used as the weights which correspond to the resins tendency to be fouled by dissolved impurities.

For each of the parameters listed in Table 15, their individual utilities were calculated using the additive utility model,

$$U_P = \sum_{A=1}^n k_A U_A. \quad (11)$$

U_P is the utility of the parameter. k_A is the importance rating for the attributes. U_A is the utility of the attributes. The attribute's utility function for the interval between 0 and 1 is

$$U_A = 1 - \sqrt{1 - X^2} \quad (12)$$

where

$$X = \frac{X_A - X_i}{X_f - X_i}.$$

X_A is either the percent removal or retained, X_i is the beginning of the interval, and X_f is the end of the interval. For the percent removal X_i and X_f are 0 and 100, respectively. These values are reversed for the percent retained. This type

of utility function gives more weight to those removal or retained percentages that are closer to their ideal values (100% for removal and 0% for retained) than to those less than 10% of their ideal value (e.g. 90% for removal and 10% for retained). The utility for each resin was then calculated using

$$U_R = \sum_{P=1}^4 k_P U_P, \quad (13)$$

where U_R is the utility of the resin and k_P is the importance rating of the parameter [56]. For a resin to achieve a utility of 1.0, all of the percent removal and retained values must be ideal.

The calculated resin utilities are given in Table 16. The best resins were found to be IRA-35, IRA-68, and IRA-93. These three resins were used in the fixed-bed resin evaluation experiments discussed in the following chapters.

Table 16: The Calculated Resin Utilities

Resin	Utility (U_R)
IRA-68	0.46
IRA-35	0.43
IRA-93	0.29
A-305	0.18
UNKNOWN	0.16
IRA-94	0.12
MWA-1	0.11
WGR-2	0.11
A-7	0.10
AFP-329	0.10
A-365	0.07

CHAPTER VI

FIXED-BED EXPERIMENTAL EQUIPMENT AND PROCEDURE

Apparatus

Initially the fixed-bed system was to provide a semi-automatic system that could utilize individually two different sized glass columns, that could provide for regeneration, carbonation, and exhaustion of an ion-exchange material, and could be left operating alone for an extended period of time. The design consisted of three approximately six-liter stainless steel tanks for the eluent, the deionized rinse water, and the regenerant. It also consisted of a number of solenoid and manually operated valves, one pressure gauge, a nitrogen tank, a 99.99% carbon dioxide tank, an adjustable pressure relief valve, two 215 psia (1480 KPa) rated glass tubes (one a 2.5 cm. I.D. column (I) and the other a 5.2 cm. I.D. column (II)), two four-outlet timers, two rotameters, two pressure regulators, a two-way valve, a check-valve and a Gilson fractional auto-sampler. Problems occurred, however, during the shakedown experiments that prompted a re-design of the system. These problems include unstable system flow-rates, high initial concentrations of sulfate, and unstable sampler flow-rates. The unstable system flow-rates had to be dealt with procedurally.

In the re-designed system, six of the manually operated valves and three of the solenoid valves were replaced with three two-way valves and a four-way valve, respectively, to reduce/remove the dead-spaces in the system, which contributed to the high initial sulfate concentrations. Due to the removal of most of the solenoids one of the timers was deleted from the system. Two isolation valves were added to the eluent and regenerant tanks to aid in the post-run system flush. The flush was also added to reduce the initial high sulfate concentrations.

In the revised system the full flow-rate through the column could be directed to the sampler, thereby eliminating the unstable sampler flow-rates caused by the flow-splitting sampling system. The schematic of the re-designed fixed-bed system is presented in Figure 3.

Experimental Procedure

After the shakedown of the original and re-designed fixed-bed systems, the experimental procedure was one of prevention and constant monitoring. The preventative measures that were necessary to provide a good run were primarily associated with the filling and flushing of the eluent and regenerant tanks. These tanks were found on-site and were modified by removing their internal baffles. The subsequent welding with a copper based welding rod caused the production

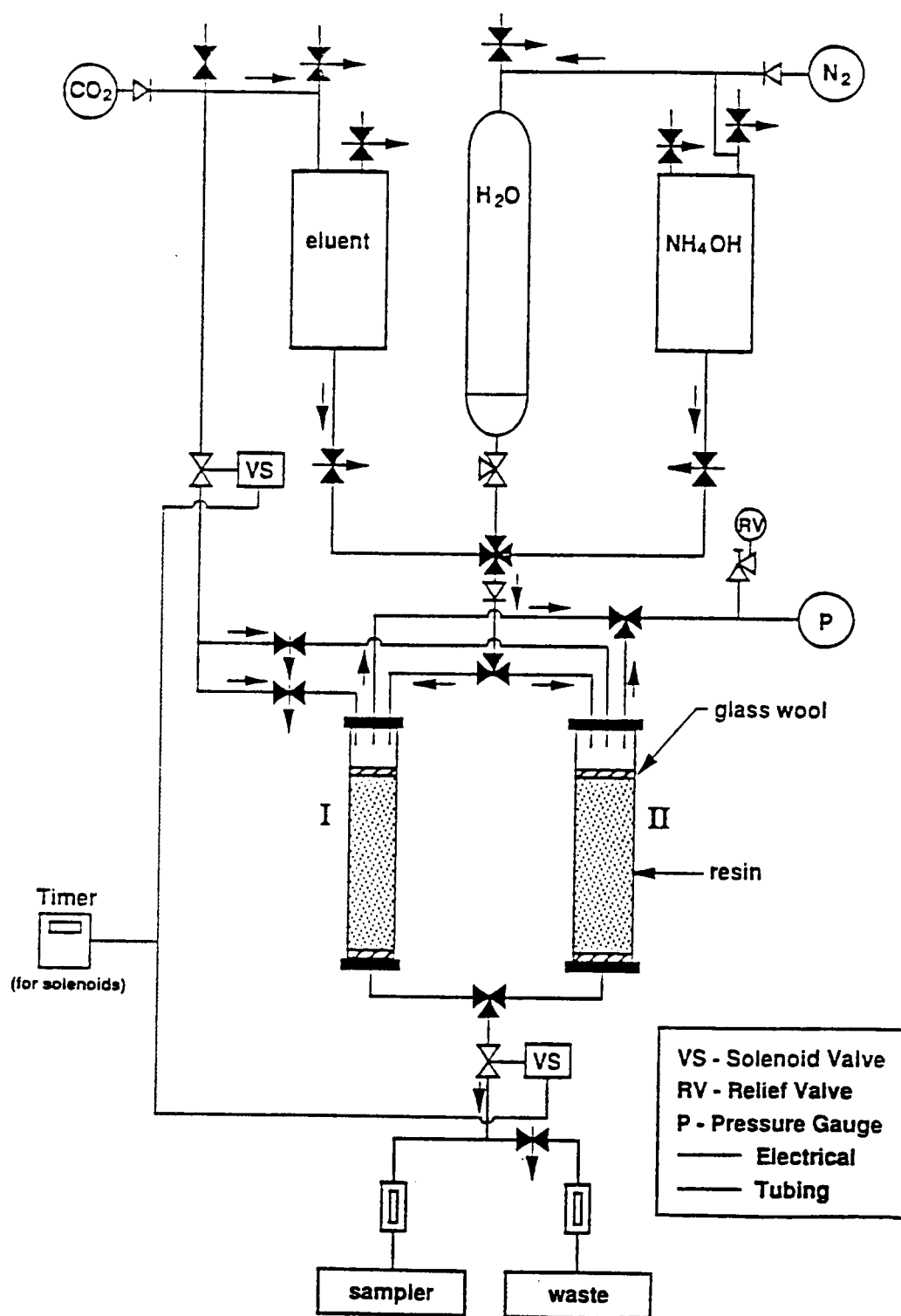


Figure 3: Fixed-Bed Schematic

of copper sulfate/hydroxide when the weld was exposed to the ammonium hydroxide (regenerant) or the potassium sulfate (eluent) solution. Therefore, these tanks could not be filled to the weld line. Another problem caused by the scavenged eluent and regenerant tanks was that of low final sulfate concentration due to a dead space in the tanks themselves. This problem could be solved by either initiating a sulfate solution rinse of the eluent tank or by using a more concentrated eluent. But due to the time required to make adjustments in sulfate solution, the former method was used. The bulk sulfate concentration of the eluent was determined by taking a few extra samples at the end of a run.

The eluent tank was flushed because of the tendency of the sulfate to precipitate out when the room temperature dropped below 20°C. Therefore, the eluent tank and its associated tubing were flushed with hot tap and deionized water, respectively. The procedure involved the isolation of the eluent tank and the removal of the tubing between the tank and the four-way valve. The tubing and tank were then flushed with hot tap-water and with deionized water. The regenerant tank could be flushed in the same manner. However, that was not necessary in the present study. The high initial sulfate concentration was thus reduced by a factor of ten (from 50 ppm to 4 ppm SO_4^{2-}).

An additional preventive measure concerned the resin's ionic form. This preventive measure consisted of performing a

initial regeneration on the fresh resin sample to ensure that it was in the free base form. The 4.0 wt% ammonia solution was used in batch mode with a mixing time of approximately 24 hours.

The unstable system flow-rates persisted throughout the experimental runs. The flow-rate could only be controlled through constant monitoring. The valve line-ups for the regeneration, rinse, and exhaustion steps are outlined in Table 17. Even though the in-column regeneration and subsequent rinse step were not used in the present investigation, Table 17 includes their line-ups for future applications.

For an experiment run these steps were followed:

- (1) remove exhausted column from its mount, (2) remove top flange from column, (3) remove glass wool plug, (4) use deionized water pump to drive the resin from the column and into an appropriate container, (5) remove bottom glass wool plug, (6) rinse column with hot tap and then with deionized water, (7) insert fresh plug of glass wool, (8) add a measured amount of settled fresh resin and water slurry to column, (9) tap column on table to settle resin, (10) insert another glass wool plug, (11) replace the columns top flange, (12) remount column, (13) rinse column using the line-up from Table 17, (14) estimate flow-rate and adjust with rotameter, (15) rinse eluent tank with an appropriate volume of the sulfate solution, (16) fill tank with the sulfate solution, (17)

reconnect the tubing to the eluent tank and to the four-way valve, (18) fill this tubing with the sulfate solution, (19) place the column under 50 psig of carbon dioxide for 20 minutes, (20) bleed system pressure off, (21) line-up all the valves except the column solenoid (closed) as indicated in Table 17, (22) pressurize the system to the appropriate pressure, (23) close the appropriate static pressure column valve, (24) create an approximately one psig positive pressure differential between the regulator's pressure and the system's pressure gauge, (25) open the column solenoid,

Table 17: Valve Line-ups for the Fixed-Bed System.

Valves	Regeneration	Rinse	Exhaustion
Tank Isolation:			
Eluent	Closed	Closed	Open
Water ¹	Closed	Open	Closed
Regenerant	Open	Closed	Closed
Four-Way Tank ²	Up	Left	Down
Column Pressure ¹	Closed	Closed	Left/Right
Static Pressure:			
Solenoid	Closed	Closed	Open
Column I	Closed	Closed	Open/Closed
Column II	Closed	Closed	Closed/Open
Column Valves:			
Column I:			
Inlet ¹	Left	Left	Left
Outlet ¹	Left	Left	Left
or Column II:			
Inlet ¹	Right	Right	Right
Outlet ¹	Right	Right	Right
Column Solenoid	Open	Open	Open
Flow Splitting	Open	Open ³	Closed

¹ Two-way valves with arrow shaped-handle: Left, Right, or Closed Positions.

² Four-way valve with arrow-shaped-handle: Left, Right, Up, or Down Positions.

³ Flow Splitting valve used opened to aid in rinsing.

(26) adjust the flow-rate with the rotameter and start the auto-sampler, (27) store the samples appropriately, (28) analyze samples for sulfate, and (29) flush system with deionized water.

The breakthrough curves obtained from the procedure above have good reproducibility and compare well with Modeste's results. Figure 4 is a comparison of a typical breakthrough curve from Modeste's work [2] with a similar one from the present study. The test conditions for this comparison are listed in Table 18. Although the pressure, flow-rate, and bed

Table 18: Test Conditions for IRA-68 Breakthrough Curve Comparison

Basis: 0.028 gm SO ₄ ⁻ / ml Solution		
Test Conditions	Present Study	Modeste's Study [2]
CO ₂ -Pressure (psig)	10	5
Solution Flow-rate (cm/min)	11	10
Resin Bed Height (in.)	16	18

height were slightly different, the breakthrough curve from this study compares well with the Modeste curve. A check for the reproducibility was also performed. The results, in the form of breakthrough curves, are shown in Figure 5. From these curves, the fixed-bed system and procedure provides the necessary stability to ensure an adequate run reproducibility. The test conditions used in this investigation to evaluate the effect of major process variables include: CO₂-pressure (10 -

120 psig), solution concentration ($0.006 - 0.028 \text{ gm SO}_4^{2-} / \text{ml}$), product inhibition (0, 0.1, & 1.0 molar ratios of $\text{KHCO}_3 / \text{K}_2\text{SO}_4$), resin bed height (20.3 & 40.6 cm), dissolved impurities (spent seed), and superficial velocity ($0.009 \text{ \& } 0.037 \text{ cm/s}$). Results from this process variables study are discussed in the next chapter.

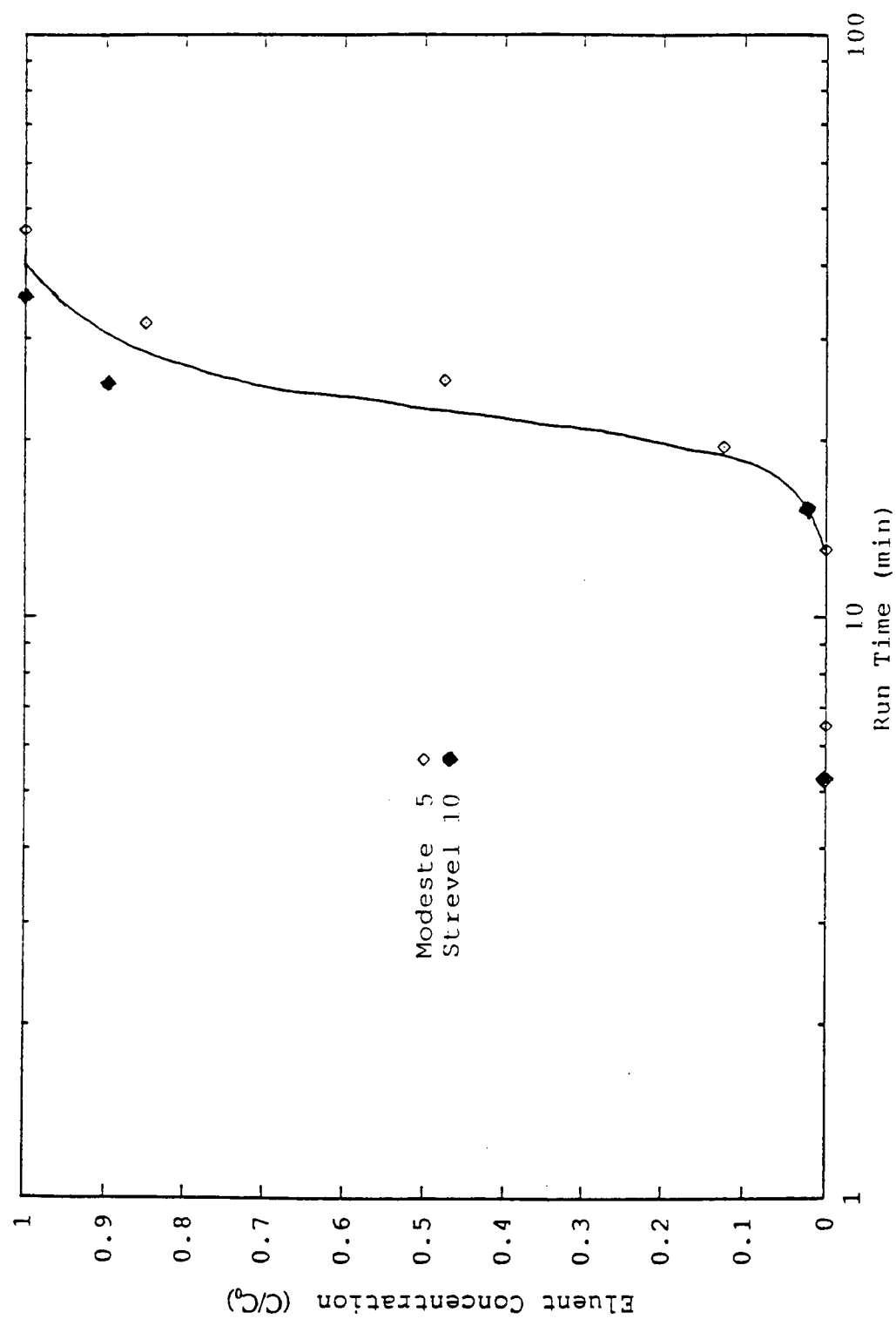


Figure 4: Comparison of Strevel's and Modeste's Breakthrough Curves

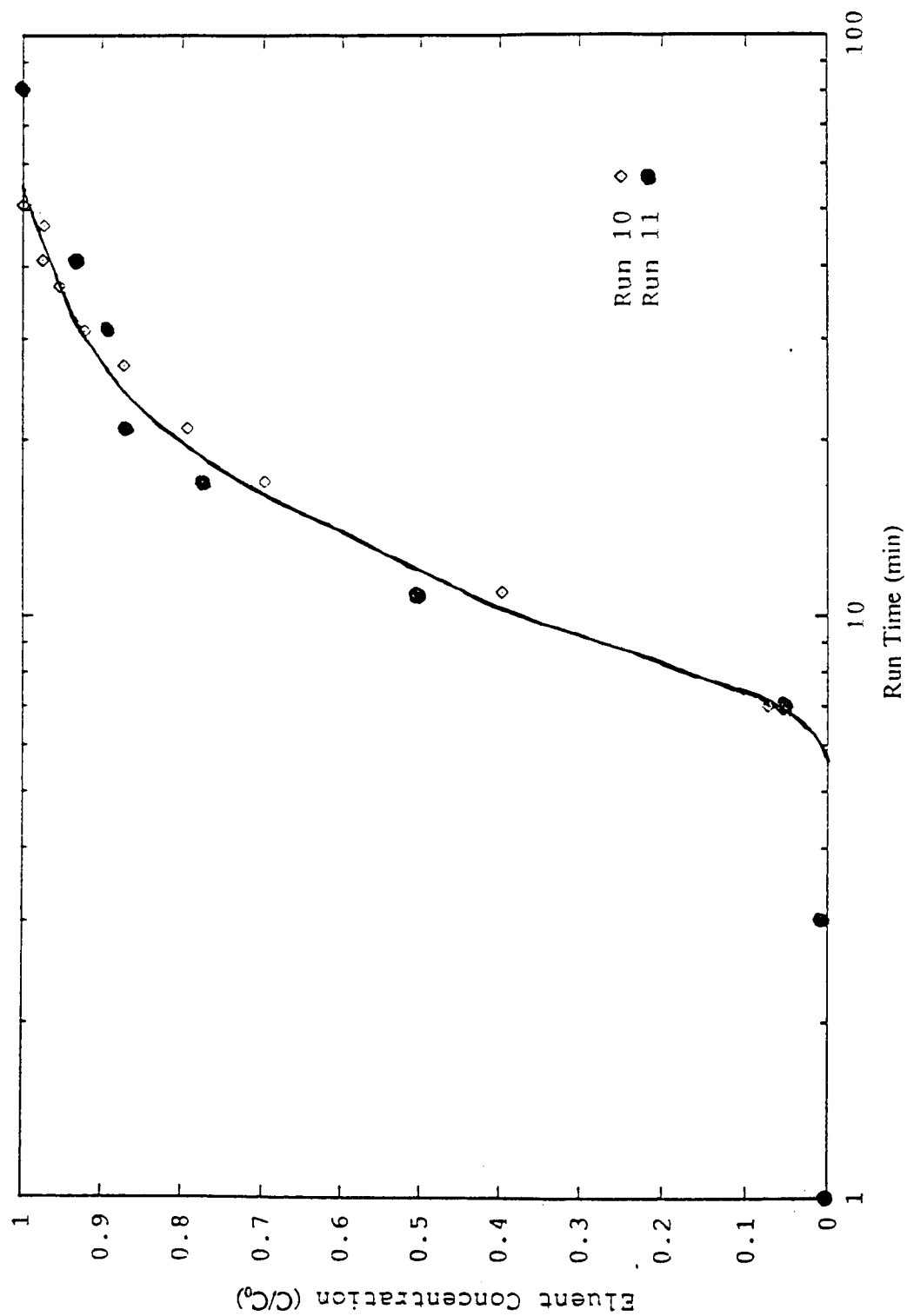


Figure 5: Reproducibility Check for IRA-35 at 10 psig, 0.014 gm SO_4/ml , 20.3 cm Bed Height, and 10.8 cc/min.

CHAPTER VII

FIXED-BED RESULTS AND DATA ANALYSIS

In this chapter the results of the process variables study using the redesigned fixed-bed system are presented. The chapter is divided into an equilibrium capacity, mathematical model, and effects of process variables sections. For all the experimental runs, the respective test parameters and breakthrough curve data and results are presented in Appendix B.

Equilibrium Capacity

The determination of the equilibrium capacity is based on the breakthrough curve data. The breakthrough curve can be modeled by the material balance for the ion-exchange system. The material balance equation is

$$VC_0 - VC = V_{resin} \frac{dq}{dt}, \quad (14)$$

where V_{resin} is the volume of the resin without standing water, V is the volumetric flow-rate, C_0 is the inlet concentration of the sulfate solution, C is the effluent concentration, and q is the average concentration of sulfate on the resin. After the separation of variable technique of integration is applied, the equation becomes:

$$q_{\infty} = \frac{VAC_0}{V_{resin}}, \quad (15)$$

where q_{∞} is the equilibrium capacity (gm SO_4^{2-} / ml resin) and A is the area under the $(1 - C/C_0)$ vs. time curve. The area under the curve was determined using a modified version of Modeste's program [2], which uses the method of trapezoids. This program and examples of the typical input and output are given in Appendix A. The equilibrium capacities for each resin are tabulated versus CO_2 -pressure in Table 19. Table 19 also includes the equilibrium capacities for IRA-68 that were determined by Butler [1] and Modeste [2].

Table 19: Effect of CO_2 -Pressure on Equilibrium Loading

Basis: 0.028 gm SO_4^{2-} / ml solution

CO_2 - Pressure (psig)	IRA-35 (g SO_4^{2-} /ml _R)	IRA-68 (g SO_4^{2-} /ml _R)	IRA-93 (g SO_4^{2-} /ml _R)
0	—	0.068 ¹	—
10	0.073	0.065	0.074
20	—	0.087 ²	—
40	0.098	0.124 ²	0.096
80	0.130	—	0.164
120	0.126	0.136	0.168

¹ Butler [1]

² Modeste [2] with 0.039 gm SO_4^{2-} / ml solution
R is for resin

In order to use Antonson's fixed-bed model, the relationship between the Langmuir isotherm and the reversible adsorption rate must be determined. The Langmuir isotherm is

defined as

$$q_{\infty} = \frac{a_1 C_0}{1 + a_2 C_0}, \quad (16)$$

The kinetic rate of reversible adsorption can be written as

$$\frac{dq}{dt} = k_1 C_0 (C_T - q) - k_2 q, \quad (17)$$

where k_1 is the forward reaction (adsorption) rate constant, k_2 is the backward reaction (desorption) rate constant, and C_T is the total concentration of available adsorption sites. When the ion-exchange system is at equilibrium, equation (17) is equal to zero and q is maximum, q_{∞} . By setting q_{∞} equal to the Langmuir isotherm, the Langmuir constants, a_1 and a_2 , can be defined in terms of the rate constants, k_1 and k_2 , and the concentration of available exchange sites, C_T :

$$a_1 = \frac{k_1}{k_2} C_T \quad (18)$$

$$a_2 = \frac{k_1}{k_2}. \quad (19)$$

From equations (18) and (19), C_T can be derived in terms of the Langmuir constants:

$$C_T = \frac{a_1}{a_2}. \quad (20)$$

In other words C_T is a constant for a given resin and process conditions and should not change with any parameter. However the Langmuir constants, a_1 and a_2 , would change with the reaction conditions, such as the CO_2 -pressure changes investigated in this study.

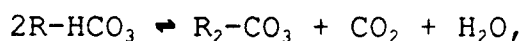
Using the fitted data from Butler [1], Modeste [2] and the present investigation, a maximum experimental C_T -value, $\bar{C}_T$, can be determined for IRA-68. These $\bar{C}_T$ -values and their corresponding Langmuir constants are presented in Table 20. The pre-run CO_2 -pressure is the static CO_2 -pressure applied to the system prior to the exhaustion /carbonation step. The $\bar{C}_T$ -values seem to be dependent on the static CO_2 -pressure during the pre-run and the carbonation /exhaustion step. It is believed that the higher static CO_2 -pressures would create more bicarbonate ions on the resin. Since the bicarbonate ions can be easily replaced on the resin by the sulfate ions, the maximum concentration of sulfate ions that can be removed

Table 20: $\bar{C}_T$ Values for IRA-68

Study	a_1 (g SO_4^- /ml)	a_2 (dimension less)	$\bar{C}_T$ (g SO_4^- /ml)	CO_2 - Pressure (psig)	Pre-Run CO_2 - Pressure (psig)
Butler	24.23	318.7	0.076	0	None*
Modeste	74.07	830.2	0.089	20	20 (5 min)
	42.73	322.2	0.133	40	40 (5 min)
Present	3.13	19.0	0.165	10	50 (20 min)

* Butler carbonated the resin at atmospheric pressure with a CO_2 bubbling apparatus.

by the resin is approached as the CO_2 -pressure is increased. The CO_2 -pressure effect on the resin sites can be represented by the following reaction:



where R is the complex cation group on the resin. In other

words the capacity of the resin for sulfate would increase with CO₂-pressure. This conjecture is supported by the results in Table 19, which shows the equilibrium loading increases as the static CO₂-pressure is increased.

From Table 19 the resin's equilibrium loading seems to level-out around 80 psig. Therefore, the $\bar{C}_T$ -values should level-out at the same pre-run CO₂-pressure. This means that the $\bar{C}_T$ -value for IRA-68 would approach a constant value at higher CO₂-pressures. Therefore, the highest experimental C_T -value of 0.165 g SO₄²⁻/ml resin was used to calculate the Langmuir constants for IRA-68 at higher static CO₂-pressures. These calculations were based on a linearized form of the Langmuir isotherm,

$$\frac{1}{a_1} = \frac{C_0}{q_{\infty}} - \frac{1}{C_T} C_0, \quad (21)$$

and the experimental values of C_0 and q_{∞} . These calculated values are presented in Table 21.

Table 21: Calculated Langmuir Constants for IRA-68

CO ₂ - Pressure (psig)	$1/\bar{C}_T$ (g SO ₄ ²⁻ / ml)	a_1 (g SO ₄ ²⁻ / ml)	a_2 (dimensionless)
10	6.070	3.13	19.00
40-80	"	4.19	25.43
120	"	30.14	182.95

The $\bar{C}_T$ -values and respective Langmuir constants for IRA-35 and IRA-93 were obtained from fitting the experimental data

at 10 psig. The same Langmuir constants were used for the higher CO₂-pressures because the actual experimental data were limited and the results from equation (21) would give a negative intercept. The $\bar{C}_T$ -values and the Langmuir constant used for the IRA-35 and IRA-93 resins are presented in Table 22.

Table 22: Calculated Langmuir Constants for IRA-35 and IRA-93

Resin	CO ₂ - Pressure (psig)	$1/\bar{C}_T$ (g SO ₄ ⁻ / ml)	a_1 (g SO ₄ ⁻ / ml)	a_2 (dimensionless)
IRA-35	10	13.58	12.66	171.9
IRA-93	10	12.27	20.07	246.3

Equation (21) solved for the C_0 / q_∞ gives

$$\frac{C_0}{q_\infty} = \frac{1}{a_1} + \frac{1}{\bar{C}_T} C_0. \quad (22)$$

This linearized Langmuir equilibrium isotherm is plotted for IRA-35, IRA-68, and IRA-93 in Figures 6-8. These plots represent the least squares fits to the concentration and equilibrium loading data at a static CO₂-pressure of 10 psig. The calculated regression coefficients are $1/a_1$ (intercept) and $1/\bar{C}_T$ (slope) of equation (22). From these coefficients the second Langmuir constant, a_2 , was determined. In Figure 7 the fit for IRA-68 has a slope that is less than those found by Butler [1] and Modeste [2] (Table 20). This difference in slope is believed to be caused by the different pre-run CO₂-

pressures used in each investigation. This effect seems to be greater at low sulfate concentration. In future work this needs to be resolved. The calculated values of q_e at various solution concentrations for IRA-35, IRA-68, and IRA-93 at a CO_2 -pressure of 10 psig are shown in Figure 9. IRA-93 seems to have the highest equilibrium loading at a given solution concentration.

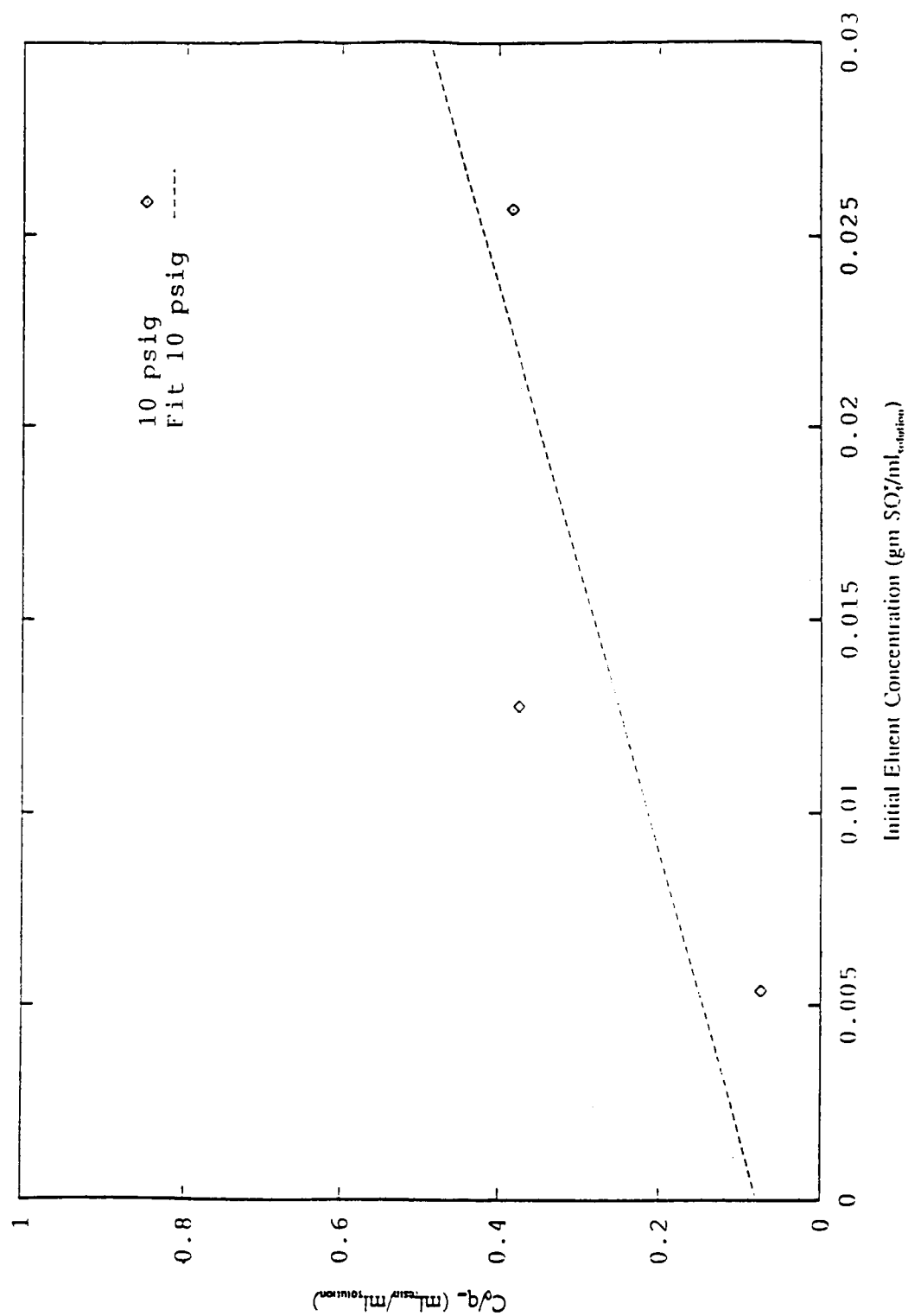


Figure 6: Plot of Fitted Linearized Langmuir Isotherm for IRA-35

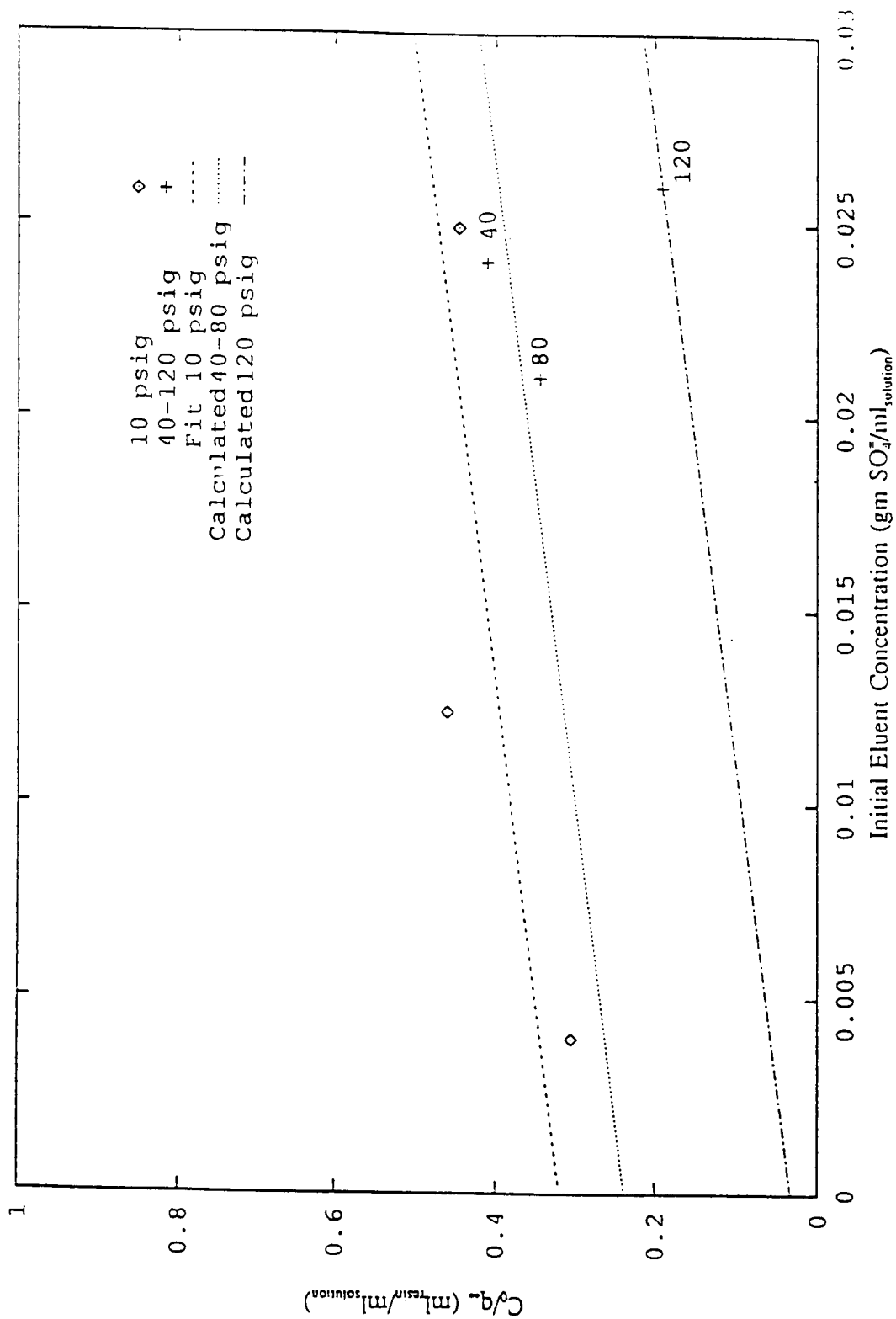


Figure 7: Plot of Fitted Linearized Langmuir Isotherm for IRA-68

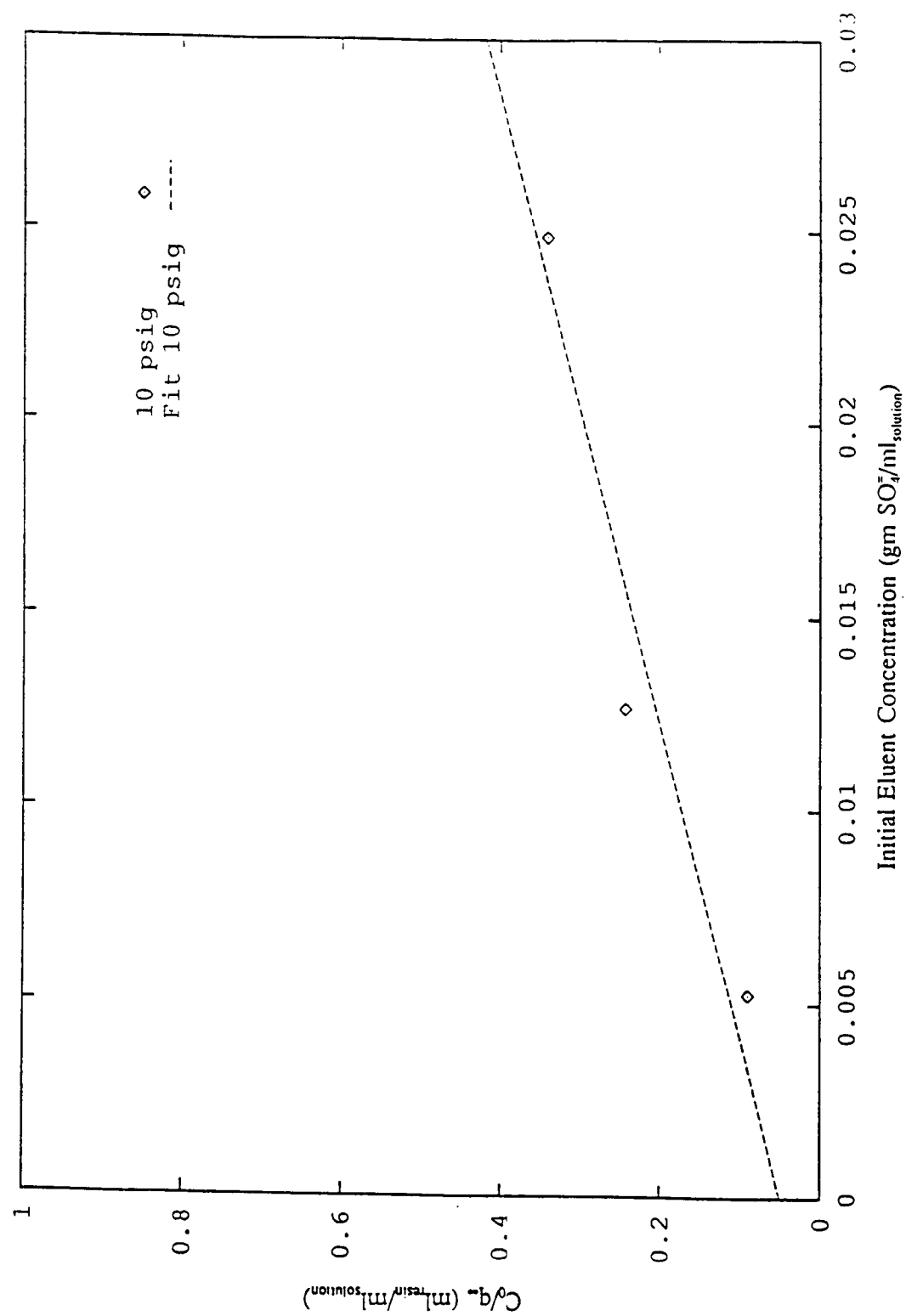


Figure 8: Plot of Fitted Linearized Langmuir Isotherm for IRA-93

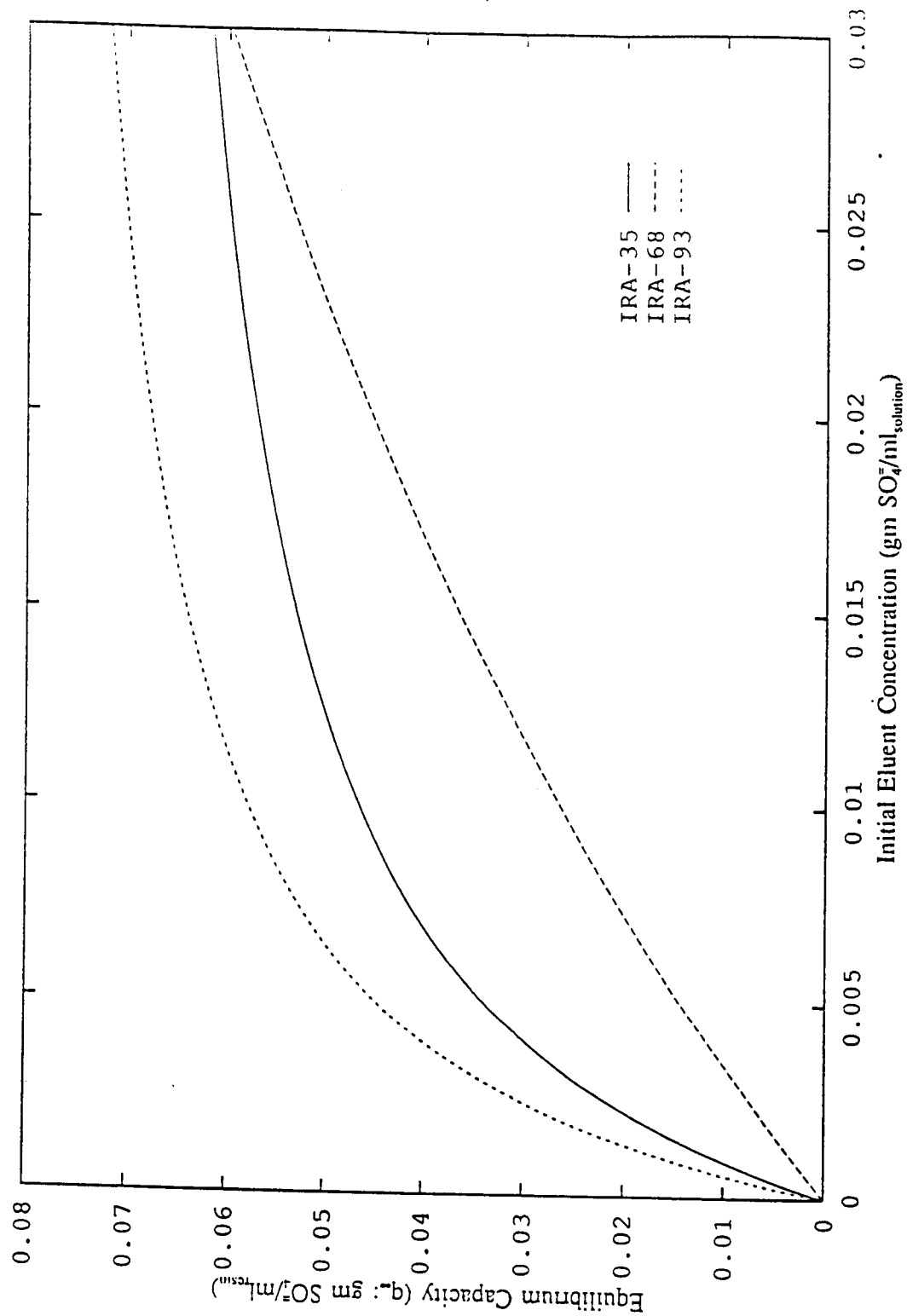


Figure 9: Langmuir Equilibrium Isotherms for IRA-35, IRA-68, and IRA-93 at 10 psig CO_2 -Pressure

Mathematical Model

Antonson's fixed-bed model requires two inputs. These are a_2C_0 and X , the dimensionless column length defined in Chapter III. With these inputs, the model will generate a breakthrough curve which can be fitted to an experimental curve. Examples of the effect of X on C/C_0 at a fixed a_2C_0 and of a_2C_0 on C/C_0 at a fixed X are shown in Figures 10 and 11, respectively. In Figure 10 the effect of increasing dimensionless column length, X , on the model's C/C_0 -values represents an increasing diffusion parameter, D/R^2 , or rate of intraparticle diffusion, an increasing resin bed height, z , and/or a decreasing linear velocity, v , for a given resin with a given void-to-resin ratio, m , and first Langmuir constant, a_1 . The model responds by shifting the curve's origin to the right and their slopes from positive to near infinite. In Figure 11 the effect of increasing a_2C_0 on the model's C/C_0 -values represents the change from a non-linear equilibrium to a more linear equilibrium; the curve's slopes change from near infinite to positive. In other words the denominator of the non-linear Langmuir isotherm becomes dominate. An example of the typical best fit for a run is shown in Figure 12. From the best fit the diffusion parameter can be determined using the equation for the dimensionless column length. The diffusion parameter is presented in this thesis and the literature as the intraparticle diffusion coefficient, D , divided by the

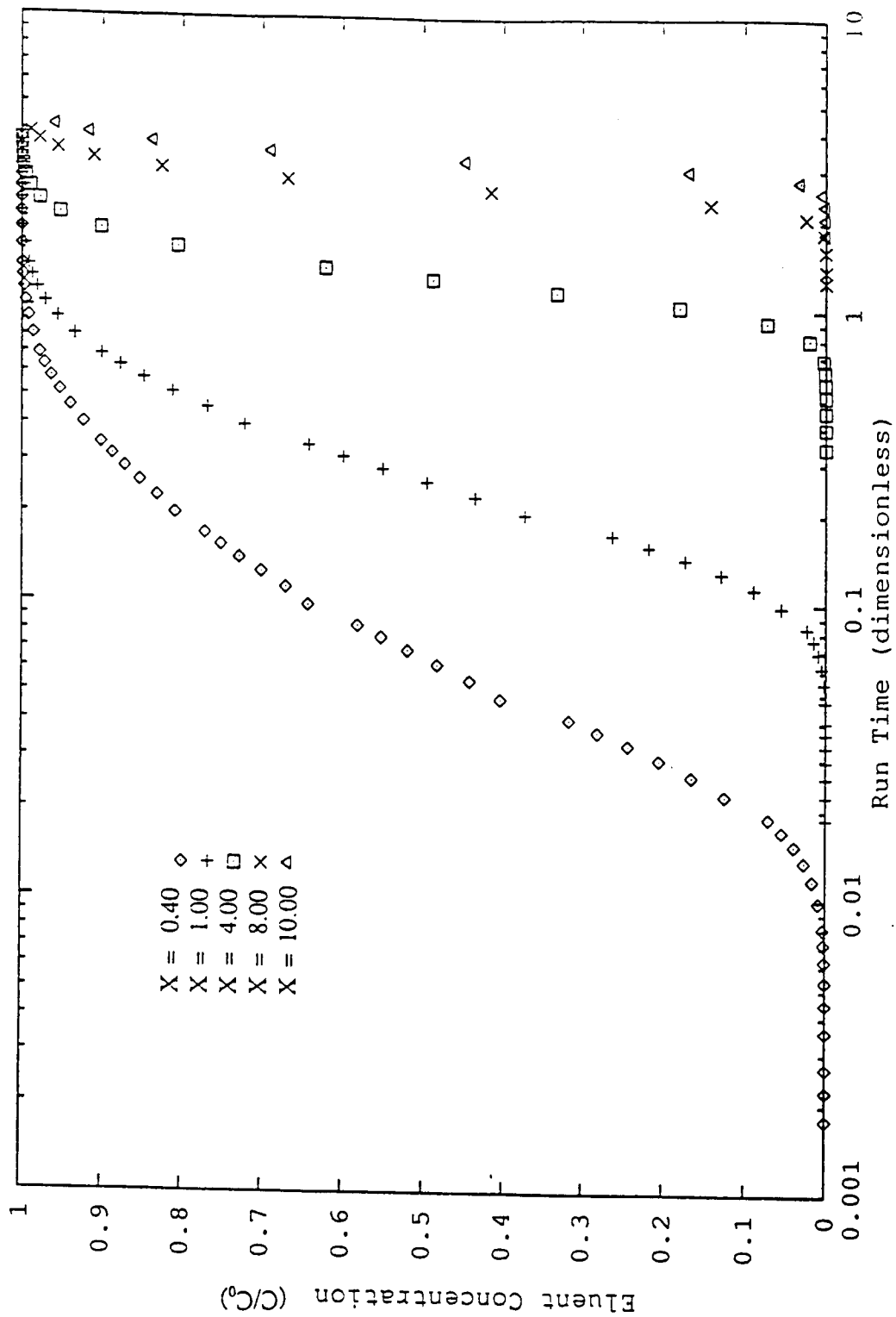


Figure 10: Effect of X on C/C_0 at $a_2C_0 = 1.0$

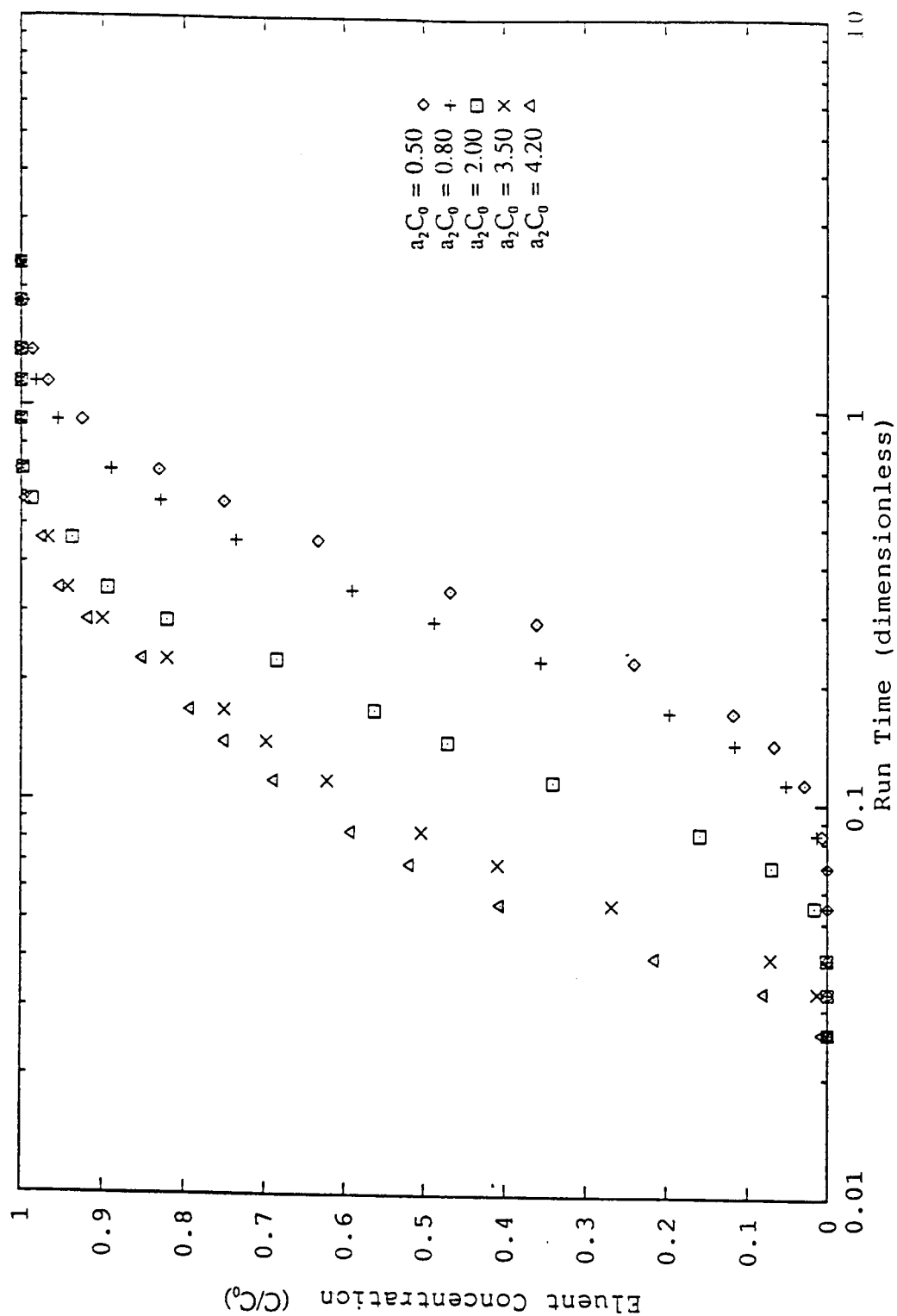


Figure 11: Effect of a_2C_0 on C/C_0 at $X = 1.0$

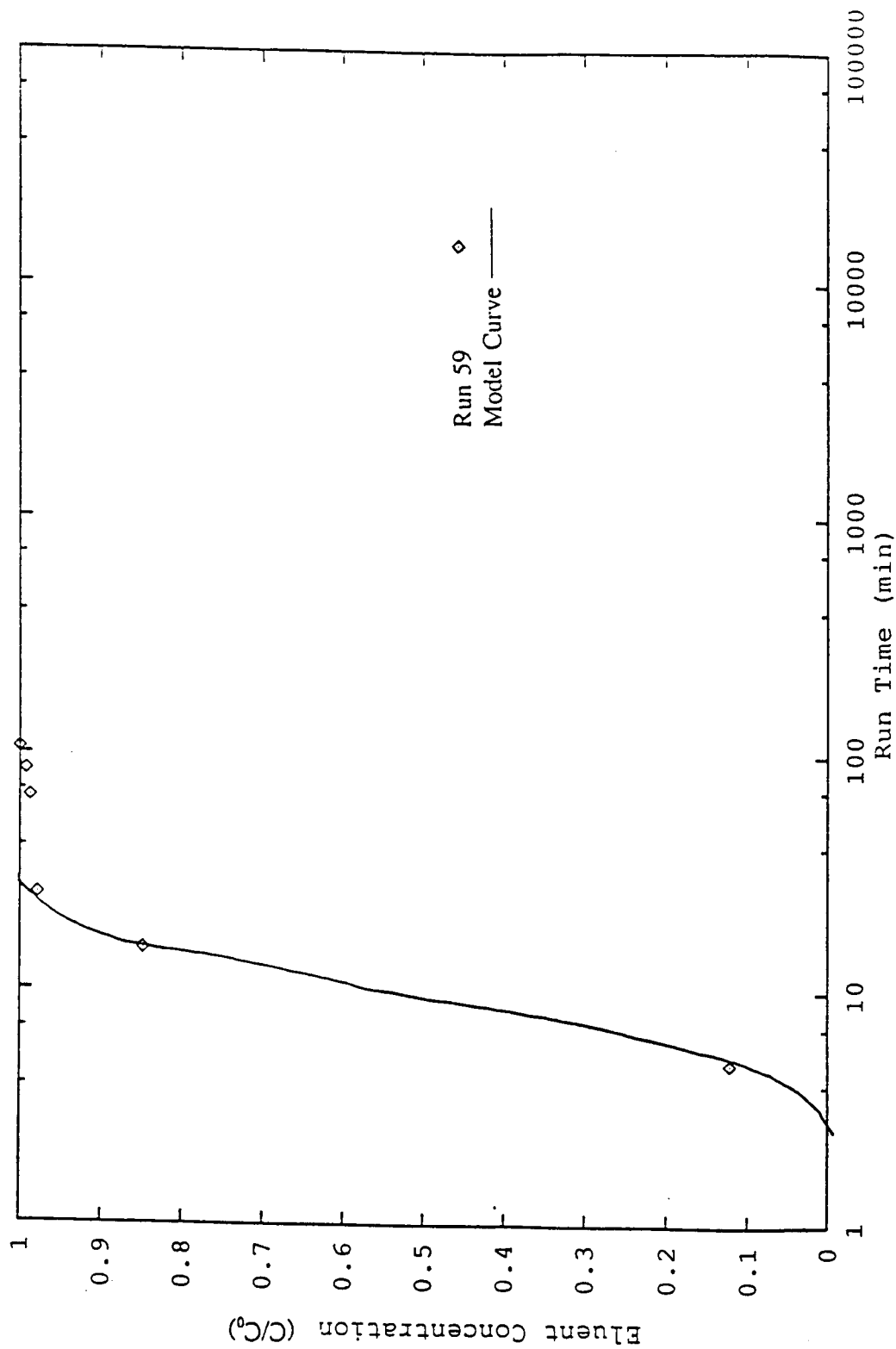


Figure 12: Typical Best Fit: Run 59 (IRA-68, 10 psig, 0.004 g $\text{SO}_4^{2-}/\text{ml}$, 20.3 cm Bed Height, 4.96 cm^2 Column Area, and 11.0 cc/min)

square of the particle diameter, R . The theoretical time, θ , as defined in Chapter III is related to the actual time by

$$\ln(\theta_g) = \ln(\theta) + \ln\left(\frac{2D}{R^2}\right). \quad (23)$$

This semi-log relationship makes the comparison of the actual and theoretical time a mere displacement along the abscissa [4]. The calculated diffusion parameters for IRA-35, IRA-68 and IRA-93 are given in Table 23. When dissolved impurities (spent seed) are present in the test solution, the diffusion parameters are roughly the same for IRA-35 and IRA-93. However IRA-68's diffusion parameter for dissolved impurities is approximately half that of the parameter for the pure K_2SO_4 solution. The probable cause for this effect is the temporary fouling of the pores caused by large ions or non-ionic impurities present in the spent seed extract. IRA-35 and IRA-93 have a polymer matrix that possibly prevents large ions or particles from entering the porous resin bead by reducing the size of the pores. In Table 24 the range of diffusion parameters for this investigation are compared with those found in the literature. The D/R^2 range found by Modeste [2] for IRA-68 compares well with the values found in the present investigation.

The diffusion parameters for each resin are plotted against CO_2 -pressure and solution concentration in Figures 13 and 14, respectively. In Figure 13 the general trend of the

Table 23: Calculated Diffusion Parameters for IRA-35, IRA-68, and IRA-93

C_0 (g SO_4^{2-} /ml)	a_2C_0	CO ₂ - Pressure (psig)	Column (no.)	X (no units)	D/R ² (s ⁻¹) x 10 ⁻³
IRA-35					
0.005	0.930	10	I	1.0	0.017
0.013	2.188	10	I	2.5	0.043
0.026	4.411	10	I	3.0	0.054
0.024	4.210	40	I	1.5	0.026
0.027	4.567	80	I	2.0	0.034
0.026	4.548	120	I	0.9	0.016
0.021*	3.531	10	I	3.0	0.052
0.026	4.504	10	II	2.0	0.008
IRA-68					
0.004	0.076	10	I	2.0	0.143
0.012	0.228	10	I	0.6	0.043
0.025	0.475	10	I	3.0	0.215
0.024	0.610	40	I	2.0	0.018
0.021	0.534	80	I	2.5	0.022
0.026	4.757	120	I	0.8	0.006
0.021*	0.399	10	I	1.5	0.108
0.027	0.513	10	II	2.0	0.034
IRA-93					
0.005	1.293	10	I	2.0	0.024
0.013	3.108	10	I	2.0	0.024
0.025	6.116	10	I	4.0	0.048
0.026	6.470	40	I	5.0	0.060
0.027	6.657	80	I	3.0	0.036
0.028	6.955	120	I	4.0	0.048
0.021*	5.145	10	I	5.0	0.060
0.027	6.537	10	II	4.0	0.011

* Spent Seed extract

Table 24: Comparison of the Diffusion Parameters with the Literature

System	Reference	Temperature (°C)	D/R^2 (s ⁻¹) x 10 ³
SO ₄ ²⁻ / IRA-35	Present	21	0.008-0.054
SO ₄ ²⁻ / IRA-68	[2]	20	0.050-0.183
SO ₄ ²⁻ / IRA-68	Present	21	0.006-0.215
SO ₄ ²⁻ / IRA-93	Present	21	0.011-0.060

diffusion parameters with increasing CO₂-pressure is downward. Above 40 psig all the resins show roughly the same downward trend of decreasing D/R^2 values. However, the point at 10 psig for IRA-68 seems to be in error. In Figure 14, as the solution concentration increases, the diffusion parameters also increase in value. The diffusion parameters for IRA-68 at 10 psig CO₂-pressure from this study compare well with those found by Modeste [2] at 20 psig and 40 psig CO₂-pressure and in general show a higher average value than for the other two resins. IRA-35 and IRA-93 have average diffusion parameters that are similar. The effective diffusion parameters seems to decrease in value as the superficial velocity increases. These observations are discussed in greater detail in the following section.

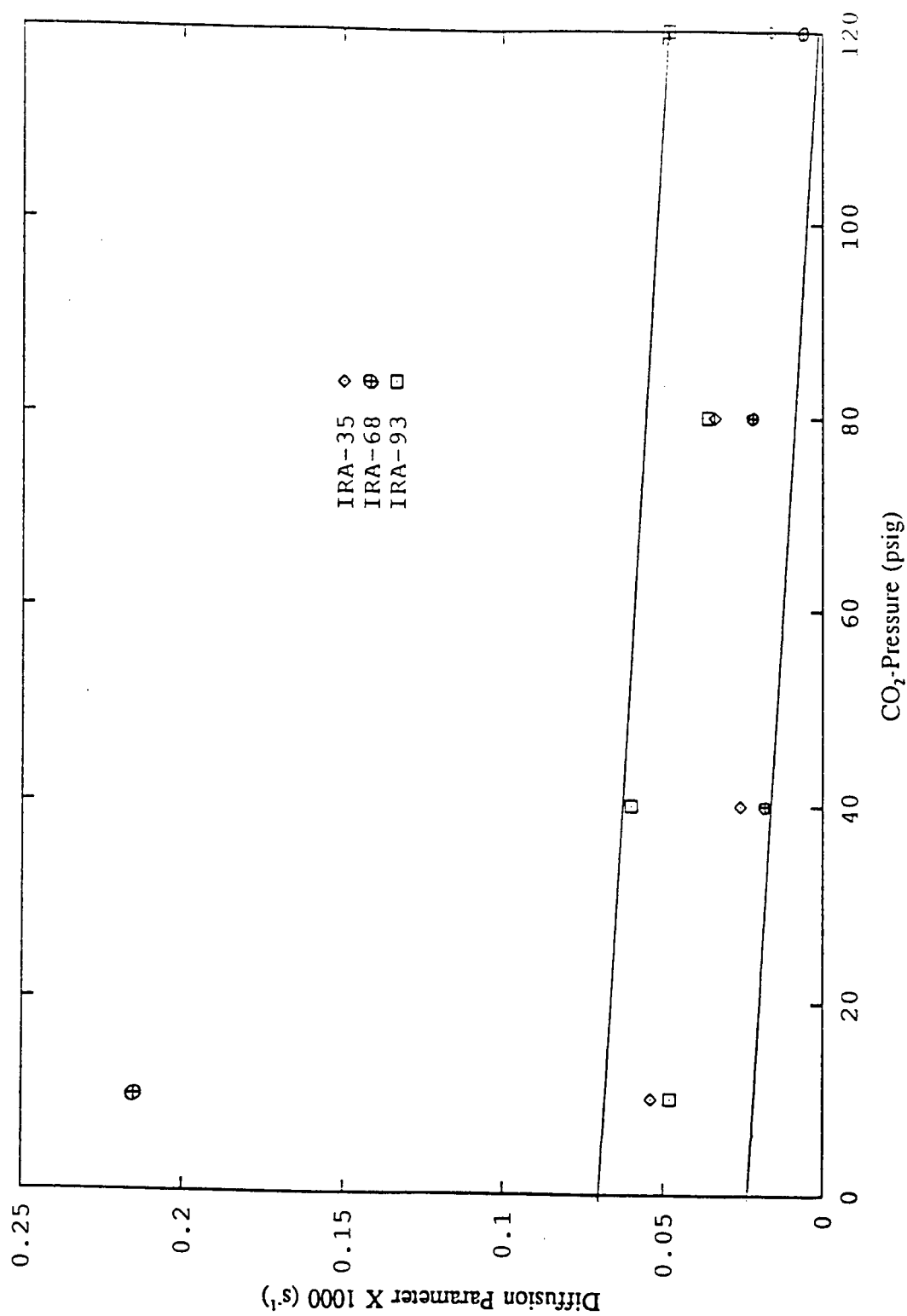


Figure 13: Effect of Static CO₂-Pressure on Diffusion Parameters

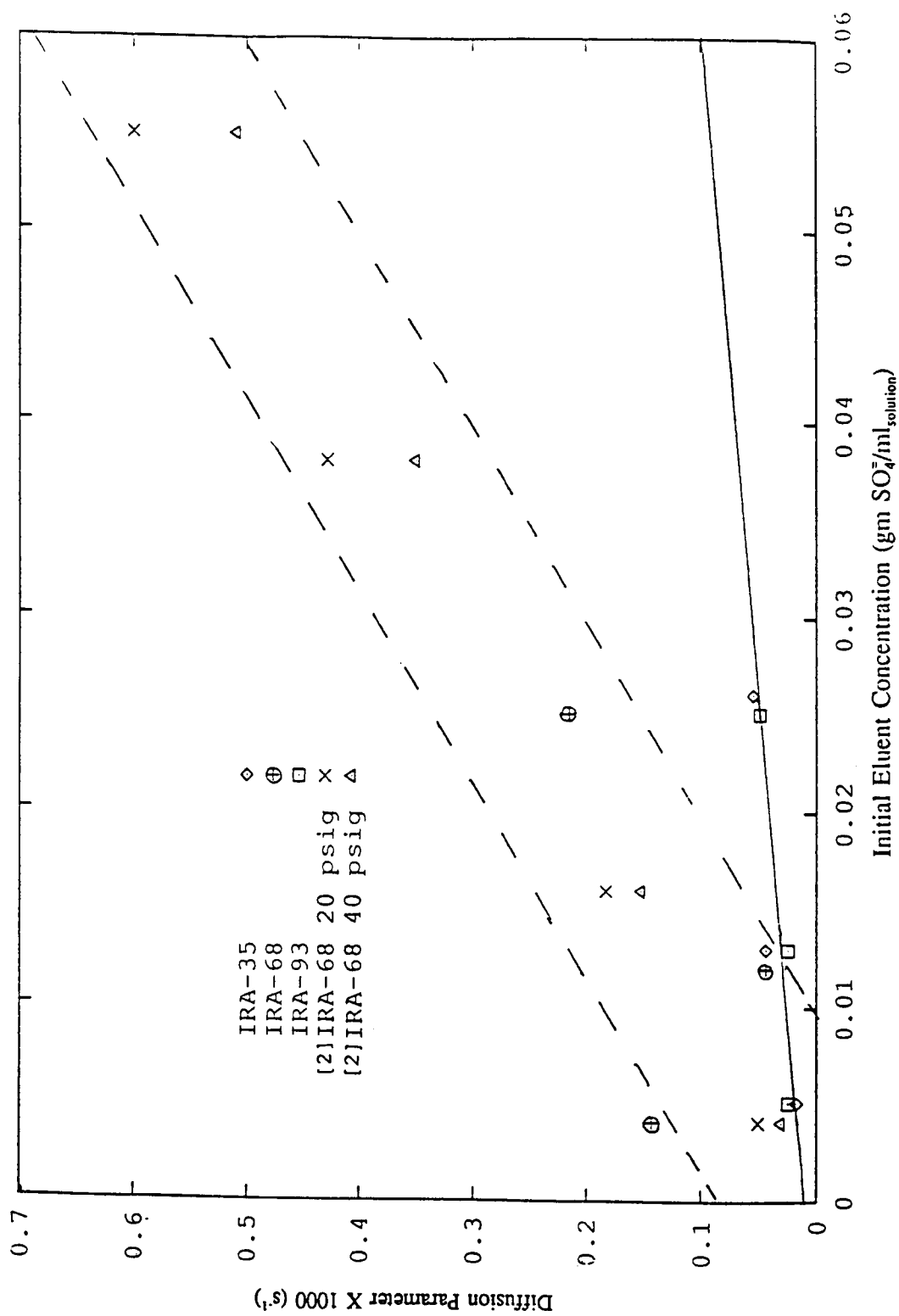


Figure 14: Effect of Solution Concentration on Diffusion Parameters

Effect of Process Variables

The process variable effects that will be discussed in this section include the effects of CO₂-pressure, solution concentration, product inhibition, resin bed height, dissolved impurities, and superficial velocity. The effects of these parameters on resin performance will be determined from their breakthrough curves and equilibrium loading.

Effect of Static CO₂-Pressure on the Equilibrium Loading

In Table 19 the effect of static CO₂-pressure on equilibrium loading was given. From the table the upward trend in equilibrium loading can be easily seen. The optimum static CO₂-pressure seems to be around 80-120 psig. IRA-93 seems to have the highest equilibrium loading at a given solution concentration.

Effect of Static CO₂-Pressure on the Ion-Exchange Kinetics

The typical effect of CO₂-pressure on the ion-exchange kinetics can be seen in Figure 15 for IRA-93. Figure 15 shows that increased static CO₂-pressure slightly alters the shape of the breakthrough curve. The curve's shape changes from a somewhat steep S-curve at 10 psig and 40 psig CO₂-pressure to a slightly more linear curve at 80 and 120 psig CO₂-pressure.

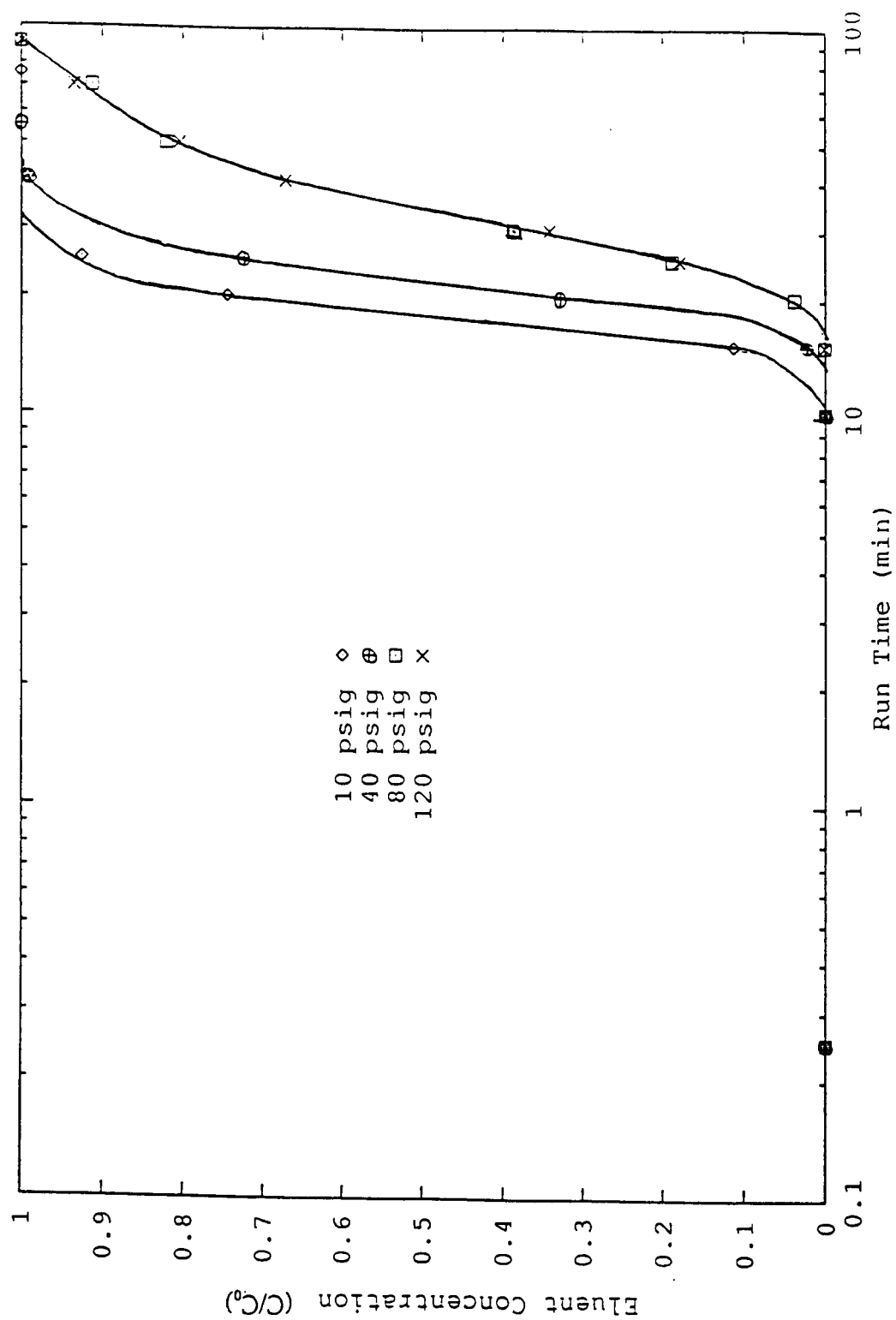


Figure 15: Effect of Static CO₂ Pressure on IRA-93

This change in shape is possibly due to the increased sulfate loading on the resin at higher CO₂-pressures, which would slightly decrease the diffusion parameter, causing the overall X parameter to be slightly lower (see Figure 10).

Effect of Solution Concentration on the Equilibrium Loading

The typical effect of concentration on the equilibrium loading is noted in Figure 9. From this figure of the non-linear Langmuir isotherms for IRA-35, IRA-68, and IRA-93, IRA-93 seems to respond better as the solution concentration increases.

Effect of Solution Concentration on the Ion-Exchange Kinetics

The solution concentration affects the ion-exchange kinetics of IRA-93 very little as shown by the breakthrough curve's shapes in Figure 16. The breakthrough curve shape and the diffusion parameters of Figure 16 and Table 23 for IRA-93 seem to show only a slight effect. Since the breakthrough curve's shape and the diffusion parameter are related, the effect of solution concentration on the ion-exchange kinetics of IRA-35 seems also to be very slight when considering the experimental scatter. From the diffusion parameters for IRA-68 in Table 23 and Figure 14, the effect of solution concentration on the diffusion parameters is significant. The

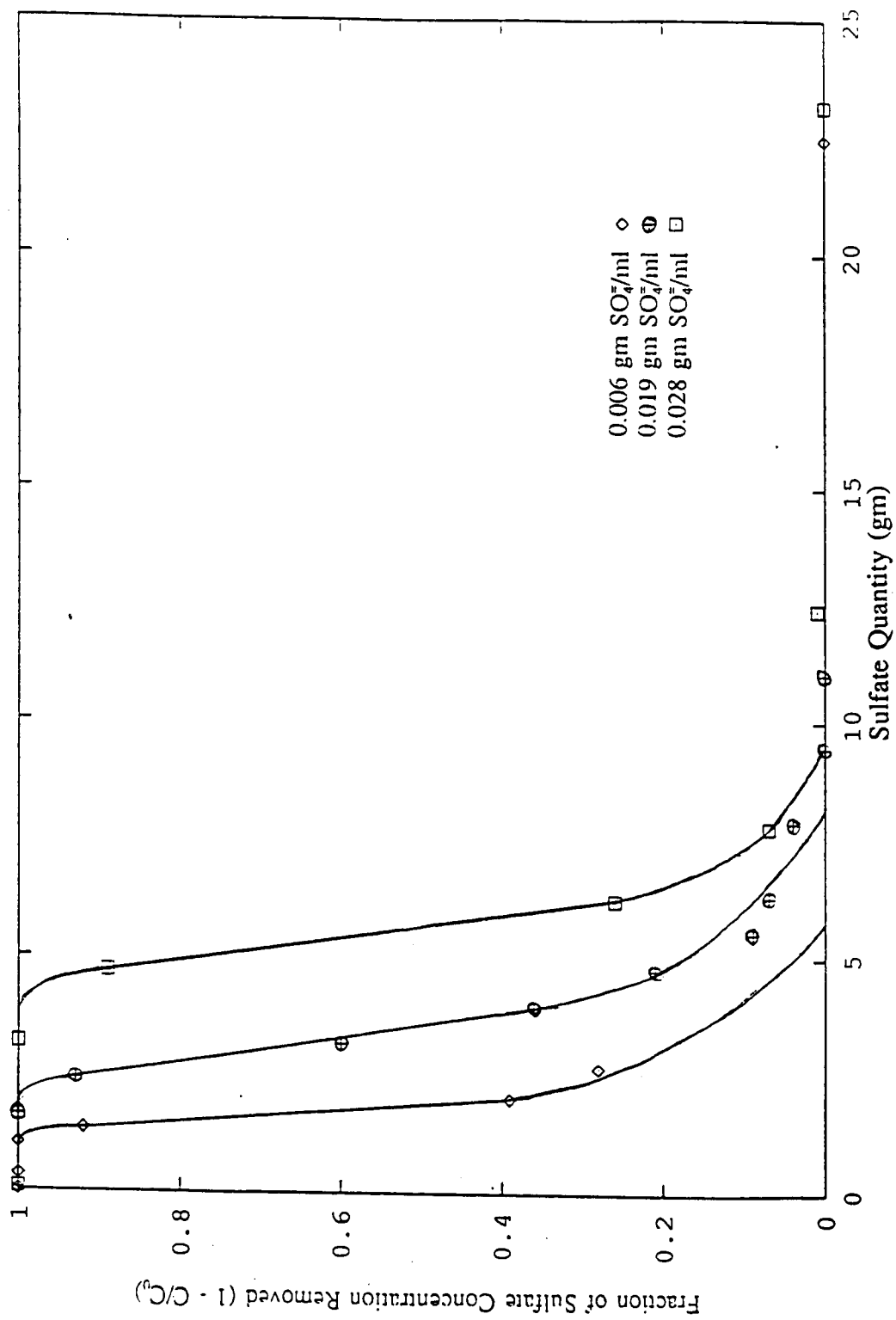


Figure 16: Effect of Solution Concentration on IRA-93

increasing diffusion parameters means an increasing X parameter, which means the effect on the breakthrough curves is the same as those presented in Figure 10. This phenomenon may also be caused by the gel-type matrix of IRA-68 because gel resins have larger pores and, therefore, better intraparticle diffusion.

Effect of Product Inhibition on the Equilibrium Loading

Product inhibition (PI) is the interference of the product, KHCO_3 , with the operation of the ion-exchange resin. By competing for or by forcing the SO_4^{2-} ions from the complex sites on the resin, the product reduces the resin's ability to remove SO_4^{2-} ions from the bulk phase solution. The magnitude of product inhibition for the experimental runs in this investigation is determined using solutions containing known molar ratios of $\text{KHCO}_3/\text{K}_2\text{SO}_4$. The pH of the $\text{KHCO}_3/\text{K}_2\text{SO}_4$ solution also changes with the molar ratio. The resulting pH values are given for the readers information in Table 25. The effects of product inhibition on equilibrium loading for the present and Butler's [1] investigations are presented in Table 25. Within experimental scatter, there seems to be no effect of product inhibition on the equilibrium loading of IRA-35. However, IRA-68 and IRA-93 seem to be affected by product inhibition. For IRA-68 Butler [1] saw a similar effect of increase in equilibrium loading at the 0.1 molar ratio, but

Table 25: Effect of Product Inhibition (PI) on Equilibrium Loading

Basis: 0.028 gm SO₄ / ml solution and 10 psig CO₂-Pressure

Molar Ratio (PI)	IRA-35 (g SO ₄ ²⁻ /ml _R)	IRA-68 (g SO ₄ ²⁻ /ml _R)		IRA-93 (g SO ₄ ²⁻ /ml _R)	Solution pH
0.0	0.073	0.065	0.063 _B	0.074	6.5
0.1	0.068	0.095	0.087 _B	0.098	9.1
1.0	0.072	0.061	0.047 _B	0.088	8.5

B is for Butler [1] runs at atmospheric pressure

R is for resin

at a molar ratio of 1.0 the decrease was significant. This increase in equilibrium loading for the 0.1 molar ratio was probably due to the extra bicarbonate ions eluting some hydroxide ions off the resin with help from the sulfate ions and leaving a sulfate ion in its place. For the molar ratio of 1.0, the ionic mobility for the sulfate/bicarbonate ions in solution could be affecting the affinity of the resin for the sulfate ions. The decrease in equilibrium loading for the molar ratio of 1.0 could also be caused by the extra bicarbonate ions eluting some sulfate ions off the resin and leaving a bicarbonate or hydroxide ion in its place.

Effect of Product Inhibition on the Ion-Exchange Kinetics

From Figure 17 the effect of product inhibition can be seen. The ion-exchange kinetics for IRA-68 measured in terms of breakthrough curve shape does not seem to change with the increasing ratio of product (KHCO₃) in the bulk solution.

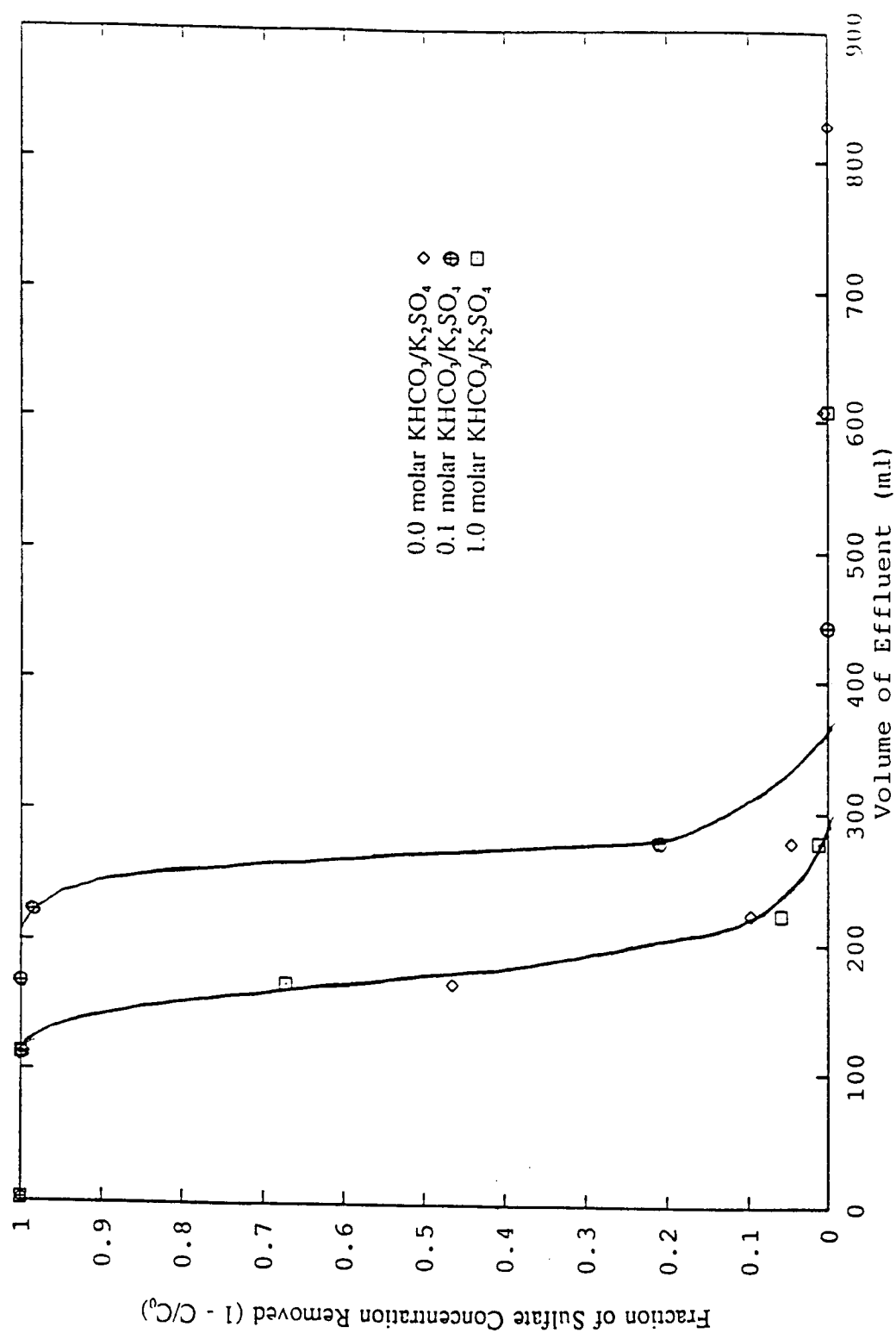


Figure 17: Effect of Product Inhibition on IRA-68

However the volume of eluent needed to exhaust the resin increases for the 0.1 molar ratio of $\text{KHCO}_3/\text{K}_2\text{SO}_4$. Butler [1] saw a similar effect of product inhibition on IRA-68.

Effect of Resin Bed Height on the Ion-Exchange Kinetics

Height of the resin bed should not affect the equilibrium loading of the resin measured in terms of gm SO_4^{2-} /ml of resin. Hence only the kinetic effect was evaluated. The resin bed height affects the ion-exchange kinetics only slightly, if at all, when considering experimental error. The typical breakthrough curves presented in Figure 18 for IRA-93 as the fraction of sulfate removed versus the number of bed volumes shows this result. Bed volume is defined as the volume of the bulk phase solution at any time divided by the volume of resin and voids in the fixed-bed. The reason for plotting these curves as sulfate removed versus the number of bed volumes was because the volume of effluent would be directly proportional to the resin volume [1], thereby forcing the curves to overlap. The fact that the curves of the present investigation do overlap within experimental error proves that no channeling occurred. Channeling would result in not all of the resin bed being utilized and would show a steadily rising curve rather than a typical S-shaped curve. Butler [1] saw a similar phenomenon of in the ion-exchange kinetics for IRA-68.

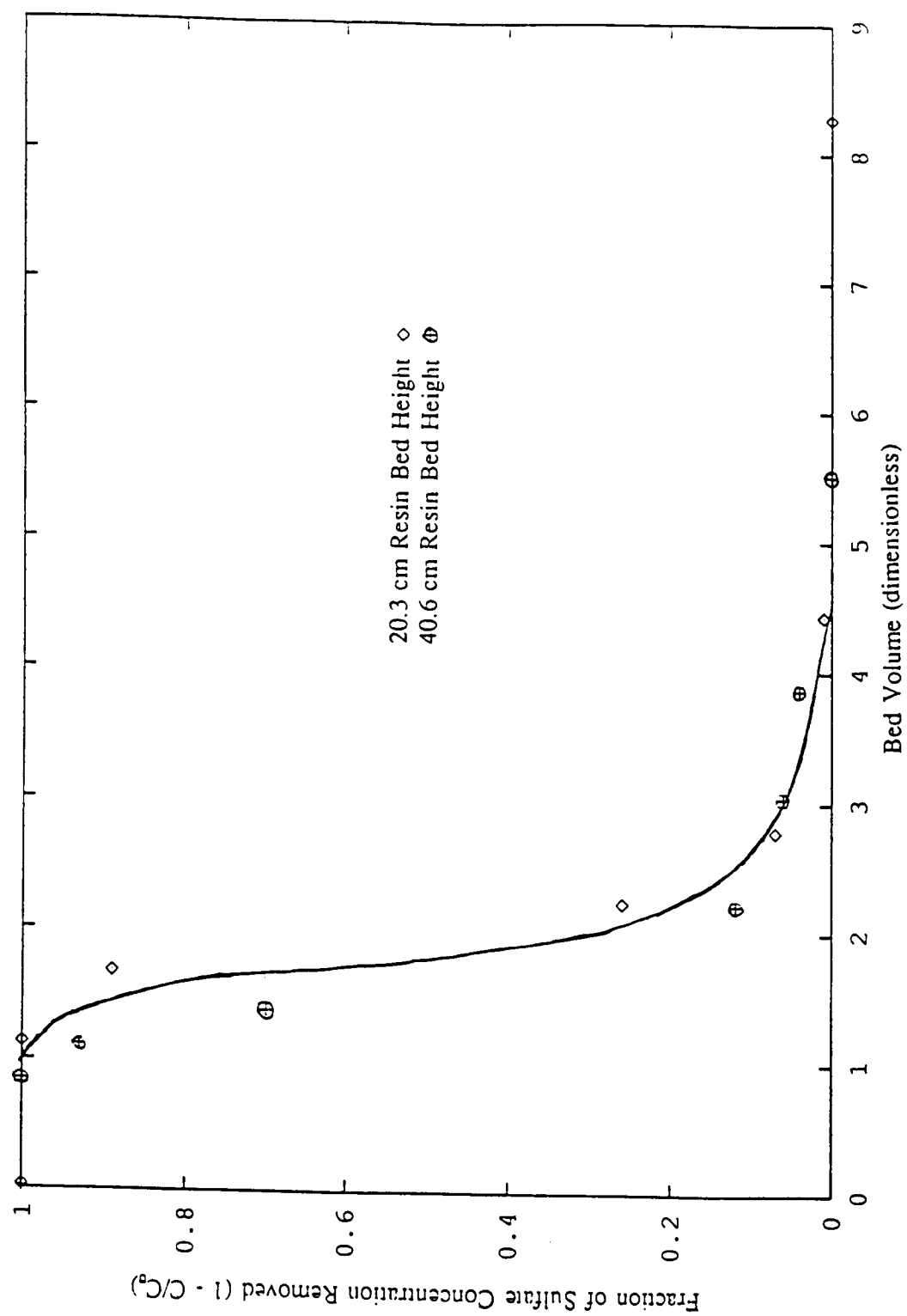


Figure 18: Effect of Resin Bed Height on IRA-93

Effect of Dissolved Impurities on the Equilibrium Loading

The effect of dissolved impurities (spent seed) on equilibrium loading and ion-exchange kinetics is evaluated below. (The spent seed extract used in the present study contained about 588 ppm chloride.) In Table 26 the effect on the resins' equilibrium loading is shown. There seems to be a slight effect on IRA-35; however, this could be the result of experimental error. On IRA-68 and IRA-93 resin, no change in equilibrium loading values were observed suggesting that low levels of dissolved impurities possibly did not change the capacity of these two resins. However, depending upon the spent seed material, the concentrations of dissolved impurities could change and subsequently could cause a significant change in the resin's capacity for the sulfate ions. For the spent seed taken from the UTSI MHD plant, the composition of the spent seed could change with every test run because the facility tests different parameters for every test run (not a steady-state facility).

Table 26: Effect of Dissolved Impurities on Equilibrium Loading

Basis: 10.0 psig CO₂ and 0.028 gm SO₄²⁻/ml

SO ₄ ²⁻ Source (g SO ₄ ²⁻ /ml)	IRA-35 (g SO ₄ ²⁻ /ml _R)	IRA-68 (g SO ₄ ²⁻ /ml _R)	IRA-93 (g SO ₄ ²⁻ /ml _R)
Reagent	0.073	0.065	0.074
Spent Seed	0.058	0.060	0.076

R is for resin.

Effect of Dissolved Impurities on the Ion-Exchange Kinetics

The typical effect of dissolved impurities on the ion-exchange kinetics is shown in Figure 19. The figure shows the breakthrough curves for the runs using a reagent grade potassium sulfate and a spent seed solution. Within the experimental error, the shape of the curves are approximately the same. Therefore, no change in the ion-exchange kinetics can be detected. From the batch results discussed in Chapter V, the diffusion parameters of Table 23, and Figure 19, there seems to be little or no effect of dissolved impurities on the ion-exchange kinetics of the three candidate resins. Butler [1] also showed a similar slight to no kinetic effect due to dissolved impurities.

Effect of Superficial Velocity on the Ion-Exchange Kinetics

Superficial velocity is not expected to affect the equilibrium loading except at very high values. These high velocities could cause the bulk solution to partially or completely by-pass the ion-exchange material resulting in low equilibrium capacities. Since we did not use such a high velocity, we evaluated only the effect on the ion-exchange kinetics for the three candidate resins.

From the typical normalized curves of C/C_0 versus the grams of sulfate ($\text{gm SO}_4/\text{ml}_{\text{resin}}$) shown in Figure 20 for IRA-35

and the diffusion parameters of Table 23, there is a definite effect of superficial velocity on the ion-exchange kinetics. This effect is considered to be the result of the type of mass transfer step that is controlling the overall mass transfer. For instance, in the case of IRA-35 at the higher superficial velocity of 0.036 cm/s, the shallow **S**-curve of Figure 20 and the calculated effective diffusion parameter of Table 23 are believed to be the result of the mass transfer being controlled by the solid-phase (intraparticle) diffusion. Whereas the near-vertical (steep) **S**-curve of Figure 20 and the calculated effective diffusion parameter of Table 23 at the slower superficial velocity of 0.009 cm/s are believed to be due to the mass transfer being controlled by the liquid-film diffusion. For the former the model developed by Antonson [3] and used in the present work and that of Modeste [2] would be a more appropriate model. For the latter the Selke and Bliss model which Butler [1] used would be preferable. Butler [1] using the Selke and Bliss model also saw a significant effect of superficial velocity on the ion-exchange kinetics of IRA-68 measured in terms of the parameter $K_L S$, which is the liquid-film mass transfer coefficient (K_L) and the resin's effective surface area (S). Based on these preliminary results, it is necessary to use a model or models that can use different mass transfer controlling steps at different superficial velocities.

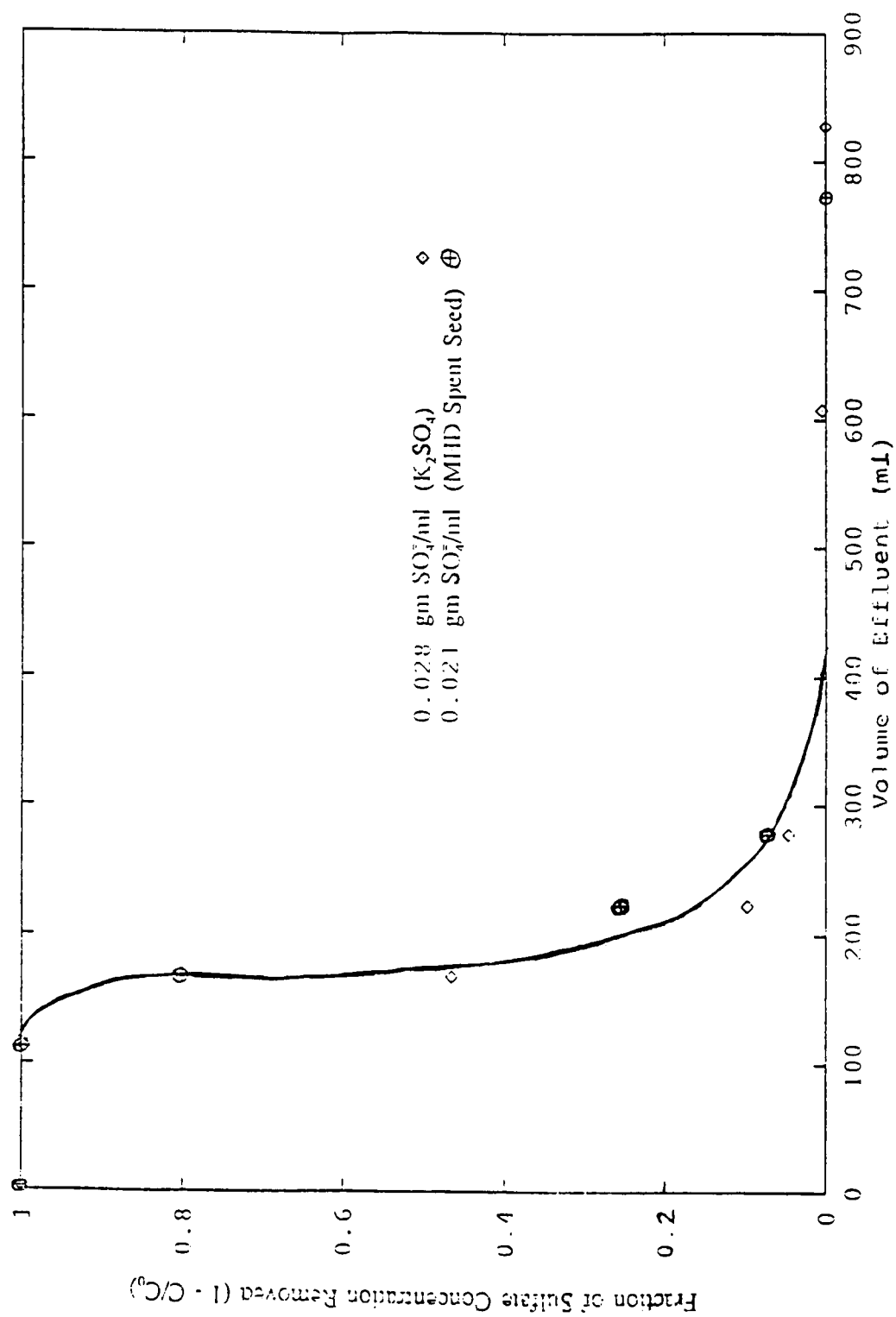


Figure 19: Effect of Dissolved Impurities on IRA-68

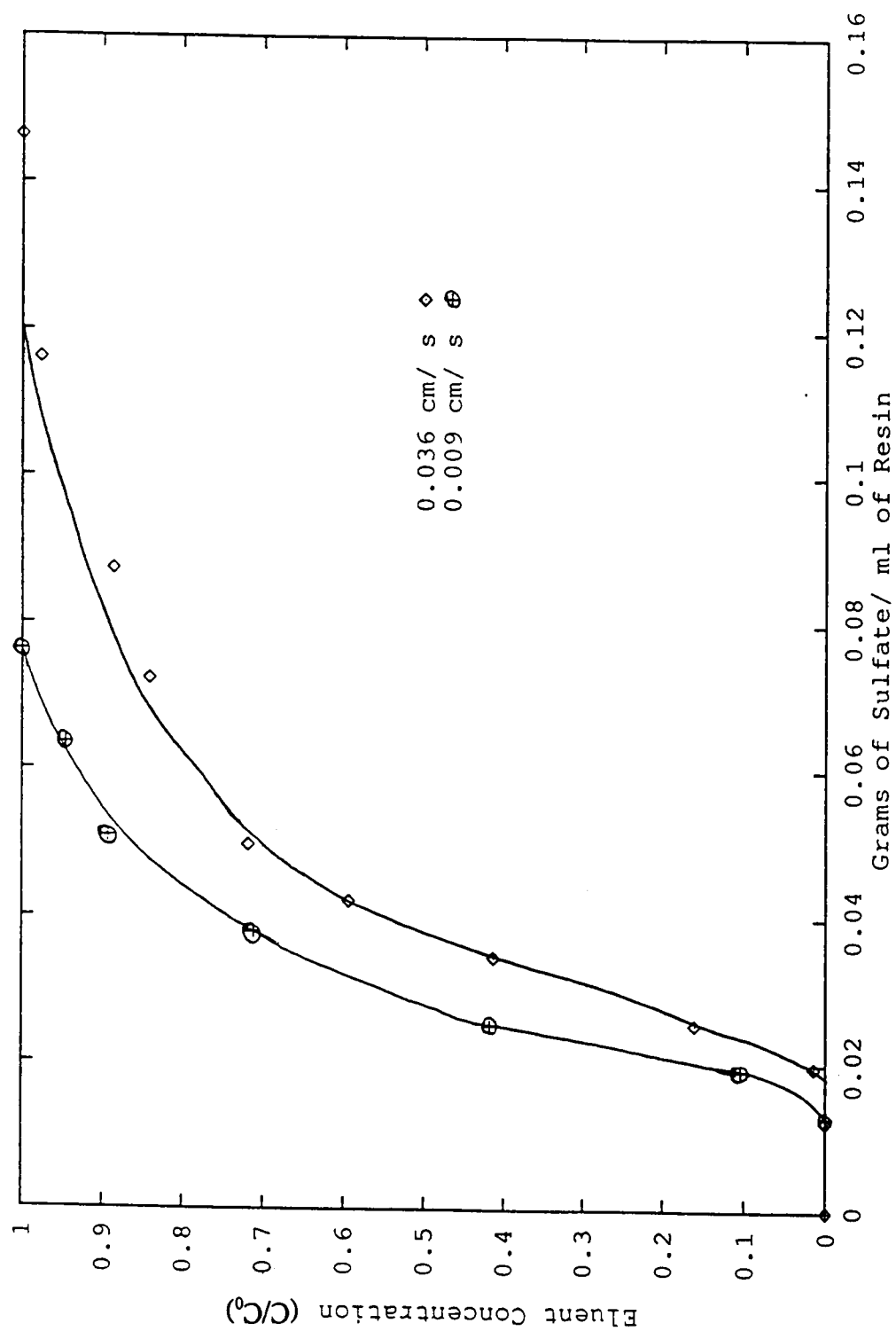


Figure 20: Effect of Superficial Velocity on IRA-35

CHAPTER VIII

CONCLUSIONS AND RECOMMENDATIONS

For industrial applications the most important attributes of an ion-exchange resin are high equilibrium capacity, high resistance to dissolved impurities, and high diffusion parameters. From the discussion of Chapter VII, none of the three candidate resins performed significantly better than the others for the attributes above. Therefore, no determination as to the best resin could be made with the available data. However the data provides a basis for other investigators in evaluating these and other ion-exchange resins.

For the resins of the present investigation, work is in progress that could determinate the best resin for the application of MHD spent seed regeneration. This work consists of investigating the resins performance during cyclic operations and the optimization of the resin's regeneration step.

For future study the following should be considered:

- pre-run static pressure should be investigated as a possible process variable.
- more experimental runs should be carried out to decrease the experimental scatter.

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LIST OF REFERENCES

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APPENDIXES

APPENDIX A

COMPUTER PROGRAMS

Antonson's Model 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(3,1000),TAU(1000),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
C  DIFFERENCE 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(1)=' ,n
do j= 1,n
  write(15,*) 'j=',j,' de(1,j)=' ,DE(1,J)
  write(15,*) 'e(1,j)=' ,E(1,J)
enddo
write(15,*) 'EE(1)=' ,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=',1,' nn(1)=' ,nn(1)
  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(1,j)
    write(15,*) 'j=',j,' de(1,j)=' ,DE(L,J)
    write(15,*) 'e(1,j)=' ,E(L,J)
  enddo
  write(15,*) 'ee(1)=' ,ee(1),' 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)
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/CO
*')
          write(16,201) x,tau(1),phi(2,1),k2
201      format(1x,f10.6,2x,f10.5,2x,f12.8,2x,'k1=',i3)
          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 + 0.5d+00
      if (t.gt.10.0d+00) t = 1.5d+00
      chk = 10.0 * (10.0**(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

```

Antonson's Model I/O

Input:
(FOR008.DAT)

\$CONTROL

KK= 571,N= 160,M2=10,IH= 7,EL= 0.0000900,CUT= 1.0,
XZERO= 0.0000000,I1= 1,I2= 1,K2= 1,NJ= 1,CON= 4.2

\$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, 0.0000000000E+00
$END

```

```

(FOR010.DAT)
$XINC
HINC=0.00031250,0.00062500,0.00125000,0.00250000,
0.00500000,0.01000000,0.02000000,0.00000000,
0.00000000,0.00000000,0.00000000,0.00000000,
0.00000000,0.00000000,0.00000000,0.00000000,
0.00000000,0.00000000,0.00000000,0.00000000
$END

```

Output:

```

(FOR015.DAT)
-last of file-
l=          9  nn(l)=  11.39574819258996
j=          1  de(l,j)= 0.8925275988720041
e(l,j)= 0.9452457370808359
j=          2  de(l,j)= 0.6345803461272869
e(l,j)= 0.8034885385536415
j=          3  de(l,j)= 0.3594139163551605
e(l,j)= 0.6260121548967610
j=          4  de(l,j)= 0.1621610205781488
e(l,j)= 0.4605622672346955
j=          5  de(l,j)= 5.8282927486142327E-02
e(l,j)= 0.3313051682058636
j=          6  de(l,j)= 1.6687049537052544E-02
e(l,j)= 0.2402354167431813
j=          7  de(l,j)= 3.8059323214744249E-03
e(l,j)= 0.1788115824735156
j=          8  de(l,j)= 6.9148995536009383E-04
e(l,j)= 0.1373306220995695
j=          9  de(l,j)= 1.0008154455255385E-04
e(l,j)= 0.1085723628919856
j=         10  de(l,j)= 1.1538927139468183E-05
e(l,j)= 8.7951401479660329E-02
j=         11  de(l,j)= 1.0597908646899742E-06
e(l,j)= 7.2687870367782662E-02
j=         12  de(l,j)= 7.7538647390263097E-08
e(l,j)= 6.1078062178106253E-02
j=         13  de(l,j)= 4.5191793632202719E-09
e(l,j)= 5.2042849679711040E-02
j=         14  de(l,j)= 2.0981872562319753E-10
e(l,j)= 4.4873681804964458E-02
j=         15  de(l,j)= 7.7601875933333816E-12
e(l,j)= 3.9089962824667501E-02

```

```

ee(l)= 4.756525517000000      sum= 4.189287678514942
l=      10 nn(l)= 8.190694013424036
j=      1 de(l,j)= 0.7966055147482250
e(l,j)= 0.8944518225707960
j=      2 de(l,j)= 0.4026922156910272
e(l,j)= 0.6566832867291596
j=      3 de(l,j)= 0.1291783632697543
e(l,j)= 0.4255048175870696
j=      4 de(l,j)= 2.6296196594946786E-02
e(l,j)= 0.2676237572646299
j=      5 de(l,j)= 3.3968996363549247E-03
e(l,j)= 0.1753073016500951
j=      6 de(l,j)= 2.7845762225204553E-04
e(l,j)= 0.1221221185214646
j=      7 de(l,j)= 1.4485120835643705E-05
e(l,j)= 8.9746063627352752E-02
j=      8 de(l,j)= 4.7815835836390456E-07
e(l,j)= 6.8712792422657331E-02
j=      9 de(l,j)= 1.0016315560024821E-08
e(l,j)= 5.4291614490879781E-02
j=     10 de(l,j)= 1.3314683952995538E-10
e(l,j)= 4.3976208172236908E-02
j=     11 de(l,j)= 1.1231566768803231E-12
e(l,j)= 3.6343973700861826E-02
ee(l)= 3.216925144000000      sum= 2.834763756737204
(FOR016.DAT)
-last of file-

```

X2	THETA2	C/C0	k1= 72
1.010625	0.00000	0.00000000	
	0.01350	0.00000106	
	0.01530	0.00000687	
	0.01710	0.00003116	
	0.01890	0.00011332	
	0.02250	0.00191689	
	0.02610	0.01029521	
	0.02970	0.03356999	
	0.03330	0.07988126	
	0.03690	0.14265530	
	0.04050	0.20662756	
	0.04770	0.33892142	
	0.05490	0.39811937	
	0.06210	0.45679068	
	0.06930	0.50591441	
	0.07650	0.54690528	
	0.08370	0.58156476	
	0.09810	0.63897839	
	0.11250	0.67604897	
	0.12690	0.71020823	
	0.14130	0.73889619	
	0.15570	0.76317310	
	0.17010	0.78400287	
	0.19890	0.81550931	

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2.3723329628314027E-06	3.4369528933431148E-06
4.8950850489032360E-06	6.8672777130338036E-06
9.5043466820515787E-06	1.2993701216032494E-05
1.7566768688345724E-05	2.3507668370406631E-05
3.1163294732225455E-05	4.0954980190507917E-05
5.3391915801316581E-05	6.9086515465457965E-05
8.8771914326539469E-05	1.1332179476769566E-04
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7.6786292410904039E-04	1.2370695703006335E-03
1.9168899869327419E-03	2.8551859970022964E-03
4.1023897236620796E-03	5.7141474186632665E-03
7.7540183700686161E-03	1.0295212539152880E-02
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3.3569992946796773E-02	4.0910212351274476E-02
4.9252508654906407E-02	5.8576018684375127E-02
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1.032747472441824	1.017311365305183
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1.032747472441844	1.017311365305199
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1.130010043135698	1.032747472441845
1.017311365305200	1.011557610387003
10.80837350873025	1.130010043135698
1.032747472441846	1.017311365305200
1.011557610387004	10.80837350873025
1.130010043135699	1.032747472441846


```

1.032747472441846      1.017311365305201
  1.011557610387004      10.80837350873025
0.0000000000000000E+00  0.0000000000000000E+00

```

Modeste's Trapezoid Method Program

```

      IMPLICIT REAL*8 (A-H,O-Z)
      DIMENSION X(50),Y(50)
C
C*****
C THIS PROGRAM WILL CALCULATE THE AREA UNDER THE
C BREAKTHROUGH CURVE AND THE EQUILIBRIUM CAPACITY, USING THE
C TRAPEZOIDAL METHOD
C*****
C
      OPEN(UNIT=21,file='input.dat')
      open(unit=20,file= 'output.dat',status='new')
      read(21,*) n,c,flow,rv,iresin
C*****
C      iresin corresponds to the resin used:
C          IRESIN = 1      IRA-68
C          IRESIN = 2      IRA-35
C          IRESIN = 3      IRA-93
C*****
C
      if (iresin.eq.1) resin = 0.73
      if (iresin.eq.2) resin = 0.735
      if (iresin.eq.3) resin = 0.715
      DO 5 I= 1,N
        read(21,*) x(I),y(I)
        temp = y(i) / c
        y(i) = 1.0 - temp
        WRITE(20,*) X(I),temp
5      continue
      CLOSE (UNIT=21)
      NINT = N - 1
      AREA = 0.0
      DO 10 I= 1,NINT
        AREA = AREA + (Y(I) + Y(I+1)) * (X(I+1) - X(I)) /
*          2.0
10     continue
      WRITE(20,*) 'THE AREA IS',AREA
      CAP = FLOW * AREA * C / (resin * RV * 1000000)
      WRITE(20,*) ' THE CAPACITY IS',CAP
      close(unit=20)
      STOP
      END

```

Modeste's Program I/O

Input:
(INPUT.DAT)

10,3280,10.8,100,1
0.25,74
2.75,50
5.25,33
7.75,28
10.25,27
15.25,905
20.25,2600
25.25,3044
30.25,3144
35.25,3280

Output:
(OUPUT.DAT)

2.50000000E-001	2.2560975609756E-002
2.75000000000000	1.5243902439024E-002
5.25000000000000	1.0060975609756E-002
7.75000000000000	8.5365853658537E-003
10.25000000000000	8.2317073170732E-003
15.25000000000000	2.7591463414634E-001
20.25000000000000	7.9268292682927E-001
25.25000000000000	9.2804878048780E-001
30.25000000000000	9.5853658536585E-001
35.25000000000000	1.00000000000000
THE AREA IS	17.58041158536600
THE CAPACITY IS	8.5310751195653E-003

APPENDIX B

EXPERIMENTAL FIXED-BED DATA

Run Information

RUN	RESIN (IRA-)	RESIN MLS/"BH	EXHAUSTION CCPM/MIN	T/P °C/PSIG	SAMPLE MIN/CCPM	SOLUTION CONCENTRAION	EQ. LOADING GM SO ² /ML RESIN
001	68	200/16	10.6/BAD	21/13	1.5/4.0	5.0% K ₂ SO ₄	-
002	68	200/16	10.6/BAD	21/13	2.0/4.3	SAME	-
003	68	250/20	13.1/75	21/15	0.7/4.5	SAME	0.020
004	68	225/18	5.3/150	21/15	0.7/4.5	SAME	0.018
005	68	50/4	82.8/BAD	21/11	1.0/3.0	0.1% K ₂ SO ₄	-
006	35	25/2	9.8/BAD	21/12	2.5/1.6	SAME	-
007	35	25/2	9.8/BAD	21/12	2.0/2.7	SAME	-
008	35	25/2	11.1/260	21/10	2.0/2.7	SAME	0.068
009	35	25/2	11.1/320	21/10	2.0/2.7	SAME	0.066
010	35	100/8	10.4/80	21/10	2.0/2.7	2.5% K ₂ SO ₄	0.025
011	35	100/8	11.2/122	21/10	2.0/2.6	SAME	0.028
012	35	100/8	11.6/51	21/10	0.5/11.6	5.0% K ₂ SO ₄	0.067
013	68	100/8	11.3/BAD	21/10	0.5/11.3	SAME	-
014	68	100/8	11.6/50	21/10	0.5/11.6	SAME	0.056
015	68	100/8	10.6/66	21/10	0.5/10.6	SAME	0.075
016	93	100/8	11.0/78	21/10	0.5/11.0	SAME	0.080
017	68	100/8	11.0/78	21/10	0.5/11.0	2.5% K ₂ SO ₄	0.027
018	35	100/8	10.8/78	21/10	0.5/10.8	SAME	0.031
019	93	100/8	11.2/78	21/10	0.5/11.2	SAME	0.045
020	68	100/8	10.8/298	21/10	0.5/10.8	1.0% K ₂ SO ₄	0.009
021	35	100/8	11.0/291	21/10	0.5/11.0	SAME	0.073
022	93	100/8	11.0/341	21/10	0.5/11.0	SAME	0.058
023	35	200/16	11.0/BAD	21/10	0.5/11.0	5.0% K ₂ SO ₄	-
024	35	200/16	11.0/BAD	21/10	0.5/11.0	SAME	-
025	35	100/8	11.0/BAD	21/10	0.5/11.0	SAME	-
026	35	100/8	11.0/25	21/10	0.5/11.0	SAME	0.079
027	35	200/16	11.0/35	21/10	0.5/11.0	SAME	0.040
028	68	100/8	11.0/75	21/10	0.5/11.0	SAME	0.063
029	68	200/16	11.2/55	21/10	0.5/11.2	SAME	0.042
030	93	100/8	11.0/75	21/10	0.5/11.0	SAME	0.073
031	93	200/16	11.0/100	21/10	0.5/11.0	SAME	0.070
032	93	100/8	11.0/70	21/10	0.5/11.0	2.5% K ₂ SO ₄	0.052
033	68	100/8	11.0/70	21/10	0.5/11.0	SAME	0.028
034	35	100/8	11.0/70	21/10	0.5/11.0	SAME	0.033
035	93	100/8	11.0/55	21/40	0.5/11.0	5.0% K ₂ SO ₄	0.096
036	93	100/8	11.0/90	21/80	0.5/11.0	SAME	0.164
037	93	100/8	11.0/90	21/120	0.5/11.0	SAME	0.168
038	93	100/8	11.0/40	21/10	0.5/11.0	5.0% SP SD	0.076
039	68	100/8	11.0/55	21/10	0.5/11.0	SAME	0.060
040	35	100/8	11.0/70	21/10	0.5/11.0	SAME	0.058
041	35	100/8	11.0/115	21/40	0.5/11.0	5.0% K ₂ SO ₄	0.098
042	35	100/8	11.0/115	21/80	0.5/11.0	SAME	0.130
043	35	100/8	11.0/115	21/120	0.5/11.0	SAME	0.126
044	68	100/8	11.0/25	21/40	0.5/11.0	5.0% K ₂ SO ₄	0.058
045	68	100/8	11.0/115	21/80	0.5/11.0	SAME	0.061
046	68	100/8	11.0/115	21/120	0.5/11.0	SAME	0.136
047	68	450/8	11.0/95	21/10	0.5/11.0	5.0% K ₂ SO ₄	0.043
048	93	450/8	11.0/135	21/10	0.5/11.0	SAME	0.074
049	35	450/8	11.0/135	21/10	0.5/11.0	SAME	0.058
050	35	100/8	11.0/70	21/10	0.5/11.0	SAME pH=8.5	0.076
051	93	100/8	11.0/70	21/10	0.5/11.0	SAME	0.094
052	68	100/8	11.0/70	21/10	0.5/11.0	SAME	0.069
053	93	100/8	11.0/70	21/10	0.5/11.0	0.1HCO ₃ /SO ₄	0.098
054	35	100/8	11.0/55	21/10	0.5/11.0	SAME pH=9.1	0.068
055	68	100/8	11.0/40	21/10	0.5/11.0	SAME pH=9.1	0.095
056	68	100/8	11.0/55	21/10	0.5/11.0	1.0HCO ₃ /SO ₄	0.061

057	93	100/8	11.0/70	21/10	0.5/11.0	SAME pH=8.4	0.088
058	35	100/8	11.0/70	21/10	0.5/11.0	SAME pH=8.4	0.072
059	68	100/8	11.0/115	21/10	0.5/11.0	1.0% K_2SO_4	0.013
060	68	100/8	11.0/70	21/10	0.5/11.0	2.5% K_2SO_4	0.034
061	35	100/8	11.0/55	21/10	0.5/11.0	SAME	0.034
062	93	100/8	11.0/70	21/10	0.5/11.0	SAME	0.048

<u>Time</u> <u>(min)</u>	<u>C/C₀</u>	<u>Time</u> <u>(min)</u>	<u>C/C₀</u>
Run 3:		111.00	0.042
0.35	0.003	121.00	0.068
1.05	0.004	131.00	0.099
3.15	0.001	141.00	0.143
3.85	0.001	151.00	0.191
5.25	0.001	161.00	0.228
7.35	0.199	171.00	0.272
8.75	0.495	181.00	0.309
10.85	0.740	191.00	0.347
12.25	0.841	201.00	0.384
13.65	0.861	211.00	0.434
14.35	0.905	221.00	0.502
15.75	0.977	231.00	0.566
17.85	0.969	241.00	0.658
19.25	1.000	251.00	0.754
		261.00	0.838
		269.00	0.925
Run 4:		281.00	0.980
3.85	0.012	300.00	1.000
7.35	0.008		
10.85	0.024	Run 9:	
14.35	0.280	1.00	0.004
17.85	0.566	11.00	0.004
21.35	0.791	21.00	0.007
24.85	0.838	31.00	0.004
31.85	0.899	41.00	0.002
35.35	0.880	51.00	0.002
38.85	0.849	61.00	0.002
42.35	0.889	71.00	0.002
45.85	0.880	81.00	0.004
49.35	0.972	91.00	0.007
52.85	0.975	101.00	0.009
56.35	0.990	111.00	0.017
59.85	1.000	121.00	0.026
		131.00	0.042
Run 8:		141.00	0.074
1.00	0.000	151.00	0.107
11.00	0.005	161.00	0.155
21.00	0.002	171.00	0.229
31.00	0.002	181.00	0.312
41.00	0.002	191.00	0.404
51.00	0.002	201.00	0.476
61.00	0.005	211.00	0.568
71.00	0.005	221.00	0.660
81.00	0.007	231.00	0.756
91.00	0.026	241.00	0.867
101.00	0.026	251.00	0.915
		261.00	0.919

<u>Time</u> <u>(min)</u>	<u>C/C₀</u>
269.00	0.970
281.00	0.981
291.00	0.989
301.00	0.987
311.00	0.965
319.00	1.000

Run 10:

1.00	0.000
7.00	0.073
11.00	0.398
17.00	0.699
21.00	0.794
27.00	0.873
31.00	0.922
37.00	0.954
41.00	0.975
51.00	1.000

Run 11:

1.00	0.000
3.00	0.008
7.00	0.049
11.00	0.505
17.00	0.775
21.00	0.869
31.00	0.894
81.00	1.000

Run 12:

0.25	0.000
1.25	0.000
5.25	0.000
7.75	0.014
9.75	0.161
12.75	0.413
15.25	0.594
17.75	0.718
25.25	0.841
30.25	0.887
39.75	0.977
49.75	1.000

<u>Time</u> <u>(min)</u>	<u>C/C₀</u>
Run 14:	

0.25	0.004
1.50	0.007
5.25	0.003
7.75	0.025
10.25	0.397
12.75	0.609
15.25	0.712
17.75	0.774
20.25	0.826
25.25	0.898
30.25	0.955
40.25	0.979
50.25	1.000

Run 15:

0.25	0.000
2.75	0.000
5.25	0.000
7.75	0.000
10.25	0.037
12.75	0.175
15.25	0.306
17.75	0.452
20.25	0.561
25.25	0.727
30.25	0.836
40.25	0.940
50.25	0.996
60.25	1.000

Run 16:

0.25	0.001
5.25	0.004
7.75	0.003
10.25	0.006
12.75	0.053
15.25	0.228
17.75	0.427
20.25	0.610
25.25	0.797
30.25	0.879
35.25	0.938
50.25	0.975
60.25	1.000

<u>Time</u> <u>(min)</u>	<u>C/C₀</u>
Run 17:	
0.25	0.005
2.75	0.005
5.25	0.069
7.75	0.257
10.25	0.484
12.75	0.613
15.25	0.697
17.75	0.766
20.25	0.789
25.25	0.799
30.25	0.928
40.25	0.982
60.25	0.988
70.25	1.000

Run 18:

0.25	0.001
2.75	0.002
5.25	0.003
7.75	0.002
10.25	0.045
12.75	0.244
15.25	0.450
17.75	0.611
20.25	0.702
25.25	0.845
30.25	0.909
40.25	0.945
50.25	0.979
60.25	1.000

Run 19:

0.25	0.000
5.25	0.001
10.25	0.001
15.25	0.068
20.25	0.399
25.25	0.642
30.25	0.791
35.25	0.911
40.25	0.926
50.25	0.963
60.25	0.996
70.25	1.000

<u>Time</u> <u>(min)</u>	<u>C/C₀</u>
Run 20:	
0.25	0.023
2.75	0.015
5.25	0.010
7.75	0.008
10.25	0.008
15.25	0.276
20.25	0.793
25.25	0.928
30.25	0.958
35.25	1.000

Run 21:

0.25	0.002
5.25	0.002
10.25	0.013
15.25	0.361
20.25	0.562
30.25	0.612
40.25	0.625
50.25	0.633
60.25	0.636
100.25	0.622
120.25	0.625
190.25	0.668
240.25	0.951
290.25	1.000

Run 22:

0.25	0.002
5.25	0.002
10.25	0.001
15.25	0.003
20.25	0.081
30.25	0.608
40.25	0.723
50.25	0.726
340.25	1.000

Run 26:

0.25	0.000
10.25	0.000
15.25	0.209
20.25	0.747
25.25	1.000

<u>Time</u> <u>(min)</u>	<u>C/C₀</u>
Run 27:	
0.25	0.000
10.25	0.000
15.25	0.027
25.25	0.910
35.25	1.000

Run 28:	
0.25	0.000
10.25	0.003
15.25	0.535
20.25	0.902
25.25	0.954
40.25	0.957
55.25	0.994
75.25	1.000

Run 29:	
0.25	0.000
5.25	0.000
15.25	0.022
25.25	0.897
35.25	1.000

Run 30:	
0.25	0.000
10.25	0.000
15.25	0.113
20.25	0.744
25.25	0.925
40.25	0.992

Run 31:	
0.25	0.000
15.25	0.000
20.25	0.065
25.25	0.299
40.25	0.881
55.25	0.944
70.25	0.959
85.25	0.974
100.25	1.000

<u>Time</u> <u>(min)</u>	<u>C/C₀</u>
Run 32:	
0.25	0.000
10.25	0.000
15.25	0.012
20.25	0.326
40.25	0.952
55.25	0.991
70.25	1.000

Run 33:	
0.25	0.000
10.25	0.000
15.25	0.182
20.25	0.861
25.25	0.995
70.25	1.000

Run 34:	
0.25	0.000
10.25	0.000
15.25	0.080
20.25	0.665
25.25	0.907
40.25	0.985
70.25	1.000

Run 35:	
0.25	0.000
10.25	0.000
15.25	0.022
20.25	0.328
25.25	0.723
40.25	0.991
55.25	1.000

Run 36:	
0.25	0.000
10.25	0.000
15.25	0.001
20.25	0.037
25.25	0.188
30.25	0.387

<u>Time</u> <u>(min)</u>	<u>C/C₀</u>	<u>Time</u> <u>(min)</u>	<u>C/C₀</u>
50.25	0.820	20.25	0.673
70.25	0.912	25.25	0.837
90.25	1.000	40.25	0.910
		115.25	1.000
Run 37:		Run 42:	
0.25	0.000	0.25	0.000
10.25	0.000	10.25	0.000
15.25	0.001	15.25	0.157
25.25	0.179	20.25	0.594
30.25	0.342	25.25	0.793
40.25	0.672	40.25	0.804
70.25	0.934	70.25	0.821
90.25	1.000	115.25	1.000
Run 38:		Run 43:	
10.00	0.000	0.25	0.000
15.00	0.013	10.25	0.000
20.00	0.295	15.25	0.136
25.00	0.738	20.25	0.585
40.00	1.000	40.25	0.747
		85.25	0.958
Run 39:		115.25	1.000
0.25	0.000	Run 44:	
10.25	0.000	0.25	0.000
15.25	0.199	10.25	0.000
20.25	0.745	15.25	0.408
25.25	0.927	20.25	0.856
40.25	0.960	25.25	1.000
55.25	0.975	Run 45:	
70.25	1.000	0.25	0.000
Run 40:		10.25	0.000
0.25	0.000	15.25	0.383
10.25	0.000	20.25	0.787
15.25	0.117	25.25	0.960
20.25	0.706	50.25	0.980
25.25	0.949	115.25	1.000
40.25	0.998	Run 46:	
55.25	1.000	0.25	0.001
Run 41:		10.25	0.001
0.25	0.000	15.25	0.218
10.25	0.000		
15.25	0.192		

<u>Time</u> <u>(min)</u>	<u>C/C₀</u>
20.25	0.665
25.25	0.743
50.25	0.744
100.25	0.894
115.25	1.000

Run 47:

0.25	0.000
15.25	0.000
35.25	0.127
55.25	0.715
75.25	0.981
95.25	1.000

Run 48:

0.25	0.000
15.25	0.000
35.25	0.000
55.25	0.020
75.25	0.432
95.25	0.731
115.25	0.963
135.25	1.000

Run 49:

0.25	0.000
15.25	0.000
35.25	0.000
45.25	0.105
55.25	0.417
75.25	0.711
95.25	0.893
115.25	0.946
135.25	1.000

Run 50:

0.25	0.000
10.25	0.000
15.25	0.278
20.25	0.780
25.25	0.900
40.25	0.958
70.25	1.000

<u>Time</u> <u>(min)</u>	<u>C/C₀</u>
Run 51:	
0.25	0.000
10.25	0.000
15.25	0.035
20.25	0.444
25.25	0.826
40.25	0.967
55.25	0.981
70.25	1.000

Run 52:

0.25	0.000
10.25	0.000
15.25	0.238
20.25	0.830
25.25	0.971
40.25	0.979
70.25	1.000

Run 53:

0.25	0.000
10.25	0.000
15.25	0.043
20.25	0.405
25.25	0.816
40.25	0.974
55.25	0.988
70.25	1.000

Run 54:

0.25	0.000
10.25	0.000
15.25	0.291
20.25	0.822
25.25	0.982
40.25	0.998
55.25	1.000

Run 55:

0.25	0.000
10.25	0.000
15.25	0.000
20.25	0.015
25.25	0.789

<u>Time</u> <u>(min)</u>	<u>C/C₀</u>
40.25	1.000
Run 56:	
0.25	0.000
10.25	0.000
15.25	0.327
20.25	0.941
25.25	0.988
55.25	1.000

Run 57:	
0.25	0.000
10.25	0.000
15.25	0.075
20.25	0.581
25.25	0.903
40.25	0.982
55.25	0.986
70.25	1.000

Run 58:	
0.25	0.000
10.25	0.000
15.25	0.152
20.25	0.787
25.25	0.931
40.25	0.966
55.25	0.977
70.25	1.000

Run 59:	
0.25	0.000
10.25	0.000
15.25	0.122
25.25	0.847
35.25	0.978
75.25	0.987
95.25	0.992
115.25	1.000

<u>Time</u> <u>(min)</u>	<u>C/C₀</u>
Run 60:	
0.25	0.000
10.25	0.000
15.25	0.322
20.25	0.868
25.25	0.959
30.25	0.969
40.25	0.972
70.25	1.000

Run 61:	
0.25	0.000
10.25	0.000
15.25	0.225
20.25	0.784
25.25	0.958
30.25	0.971
40.25	0.988
55.25	1.000

Run 62:	
0.25	0.000
10.25	0.003
15.25	0.004
20.25	0.225
25.25	0.637
30.25	0.840
40.25	0.961
55.25	0.988
70.25	1.000

VITA

Sterling Dan Strevel was born in Knoxville, Tennessee on December 22, 1959. He attended Giffin and Rockford elementary schools and Eagleton Junior, Everett, and Heritage High Schools. Sterling graduated from Heritage High School on the 29th day of May, 1978. In the summer of 1980, he received with honors an Associate Degree in Chemical Engineering Technology from the State Technical Institute at Knoxville (Pellissippi State Technical Community College). He then worked for approximately six-and-a-half years in the nuclear industry as a Radiochemical Technician before returning to school for his bachelor's degree. In the spring of 1990, Sterling received with honors his degree of Bachelor of Arts in Computer Science/ Math and / Physics from Maryville College. In December, 1992 Sterling received his Master of Science degree in Engineering Science and Mechanics from the University of Tennessee, Knoxville. (He attended the University of Tennessee Space Institute in Tullahoma, Tennessee.)