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THE ANION-EXCHANGE RESIN-BASED DESULFURIZATION PROCESS FOR SPENT SEED REGENERATION IN AN MHD POWER PLANT

A Thesis

Presented for the

Master of Science

Degree

The University of Tennessee, Knoxville

Rajeev S. Dharmapurikar

May 1994

ACKNOWLEDGEMENTS

I would like to express my special gratitude to my Advisor Dr. Atul C. Sheth whose guidance and encouragement have made this work possible. His judicious supervision and insight have made working with him a wonderful and rewarding experience. I owe special thanks to Dr. Lloyd Crawford for his conscientious advice. I consider myself fortunate to benefit from his academic wisdom as well as personal care and affection. I would like to extend my sincere thanks to Dr. James Chapman for his guidance and assistance in the economic analysis of the project.

I am thankful to Phil Sherill, Teresa Young and Kathy Parks from Chem-Lab., for their assistance in sample analysis and solutions preparations. I am thankful to the Department of Energy for the financial support. My sincere appreciation to Jeff Holt, Sterling Strevel and my friend S. Parthasarathy for their helping hand and also to the library staff for their wonderful assistance.

And finally, I am deeply indebted to my parents and my friends Dr. G.K. Raviprakash, Aye Naing, Deepak and Uday for their support, encouragement and for being there for me.

ABSTRACT

Ion-exchange resin-based desulfurization concept is being considered for the recovery and recycle of spent seed from a coal-fired MHD power plant. The concept has been put forth at UTSI. Strevel, (UT 1992) has carried out process variables studies for this concept. This thesis includes the continuation of Strevel's work in the area of process variable studies. Experimentation also included investigation about the location of the carbonate ion in the resin's affinity chart and determination of the cycle efficiencies. The multiattribute analysis of the fixed-bed results was carried out and IRA-68 resin was selected as the most suitable resin for this process. Based on this resin, a process design was carried out for a 300 MW_t MHD plant burning high sulfur Illinois no. 6 coal. Economic analysis was carried out to determine the cost of MHD seed regeneration. The cost figures were compared with those presented for alternative processes such as the Econoseed Process; (Westinghouse, 1992). The analysis was also extended to determine the cost of sorbent regeneration for dry sodium-based FGD system.

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LIST OF SYMBOLS

a_1 : First Langmuir constant (dimensionless)

a_2 : Second Langmuir constant (ml/gm)

C_0 : Sulfate concentration in bulk (gm/cc)

D : Intraparticle diffusion coefficient (cm^2/s)

m : Ratio of void-to resin volume (dimensionless)

μ : t-(z/v) (s)

μ^*: $2D\,\mu/R^2$ (dimensionless)

q_∞ : Equilibrium resin capacity (gm/ml_R)

R : Resin particle radius (cm)

t : Time (s)

v : Linear velocity in packed bed (cm/s)

V : Volumetric flow rate (cc/min)

x : Dimensionless column length ($3Da_1z/mvR^2$)

z : Resin bed height (cm)

CHAPTER 1

Introduction

Magnetohydrodynamics is a branch of fluid mechanics that deals with the flow of an electrically conducting fluid in the presence of a magnetic field. This flow can be utilized to generate electrical power by using Faraday's laws. The concept of MHD power generation is based on this principle.

A combined cycle, coal-fired MHD system consists of an MHD topping cycle with a steam bottoming cycle. In the topping cycle, power is produced by passing conductive plasma through strong magnetic field. The bottoming cycle utilizes the thermal energy of the gases to produce high pressure steam for conventional power generation.

In order to provide sufficient electrical conductivity to the plasma, potassium salt is injected as a seeding material. The salt (usually K_2CO_3) is ionized at the combustor temperatures to provide positively charged potassium ions and free electrons. Typical downstream temperatures in MHD combined cycle system allow the reactions between alkali metals with the fossil fuel derived sulfur containing gases. As a result of these reactions the seed is converted

to alkali metal sulfates.

From an environmental point of view, the spent seed can not be acceptably disposed in a landfill. The alkali metal sulfates being water soluble, would pose a problem of leaching in the ground water. Surface runoffs from such sites would alter the soil pH.

From economic standpoint, the cost of replacement material is an important factor influencing the overall economics of the process. The spent seed rich in K_2SO_4 does not have a significant commercial value due to possible presence of impurities and low demand. Thus, it is necessary to recover the spent seed material, desulfurize it and then recycle the regenerated seed material.

Ion-exchange resin-based desulfurization concept developed by Sheth *et. al.*, (1), utilizes commercially available weak-base anion-exchange resin to remove sulfur from alkali metal sulfates. The proof of concept was performed by Butler, (2). The three-step process studied by Butler consists of regeneration, carbonation and exhaustion of the resin. The anion-exchange resins are supplied in hydroxide form by the manufacturer. The affinity of these resins for different anions is reported in literature, (3), as :

$$OH^- > SO_4^{-2} > \ldots\ldots\ldots\ldots > Cl^- > HCO_3^-$$

Thus, in order to exchange sulfate from the solution, it is necessary to convert the resin into bicarbonate form before exhaustion. This is done during carbonation by the following reaction.

$$R\text{-}OH + CO_2 \rightarrow R\text{-}HCO_3$$

Here R represents the complex cation group on the resin. The resin is then exhausted according to the reaction :

$$2R\text{-}HCO_3 + K_2SO_4 \rightarrow R_2\text{-}SO_4 + 2KHCO_3$$

The exhausted resin is then converted back to hydroxide form using ammonium hydroxide solution :

$$R_2\text{-}SO_4 + 2NH_4OH \rightarrow 2R\text{-}OH + (NH_4)_2SO_4$$

This process was modified to a two-step process by Modeste (4), by combining the carbonation and exhaustion steps into one step.

Strevel (5), developed the best resin testing procedure and performed process variable studies on the three selected resins, IRA-68, IRA-35 and IRA-93.

The present work includes :

* Continuation of Strevel's work to improve the resin's performance by evaluating the effect of performance enhancers and locating relative positions of carbonate and sulfate ions in the affinity chart.

* Optimization of the resin regeneration step and determination of the cycle efficiency of the candidate resins; and,
* Development of the best process schematic and related economics.

CHAPTER 2

Literature Review

The literature survey covering the mathematical model for ion-exchange kinetics and resin testing procedure has been carried out by Strevel, (5). The models studied by him include:

* Nearnst Plank mass transfer in ternary systems with constant self diffusivities and particle diameter, (6).
* Multicomponent model for mass action equilibria which discusses the inversion of resin affinities, (7).
* Thermodynamic model which defines surface excess as the separative characteristics of ion exchangers, (8).
* Dimensionless numerical model for the constant pattern pore and solid diffusion mechanisms which includes external mass transfer for irreversible equilibrium, (9),
* Zone height model based on counter current system with infinite bed height, (10).
* Linear mass transfer model for cyclic operation and cocurrent regeneration, (11).
* Multicomponent model which predicts the ion-exchange

equilibria from binary data, (12).

* Pore diffusion model based on the orthogonal collocation method which utilizes both batch and fixed-bed data, (13).
* Shrinking core model for batch experiments with Ligand exchange, (14).
* Model for systems with concave Langmuir isotherms, (15).
* Shell progressive, shrinking core, model with changing concentration and column volume, (16).

The literature on resin testing included :

* Determination of quality and deterioration by analyzing total chemical capacity and physical strength, (17).
* Testing of anion-exchange resin for sulfate leakage, (18).
* Testing of anion-exchange resins for stability and regenerant efficiency, (19).

Additional literature search was carried out in the present studies for the process design/development part of the project.

Concentration/drying of the regenerated seed solution is a very important unit operation in this process. Conventional evaporation can be used for concentrating these kind of solutions. However, Reverse Osmosis (R.O.) can be considered as a viable alternative for

the initial concentration of dilute solutions. Madsen *et. al.*, (20) have discussed the experience with the concentration of industrial solution with reverse osmosis. They have presented membrane data and case specific studies for different solutions. They are concerned in their studies with mostly the organic solutions of species such as enzymes, lactose and whey proteins.

An evaluation of a R.O. system for brackish water has been presented by Wowk & Suffet, (21). The system utilizes very dilute streams with concentration range much lower than that of present interest. Concentration of dilute pulping waste by reverse osmosis by Weily *et. al.*, (22), considers the system consisting of wastewater stream from paper and pulp industry. The chief contents of these wastewaters are sulfates in the concentration range of 10 to 20 gm/Ltr (1 -2 % wt.).

A detailed comparison of the concentration of sugar solution by R.O. and evaporation has been presented by Blomgren (23). He has shown that the reverse osmosis would be more expensive as compared to evaporation in the specific case of sugar solution concentration. Sambrilo *et. al.*, (24), Friedlander *et. al.*, (25) and Miller, (26), all have presented the design procedure and economic

analysis for the desalting by reverse osmosis. In absence of the data for the specific system (e.g. for sodium and potassium carbonate /bicarbonate), the procedure followed in the above mentioned literature was applied with proper modifications for the economic evaluation of the R.O. concentration in the present system.

In order to perform the overall economic analysis, it is necessary to carry out the process design. Rohm & Haas' Desal Process, (27), presents a design for the sea-water desalination. It utilizes Amberlite, IRA-68 anion-exchange resin with IRC-84 cation exchanger. The reactions involved are:

$$R\text{-}N + H_2O + CO_2 \rightarrow R\text{-}(NH)HCO_3$$

$$R\text{-}(NH)HCO_3 + NaCl \rightarrow R\text{-}NHCl + NaHCO_3$$

and,

$$R\text{-}COOH + NaHCO_3 \rightarrow R\text{-}COONa + H_2O + CO_2$$

Regeneration :

$$R\text{-}NHCl + NH_4OH \rightarrow R\text{-}N + NH_4Cl + H_2O$$

$$2R\text{-}COONa + H_2SO_4 \rightarrow 2R\text{-}COOH + Na_2SO_4$$

A flow sheet illustrating the three step process is presented with the subsequent economic analysis in this Rohm & Haas report.

Westinghouse Corporation has approached the problem of MHD

spent seed regeneration based on the TRW process called the Econoseed process, (28). In this process the spent seed is converted to potassium formate by reacting it with calcium formate. The potassium formate is then subsequently oxidized to give potassium carbonate. Sulfur is removed from the process as gypsum ($CaSO_4$). calcium formate needed in the process is produced from the high temperature, high pressure reaction between slaked-lime and carbon monoxide.

The Westinghouse report presents a site-specific conceptual design of a coal-fired MHD system for retrofit to the Scholz generating station at Sneads, Florida. The design includes process, system and equipment descriptions, an overall plant layout and related costs. The present study uses similar assumptions as made by Westinghouse Corporation in their work.

The literature survey also included the EPRI report, (29), which provides the guidelines for the technical assessment and procedure for performing the economic analysis of the desulfurization plant.

CHAPTER 3

Theory

In ion-exchange resin-based process, an exchange of ions takes place between the resin which is a stationary phase and the solution which is a mobile phase. Ideally, the mobile phase should pass through the stationary phase in a plug flow. The stationary phase is subjected to the mobile phase concentration in a stepwise manner. The effluent concentration in the mobile phase will be very low in the beginning as all the ions are exchanged by the stationary phase. However, as the resin starts getting saturated, the effluent concentration increases rapidly during a short time interval. This phenomenon is called a breakthrough. The plot of the effluent concentration versus time is termed as a breakthrough curve.

The differential material balance for a fixed-bed is represented by the equation :

$$\frac{\partial C}{\partial x} + \frac{1}{m}\left(\frac{\partial q}{\partial \mu}\right) = 0 \qquad \text{.....(3.1)}$$

and

$$\frac{\partial q_i}{\partial \mu} = \frac{D}{R^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial q_i}{\partial r}\right) \quad \text{.....(3.2)}$$

$$q(x, \mu) = \frac{3}{R^2}\int_0^R q_i(r, x, \mu,)r^2 dr \quad \text{.....(3.3)}$$

$$q_i\ (R, x, \mu,) = \frac{a_1 C_s}{1 + a_2 C_s} \quad \text{.....(3.4)}$$

with the initial and boundary conditions given by:

$q(\mu=0\ ) = 0$

$C\ (x = 0\ ) = C_0$

$\frac{\partial q_i}{\partial r}\ (r = 0) = 0$

where:

v=velocity in packed bed

z = bed height

q = concentration of ions under consideration in stationary phase

m= ratio of void-to-solid fraction in stationary phase

C = concentration of ions under consideration in mobile phase

$x = z/mv$

$\mu = t-(z/v)$

q_i = local concentration of ions under consideration in stationary phase

D = intraparticle diffusion coefficient

C_s = concentration of ions under consideration at the surface of resin particle

C_0 = concentration of ions under consideration at the inlet

Antonson has solved these equations and the resulting solution is given by:

$$\frac{\partial \phi}{\partial x^*} = -2 \sum_{n=1}^{\infty} \int_0^{\mu} \frac{\partial \left[\frac{\phi}{1+a_2 C_0 \phi} \right]}{\partial \lambda} e^{\left\{ -\frac{1}{2} n^2 \pi^2 (\mu^* - \lambda) \right\}} d\lambda \quad \text{.....(3.5)}$$

where

a_1, a_2 = first and second Langmuir constants from Langmuir adsorption isotherm given by equation 3.4

$x^* = 3D\, a_1 x/R^2$

$$\mu^* = 2D\,\mu/R^2$$

This partial integro-differential equation can be solved by using finite difference method. The computer scheme for this solution is given by Antonson and was used by Strevel and in the present analysis. Antonsons's fixed-bed model requires two inputs. These are a_2C_0 and x, the dimensionless column length. With these inputs, the model will generate a breakthrough curve which can be fitted to experimental data.

A typical best fit is shown in Figure 3-1. From the best fit, the diffusion parameter can be determined using the equation for the dimensionless column length. The diffusion parameter is defined as D/R^2 where D is the intraparticle diffusion coefficient and R is spherical particle radius. The theoretical time μ, as defined in equation 3.1 can be related to the actual time by :

$$\ln(\mu_E)= \ln(\mu)+\ln(2D/R^2).....(3.6)$$

Where μ_E is the actual time. This semi log relationship make the comparison of the actual and theoretical time a mere displacement along the abscissa. The diffusion parameters calculated for cycle efficiency experiments are presented in Figure 5-8. The results of these cycle efficiency experiments are also discussed in

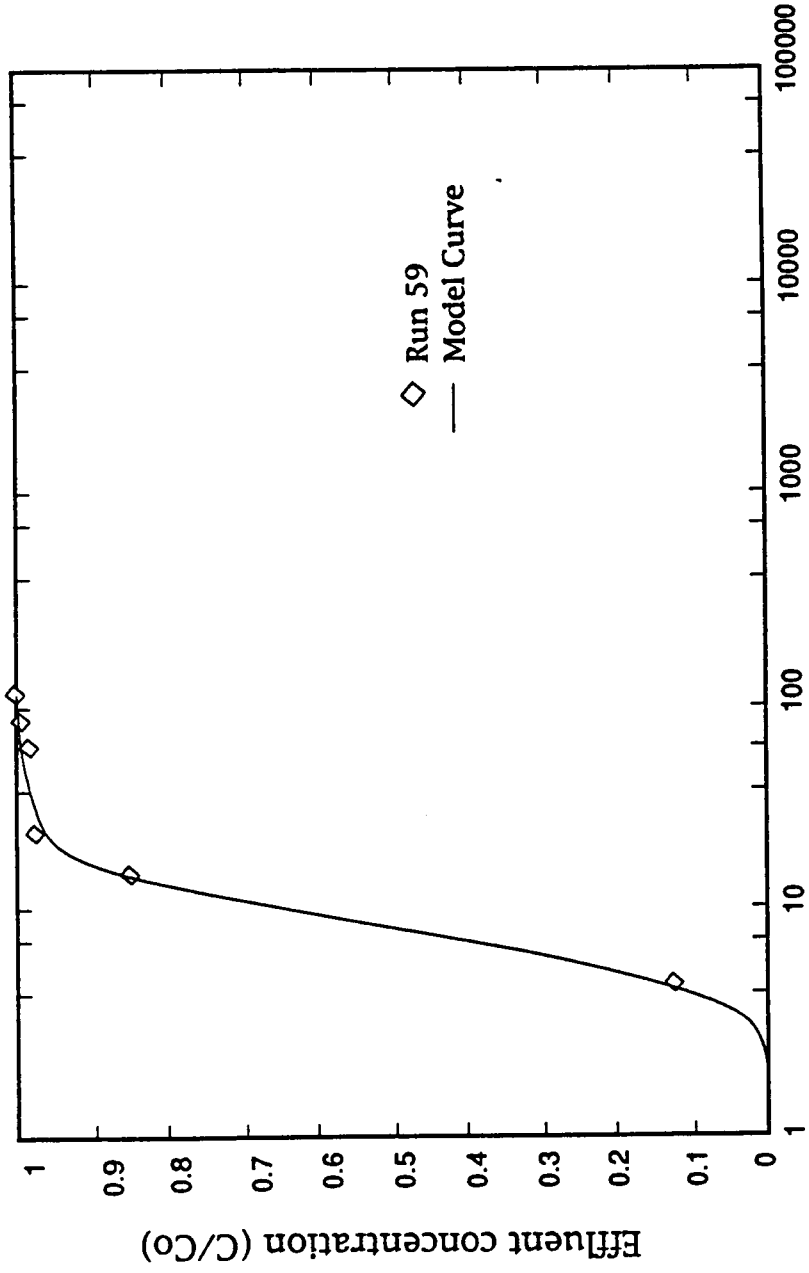


Figure 3-1. Typical Best Fit: Run IRA-68, (5)

detail later in Chapter five.

The effects of different process parameters such as CO_2 pressure, solution concentration, superficial velocity, product inhibition, dissolved impurities and resin bed height on the equilibrium loading and ion-exchange kinetics were studied by Strevel. Some of his results are reproduced here in Figures 3-2 to 3-6 and Table 3.1. It is observed from Table 3.1 that the static CO_2 pressure causes an upward trend on the equilibrium loading for the candidate resins. The highest equilibrium loading values are achieved in the pressure range around 80 to 120 psig. A static pressure of 90 psig was assumed for the process calculations based on these results. Strevel's experiments suggested that there was a little or no effect of dissolved impurities, product inhibition and resin bed height on the equilibrium loading and on ion-exchange kinetics for the candidate resins. Thus, these parameters were not considered as design parameters in the present study.

The solution concentration had a significant effect on the ion-exchange kinetics of IRA-68 resin. On the other hand it did not affect the ion-exchange kinetics of IRA-93 or IRA-35. The increasing solution concentration increases the equilibrium loading and the

Table 3.1. Effect of Static CO_2 Pressure on Equilibrium Loading[a]

Basis :
0.028 gm of sulfate /ml solution

Static CO_2 Pressure (psig)	Equilibrium Loading (gm sulfate/ml_R) IRA-35	IRA-68	IRA-93
0	-	.068	-
10	.073	.065	.074
20	-	.087	-
40	.098	.124	.096
80	.130	.136	.164
120	.126	.136	.168

a- Reproduced from Strevel (5)

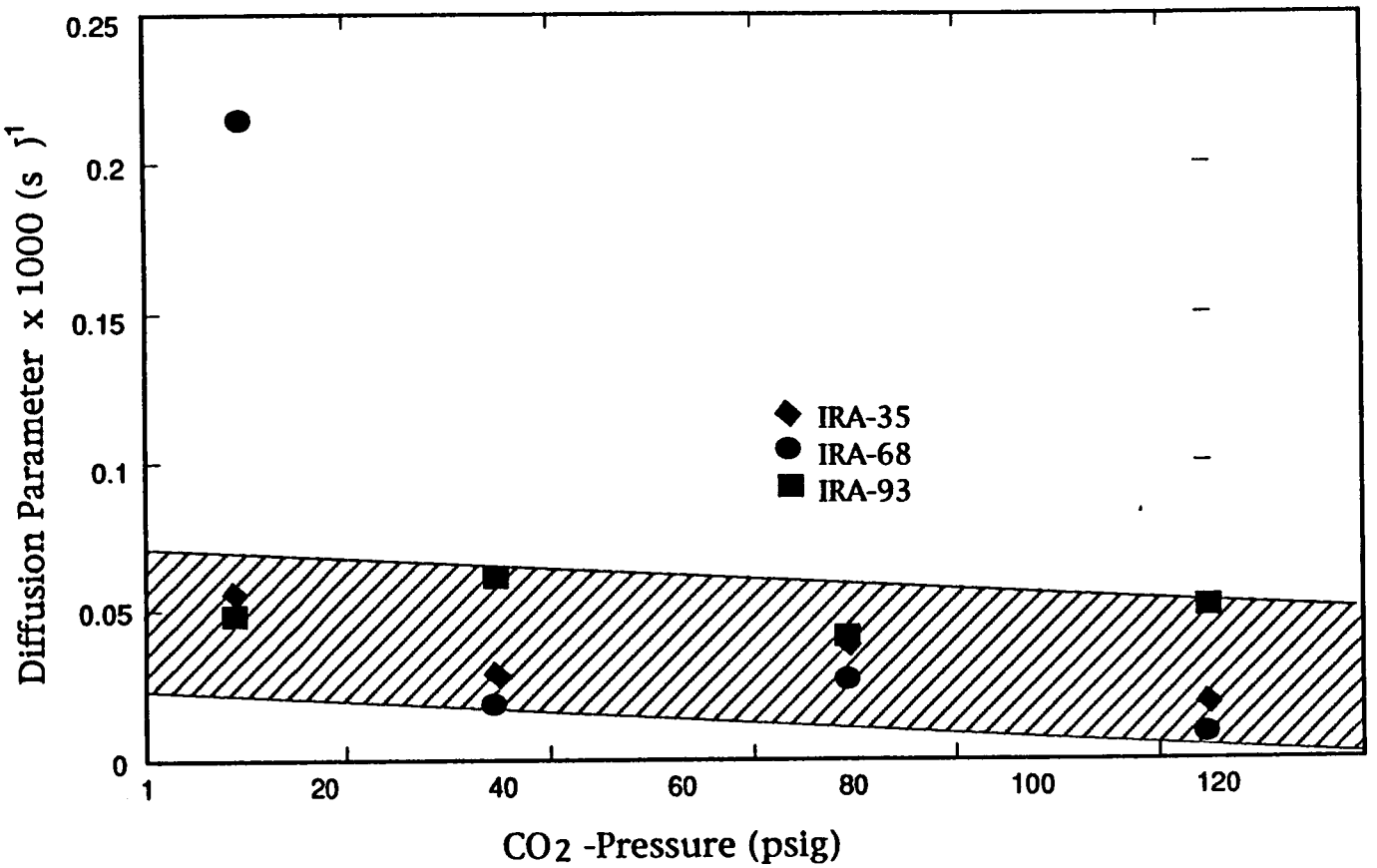


Figure 3-2. Effect of Static CO2 -Pressure on Diffusion Parameter, (5)

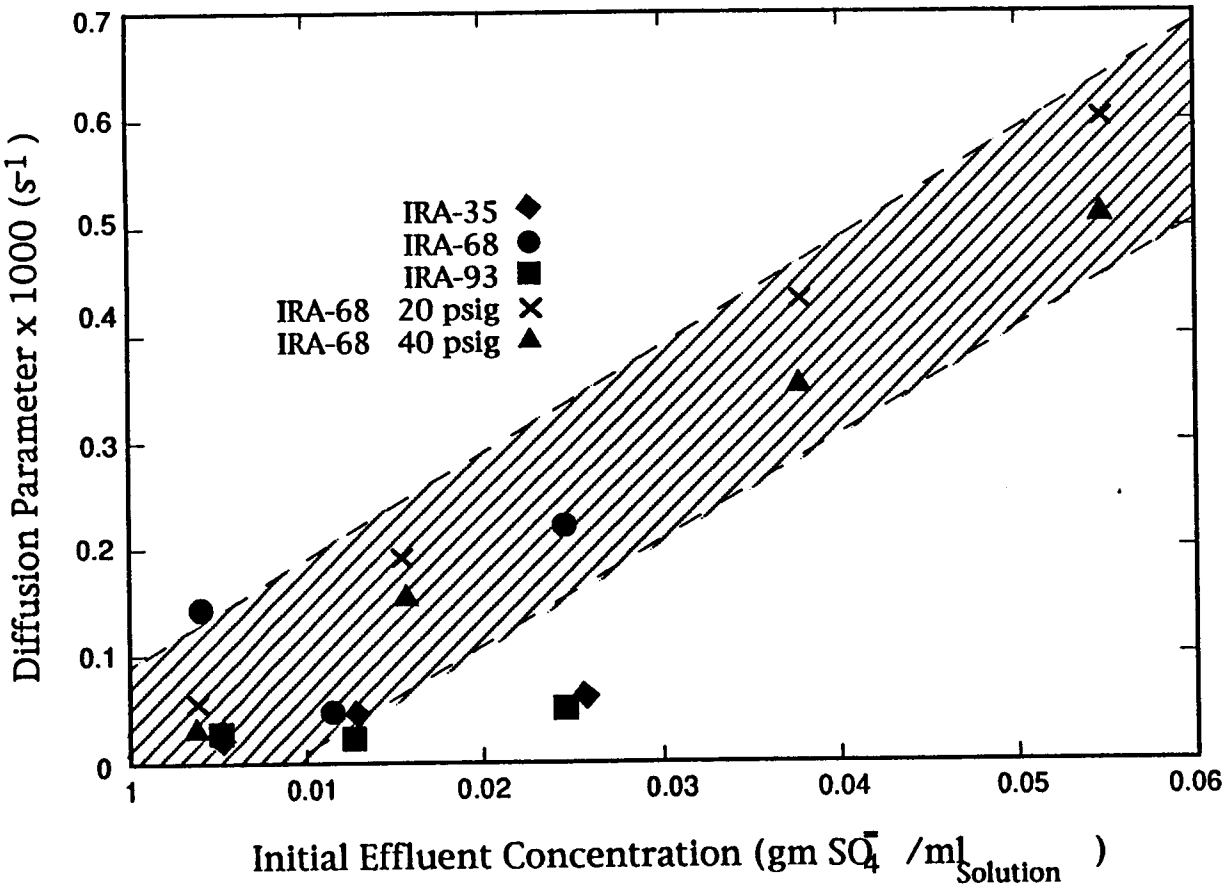


Figure 3-3. Effect of Solution Concentration on Diffusion Parameter, (5)

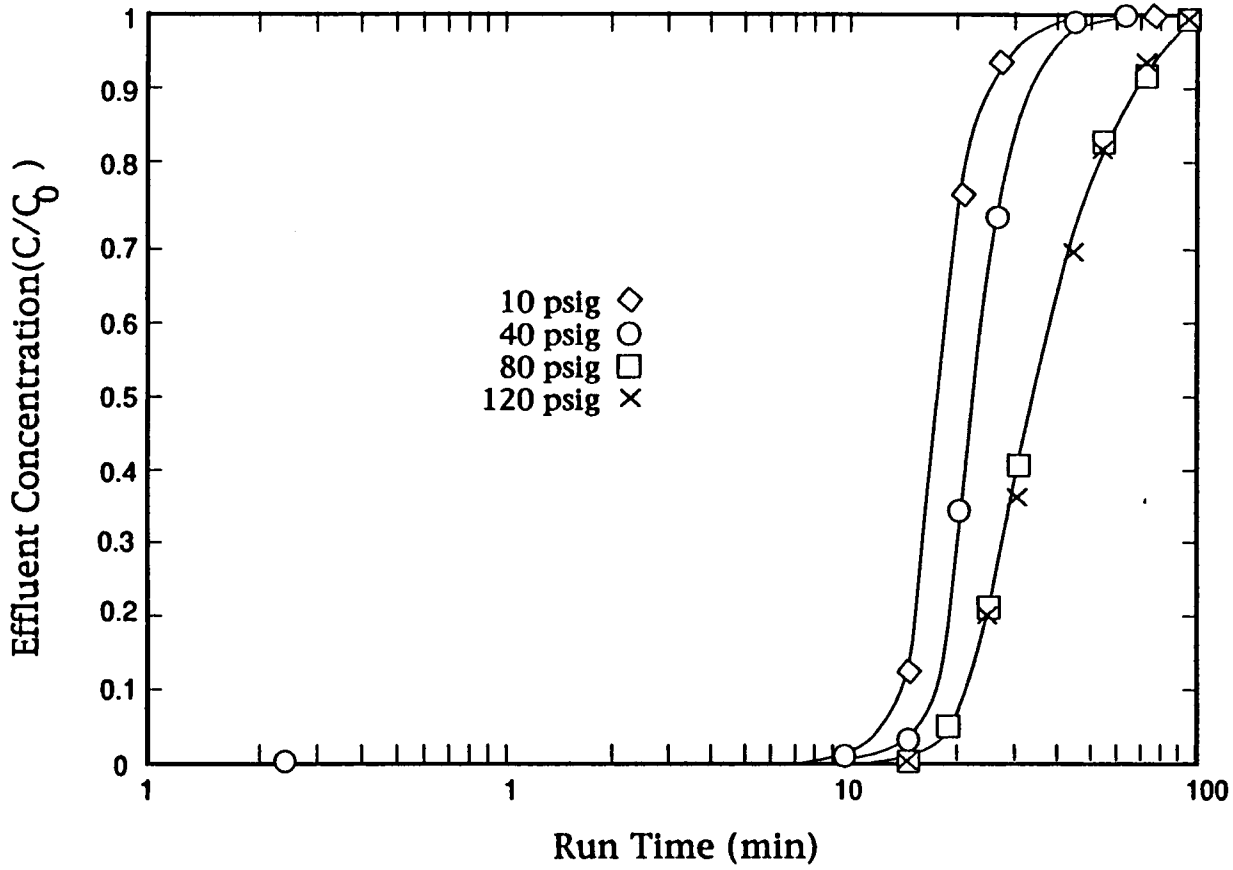


Figure 3-4. Effect of Static CO_2 -Pressure on IRA-93, (5)

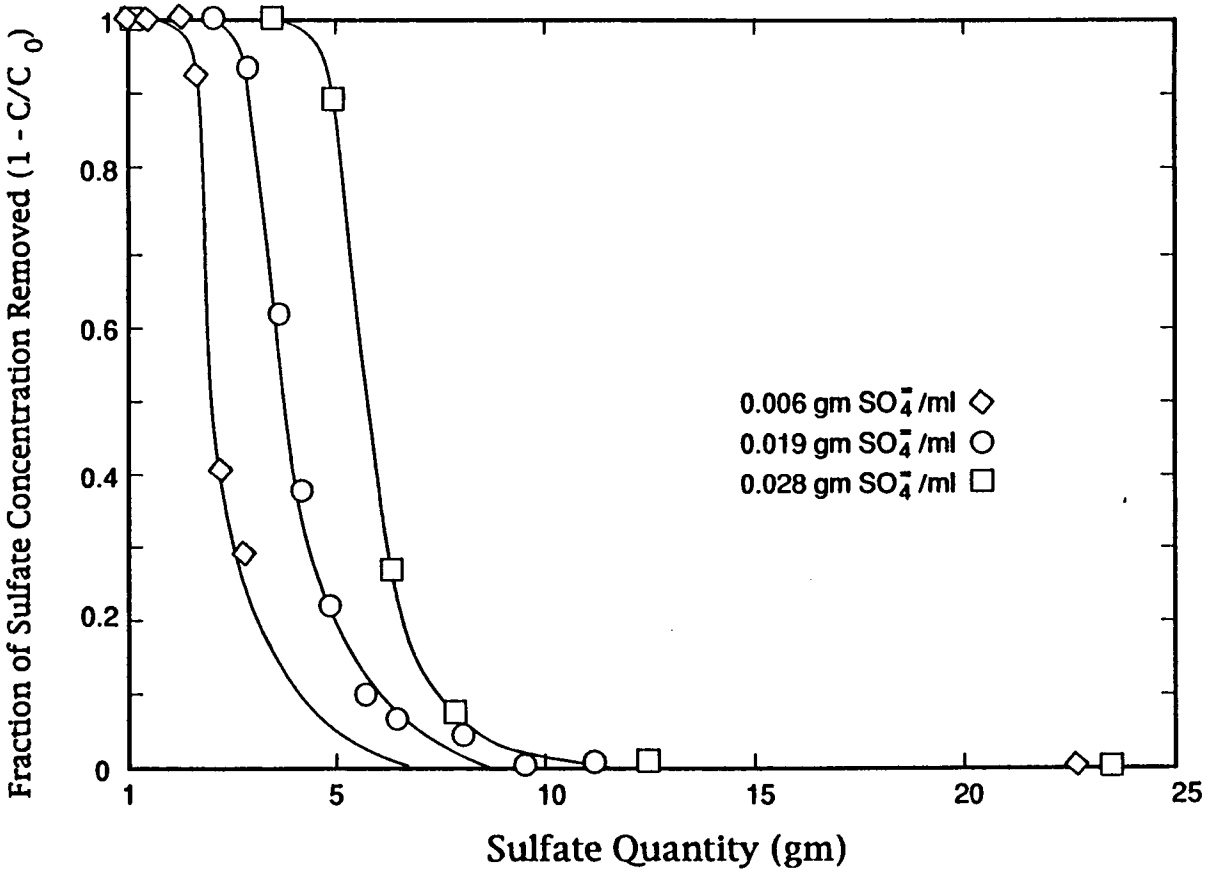


Figure 3-5. Effect of Solution Concentration on IRA-93, (5)

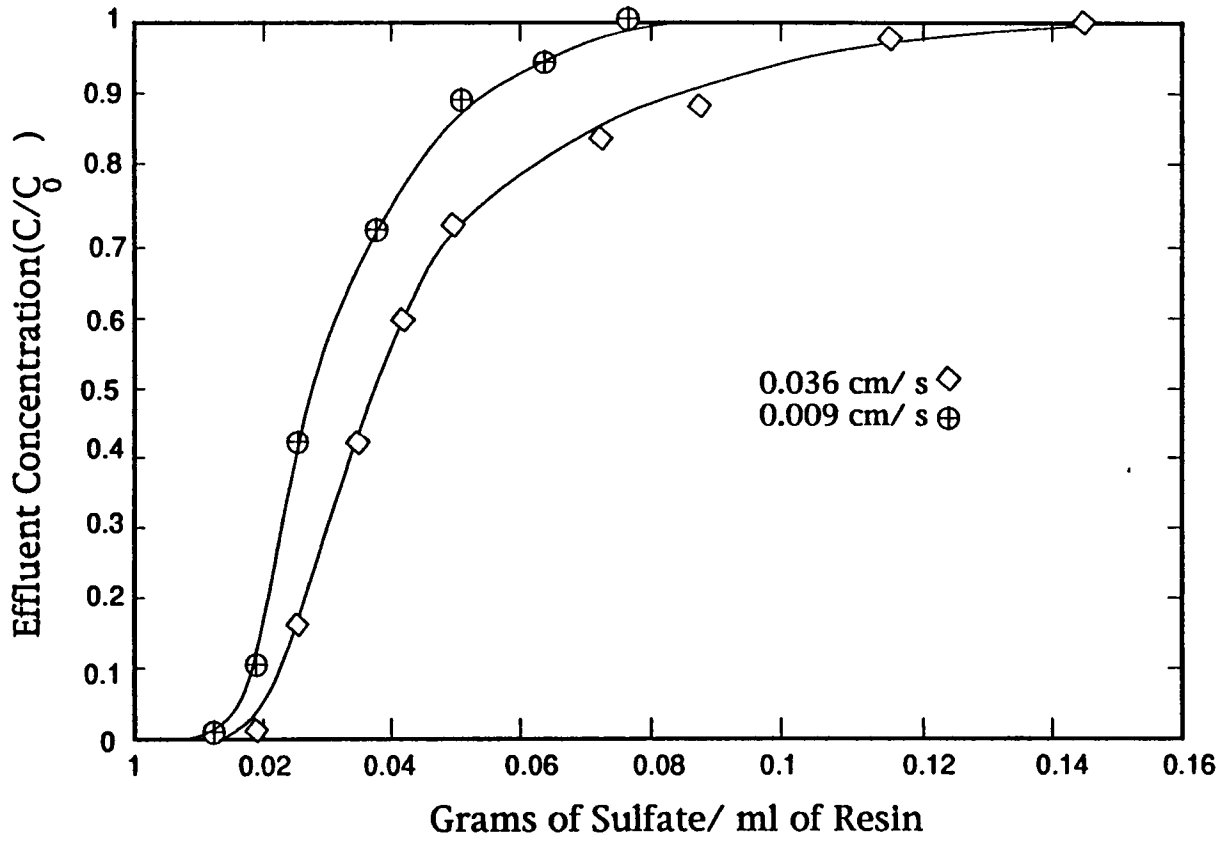


Figure 3-6. Effect of Superficial Velocity on IRA-35

diffusion parameter for IRA-68. Since the final choice of resin based on the multiattribute analysis (presented in chapter five), was IRA-68, it was necessary to correlate the equilibrium resin capacity to the solution concentration at higher CO_2 pressure. As the data for the specific values of interest were not available, this was done by using a least square best fit method. Using the data from Strevel (5), the resin capacity was related to the solution concentration as:

$$q_\infty = 0.1867 + \log (c) \quad \text{.....(3.7)}$$

where:

q_∞ = equilibrium resin capacity in gms/ml of resin

c = sulfate concentration as weight fraction in the bulk solution.

At lower superficial velocities, (~ .009 cm/s) the liquid film mass transfer becomes important and Antonson's model no longer represents the ion-exchange mechanism. However this situation can be well represented by the Selke and Bliss' model (31). In the present design, all the superficial velocities used were well above this values. As a result, Antonson's model was assumed to be valid for conditions employed in the present study.

CHAPTER 4

Experimental Procedure

The experiments are primarily divided into two parts. Batch mode experiments and fixed bed experiments. Based on Strevel's preliminary analysis, three resins were selected. They were IRA-68, IRA-93 and IRA-35.

Batch Mode Experiments

Batch mode experiments were carried out to determine the effect of performance enhancers, to determine the position of the carbonate ion in the resin's affinity chart and for the optimization of the resin regeneration step. The apparatus used for batch mode experiments is shown in Figure 4-1. The equipment consists of a 500 ml plastic jar, a carbonation device consisting of a flow regulator /rotameter and a 1.6 mm diameter steel tube which could be inserted into the jar through the lid. The flowmeter was equipped with appropriate connectors so as to attach to the carbon dioxide cylinder tank. The general procedure used the following steps:

(1) The resin supplied by manufacturer was treated with a 4

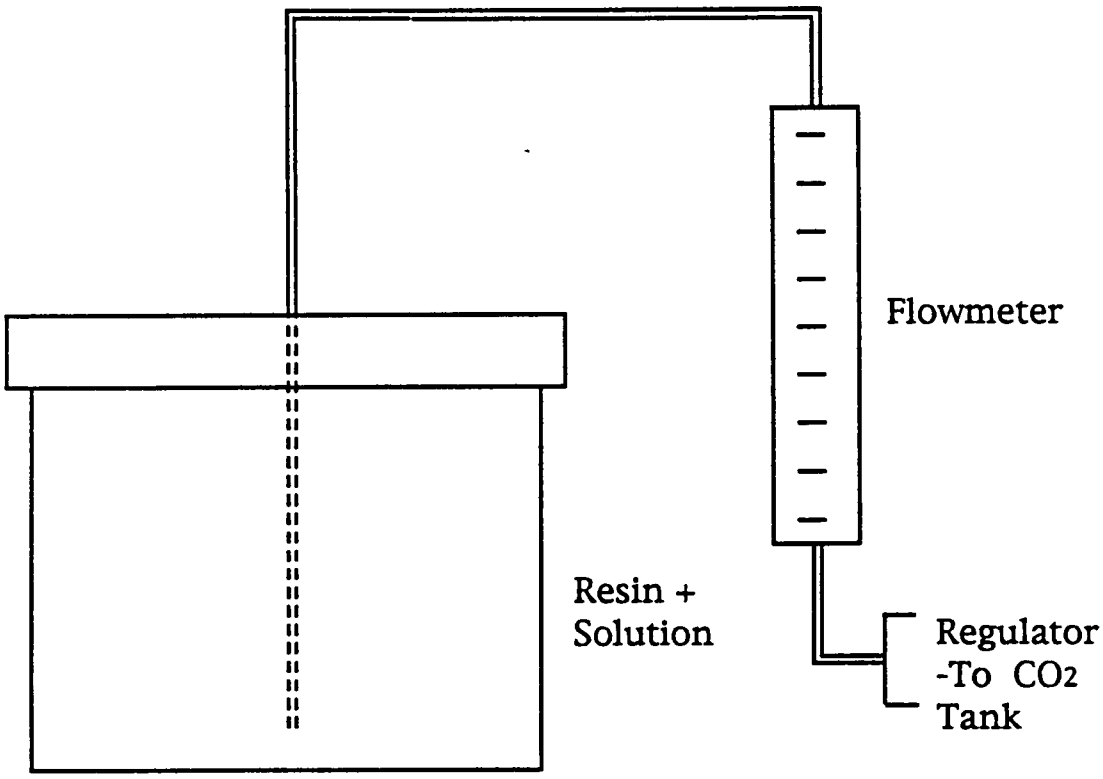


Figure 4-1. The Batch Apparatus

wt% ammonia solution for two hours to ensure complete conversion to R-OH form. Excess ammonia was removed by washing the sample with deionized water.

(2) Resin sample measured according to the desired sample size was then carbonated by bubbling CO_2 for 30 minutes to convert it into R-HCO_3 form. The carbonated resin was then filtered and dewatered.

(3) The resin sample thus obtained was then exhausted using potassium sulphate solution according to the predetermined conditions. (concentration, resin-to-solution ratio etc).

(4) The mixture was then filtered and the filtrate was analyzed for sulfate ion concentration.

In the regeneration experiments, the sulfate form of resin (e.g. R_2-SO_4) freed from excess sulfate by washing and filtration, was treated with ammonia solution by fixing the parameters as desired. After mixing for a certain time period, the sample was filtered and the filtrate was analyzed for the sulfate ions removed by the regenerating solution. To determine the effect of performance enhancers, measured amounts of concentrated organic acid solutions

(1 to 8 ml) were added to a batch of 50 ml of resin. The resin was then exhausted using a 5% potassium sulfate solution for 30 minutes. A resin-to-solution ratio of 1:2 was used during the experiments. The experiments were carried out by using 50% (v/v) solutions of formic, acetic, butyric and palmitic acids. Since palmitic acid is insoluble in water, it was dissolved in warm alcohol and the experiments were carried out at higher temperature to avoid separation of palmitic acid from alcohol.

In order to determine the position of the carbonate ion in the affinity chart, a series of experiments was carried out. The samples of sulfate form of resins (obtained by following the procedure up to step 4) were regenerated with different concentrations of potassium carbonate solutions for 30 minutes. The resulting filtrate samples were analyzed for sulfate ion concentration. Additional experiments were carried out in which, the bicarbonate form of resin was treated with potassium carbonate solution for sufficient time (45 min) in order to convert it partially to carbonate form. These samples were then exhausted with sulfate solution by following the usual procedure and filtrate samples were analyzed for the sulfate ion concentrations.

In order to optimize the resin regeneration step, the experiments were carried out to study the effect of ammonia solution concentration, mixing time and resin-to-solution ratio on regeneration efficiency. The parameter to be studied was varied for different batches keeping the other parameters fixed.

Fixed-Bed Experiments

The fixed-bed experiments were carried out by using an apparatus shown in Figure 4-2. The apparatus consists of two different diameter glass columns for carbonation/exhaustion and regeneration. These columns are supported with an assembly of tanks, valves and necessary instrumentation to ensure semi-automatic operation. The assembly consists of an eluent tank and regenerating solution tank of approximately 1.5 gallon capacity. A water tank was provided for deionized rinse water. A nitrogen tank was provided to apply necessary pushing force for regenerating solution and rinse water. A 99.9% pure carbon dioxide tank was used to supply CO_2 for carbonation. The glass columns were of 2.5 and 5.2 cms in diameter and were rated for 215 psia pressure.

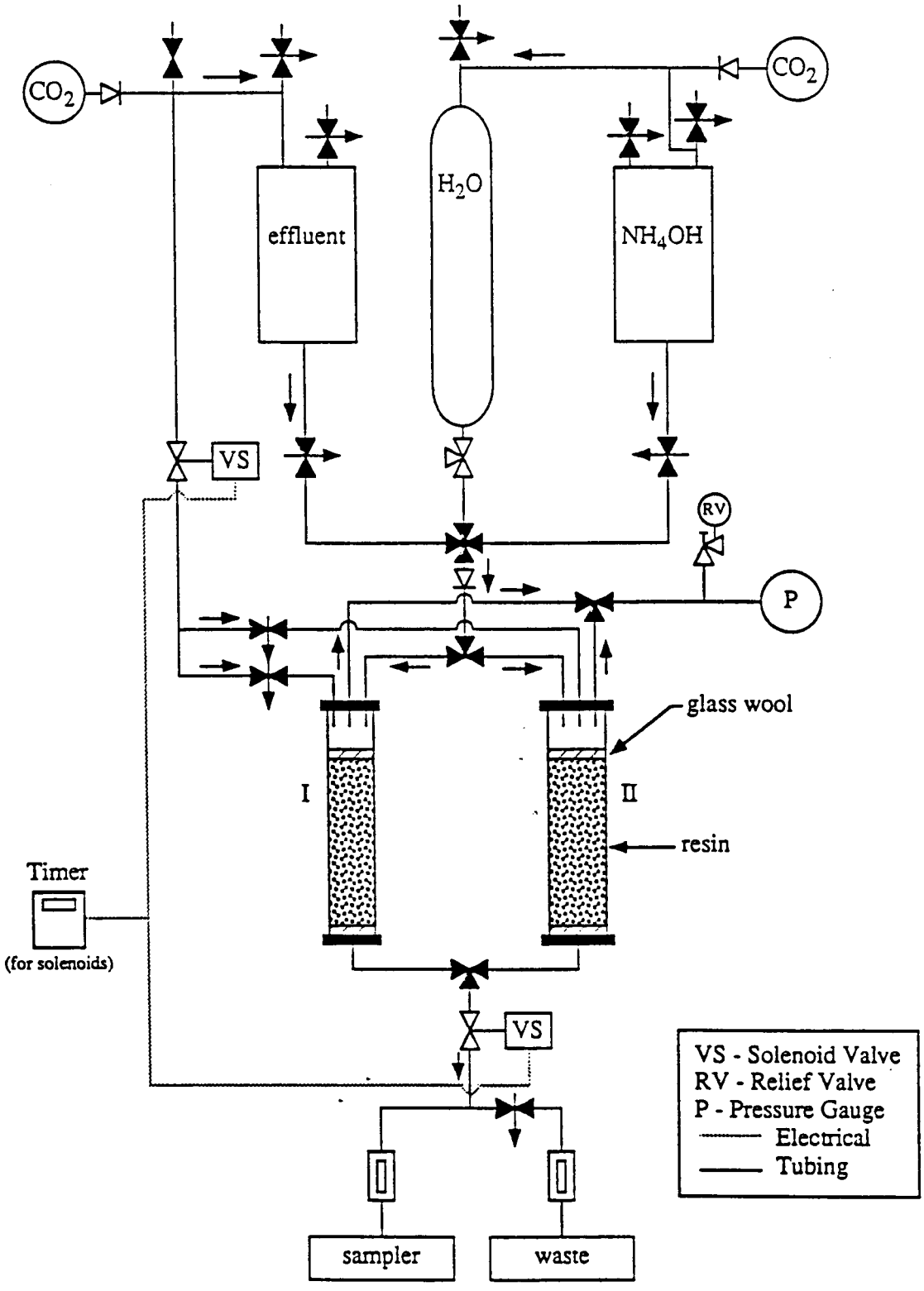


Figure 4-2. Fixed-Bed Schematic

The instrumentation included two solenoid valves to control the gas flow rate and the sample flow rate to the sample collecting device, two pressure gauges, two rotameters for flow measurements, a relief valve, several manual valves and a Gilson fractional sampler. The auto-sampler could be set to collect samples at a predetermined time interval or number of drops.

The system was supposed to operate in a semi-automatic manner but the problem of unstable flow rates was encountered frequently. It required constant monitoring and manual regulation to keep the flow rate constant. A few other problems such as air entrainment and resin particle entrainment were also encountered but they were rectified readily with proper care.

The fixed-bed runs were carried out by using the following procedure:

(1) The column was removed from the assembly , washed and charged with measured amount of regenerated resin. Glass wool plugs were used to prevent resin particle entrainment in the flow.

(2) All the liquid tanks were flushed, rinsed and filled with the appropriate solutions (sulfate, ammonia and deionized

water). All the piping was flushed with water and then rinsed with the appropriate solution. The column was reassembled on the mount and rinsed with deionized water.

(3) The resin was then carbonated for 20 minutes under 50 psig of CO_2 pressure.

(4) The system was bled free of pressure and then repressurized at the desired pressure during the exhaustion. A small positive pressure gradient was maintained between the column pressure and the eluent tank pressure to provide the necessary driving force for the eluent.

(5) The flow rate was adjusted using rotameters. The sampler was preset to the desired time interval (0.5 min.).

(6) The solenoid valves and the auto sampler were then turned on to start the exhaustion run.

(7) The collected samples were then analyzed for sulfate concentration.

For the cycle efficiency runs, following additional steps were taken:

(8) The exhausted resin sample was washed with deionized water without removing the column from the assembly.

(9) The resin was then regenerated in-situ by using ammonia solution. The ammonia tank was pressurized with nitrogen to provide the driving force. The reaction was carried out by using 4 wt% ammonia solution at a flow rate of 25 cc/min. Regenerated resin was then washed again and freed from any excess ammonia solution.

(10) The procedure from step 2 through step 9 was then repeated to complete each cycle of experiments.

Fixed-bed experiments were carried out to determine the effect of solution pH on the breakthrough curve and to determine the cycle efficiency.

To determine the effect of the solution pH, experiments were carried out by using potassium sulfate solutions of pH 7.00 and 4.25. The pH was lowered by using small amounts of 50% (v/v) solution of acetic acid. The exhaustion was carried out at a pressure of 10 psig. Exhaustion solution flow rate was 11 cc/min. The samples were spaced 5 minutes apart. A typical sample size was 5.5 cc.

During the cycle efficiency experiments the same sample of

resin was subjected to repeated carbonation/exhaustion and regeneration by following the above mentioned procedure. In order to ensure complete regeneration, effluent from the regeneration run was sampled and analyzed for sulfate for the first few runs. The regeneration was carried out for excess amount of time (≈ 90 min) with a higher flow rate (25 cc/min) in order to ensure complete regeneration of resin.

Sulfate analysis for fixed-bed as well as batch mode experiments was carried out using a Dionex ion-chromatograph.

The results from these experiments are discussed in the next chapter.

CHAPTER 5

Experimental Results and Analysis

Batch Mode Experiments:

Effect of Performance Enhancers

The results of the experiments carried out to determine the effect of the performance enhancers (organic acids) on the exhaustion efficiency of candidate resins are presented in Tables 5.1 to 5.4. From these results it is evident that in most cases, the small dosage of organic acids would improve the performance of the resins to a significant extent. The performance enhancement increases as the dosage is increased. It is also seen that as we go from formic to butyric acid the enhancement effect at the same dosage also increases. However, palmitic acid does not give any significant improvement. This can be attributed to the fact that palmitic acid has very poor solubility in water. Due to this poor solubility, it would not dissociate in the solution and therefore would not be effective as a performance enhancer.

Table 5.1. Performance Enhancement by Addition of Formic Acid Solution

Basis:

* 5 wt % K_2SO_4 solution
* Batch size of resin = 50 ml
* Mixing time = 30 min
* Resin-to-solution ratio = 1:2

Resin Type	Amount of Acid Added (ml/100 ml_R)	% Sulfate Removed	% Improve-ment
IRA-35	0	51.1	-
	2	57.3	12.0
	4	62.1	21.5
	6	62.6	22.6
	8	64.1	25.4
IRA-93	0	50.0	-
	2	55.3	10.6
	4	54.5	8.0
	6	56.6	13.1
	8	59.6	19.2
IRA-68	0	53.6	-
	2	56.5	5.3
	4	57.5	7.3
	6	59.8	11.5
	8	67.9	26.6

Table 5.2. Performance Enhancement by Addition of Acetic Acid Solution

Basis:

*5 wt % K_2SO_4 solution
*Batch size of resin = 50 ml
*Mixing time = 30 min
*Resin-to -solution ratio = 1:2
*Acid concentration = 50% (v/v)

Resin Type	Amount of Acid Added (ml/100 ml_R)	pH Initial/ Final	% Sulfate Removed	% Improve -ment
IRA-35	0	5.2/7.5	51.2	-
	2	4.9/7.5	52.6	2.3
	4	4.6/7.5	55.8	9.3
	6	4.3/7.5	58.1	13.7
	8	4.1/7.5	67.0	31.3
IRA-93	0	5.2/7.5	50.0-	
	2	4.9/7.5	51.7	3.3
	4	4.6/7.5	57.8	15.7
	6	4.3/7.5	62.2	24.4
	8	4.1/7.5	70.4	40.9
IRA-68	0	5.2/7.5	53.6	-
	2	4.9/7.5	63.5	18.4
	4	4.6/7.5	65.7	22.5
	6	4.3/7.5	70.6	31.6
	8	4.1/7.5	72.9	35.9

Table 5.3. Performance Enhancement by Addition of Butyric Acid Solution

Basis:

* 5 wt % K_2SO_4 solution
* Batch size of resin = 50 ml
* Mixing time = 30 Min
* Resin-to-solution ratio = 1:2
* Resin used IRA-68
* Acid concentration = 50% (v/v)

Amount of acid Added (ml/100 ml_R)	% Sulfate Removed	% Improvement
0	58.0	-
2	64.5	11.0
4	77.1	33.0
6	83.8	44.4
8	90.3	55.5

Table 5.4.Performance Enhancement by Addition of Palmitic Acid Solution (in Warm Alcohol)

Basis:

* 5 wt % K_2SO_4 solution
* Batch size of resin = 50 ml
* Mixing time = 30 min
* Resin-to-solution ratio = 1:2
* Resin used IRA-68
* Acid concentration = 50% (v/v)

Amount of Acid Added (ml/100 ml_R)	% Sulfate Removed	% Improvement
0	56.0	-
2	57.1	2.2
4	56.5	1.0
6	55.5	-1.0
8	56.7	0.4

According to the resin manufacturer, weak-base anion-exchange resins are recommended for the use in the medium with pH ≤ 7.0. However, although the starting pH of K_2SO_4 is neutral, as more and more exchange with bicarbonate ions takes place, more and more bicarbonate ions are accumulated in the solution. Since bicarbonate ions are alkaline, the solution pH does not remain neutral. As a result the exhaustion efficiency may be reduced progressively. By addition of small amounts of mild but concentrated organic acids, the initial solution pH is lowered without unduly diluting the bulk solution. Thus the overall pH remains neutral for most of the time and the overall exhaustion efficiency is improved significantly. The organic acids thus seems to behave more like a buffering agent to produce the desired effect.

The enhancement caused by each acid in the performance of IRA-68 resin for the highest dosage is reported in Table 5.5 with the corresponding pKa values obtained from the literature and the molecular weight of the corresponding acids. It is seen that the performance enhancement increases with increase in the pKa value of the acid and the weight of the corresponding anion. The strongest of the acids (formic) with lowest pKa value gives the lowest

Table 5.5. Relationship Between Performance Enhancement & pKa Value and Molecular Weight of Organic Acids

Basis:

*Performance enhancement by 8 ml of acid (50% v/v)
*IRA-68 resin

Type of Acid	pKa	Molecular Weight	% Improvement
Formic	3.75	46	26.6
Acetic	4.75	60	35.9
Butyric	4.81	88	55.5

enhancement. This is opposite of what one would expect. One possible reason for such behavior could be the simultaneous adsorption of the anions from the organic acid on the resin. As the anion becomes bulkier (e.g. increase in molecular weight), its mobility could be reduced; and thus, it is less likely to be adsorbed on the resin to occupy any sites. Hence for higher acids, this interference could be reduced resulting in better performance. Further investigation in the chemistry of ion-exchange in the presence of organic acids is necessary to explain this hypothesis.

Relative Location of Carbonate and Sulfate Ions in Affinity chart:

Information regarding the location of the carbonate ion with respect to the sulfate ion in the affinity chart is important as it can determine whether the carbonate form of resin (R_2-CO_3) can also exchange the anions with the K_2SO_4 as the bicarbonate form (R-HCO_3) does normally.

Results from the series of experiments described in Chapter four are given in Table 5.6 and Table 5.7. From Table 5.6, it is seen that the carbonate ion from the solution can replace sulfate ion present on the resin. However, the extent of the exchange depends on

Table 5.6. Exchange of Carbonate Ions with R_2-SO_4 Form of Resin

Basis:

* 5 wt % K_2SO_4 solution used for exhaustion
* Batch size of resin = 50 ml
* Mixing time = 30 min
* Resin-to-solution ratio = 1:2

Resin Type	Concentration of K_2CO_3 (PPM)	% Sulfate Removed
IRA-68	5,000	9.1
	10,000	24.0
	500,000	68.1
IRA-93	5,000	12.3
	10,000	31.1
	500,000	70.2
IRA-35	5,000	8.7
	10,000	22.0
	500,000	67.6

Table 5.7. Exchange of Sulfate Ions with Mixture of R-HCO3 and R_2-CO_3 Forms of Resins

Basis:

* Some R-HCO_3 converted to R_2-CO_3 by using 5 wt % K_2CO_3 solution.
* Batch size of resin = 50 ml
* Mixing time = 30 min
* Resin-to-solution ratio = 1:2

Type of Resin	Sulfate Concentration (ppm) Initial	Final	% Sulfate Removed
IRA-68	26,574	17,900	32.6
IRA-93	26,574	18,320	31.1
IRA-35	26,574	17,840	32.9

the concentration of the carbonate ion in the solution. As the bulk concentration increases, the extent of sulfate replacement also increases. Hence, based on these results, one can say that the position of the carbonate ion in the affinity chart is very close to the sulfate ion. However it does not clearly indicate whether it is on the left or right of the sulfate ion. The results from Table 5.7 shed further light on this matter. In this table results from the exhaustion with the mixed (R-HCO_3 & R_2-CO_3) form of resin are reported. The typical exhaustion efficiencies are around 31 to 33 % for the three candidate resins. However, efficiencies with only bicarbonate form of resin under similar conditions were found by Strevel to vary between 42 to 60% (5). Hence the removal efficiency of the candidate resins seems to decrease by about 46% for IRA-68 to 27% for IRA-93. This decrease can be attributed to the possible inability of the carbonate ions on the resin from being exchanged by the sulfate ions in the bulk solution. Hence, the most likely position of the carbonate ion would be to the left of sulfate ion as shown below.

$$OH^- \rightarrow\rightarrow CO_3^{-2} \rightarrow SO_4^{-2} \rightarrow\rightarrow HCO_3^-$$

This conclusion would also explain the observed increase in the

resin's capacity during carbonation/exhaustion cycle as the CO_2-pressure is increased. Because at higher CO_2-pressure, the R_2-CO3 form is significantly reduced in comparison to R-HCO_3 form as per the following reaction:

$$2R\text{-}HCO_3 = R_2\text{-}CO_3 + H_2O + CO_2$$

Optimization of Resin Regeneration step

To optimize the resin regeneration step, effects of regenerant concentration, mixing time, and resin-to-solution ratio were studied by performing batch mode experiments. The results from these experiments are presented in Table 5.8 and 5.9

From Table 5.8 it is observed that as the ammonia concentration increases, the percent of sulfate retained on resin decreases. This increase is observed till the concentration reaches around 4 wt%. After this value, almost complete regeneration is realized. These values compare very well with those reported by Strevel (5) and also with the value suggested by the manufacturer.

The effect of resin-to-solution ratio is reported in Table 5.9. There is no significant effect on the percentage sulfate retained on the resin as the resin-to-solution ratio increases from 1:1 to 1:3 .

Table 5.8. Effect of Solution Concentration on Resin Regeneration

Basis:

* Exhaustion using 5 wt % K_2SO_4 solution.
* Batch size of resin = 50 ml
* Mixing time = 30 min
* Resin-to-solution ratio = 1:2

Ammonia Concentration (wt %)	Percentage Sulfate Retained by Resin IRA-68		IRA-93	IRA-35
.58	76.4	77.7[b]	74.3	72.6
1.16	45.6	44.4[b]	41.2	41.7
1.74	29.7	29.2[b]	31.1	32.6
2.90	15.1	13.4[b]	14.6	14.8
3.84	11.9	11.2[b]	12.1	13.9
4.35	11.0	11.6[b]	13.3	12.4
4.64	9.9	8.5[b]	12.7	13.8

b- Strevel, (5)

Table 5.9. Effect of Resin-to-Solution Ratio on Resin Regeneration

Basis:

*Exhaustion by using 5 wt % K_2SO_4 solution.
*Batch size of resin = 50 ml
*Mixing time = 30 Min
*Ammonia concentration 4%(wt)

Resin to--Soluton Ratio	Percentage Sulfate Retained by Resin IRA-68	IRA-93	IRA-35
1:1	11.4	19.0	14.0
1:2	10.8	18.6	13.5
1:3	10.2	17.8	13.3

It is seen from Table 5.10 that for the three resins, the percentage of sulfate retained decreases monotonically as the mixing time is increased from 5 minutes to 30 minutes. Beyond that, mixing time has little effect considering the experimental error.

Fixed-Bed Experiments

Effect of Solution pH

Effect of initial solution pH on the resin's performance was evaluated using 5% K_2SO_4 solution for the three candidate resins. The resulting effect for all the three resins was similar in that the breakthrough curves for pH 4.25 moved slightly to the right of the curve for pH 7.5. However the shape of these curves did not change significantly as can be seen from the representative curve for IRA-68 given in Figure 5-1. This can be attributed to the hypothesis that slightly acidic solution at the inlet either helps in maintaining the acidic to neutral conditions throughout the bed as recommended by manufacturer and thereby improves the resin capacity, or it improves the ionic mobility of the sulfate ions. However the results from the effect of performance enhancers suggest that the improvement in the exhaustion efficiency tends to be possibly due to

Table 5.10. Effect of Mixing Time on Resin Regeneration

Basis:

* Exhaustion using 5 wt % K_2SO_4 Solution.
* Batch size of resin = 50 ml
* Resin-to-solution ratio = 1:2
* Ammonia concentration 4 wt %

Mixing Time (Minutes)	Percentage Sulfate Retained by Resin IRA-68	IRA-93	IRA -35
5	30.0	32.2	31.6
10	21.0	24.1	23.6
20	16.0	18.2	32.0
30	10.8	12.7	19.0
40	10.9	13.1	16.5

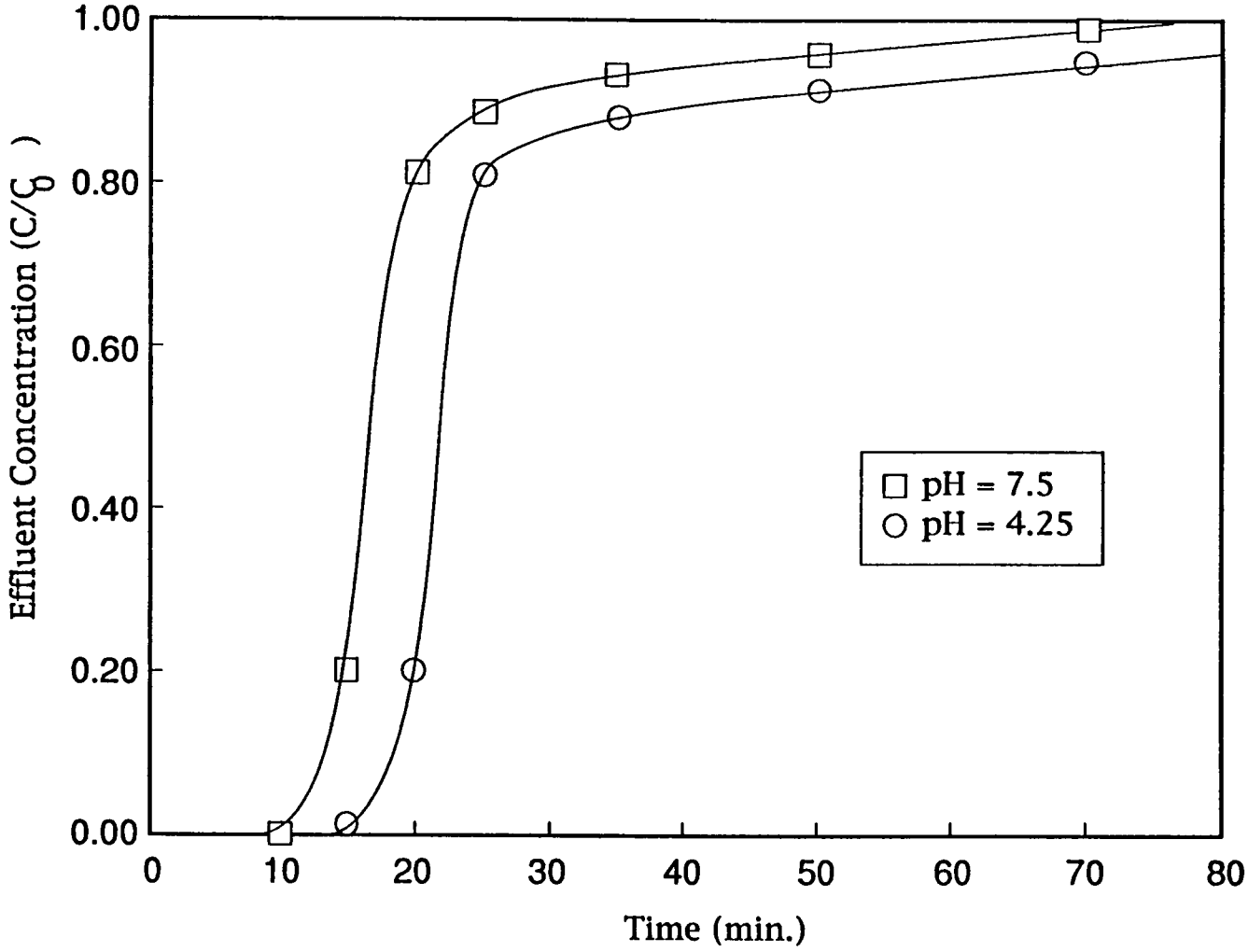
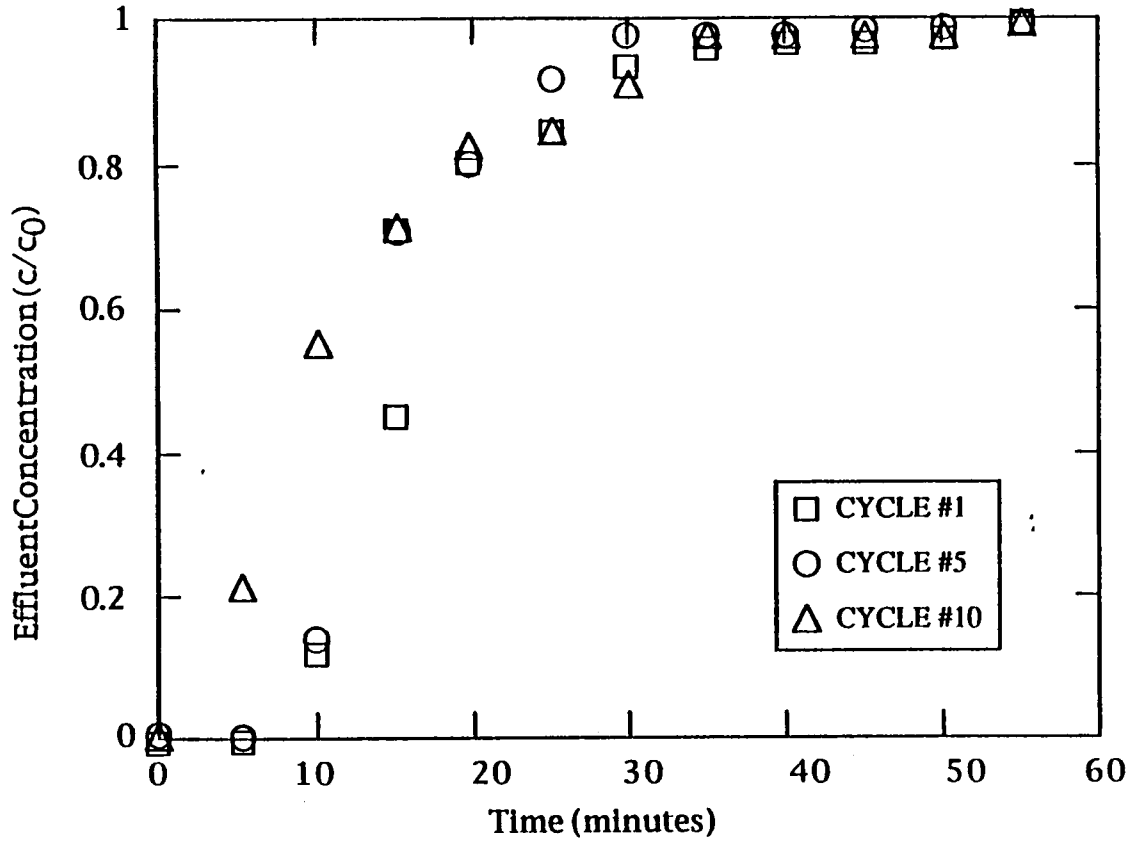


Figure 5-1. Effect of Solution pH on Breakthrough Curve for IRA-68.

the acidic conditions. From the similar shapes of the breakthrough curves, it can be inferred that the change in solution pH does not affect the diffusion parameter D/R^2.

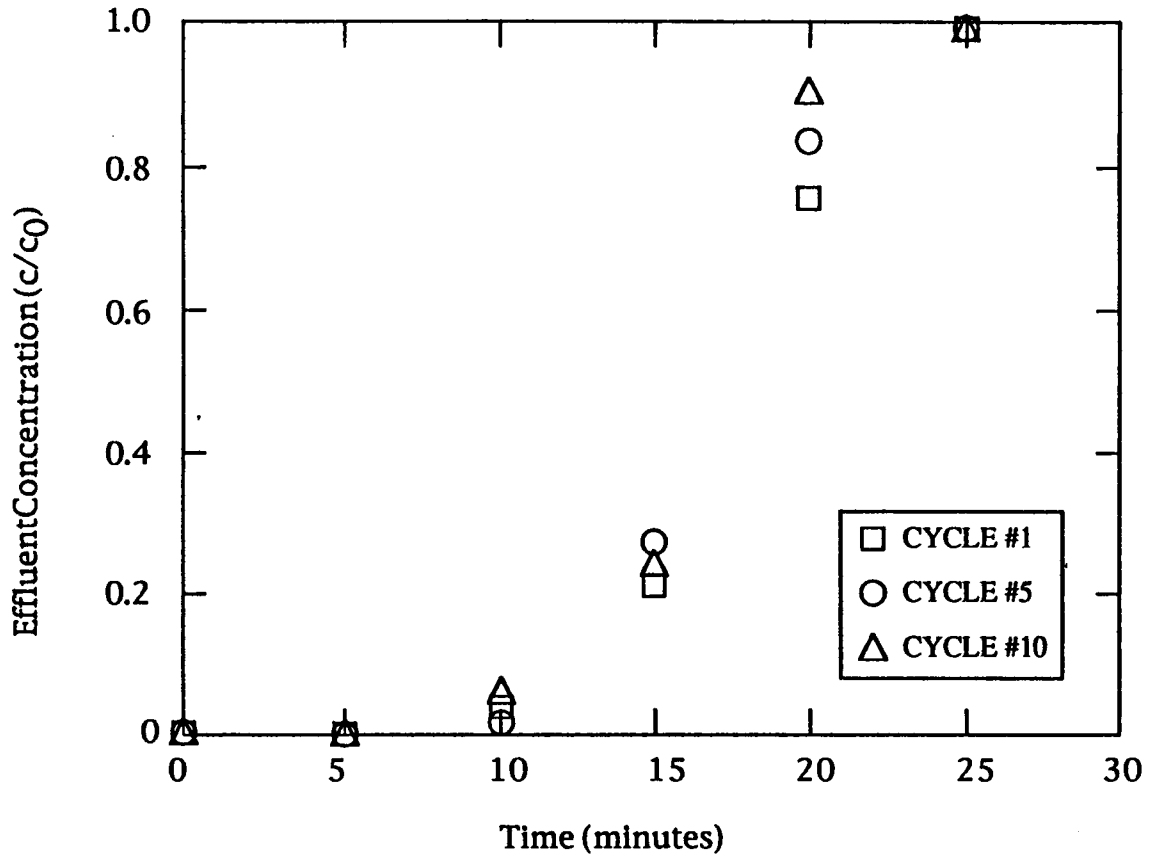
Determination of Cycle Efficiency

Ten consecutive cycles of regeneration and carbonation /exhaustion were performed on the same sample of resin for all the three candidate resins by using the procedure described in Chapter 4. The experimentally determined breakthrough curves for IRA-68, -35 and -93 are given in Figures 5-2 to 5-4. From these experiments it can be seen that the resins showed no degradation in performance. To further confirm this, the equilibrium resin capacity was computed for each cycle using numerical integration. The calculated resin capacities as a function of corresponding cycle number are plotted in Figure. 5-5 to 5-7. From these figures, it is evident that the capacities vary within an error band of ± 10%. There is no upward or downward trend in the resin capacity. These variations can be attributed to the possible experimental scatter. To study the effect of the cyclic operation on the kinetics, the diffusion parameters were computed for the candidate resins using Antonson's model. The calculated



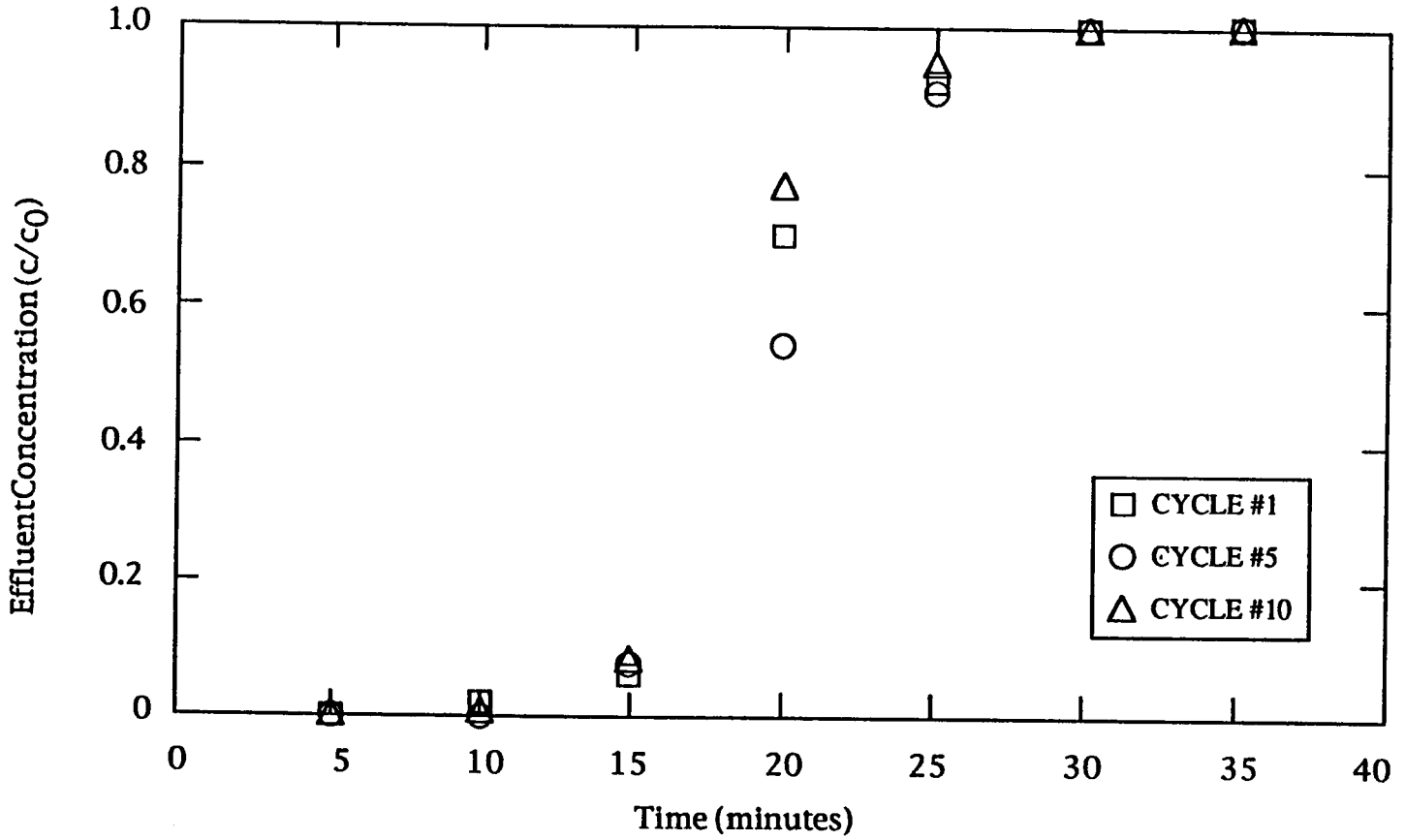
- Flow Rate of K_2SO_4 Solution = 11 cc/min
- Resin volume = 100 cc
- 5 wt% K_2SO_4 solution
- CO_2 Pressure = 10 psig.

Figure 5-2. Cycle Efficiency Experiments For IRA-68 Resin



- Flow Rate of K_2SO_4 Solution = 11 cc/min
- Resin volume = 100 cc
- 5 wt% K_2SO_4 solution
- CO_2 Pressure = 10 psig.

Figure 5-3. Cycle Efficiency Experiments For IRA-93 Resin



- Flow Rate of K_2SO_4 Solution = 11 cc/min
- Resin volume = 100 cc
- 5 wt% K_2SO_4 solution
- CO_2 Pressure = 10 psig.

Figure 5-4. Cycle Efficiency Experiments For IRA-35 Resin

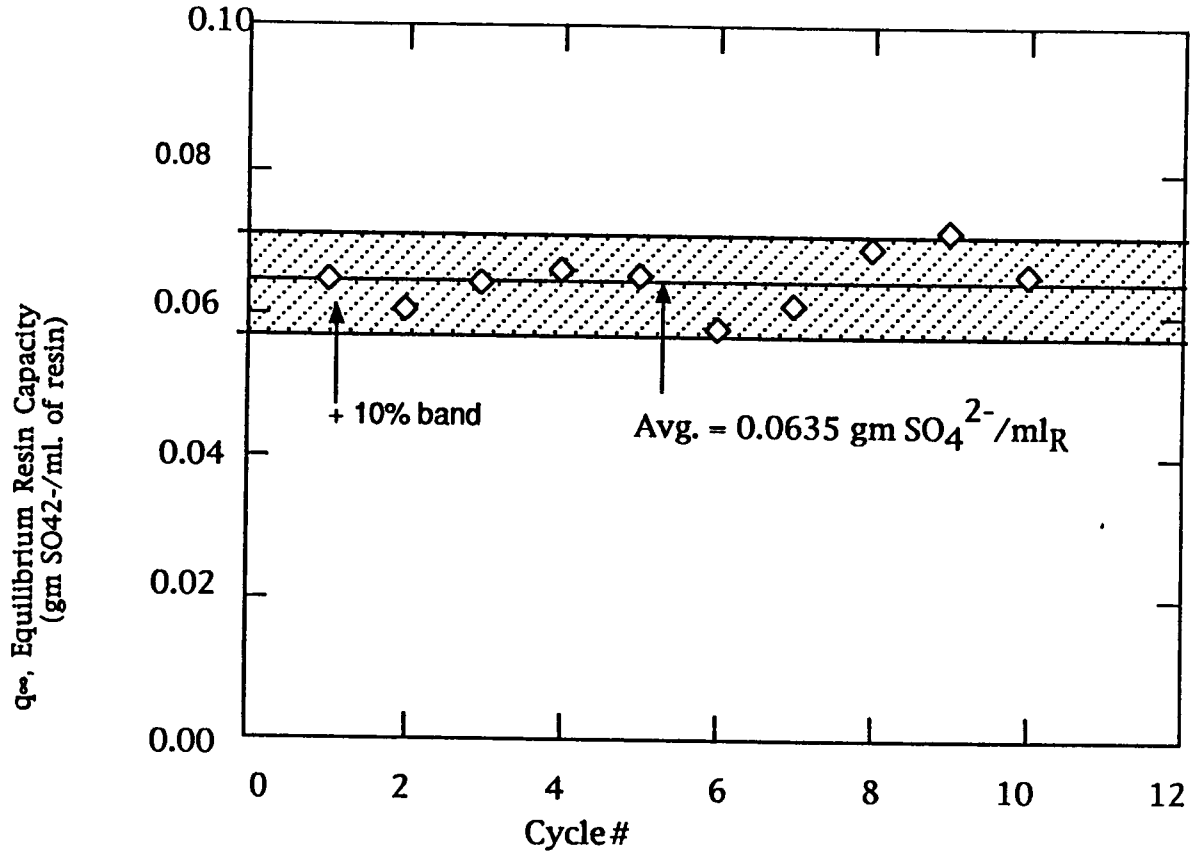


Figure 5-5. Calculated Equilibrium Capacity of IRA-68 Resin As a Function of Cycle Number

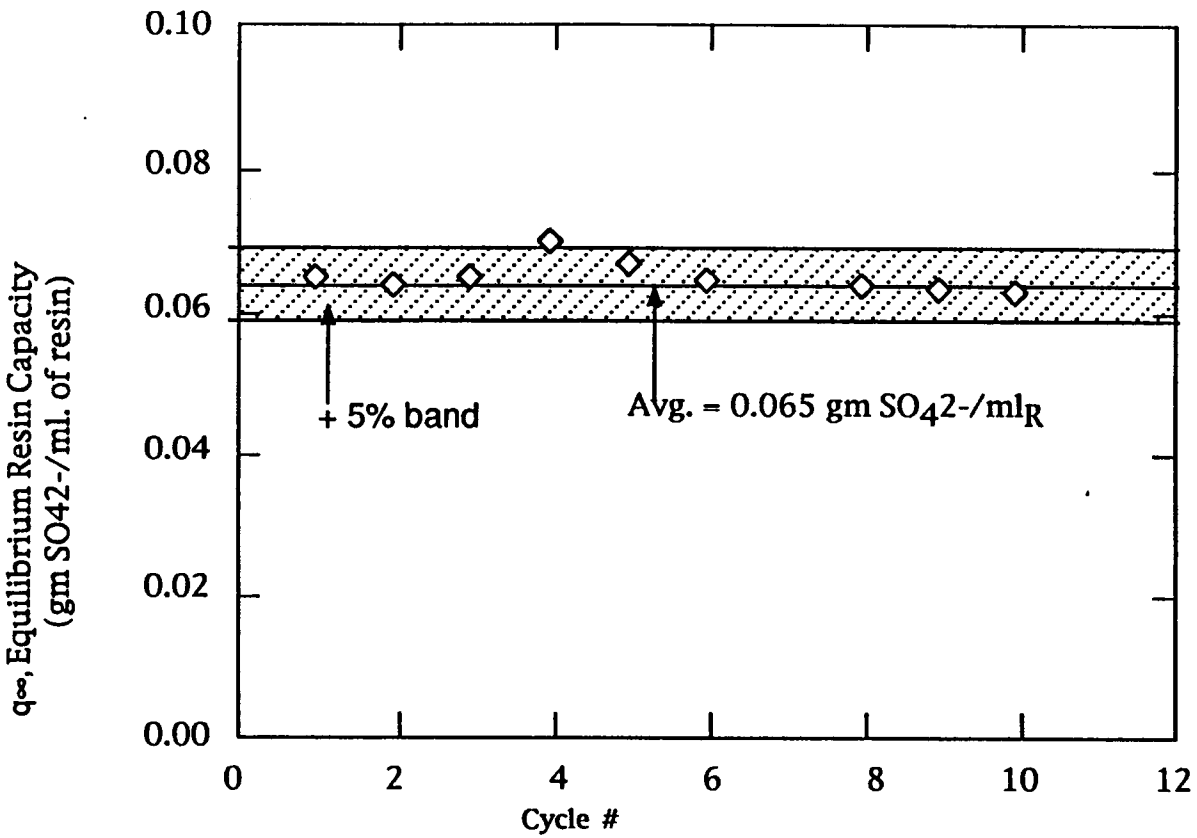


Figure 5-6. Calculated Equilibrium Capacity of IRA-93 Resin As a Function of Cycle Number

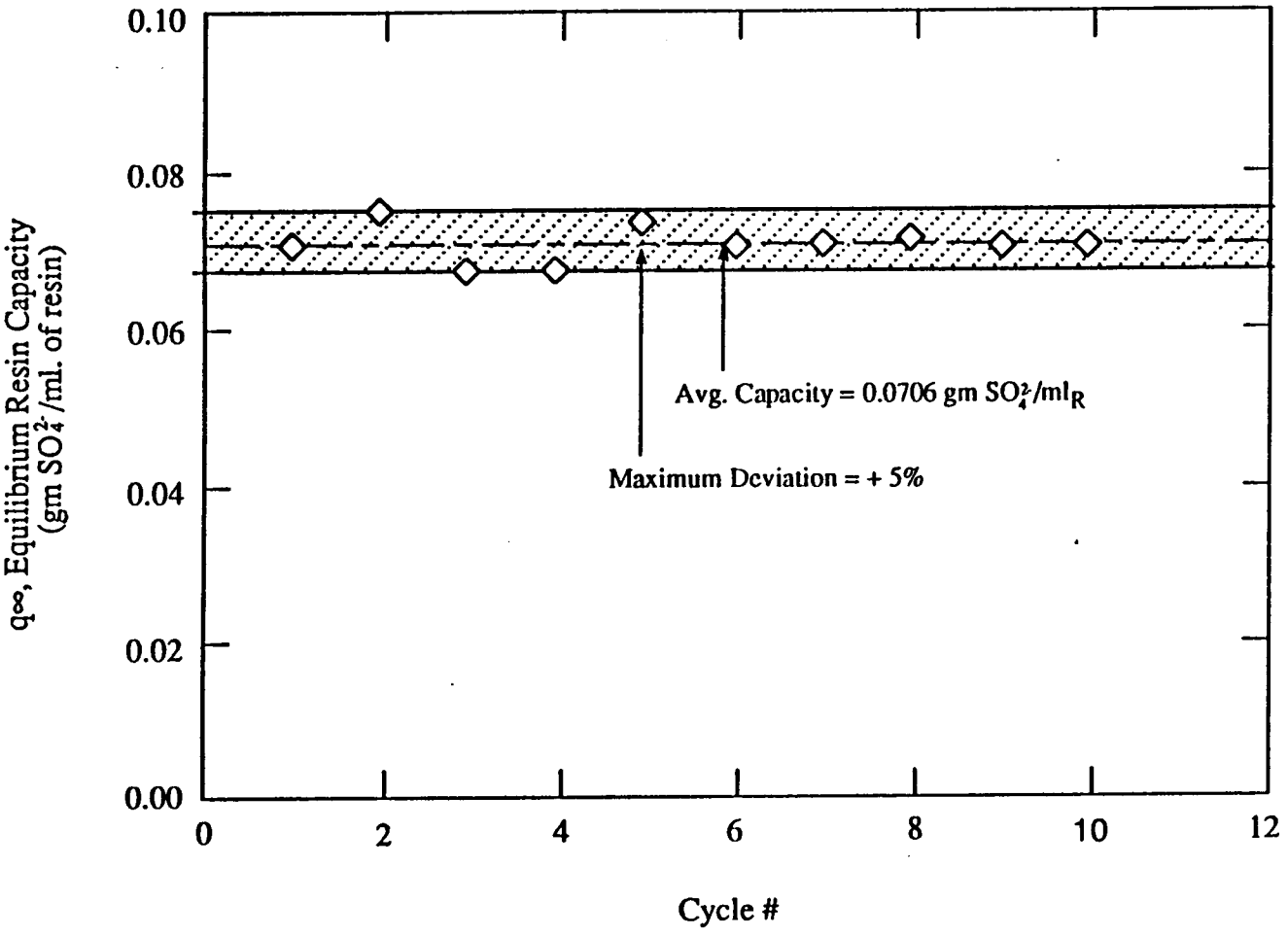


Figure 5-7. Calculated Equilibrium Capacity of IRA-35 Resin As a Function of Cycle Number

values of D/R^2 are plotted against cycle number in Figure 5-8. The value appears to be unchanged within the experimental scatter. Thus the ion-exchange kinetics does not appear to change during the cyclic operations.

Multiattribute Analysis of Fixed-Bed Results:

In multiattribute analysis, importance rating is given to each attribute affecting the decision making process. The attributes are then used to determine the utility value for each alternative. The best alternative is the one with the highest calculated attribute (32). The major parameters considered in this analysis include : resin capacity, cycle efficiency, resin cost, solution concentration, dissolved impurities and cation effect. From the evaluation of Strevel's preliminary results, (5), certain parameters were found to have very little or no effect on the resin's performance. These parameters were removed from any further consideration. The list of such parameters is given in Table 5.11.

An additive utility model was used for this analysis. In the additive model the utility U(x) for any combinations of outcomes for n attributes ($x_1, x_2, \ldots x_n$) can be expressed as :

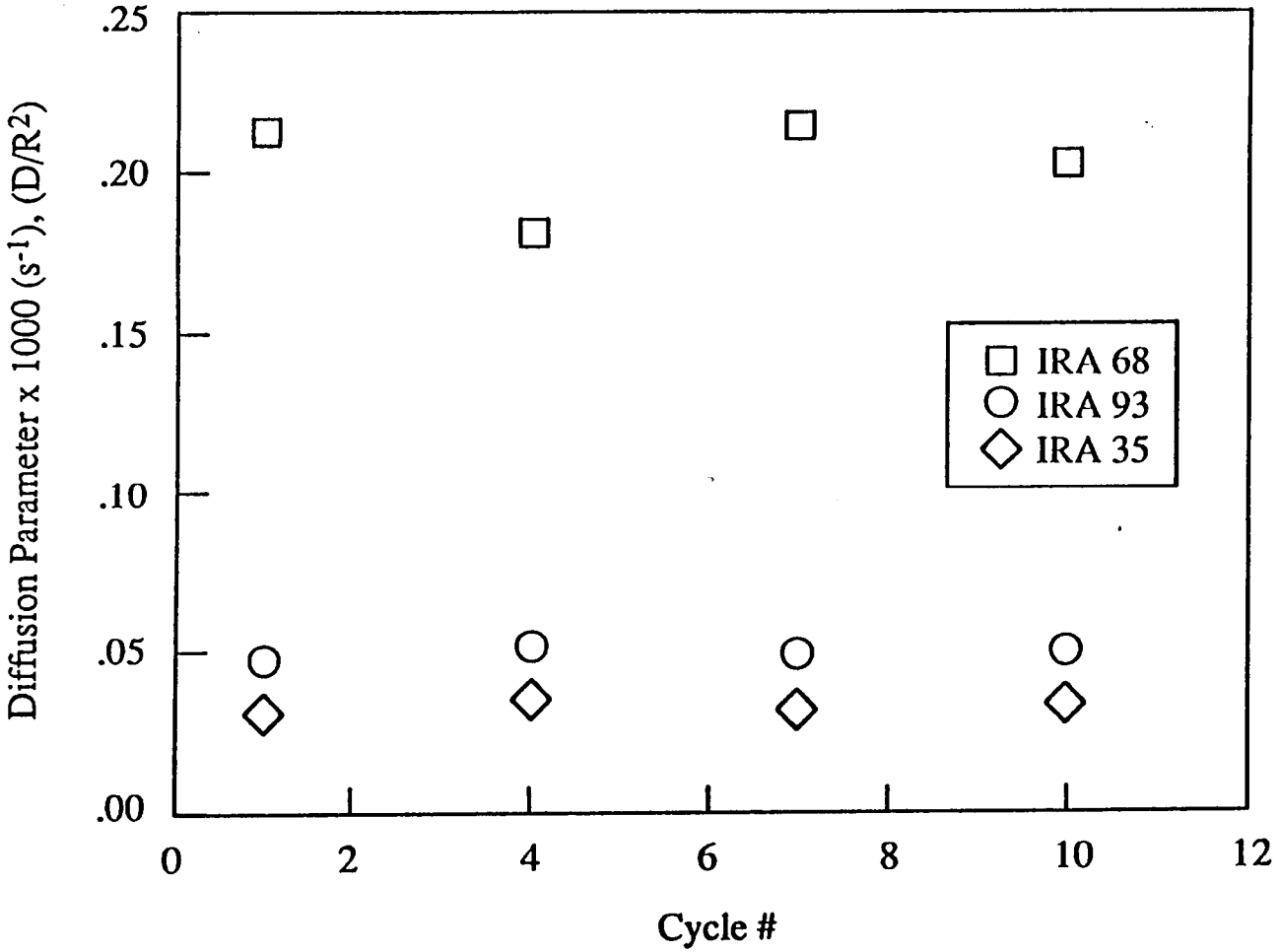


Figure 5-8. Variation in Diffusion Parameter as a Function of Cycle Number.

Table 5.11. Effect of Various Parameters on Resin's Performance

Parameter	Contribution in Resin Performance/Selection	Value Assigned to Attribute
Resin Capacity	Significant	.30
Cycle Efficiency	Significant	.25
Cost of Resin	Significant	.30
Solution Concentration	Small Effect	.15
Dissolved Impurities	No Effect	-
Cation	No Effect	-

$$U(x)=\sum_{i=1}^{n} x_i U_i(x_i) \ldots\ldots\ldots \quad (5.1)$$

where:

x_i = weight (scaling factor) for i th attribute and

$U_i(x_i)$ = utility of the outcome x_i for i th attribute.

To use this model, a utility function must be specified for each attribute x_i where, $U_i(x_i^0) = 0$ and $U_i(x_i^*) = 1.0$. Or in words, the worst outcome for each attribute should be assigned a utility of zero and the best outcome should be assigned a utility of 1.0. The shape of the utility function is then determined by subjective judgement on the relative desirability of various outcomes. For example, in the present case, it is desired to determine the utility function for equilibrium capacity for each resin. The best value that can be realized is 0.168 gm sulfate /ml resin, (5). This value is given $U(x^*)=1$ and the worst case (i.e. capacity = 0.068 gm of sulfate/ml resin) is given $U(x_0)=0$. A typical utility function for this case is :

$$U= 1-\{(1-x^2).5\}$$

where

$x = (x_i - x_0)/(x^* - x_0)$

For IRA-68, $x_i = .136$

Thus ,

$x = (.136-.068)/(.168-.068)$

$x = 0.068$

$U = 1-x\ \{(1-.68^2).5\}$

$U = 0.267$

Similar procedure is utilized to determine the U_p values for each resin for each attribute. These values are listed in Table 5.12.

These values were then substituted in the additive model to determine the utilities of the three resins. The calculated utilities are reported in Table 5.13. Based on these values, IRA-68 resin was selected as the best choice for further work to develop the best process schematic and related process economics. However, IRA-35 and IRA-93 resins follow closely in the utility values. Hence all the candidate resins are expected to perform well in the desulfurization of alkali metal sulfates.

Table 5.12. Individual Utilities of Selected Process Variables (U_p)

Parameter	Utility (Up) IRA-68	IRA-93	IRA-35
Resin Capacity	0.267	0.291	0.335
Cycle Efficiency	0.62	0.61	0.65
Concentration	0.393	0.108	0.248
Cost	0.62	0.48	0.465

Table 5.13. Calculated Resin Utilities

Resin Type	Utility (U_R)
IRA-68	.48
IRA-35	.44
IRA-93	.40

CHAPTER 6

Process Design

Based on the analysis of the experimental data, IRA-68 resin was selected as the final choice for process design. The resin was used in a 5+5 column configuration (i.e. 5 columns in parallel configuration undergoing carbonation/exhaustion and 5 columns in parallel configuration undergoing regeneration). This was done on the basis of the typical flow rates suggested by the manufacturers and the range of superficial velocity required to achieve solid phase diffusion controlled regime as well as reasonable cycle time. In absence of the fixed-bed data for regeneration, same cycle time was assumed for regeneration. However, if the studies in future suggest otherwise, a merry-go-round type configuration can be used to compensate for any slack/lead time.

Before the actual design of the process, it is necessary to determine the spent seed flow rates and compositions to be treated in the plant. An overall material and energy balance was performed for a typical 300 MW_t coal-fired MHD plant. The assumptions made for this program are consistent with those made by the

Westinghouse (28) for similar calculations. The important assumptions are listed below:

* Combustor thermal input = 300 Mw_t.
* Ash rejection = 70%
* Moisture in prepared coal = 2 wt%
* K_2CO_3/S molar ratio =1.2
* Desired potassium in channel =1.5 wt%
* Sulfur removal efficiency = 100%
* Molar ratio of Na/K in recycled seed = 0.1667
* Oxygen in the air= 35 vol%
* Amount of primary air supplied= 95% of stoichiometric requirement

The program uses the coal analysis, plant efficiency and availability as input parameters to carry out material and energy balance computations. Major variables considered at different stages of MHD plant are shown in Figure 6-1. Figure 6-2 presents an information flow chart for the computer program. Actual FORTRAN code with a typical input and output is listed in the Appendix A. The actual material balance for sulfur and potassium containing species as well as other important species is presented in Table 6.1. for low

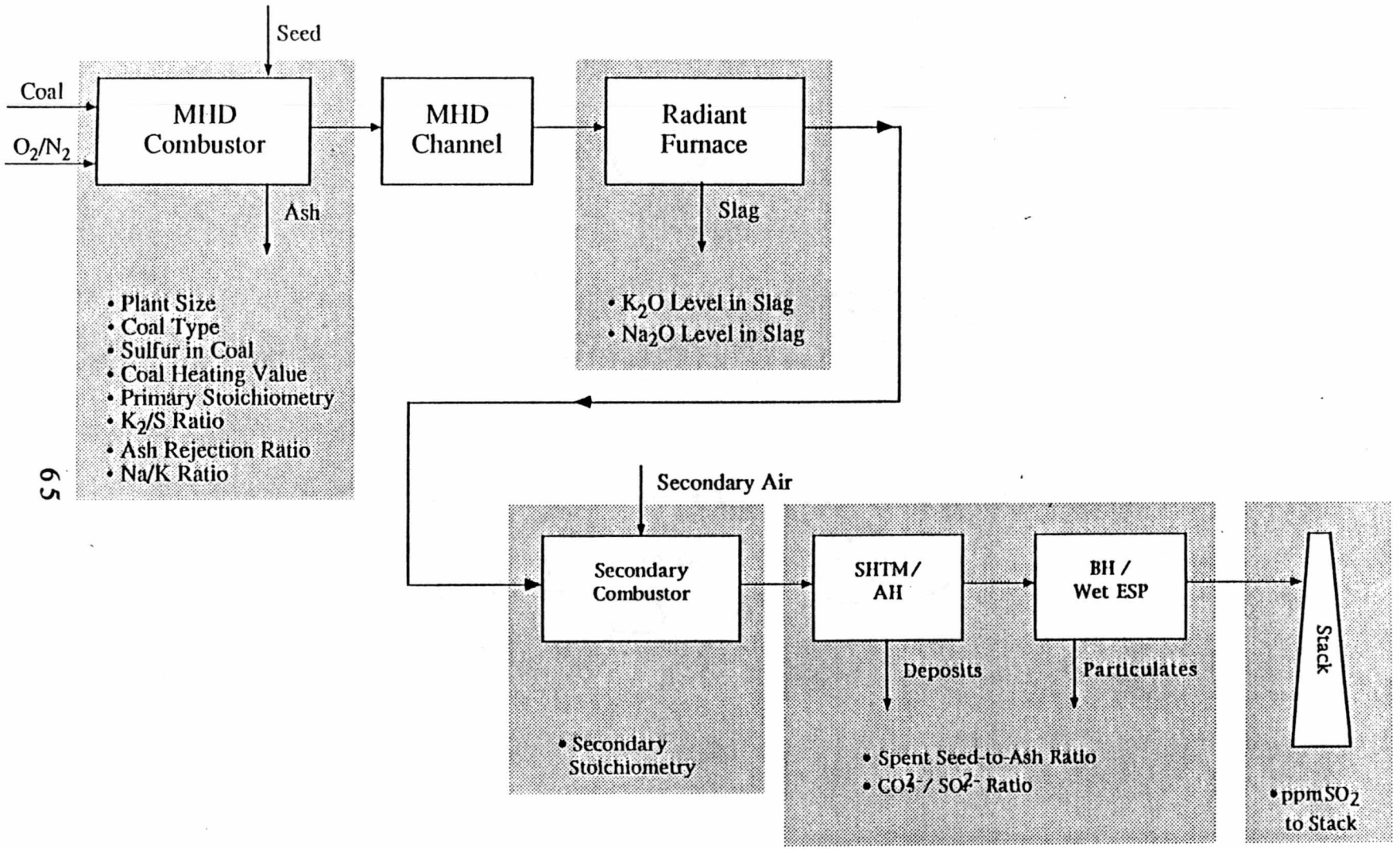


Figure 6-1. Major Variables Included in Calculations of Spent Seed Flow Rate and Composition.

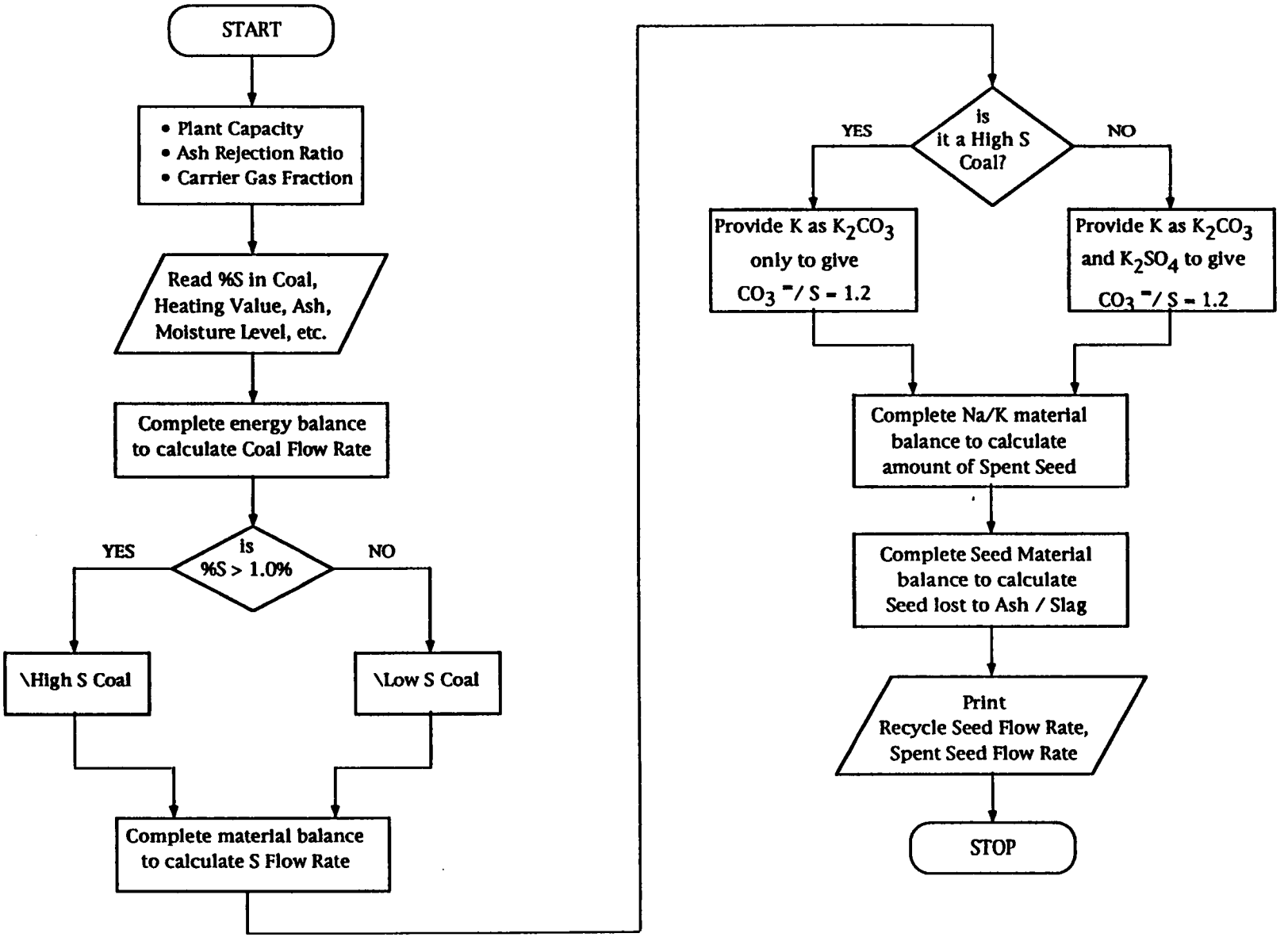


Figure 6-2 Information Flow Chart for Calculating Spent Seed Flow Rate and Composition.

Table 6.1. Material Balance for a 300 MW_t MHD Plant

Component	Flow Rate (lb/hr) 4.29% S case	1.28% S case
Prepared Coal	81,840	90,840
Coal Carrier Gas	818.4	908.4
Slag/Ash (Rejected)	5,550	7,567
Combustor Air (total)	393,064	400,650
Sulfur in Slag	77.7	423.7
Net Mass at Combustor Outlet	521,800	528,800
Slag/Ash Carryover	2,379	3,243
Potassium in the Carryover Ash	37.5	8.9
Sodium in the Carryover Ash	10.6	9.4
Sulfur in the Carryover Ash	33.3	181.6
Sulfur in the Reminder Coal	3,441	1,140
Total Sulfur from the Coal & Ash	3,474	1,321
Sodium Carbonate in Seed	1,972	751.9

Table 6.1 (continued)

Component	Flow Rate (lb/hr) 4.29% S case	1.28% S case
Potassium Carbonate in Seed	15,403	5,862
Sulfur Removed by Carbonate	3,472	1,321
Unused Sodium Carbonate	394	150.38
Unused Potassium Carbonate	3,080	1,172
Potassium Tied-up in Slag	120	27.6
Potassium Tied-up in ash	68.8	59.8
Total Potassium Tied-up	188.8	88
Potassium from Coal	151.4	78.6
Sodium Sulfate in Spent Seed	2,183.2	1,169
Potassium Sulfate in Spent Seed	16,069	8,608
Makeup Seed (as K_2SO_4)	2,363	1,265

and high sulfur coals.

Cost of evaporation/concentration of the regenerated seed solution can be a major factor influencing the overall process economics. Since the inlet solution concentration to the seed regeneration plant is a variable under consideration, two different schematics for concentration of aqueous solution of regenerated seed were considered. Reverse osmosis was considered in combination with multi-effect evaporation for low concentration ($\approx$1%) solutions as shown in Figure 6-3. Whereas for higher concentration, evaporation alone was used. This schematic is shown in Figure 6-4.

Economic calculations were carried out for 1 to 5-effect evaporators to determine fixed as well as operating costs of evaporation.From this, the annualized cost for evaporation of 1000 lb/hr of seed solution was calculated for various seed inlet concentrations. The exit concentration was assumed to be 47 wt%. In each case the annualized cost for 5-effect evaporator was assumed to be a basis. Relative cost of evaporation was defined as the ratio of the annualized cost incurred for that particular evaporator to the similar cost for a five-effect evaporator. Relative cost of evaporation as a function of number of effects is shown in Figure 6-5. It is

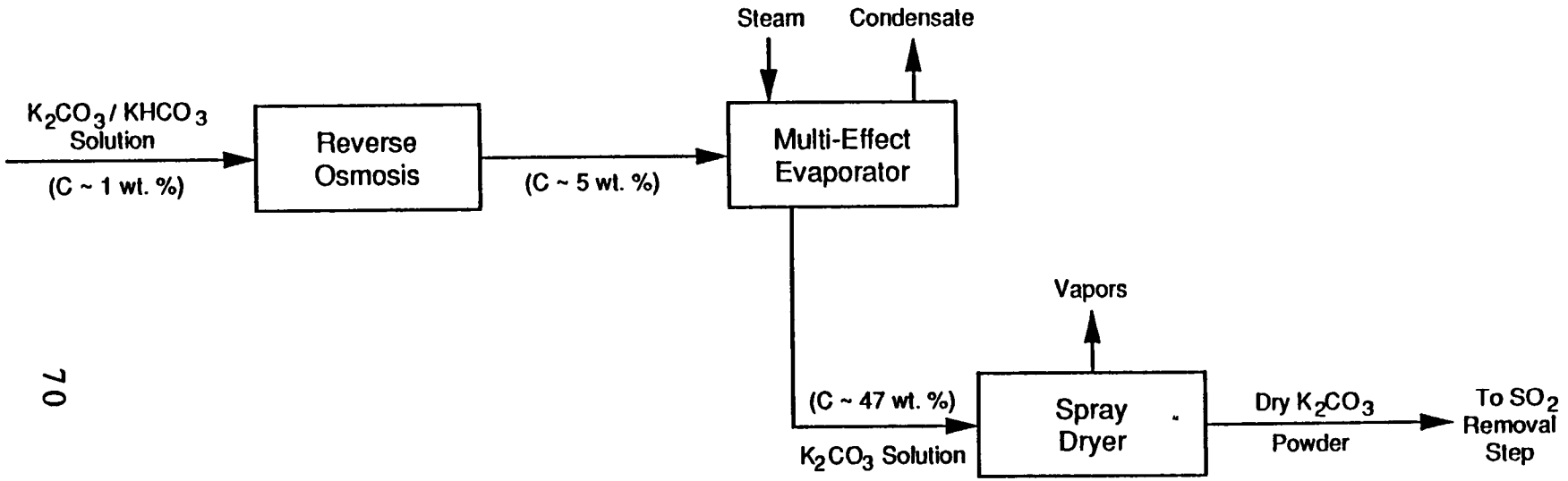


Figure 6-3. Process Schematic for Dilute Effluents

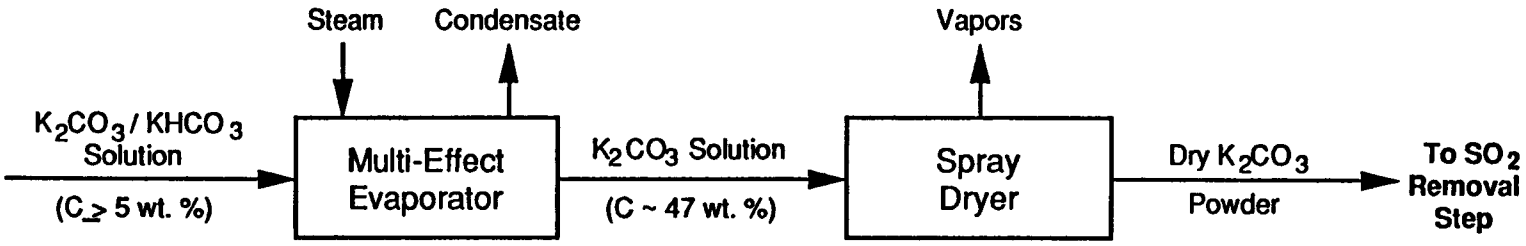


Figure 6-4. Process Schematic for Concentrated Effluents

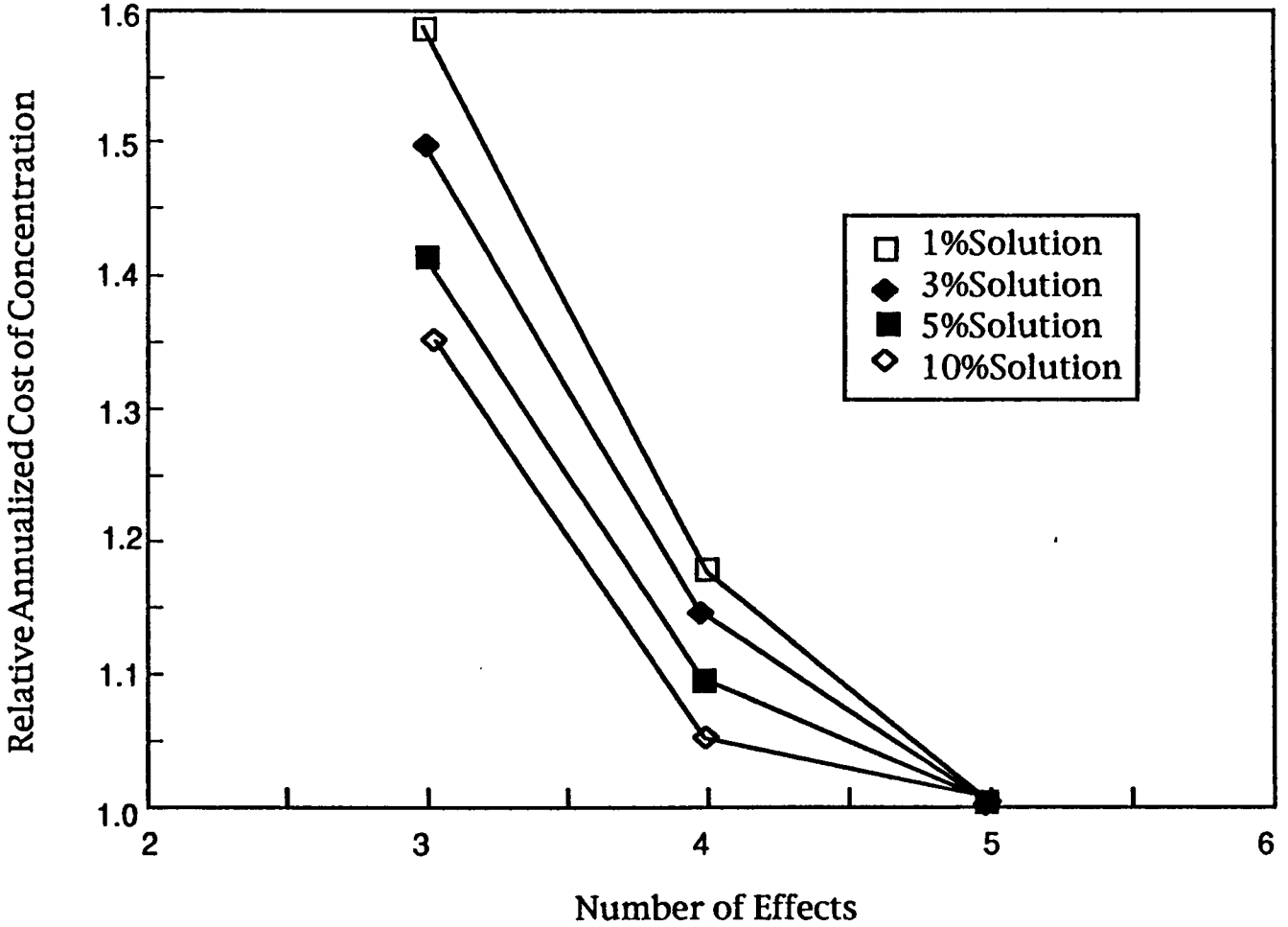


Figure 6-5. Effect of Solution Concentration and Number of Evaporator Effects on Relative Cost of Concentration

observed that the relative cost goes down as the number of effects go up due to increased steam economies. However after about 5 to 6-effects, the increase in steam economy is not very high and it is compensated by the corresponding higher capital costs. Thus a 5 to 6-effect evaporator with steam economies between 3 to 3.5 would be an optimum choice.

Steam economy of an evaporator is defined as the amount of water/liquid evaporated per unit weight of steam consumed. Steam economy of a six-effect evaporator was calculated for the given system ($KHCO_3/K_2CO_3$) for various inlet concentrations by following the procedure for evaporator calculations (32,33). The data is presented in Table 6.2. These data were then correlated to find the steam economy as a function of initial concentration. The relationship obtained is given by:

$$\text{Economy} = 3.144 - 0.107\log(c) \quad \text{..... (6.1)}$$

Where the concentration c is expressed as weight fraction and steam economy is in lb of water/lb of steam. The steam economy changes with the concentration because of the different level of boiling point elevation caused by different concentrations.

Table 6.2. Steam Economies for 6-Effect Evaporator

Basis:

* Concentration of 1000 gal./min of $K2CO_3/KHCO_3$ solution.

Initial Concentration (Wt %)	Steam Economy
1	3.35
5	3.30
10	3.25
20	3.22
25	3.20

Table 6.3. Costs of Concentration by Evaporation and Reverse Osmosis

Basis:

* Costs for 1000 cubic meters/hr of concentration capacity

Cost Component	Cost ($/m^3)
Evaporation	
Plant Amortization	1.43
Steam Cost	1.52
Operating Costs	0.70
Total	3.65
Reverse Osmosis:	
Plant Amortization	1.11
Membrane Replacement	0.92
Energy Consumption	0.81
Operating Costs	1.52
Total	4.36

Reverse osmosis calculations for the concentration of 1000 m^3/hr of water were performed and the costs are presented against the costs of evaporation by using conventional evaporation, in Table 6.3. While doing these calculations, a feed concentration of 10,000 ppm (1wt%) was used. The solution was concentrated to 50,000 ppm (5 wt%). The cellulose type of membranes are not found very suitable for such a high concentration of feed. Hence, poly(vinyl isobutyl ether) or polytetrahydrofuron type of membrane were considered. Membrane life was assumed to be one year for present applications. The membrane price was taken at $\$200/m^2$ of membrane area used. The amortization was carried out by using 30 years of plant life and 6% interest rate. Electricity consumption was assumed to be 10 Kwh per cubic meter of the water permeate. These assumptions are based on similar analyses but for different applications, (23,25,26). Based on the calculations, as shown in Table 6.3, the Reverse Osmosis proved to be about 20% more expensive compared to the evaporation alone. This R.O. based alternative would become further unattractive as the sensitivity analysis presented in the next chapter suggests that the operation of the desulfurization plant at higher concentrations ($\approx$ 10%) would be more economical.

In an MHD plant it is necessary to have greater than 1 wt% potassium in plasma, in order to achieve the desired electrical conductivity. The material and energy balance computations suggest that, for low sulfur coal, the amount of seed required as K_2CO_3 for sulfur removal would not make up this percentage. It is thus more economical to recycle some of the spent seed in the sulfate form as recycled potassium seed. For high sulfur coal the amount of seed required as K_2CO_3 for sulfur capture can be more than 1.5 wt% of plasma depending upon the sulfur level in the coal and the oxygen enrichment used. Thus it will be necessary to regenerate all or most of the seed in this case. Figure 6-6 represents the process schematics for high sulfur coal. In this case, the K_2/S ratio is lower and is determined solely by the stoichiometry of the reaction between the sulfur and potassium. In the present analysis a carbonate-to-sulfate molar ratio of 1.2 is assumed for complete sulfur removal. Figure 6-7 represents the case for a low sulfur coal. Figure 6-8 represents different variables considered while designing an ion-exchange resin-based desulfurization process.

In the case of low sulfur coal it is necessary to base the calculations on the percentage of potassium in the plasma. Thus, a higher value of

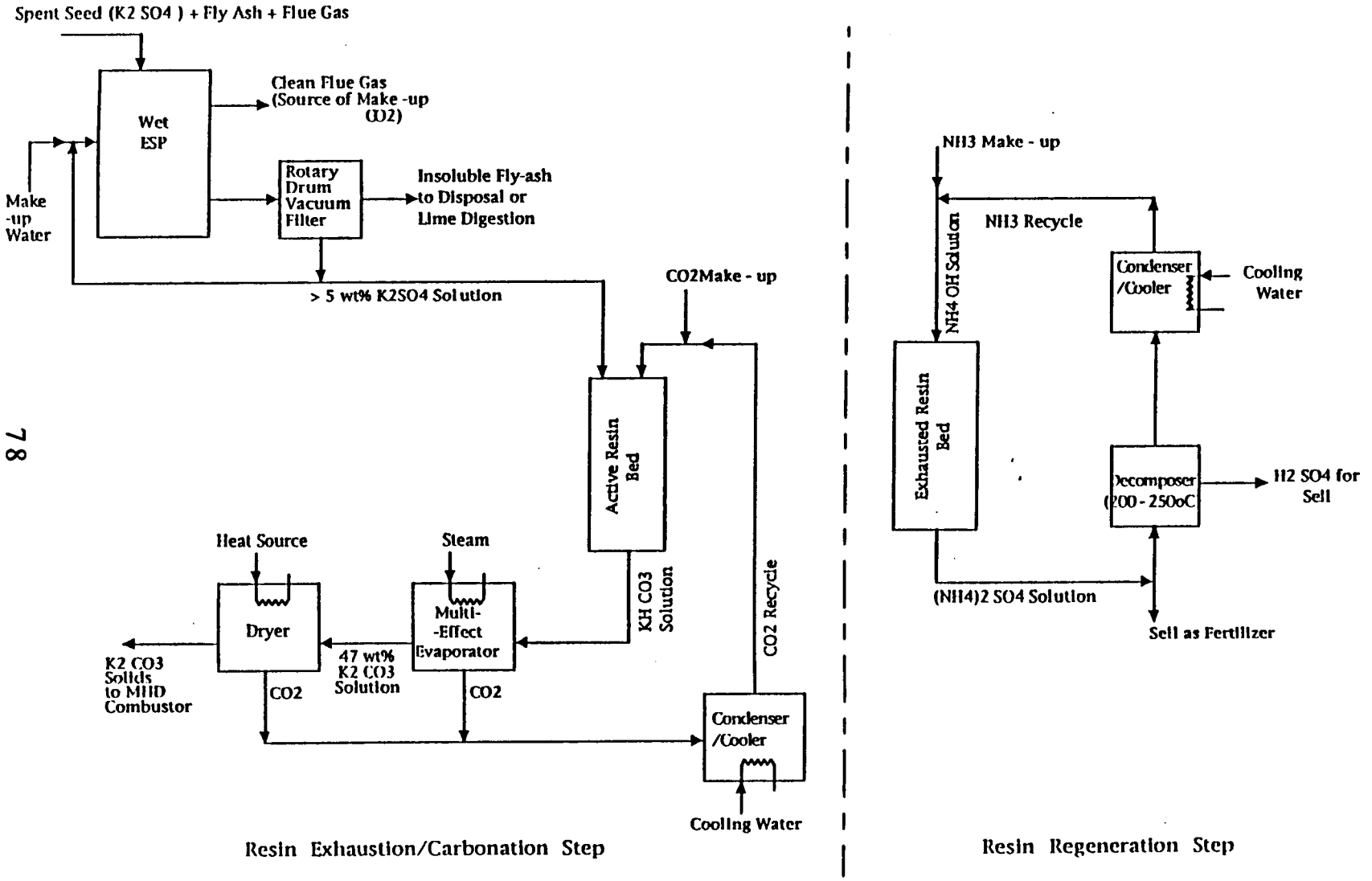


Figure 6-6. Process Schematic for Ion-Exchange Resin-Based Seed Regeneration Process (Low K2/S Ratio)

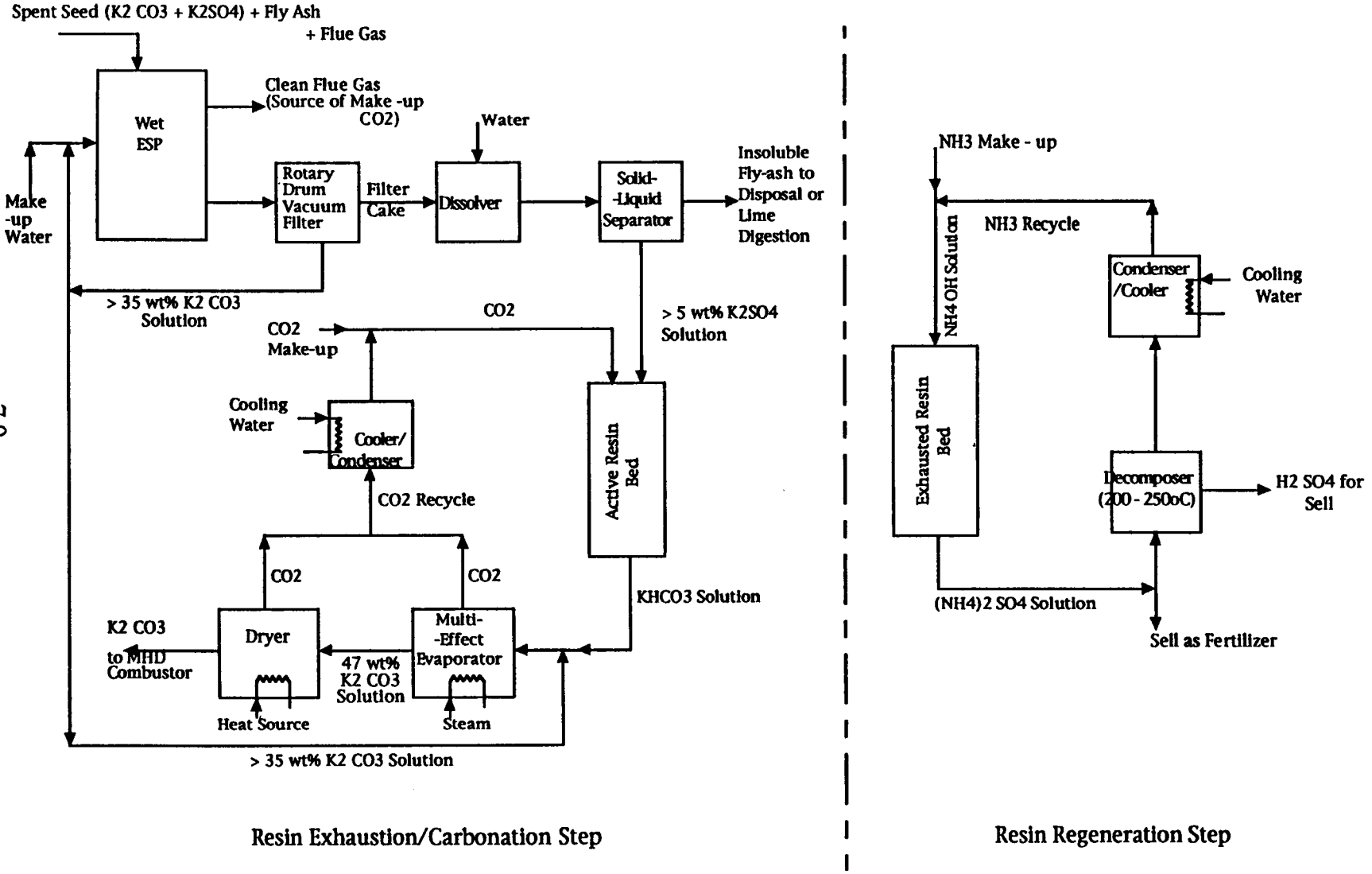


Figure 6-7. Process Schematic for Ion-Exchange Resin-Based Seed Regeneration Process (High K2/S Ratio)

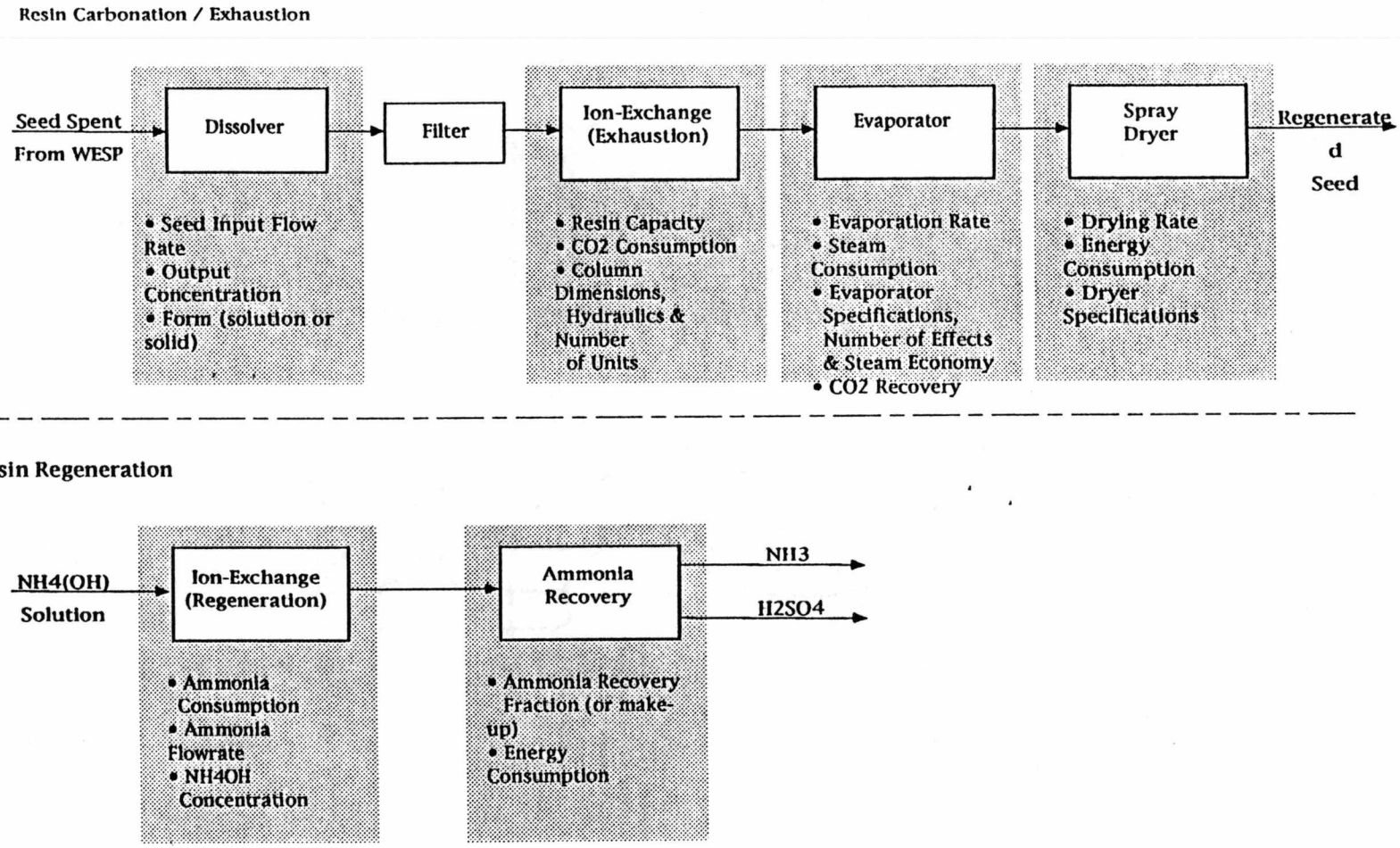


Figure 6-8. Major Variables Included in Simulation of Spent Seed Regeneration Based on Ion-Exchange Resin Concept.

K_2/S ratio is realized in this case. However, in order to make the process economical, one may fix the carbonate-to-sulfur ratio at 1.2 and thus recycle some of the spent seed in the sulfate form.

In order to determine the resin capacity, data from Strevel's experiments was correlated by a least square method. Equation (3.7) represents the equilibrium resin capacity as a function of solution concentration for IRA-68. This correlation is used for a carbonation pressure of 90 psig and superficial velocities higher than 0.03 cm/s so that the rate controlling step would be intraparticle diffusion and the Antonson's model would satisfy the kinetics. The desulfurization process can not be designed according to the equilibrium loading as the exit sulfate concentration should not exceed 5% of the initial concentration to provide relatively pure product. Thus, the resin capacity which can be realized in practice would be slightly lower than the equilibrium value. The actual resin capacity was computed by terminating the numerical integration before the breakthrough point. The usable resin capacity as a fraction of the equilibrium capacity was calculated by taking the mean value of the fractional capacities realized for four typical runs. The results are as shown in Table 6.4.

Table 6.4. Useable Resin Capacity for IRA 68

* Numerical integration terminated at $C/C_o=0.05$

Run Number	q/q_∞
1	0.798
2	0.813
3	0.821
4	0.791
Avg	0.805

This procedure ensures that the effluent does not contain any significant amount of sulfate.

The cycle time to switch from carbonation/exhaustion to regeneration step was found to be inversely proportional to the sulfate concentration and to the square root of the superficial velocity. Best fit correlation from the data obtained by Strevel, (5) is given by:

$$t = \{ 2.0\ q/(0.136\ c) \}\ \{ (0.009/v)^{0.5} \} \quad \ldots\ldots\ldots (6.2)$$

where t is the cycle time in minutes, q is the usable resin capacity expressed as gms of sulfate/ml of resin volume, c is the seed solution concentration expressed as weight fraction and v is the superficial velocity in cm/s. This correlation was determined from the limited data available and should not be extrapolated for commercial design.

This correlation was used in the process design calculations. This part of the process calculation is included in the computer program developed for economic analysis. The information flow chart for this program is given in Figure 6-9. The actual FORTRAN program is listed in the Appendix-A. The program calculates the resin capacity based on the input sulfate solution concentration.

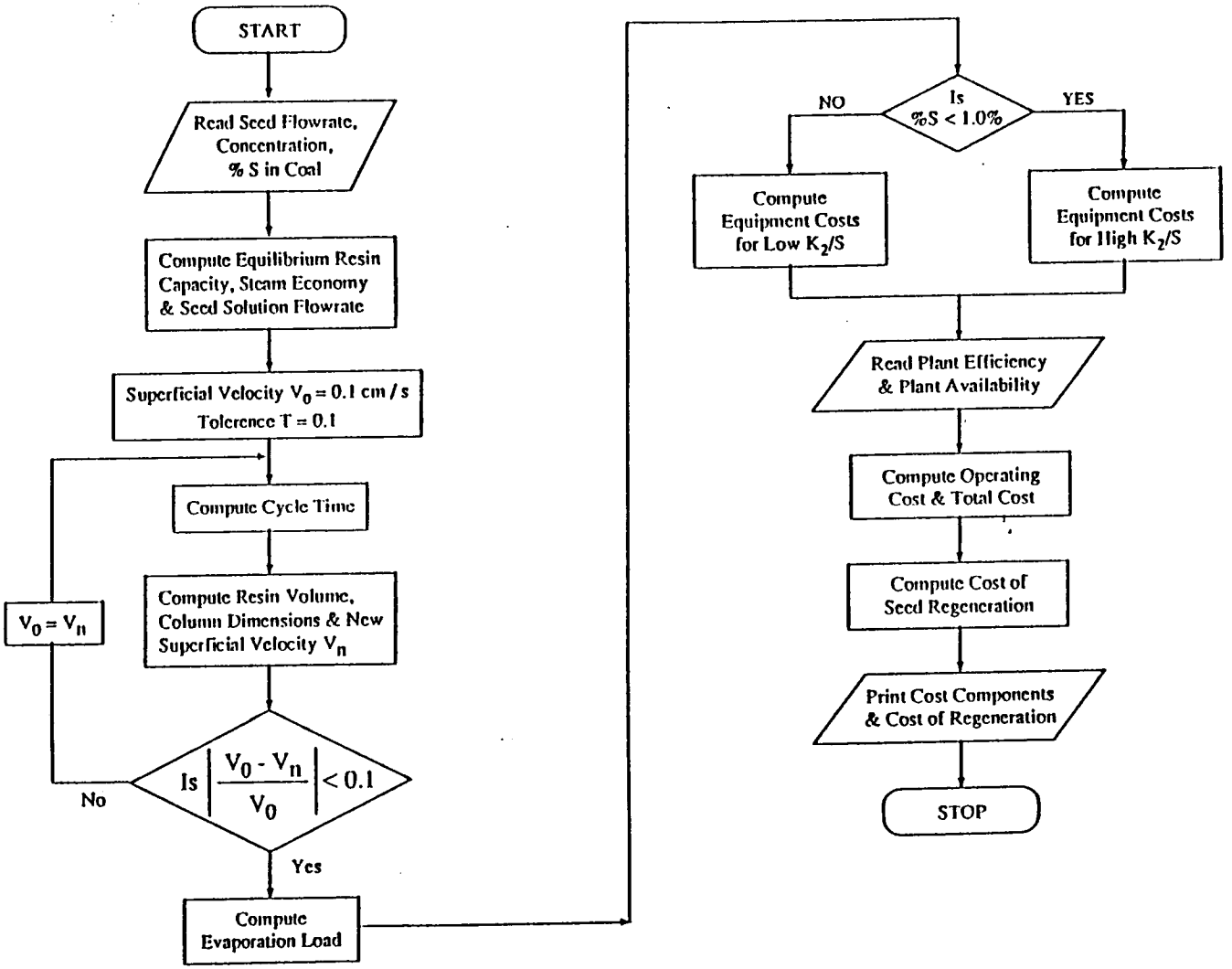


Figure 6-9. Information Flow Chart to Perform Process Engineering & Economic Calculations for Resin-Based Desulfurization System.

The above correlation is used in conjunction with an initial guess value of the superficial velocity to calculate the cycle time and column dimensions. After the column dimensions are determined, a better value is determined for the superficial velocity. These iterations are stopped when the change in superficial velocity between two successive iterations is less than the tolerance which was set at 10%.

A base case of a 300 Mw_t plant burning Illinois no. 6 (Scholz plant design) coal was considered for process design. The calculations were done for the flow scheme represented in Figure 6-6. Input spent seed was assumed to be in the form of solution of 10 wt% concentration. (For low sulfur coal, the spent seed is obtained in the form of a wet cake which then needs to be dissolved in a dissolver to obtain the solution of desired concentration. This solution must then be filtered to remove insoluble ash.) The solution stream was then divided into five streams and passed through the ion exchangers . A simultaneous carbonation was carried out during this operation at 100 psig. The cycle time for the carbonation/exhaustion process was found to be 2.2 minutes under these conditions.

The regenerated solution was then concentrated by using a 6

effect evaporator to 47 wt% strength. The evaporator used was a long tube evaporator with countercurrent operation. The unit costing was done by using the cost data for the desalination evaporators of similar type. Steam of 150 psig pressure was used for evaporation. At 47 wt% concentration a solution of potassium carbonate/potassium bicarbonate is near its saturation point at a temperature of 98 degree Celsius. The concentrated solution was then passed through a spray dryer to obtain dry potassium carbonate. The spray dryer in consideration was a natural gas operated unit. Cost of this equipment was determined by using the data from literature, (33). The carbon-dioxide released during the evaporation and drying steps was then compressed and recycled to the carbonation step.

The exhausted resin was regenerated by using aqueous ammonia solution of 4 wt% strength as NH_3. The spent regenerant solution consisting of ammonium sulfate and excess of ammonium hydroxide was then thermally decomposed using the ammonia recovery unit. It was done by flashing the solution at 200 to 250 degree Celsius. The recovered ammonia was then cooled and recycled. The decomposition gives sulfuric acid as by-product. After

proper concentration, this can be sold if adequate demand exhists. However, the present analysis does not assume any credits or debits from any such sales or additional processing. The design uses 10% excess of CO_2 over stoichiometric requirement and ammonia makeup requirements of 20%.

Table 6.5 gives the equipment sizing for this base case. These specifications were used to calculate the costs in order to perform economic analysis. The coal analysis for different coals used for sensitivity analysis is given in Table 6.6.

Application to Desulfurization of FGD Sorbent

The ion-exchange resin-based desulfurization process can be utilized for desulfurization of the sodium-based FGD sorbent. The exhausted sorbent in this case is sodium sulfate which has to be converted to sodium bicarbonate/sodium carbonate. This sorbent is then reutilized to remove sulfur as SO_2 from the flue gases in a conventional coal-fired power plant. A material balance was carried out for 1000 Mw_t power plant for low as well as high sulfur coal. A schematic of the SO_2 removal step integrated with the sorbent reactvation/regeneration step is shown in Figure 6-10.

Table 6.5. Equipment Specifications for Seed Regeneration Plant (Base Case)

Equipment	Design Conditions	Material	Remarks
Seed Dissolver*	-	C.S.	For Low Sulfur Coal only
Rotary Drum Filter*	-		For Low Sulfur Coal only
Spent Seed Receiver	Atmospheric Pr. 3,000,000 gallons	C.S	Cone roof tank
CO_2 Receiver	Design Pr. 400 Psig Capacity 50 tons	C.S	
CO_2 Blower	Design Pr. 150 Psig Capacity 800 ft^3/Min,	S.S.	Purchased Unit Two Stage
Ion-Exchange Columns	Design Pr 150 Psig. 5.8' Dia, 8.6 ' Ht.	C.S.	10 units
Regenerated Seed Tank	Atmospheric Pr. 2,750,000 gallons	C.S	Cone roof tank

Table 6.5 (Continued)

Equipment	Design Conditions	Material	Remarks
Evaporator Train	6 Effects, long tube, Capacity 2700 lb/Hr	S.S	Steam Economies 3.00- 3.5
Dryer	Spray Dryer. Capacity 380 lb/min	S.S	Purchased unit. Natural gas fuel.
Water tanks	Atmospheric pressure capacity 4,000,000 gal.	C.S.	2 units
Reg. solution tanks	capacity 3,000,000 gal	C.S.	2 units
Ammonia Recovery System	Flash Distillation Unit capacity 1,300 lb/hr Condenser, Buffer Tank	C.S	Purchased As a Package
CO_2 Cooler/ Condenser	Water Cooled Capacity 500 lb/hr	C.S.	
Sulfuric Acid Tank	Capacity 50,000 gal.	Glass lined	
Ammonia Tank	Capacity 20 Tons	C.S.	

Table 6.6. Analysis of Low and High Sulfur Coals*

	A	C
Proximate, As Received		
Moisture	12.0%	25.3%
Ash	8.7%	9.1%
Fixed Carbon	47.8%	36.6%
Volatile Material	31.5%	29.0%
Heating Value (Btu/lb)	11,241	8,600
Ultimate, Dry		
Carbon	71.75%	65.99%
Sulfur	4.29%	1.28%
Oxygen	8.68%	14.51%
Nitrogen	1.39%	1.00%
Hydrogen	5.19%	5.21%
Ash	8.7%	12.01%
Heating Value (Btu/Lb)	12,774	11,508

Table 6.6 (continued)

	A	C
Ash Analysis		
K_2O	1.9%	0.33%
Na_2O	0.6%	0.39%
SO_3	3.5%	14.76%
Other Inorganics	94%	84.52%
Prepared Coal		
Moisture	2%	2%
Heating Value (Btu/lb)	12,520	10933

A- Scholz Plant Design

C- Corette Plant Design

* Reproduced from Westinghouse,(28)

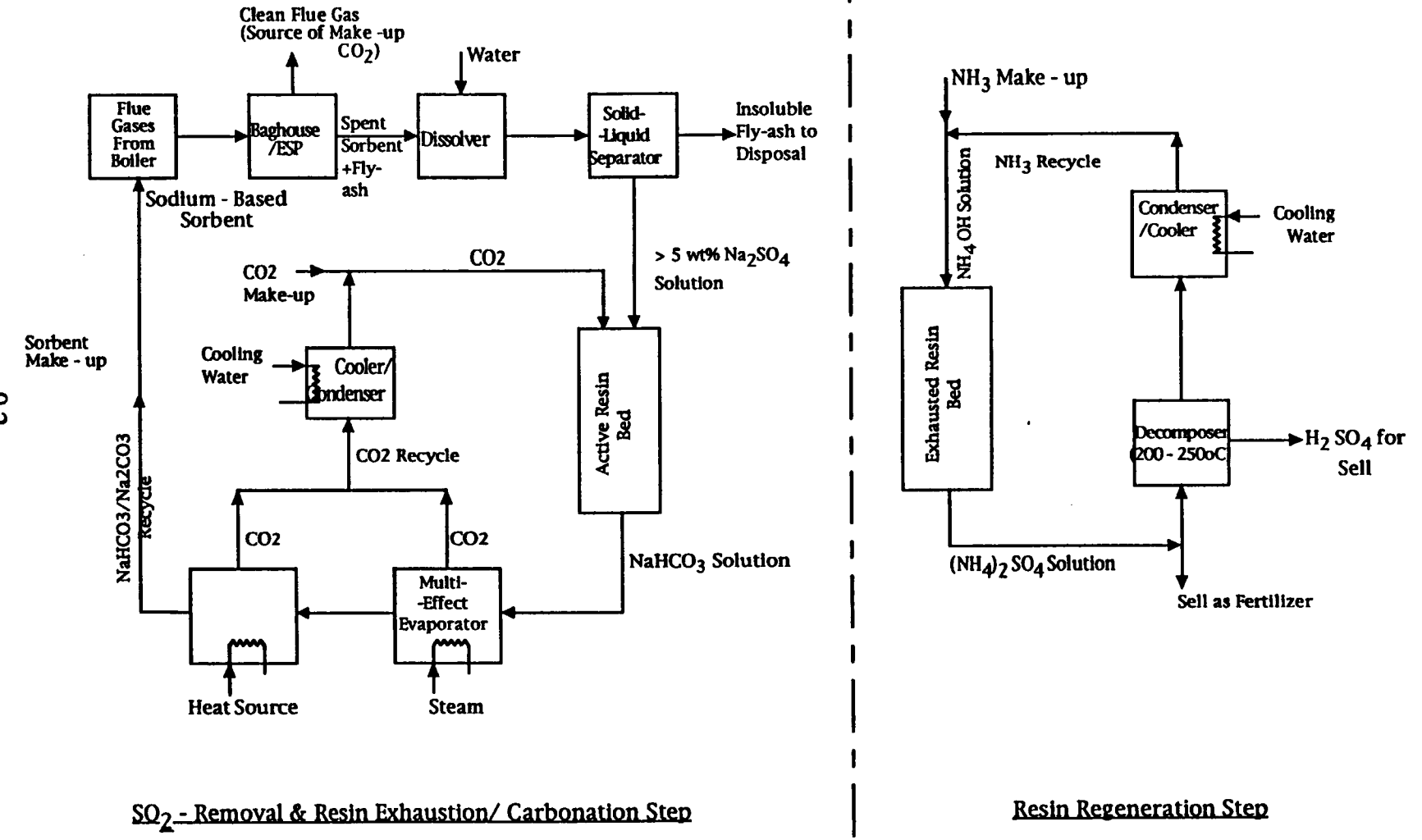


Figure 6-10. Process Schematic For Ion-Exchange Resin-Based Desulfurization of Sodium-Based FGD Sorbent

A stoichiometric amount of sodium was used for SO_2 removal and the removal of sulfur oxides was assumed to be complete. Preliminary process calculations were done for this application to perform economic analysis. The economic analysis is presented in the next chapter.

CHAPTER 7

Economic Analysis and Cost Estimation

Based on the process design described in the preceding chapter, cost estimation was carried out for a base case MHD seed regeneration plant receiving spent seed from a 300 MWt plant burning Illinois no. 6 high sulfur coal. The guidelines provided by EPRI (29), were used for this analysis. A current dollar method of analysis was used and the costs were expressed in terms of 1992 dollars. The methodology and the assumptions used are as follows :

Total Plant Cost

Total plant cost is expressed as the sum of following components.

* Process capital.
* General facilities capital.
* Engineering and home office fees.
* Project contingency.
* Process contingency.

Process capital was calculated by considering installed costs of all the processing units and storage facilities. The installed cost included costs of transfer pumps, piping and instrumentations, construction labor, taxes and freight. The Marshall & Swift index was used to correct the cost for inflation, whereever necessary,(33).

General facilities capital included cost of roads, office buildings, shops, laboratories etc. Since the plant was assumed to be in the vicinity of an already existing infrastructure (MHD power plant), minimum dues of 5% of the process capital were allotted for this purpose.

Engineering and home office fees were assumed to be 8% of the process capital.

Process contingency is the capital cost contingency factor applied to a new technology as an effort to quantify the uncertainty in the technical performance and cost of commercial scale plant. In the present case, since only bench scale data were available, process contingency was taken as equal to 30% of the process capital.

Project contingency is a capital cost contingency factor that covers the cost of additional equipments or other costs that would result from a more detailed design of a definitive project at the

actual site. For preliminary analysis (class II type) as performed here, this value is suggested to be about15% of the total process capital, engineering and home office fees and process contingency.

Total plant investment is computed by adding the Allowance for Funds During Construction (AFDC) to the total plant cost. AFDC is usually determined as interest on the capital during construction period. Since the plant was assumed to use mostly general equipment either prefabricated or site assembled, the construction was expected to be completed in one year or less. Hence, the AFDC was considered to be zero for the present case..

In order to determine the total capital requirement prepaid royalties, preproduction or startup costs, inventory capital and land cost should be incorporated in the total plant investment. The royalties were taken as 0.5% of the process capital. Preproduction costs, which are intended to cover operator training, equipment checkout and extra maintenance, were taken at 2% of the total plant investment. Initial chemical costs were calculated assuming a sixty days' inventory for chemicals and one year's inventory for the resin. The land costs were calculated at a rate of $6800/acre as suggested by EPRI. The breakup of all the equipment costs and above

mentioned cost components is presented in Table 7.1. The components of total plant cost are listed in Table 7.2. Table 7.3 lists the components of total plant investment.

Operating costs

The operating cost is made up of two components i.e. fixed operating costs which includes labor, maintenance and overhead charges; and variable component which includes consumables and fuel costs.

The operating labor requirement was determined by using the per equipment labor requirement given in Peters and Timmerhaus (32). The present process requires 120 employee hours/day. A labor rate of $19/hr was used. Overhead charges were taken at 30% of the total labor cost. Since the plant would not operate under extreme conditions of temperature, pressure or corrosion, the maintenance was taken at 1% of the total plant capital cost.

The costs of consumables such as steam, electricity, CO_2, ammonia are usually calculated by using the current market prices as quoted. In absence of these quotations in the present case, price data from EPRI-TAG, (29), was used with proper allowance for

Table 7.1. Costs of Equipment for an Ion-Exchange Resin Based MHD Seed Regeneration Plant. (Base Case)

Equipment	Installed cost (Mid. 92 $)
Spent Seed Receiver	150,230
CO_2-Receiver	100,153
CO_2- Blower	91,144
CO_2- Condenser	66,231
Ion-Exchange Columns	801,226
Regenerated Seed Tank	100,153
Evaporator	1,220,858
Dryer	3,559,680
Water Tanks	221,338
Ammonium Hydroxide Tanks	57,087
Ammonia Recovery Unit	110,183
Sulfuric Acid Tank	41,363
Ammonia Tank	41,140
Transfer Pumps	210,186
Total Equipment Cost	6,770,972

Table 7.2. Components of Total Plant Cost (Base Case)

Component	Cost (Mid. 92 $)
Process Capital	6,770,972
General Facilities Capital	338,548
Engineering & Home Office Fees	473,968
Project Contingency	1,391,435
Process Contingency	2,031,295
Total Plant Cost	11,006,218

Table 7.3. Components of Total Plant Investment (Base Case)

Component	Cost (Mid. 92 $)
Total Plant Capital	11,006,218
Total Prepaid Royalty	33,854
Preproduction Costs	230931
Land Costs	2,72,000
Initial Resin Costs	268309
Initial Inventory Cost	97,315
Total Capital investment	11,908627

inflation. The breakup of the operating costs is presented in Table 7.4.

The annualized fixed cost was calculated by considering the factors such as depreciation, interest, taxes and insurance. The breakdown of the fixed charge rate is given in Table 7.5

Total Cost of Regeneration (TCR) is given by :

TCR = Annualized fixed cost +Annual operating cost

Total Electricity Generated (TEG) in (Kwh) is given by :

TEG = Capacity x Plant Efficiency x Plant Availability x 8760

And the Cost of Seed Regeneration (Mills/Kwh) was calculated from:

Cost of Regeneration = 1000 x (TCR/TEG)

For the base case, plant efficiency of 33.33%, and plant availability of 65 % were assumed. Thus,

TEG = 300,000 x 0.65 x 8760/3

= 569,400,000 Kwh

TCR = {0.121 x 11,908,621 }+ {4,892,823}

= $6,333,766

Cost of Regeneration = {6,333,766x1000}/569,400,000

= 11.12 mils/Kwh

Thus, for high sulfur coal, the cost of seed regeneration was

Table 7.4. Components of Variable Operating Cost (Base case)

Component	Cost (Mid. 92 $)
Steam (150 psig)	1,185,255
Process Water	226,464
Ammonia (Make-Up)	113,501
CO_2 (Make-Up)	1,348,062
Natural gas	367,090
Cooling water	56,616
Resin Replacement (20% per Year)	53,661
Make-Up Seed (As K_2SO_4)	529,998
Total Variable Operating Cost	3,880647

Table 7.5. Components of Fixed Operating Cost (Base Case)

Component	Cost (Mid. 92 $)
Operating Labor	833,543
Maintenance & Overhead Charges	178,633
Total Fixed Operating Cost	1,012,176

Table 7.6. Breakdown of Fixed Charge rate

Item	Rate (%)
Cost of Money	6.5%
Depreciation (30 Yrs. Straight Line)	3.3%
Property Taxes	2.1%
Insurance	0.1%
Working Capital	0.1%
Total Fixed Charge Rate	12.1%

estimated as about 11.12 mils per Kwh of power generated. This figure is significantly lower than the cost incurred by using an alternative process such as Econoseed Process. The estimated cost figure would further go down in the absence of the high values of project contingencies, process contingencies and other add-ons suggested by EPRI for a new technology. A separate analysis was carried out for the base case assuming it to be a proven technology and overriding the EPRI guidelines. The cost of regeneration in this case was found to be about 9.9 mils/Kwh. This cost would further go down if the higher resin capacity achievable due to performance enhancement by using organic acids (as demonstrated successfully in this study) is taken into consideration.

A cost comparison with the Econoseed Process for three different sulfur levels in the coals is presented in Table 7.7. It is clearly seen from this table that the ion-exchange resin-based desulfurization process tends to be a lot cheaper than the Econoseed Process in all the cases. However this advantage seems to be particularly much higher for the high sulfur coal.

Table 7.7. Comparison of Cost of MHD Seed Regeneration Based on Ion-Exchange and Econoseed Processes

Basis:

*300 Mwt MHD plant
* Plant efficiency=33.33%
* Plant availability (Capacity factor)=65%
* Complete sulfur removal

% Sulfur in Coal	Cost of Regeneration (mills/Kwh) Ion-Exchange	Econoseed[a]
1.28 % (Corette Plant Design)	6.30	8.8
3.0% (Hypothetical)	9.01	16.8
4.29% (Scholz Plant Design)	11.12	23.1

a- Reported by Westinghouse Corporation (28)

Economic Analysis of FGD Spent Sorbent Desulfurization

Ion-exchange process can be applied for reactivating the sodium-based spent sorbent from a regenerative flue gas desulfurization option employed in conventional power plants. Based on the similar procedure, cost estimation was carried out for a dry sodium carbonate-based spent sorbent desulfurization for a 1000 Mw_t plant burning high sulfur (%S >3%) and low sulfur (%S <1%) coals. Stoichiometric amount of sodium was assumed to be used for this purpose and the sulfur removal efficiency was assumed to be 100%. The estimated costs for spent sorbent reactivation using ion-exchange resin based desulfurization option are shown in Table 7.8.

It is seen from the comparison of results presented in Table 7.9 that the ion-exchange resin-based sorbent reactivation plant would require a lower investment than the other commercially available alternatives such as Wellman Lord & MgO scrubbing processes.

Table 7.8. Costs for Spent Sorbent Reactvation for FGD System

Basis:

* 1000 Mw_t power plant

% of Sulfur in Coal	Capital Cost ($/Kw)	Cost of Regeneration (mils/Kwh)
4.29	73.2	9.9
1.28	39.9	5.5

Table 7.9. Capital Cost Estimates for Desulfurization and Regeneration in Sodium-Based FGD System

Basis:

* 1000 Mw_t power plant

Option	Capital Cost ($/Kw) Low S. Coal	High S Coal
Ion-Exchange Resin-Based Process		
Cost of Sorbent Regeneration	39.9	73.2
Cost of Desulfurization[a] (SO_2-Removal Step)	25.0	50.0
Total Capital Cost	64.9	123.2
Wellman Lord & MgO Scrubbing[a]		
Total Capital Cost	-	275

a- Sheth *et. al.* (35)

Sensitivity Analysis.

In order to determine the effect of various parameters such as % sulfur in coal, plant availability and plant efficiency on the cost of MHD seed regeneration, a sensitivity analysis was carried out. For this purpose, the economic calculations were performed using the code ECONO listed in Appendix A.

While determining the equipment costs for evaporator, dryer and some important equipments, installed costs of the equipments were correlated to the capacities by using the data for Literature (33,34). For other equipments, appropriate plant capacity factors were used to scale up or scale down the cost based on the base case. For example, for tanks and storage facilities a scaling factor of 0.57 was used whereas for pumps a factor of 0.33 was used.

Figure 7-1 shows the plot of cost of MHD seed regeneration as a function of sulfur level in coal. The three levels of sulfur in coals used for this analysis were, %S from Corrette plant design, %S from Econoseed plant design and %S from Scholz plant design. It is obvious from this plot that the cost of regeneration would be lower for low sulfur coal. However the cost does not go

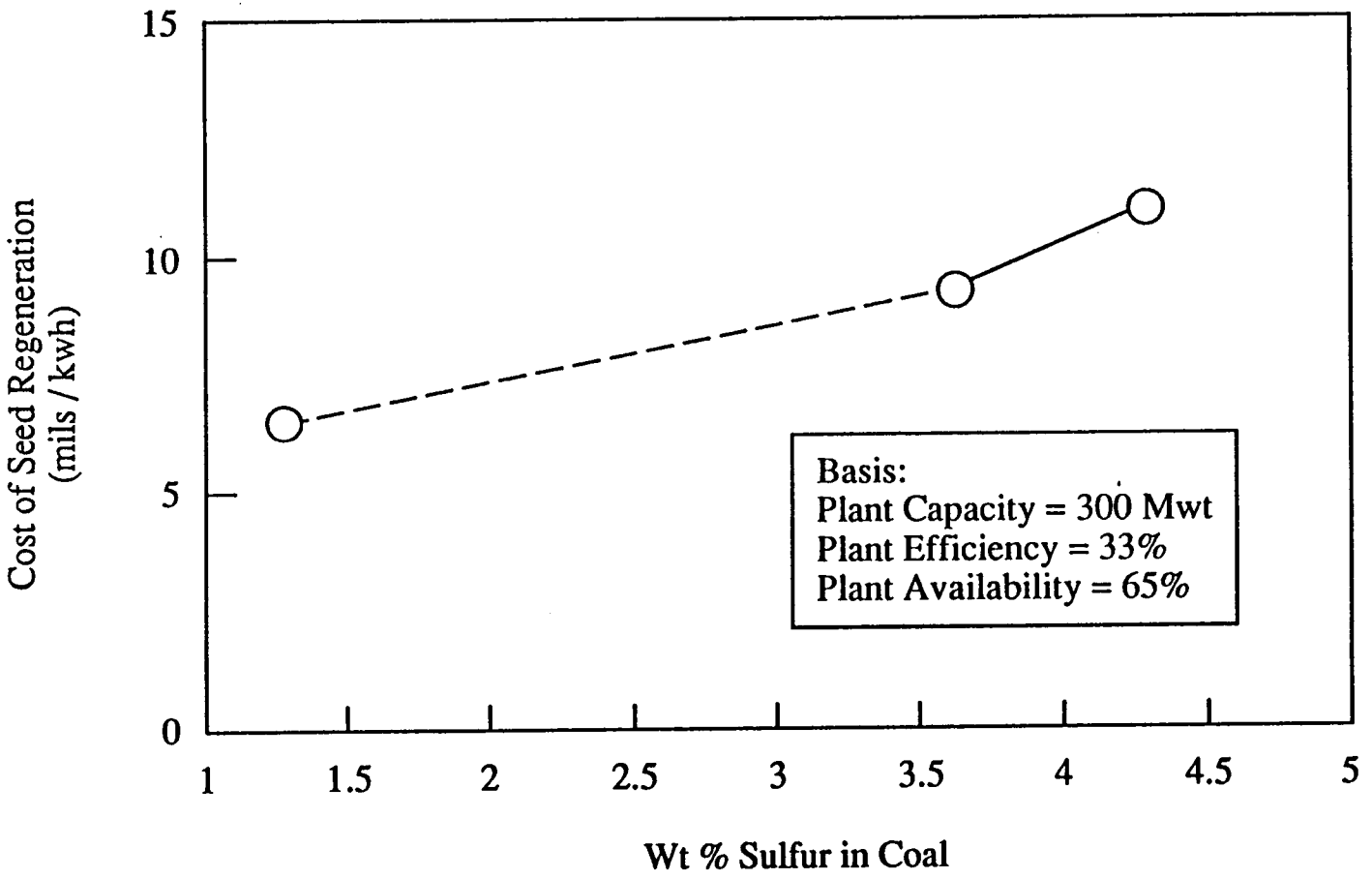


Figure 7-1. Sulfur Level in Coal vs. Cost of MHD Seed Regeneration

down in the same proportion as the sulfur percentage. This is due to the fact that the fixed cost does not decrease linearly with a decrease in the plant size. Thus, the ion exchange process would become particularly more attractive for high sulfur coals.

The variation in the cost of seed regeneration with the plant availability factor is shown in Figure 7-2. The availability factor affects only the variable operating costs. As the plant availability increases, the cost of seed regeneration decreases. In the analysis it was assumed that the availability factor for the plant is the same as that of the MHD power plant. This necessitates the design to be carried out for a much higher capacity than actually required. Since the availability of the chemical processing plant such as this seed regeneration plant can be higher than 90%, it would be economically more attractive to provide a buffer storage facility and carry out the seed regeneration plant operation independent of the availability of the MHD power plant.

The cost of regeneration goes down with increase in the overall energy conversion efficiency, as seen from Figure 7-3. This is due to the reduced coal consumption and hence lower seed rates to be processed for a specific electrical output.

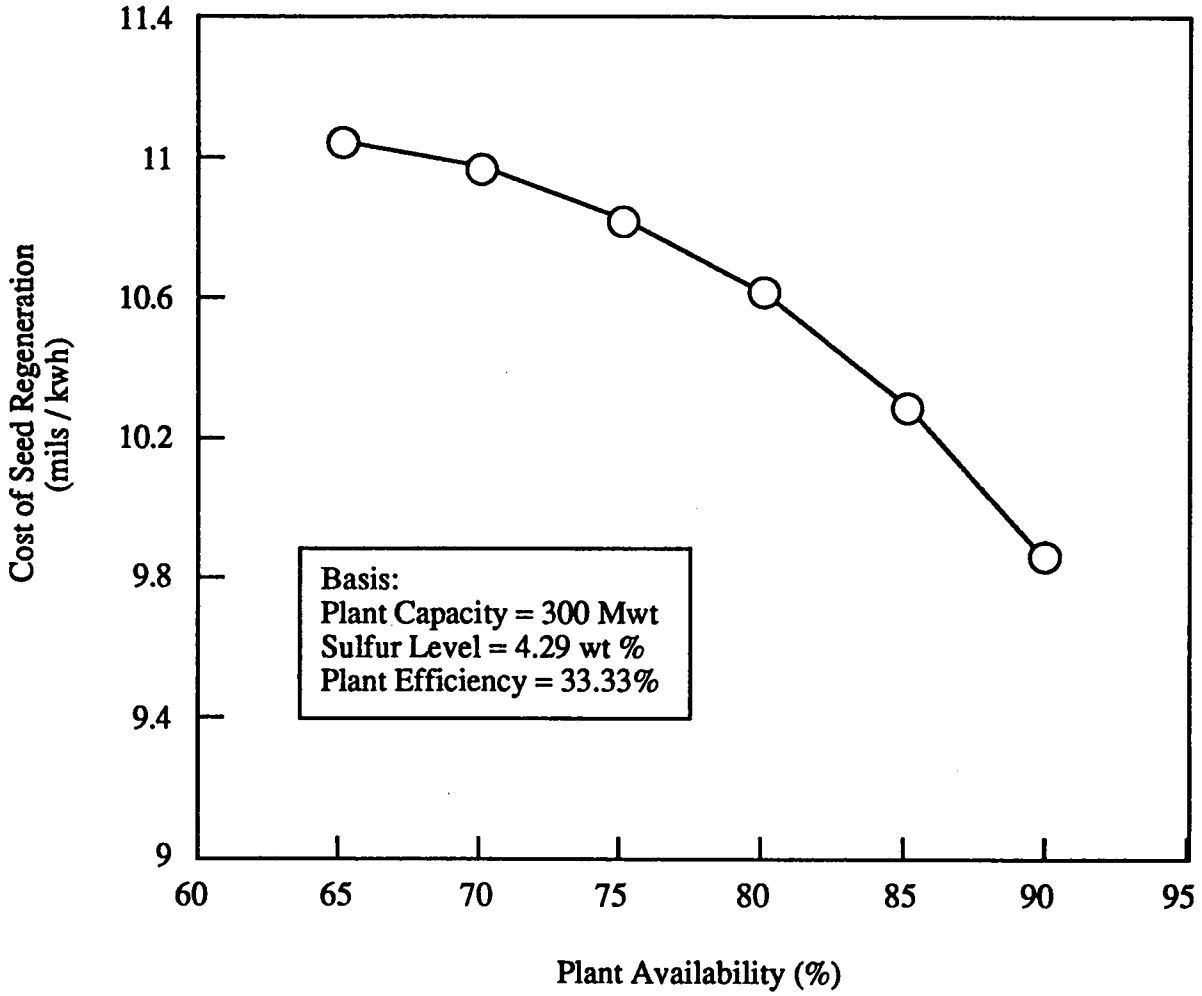


Figure 7-2. Plant Availability vs. Cost of MHD Seed Regeneration

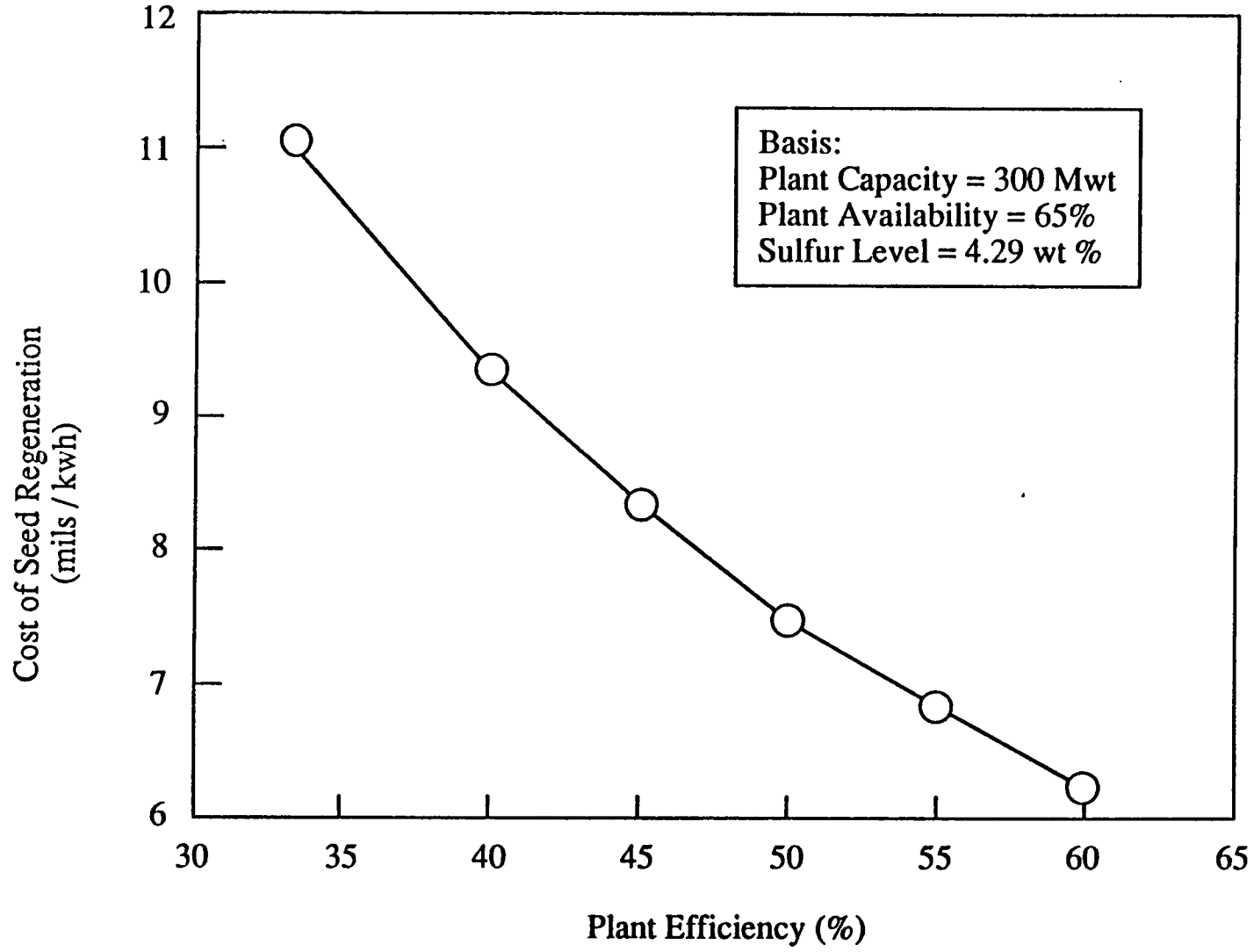


Figure 7-3. Plant Efficiency vs. Cost of MHD Seed Regeneration

The sensitivity of the cost to the seed solution concentration is shown in Figure 7-4. For low concentrations, the evaporation load is very high, and the resin capacity (q_∞) is relatively lower. Combined effect of these two factors makes the cost of regeneration very high at low solution concentrations. As the concentration increases, the cost goes down initially with a very high rate. However, at concentrations of about 10%, the curve flattens suggesting only marginal decrease. Resin performance data at high concentrations will be necessary to throw more light on this option. Beyond 10% concentration one may have to operate the resin column at higher temperatures to keep the potassium sulfate in solution. This may make the plant operating costs to go slightly higher and may offset the advantage of reduced evaporation costs and slightly lower equipment costs.

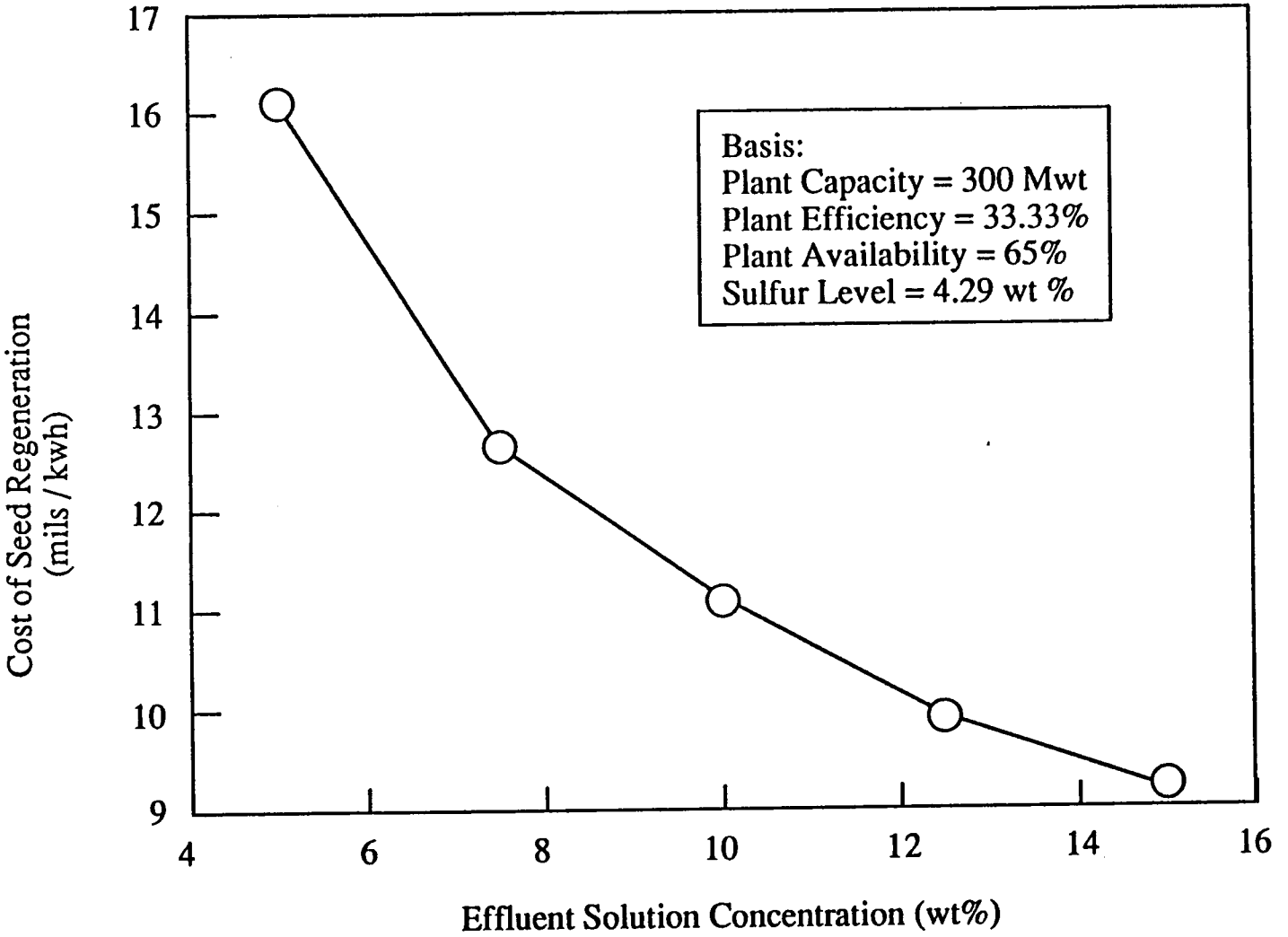


Figure 7-4. Effluent Solution Concentration vs. Cost of MHD Seed Regeneration

CHAPTER 8

Conclusions and Recommendations

The results from Chapter five suggest that the anion-exchange resins perform better in acidic medium and have excellent cycle efficiency for repeated applications. Bicarbonate form of the resin is primarily responsible for the exchange of sulfate ions from the solution. The results also suggest that the best resin suitable for desulfurization of alkali metal sulfate would be IRA-68. However, the other two resins ie: IRA-93 and -35 are also expected to perform well in such applications.

From process engineering and economic calculations it is seen that the resin-based desulfurization process would provide a significantly cheaper alternative to the option being considered at present for MHD seed regeneration. The overall economic advantage is expected to be significantly higher for high sulfur coals.

The present analysis was carried out for a stand alone plant. Purchased carbon dioxide was used in this analysis for make-up. In actual design, carbon dioxide from the power plant stack may be used. Some utilities such as steam will also be significantly cheaper

than the values assumed here due waste steam from the nearby power plant being available.

Factors such as availability of the plant, seed solution concentration, overall plant efficiency and weight percentage of sulfur in coal are important parameters influencing the process economics.

The ion-exchange resin-based process would also prove to be an economical way of desulfurizing the spent sorbent in sodium-based FGD process. The preliminary economic analysis carried out in this study suggests that the ion-exchange resin-based process would require lower capital investment as compared to the existing commercially available alternatives.

The following points should be considered for further studies

* Fixed-bed data for higher concentration and possibly at higher temperatures should be collected in order to explore the possibility of processing high concentration seed solution.

* The kinetics of resin regeneration step needs to be studied for an improved design and cost analysis.

* Th effect of performance enhancers should be determined for fixed bed operation for improved design.

* Since the process has very high potential for commercial application, pilot scale studies are recommended.

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APPENDICES

APPENDIX A

Computer Programs

```
*         THIS PROGRAM COMPUTES THE FLOWRATES OF VARIOUS
*         STREAMS IN A 300 MW MHD COMBUSTOR BY PERFORMING
*         MATERIAL AND ENERGY BALANCE CALCULATIONS
*         LIST OF VARIABLES:
*         PROXIMATE ANALYSIS
*         RMAR=MOISTURE PRECENTAGE
*         ASH= ASH FRACTION
*         CARB=CARBON FRACTION
*         VOLT=VOLATILE MATTER  FRACTION
*         HVAR=HEATING VALUE BTU/LB
*         ULTIMATE ANALYSIS
*         S= SULFUR FRACTION IN COAL (DRY ASH FREE)
*         HVD= HEATING VALUE (DRY ASH FREE, BTU/LB)
*         ASH ANALYSIS
*         RKASH= FRACTION OF K2O IN ASH
*         RNASH=FRACTION OF NA2O IN ASH
*         SASH=FRACTION OF SO3 IN ASH
*         ************************************************
          OPEN(UNIT=2,NAME='ANA2.DAT',STATUS='OLD',READONLY)
          OPEN(UNIT=3,NAME='ANA.OUT',STATUS='NEW')
          READ(2,*)RMAR,ASH,CARB,VOLT,HVAR,S,HVD,RKASH,RNASH,SASH
*        CARBONATE / SULFUR RATIO
          CO3S=1.2
*        SULFUR CAPTURE FACTOR
          SCF=.5
*        DESIRED K2 IN CHANNEL
          RK2=.015
*       THERMAL INPUT TO COMBUSTER MWT
          RQI=300
*       MOISTURE IN PREPARED COAL FRACTION
          RMP=.02
*         OXIDENT LB/HR
          ROXD=444686
*        COAL CARRIER GAS FRACTION
          CGF=.01
*        ASH REJECTION FACTOR
          SAR=.70
*        PREPARED COAL HEATING VALUE
          HVP=HVAR+((HVD-HVAR)*(RMAR-RMP)/RMAR)
*        PREPARED COAL FLOWRATE
          COI=RQI*3415*1000/HVP
          WRITE(5,*)COI
*        COAL CARRIER GAS FLOWRATE
          CCG=CGF*COI
*        MASS FRACTION IN PREPARED COAL
          RL1=ASH+CARB+VOLT
          RMT=RL1/(1.-RMP)
          RMPF=(RMT-RL1)/RMT
          ASHP=ASH/RMT
          CARBP=CARB/RMT
          VOLTP=VOLT/RMT
*        ASH REJECTION FLOWRATE
          SARF=SAR*ASHP*COI
*        SULFUR IN  ASH REJECTION FLOWRATE
          SSR=SARF*SASH*SO3*.4
*        NET COMBUSTER OUTLET FLOWRATE WITHOUT SEED
          CFWOS=COI+CCG+ROXD-SARF
          if(s.ge.0.03)go to 10
```

```
*         SEED FLOW RATE
          SEED=cfwos*0.015/73.593
*        SLAG CARRYOVER FLOWRATE
 10         SACF=(1-SAR)*ASHP*COI
*       K AND NA FLOWRATES IN ASH CARRYOVER
         RK1=SACF*RKASH*.83
         RNA1=SACF*RNASH*.7419
         WRITE(5,*)RNA1
*        SULFUR FLOWRATE IN ASH CARRYOVER
          S1=SACF*SASH*.4
*        SULFUR FLOWRATE IN REMINDER OF COAL.
          S2=(CARBP+VOLTP+ASHP)*S*COI
*        TOTAL SULFUR FLOWRATE FROM COAL LB/HR, LB MOLE/HR
          STC=S1+S2
          SCM=STC/32.
          WRITE(5,*)SCM
*        TOTAL AMOUNT OF CO3 IN THE SEED
          TM2=SCM*1.2
*        MOLES OF K2 IN CARBONATE FORM
          CK2=TM2/1.1667
*        MOLES OF NA2 IN CARBONATE FORM
          TNA2C=TM2*.1667/1.1667
*        MOLES OF K2 AND NA2 IN ASH CARRYOVER
          RIK2=RK1/78.2
          RIN2=RNA1/45.982
*        MOLES OF K2 AND NA2 LOST IN INSOLUBLE SLAG
          RK2LF=RKASH*.01992*(RIK2+CK2)/.023
          RNA2LF=RNASH*.01951*(RIN2+TNA2C)/.023
          WRITE(5,*)RNA2LF
*        MOLES OF NA2 REJECTED FROM  FLY ASH
          RNA2RR=RIN2-RNA2LF
          WRITE(5,*)RNA2RR
*        TOTAL S IN MOLES REMOVED FROM THE COAL BY CO3
          RTS=SCM
*       THE AMOUNTS OF S REMOVED BY CONVERSION TO NA2SO4 AND K2SO4
          RNRTS=RTS*TNA2C/TM2
          RKRTS=RTS*CK2/TM2
*        MOLES OF CO3 REMAINING IN THE NA2CO3 AND K2CO3 FORMS
          RNCO3=TNA2C-RNRTS
          RKCO3=CK2-RKRTS
*        MOLES OF UNUSED CO3 THAT CAN BE BYPASSED BACK TO SEED
          RNNCO3=RNCO3*(1-RLCRE)
          RNKCO3=RKCO3*(1-RLCRE)
          WRITE(5,*)' Moles bypass'
          WRITE(5,*)RNNCO3,RNKCO3
          B1=1./.1667
          B2=1/(1.1667)
          RNNA2K2=((SCM*B2)-RNA2LF+RIN2)/((SCM*B1*B2)-K2LF+RIK2)
          WRITE(5,*)RNNA2K2
*        MOLES OF K2 TIE UP IN SO4 FLY ASH
          RKS4RM=RNA2RR/RNNA2K2
         WRITE(5,*)RKS4RM
*        TOTAL K2 TIE UP
          TK2LM=RK2LF+RKS4RM
*         MAKEUP K2 FROM COAL
          MUK2=TK2LM-RIK2
```

```
*       S IN MOLES REJECTED FROM FLY ASH
          SRJ=RKS4RM+RNA2RR
*         S IN MOLES COMING OUT OF THE SYSTEM
          SEO=SCM-SRJ
*        INPUT OF K AND NA SULFATE
          RKSO4M=SEO/1.1667
         RNSO4M=.1667*SEO/1.1667
         RK2SO4=RKSO4M*174.2
          RNSO4=RNSO4M*141.98
         TT=RNSO4+RK2SO4
         FR=TT/.1
         CK3=CK2*138.2
         TNA2C3=TNA2C*105.98
          if (s.ge..03)go to 20
          seed2m=seed- rk2so4m-rnso4m
          seed3m=seed2m/1.1667
          seed4m=seed2m-seed3m
          seed3=seed3m*174.2
          seed4=seed4m*141.98
20      WRITE(3,*)'SEED INPUT TO MHD PLANT'
          WRITE(3,*)' '
          WRITE(3,*)' K2CO3, Na2CO3, K2SO4, Na2SO4,LB/HR'
          WRITE (3,*)CK3,TNA2C3,seed3,seed4
          WRITE(3,*) ' '
          WRITE (3,*)'TOTAL SLAG GENERATED LB/HR'
          WRITE(3,*)SARF
          WRITE(3,*)' '
          WRITE(3,*)'SEED PROCESSED IN ION EX.PLANT,K2SO4,NA2SO4 LB/HR'
          WRITE(3,*)RK2SO4,RNSO4
          WRITE(3,*)' '
          WRITE(3,*)' SEED SOLUTION FLOWRATE TO ION EX. PLANT LB/HR'
          WRITE(3,*)FR
          STOP
          END
```

.12,.087,.478,.315,11241.,.0429,12774.,.019,.006,.035

SEED INPUT TO MHD PLANT

K2CO3,	Na2CO3,	K2SO4,	Na2SO4,LB/HR
15431.44	1972.686	0.0000000E+00	0.0000000E+00

TOTAL SLAG GENERATED LB/HR
5550.350

SEED PROCESSED IN ION EX.PLANT,K2SO4,NA2SO4 LB/HR

16068.99	2183.249

SEED SOLUTION FLOWRATE TO ION EX. PLANT LB/HR
182522.4

```
*       THIS PROGRAM PERFORMS PRELIMINARY ECONOMIC ANALYSIS
*       OF AND ION-EXCHANGE RESIN-BASED PLANT FOR MHD SEED REGENERATION
*       BASED ON THE BASE CASE OF A PLANT TO REGENERATE SEED FROM A 300 MW MHD
*       PLANT BURNING ILLINOIS NO 6 COAL
*************************************************************
        DIMENSION COST(30),CS(20)
        OPEN (UNIT=2, NAME='ECONO.DAT',TYPE='OLD', READONLY)
        OPEN (UNIT=3,NAME='ECONO.OUT',STATUS='NEW')
        READ(2,*)RKSO4,RNASO4,C,S
        RPRICE=5.0
        RM=(RNASO4/141.98)+(RKSO4/174.2)
        STEAMEC=3.144 -(.107*ALOG10(C))

        WT=RNASO4+RKSO4
        FR=WT/C
        EVP=FR- (WT/.47)
        STEAM=EVP/STEAMEC
*       RESIN CAPACITY & COLUMN DIMENSIONS
        RCAP=.18679+(.01838*ALOG(C))
        CAP=RCAP*.795
        SUPVEL=.1
  10    TIME=(.05*RCAP*40./(C*.136))*SQRT(.009/SUPVEL)

        RESIN=(FR*.454*TIME/(CAP*60.*1000))*2.
        VOLR=RESIN/10.
        VOLC=1.15*VOLR
        VFR=(FR*.454)/(1000.*3600.)
        D=(VOLC*4.0)/(3.14*1.5)
        DIAC=D**(1./3.)
        HTC=1.5*DIAC
        AREAC=3.14*DIAC*DIAC/4.0
        SVEL=VFR/AREAC
        SVEL2=SVEL*100.
        IF(ABS((SVEL2-SUPVEL)/SVEL2).LT..2)GO TO 20
        SUPVEL=SVEL2
        GO TO 10
  20    WRITE(5,*)TIME,DIAC,HTC,RESIN
*       ******************************
*       FIXED COST
*       ******************************
*       INITIAL RESIN COST
        COSTR=RESIN*RPRICE*1000.
        WRITE (3,*) 'COST OF RESIN'
        WRITE (3,*)COSTR
        WRITE (3,*) 'EQIPMENT COSTS'
*       EQUIPMENT COSTS

*       COST OF EVAPORATOR
        GFR=EVP*2.875
        CEVP=1.6916+(.69*ALOG10(GFR))
        COST(1)=(10.**CEVP)*(904./273.)
        DRYRL=(WT/.47)-WT
*       DRYER COST
        COST(2)=EXP(.187+(1.5*ALOG(DRYRL)))
*       DISSOLVER AND FILTERS NEEDED ONLY FOR LOW SULFUR COAL
        IF(S.GT. 1.0) GO TO 11
```

```
*       DISSOLVER
        COST(3)=10.**(2.32+(.53*ALOG10(FR/7.58)))
*       FILTER
        COST(4)=62300
 11     FACT=FR/182020.
*       SPENT SEED RECEIVER
        COST(5)=150000.*(FACT**.57)
*       REGENERATED SEED TANK
        COST(6)=100000.*(FACT**.57)
*       CO2 GAS BLOWER
        COST(7)=91000*(FACT**.59)
*       CO2 RECEIVER
        COST(8)=100000.*(FACT**.57)
*       WATER TANK FOR PROCESS WATER
        COST(9)=150000*(FACT**.57)
*       WATER TANK FOR COOLING WATER .
        COST(10)=71000.*( FACT**.57)
*       AMMONIUM HYDROXIDE AND AMMONIUM SULFATE TANKS 2
        COST(11)=57000.*(FACT**.57)
*       AMMONIA RECOVERY UNIT
        COST(12)=110000.*(FACT**.62)
*       TRANSFER PUMPS
        COST(13)=210000.*(FACT**.33)
*       ION EXCHANGE COLUMNS
        COST(14)=800000*(FACT**.57)
*       CO2 CONDENSER
        COST(15)=66128*(FACT**.58)
*       SULFURIC ACID TANK
        COST(16)=41300*(FACT**.57)
*       AMMONIA TANK
        COST(17)=41078*(FACT**.57)
        COSTI=0.
        DO 40 I=1,17
        COSTI=COSTI+COST(I)
        WRITE(3,*)COST(I)
  40    CONTINUE
        Write(3,*)' Total equipment cost'
        WRITE(3,*)COSTI
*       COMPONENTS OF TOTAL PLANT CAPITAL
        WRITE(3,*)'COMPONENTS OF PLANT CAPITAL'
*       GENERAL FACILITIES
        COSTGF=.05*COSTI
*       ENGINEERING AND HOME OFFICE
        COSTEN=.07*COSTI
*       PROCESS CONTINGENCY
        COSTPRO=.3*COSTI
        CSUM=COSTI+COSTEN+COSTPRO
*       LAND COST
        COSTLN =6800.*40.
*       PROJECT CONTINGENCY
        COSTPR=.15*CSUM
        WRITE(3,*)COSTGF,COSTEN,COSTPRO,COSTPR
*       CAPTITAL COST
        CAPT=COSTI+COSTGF+COSTEN+COSTPRO+COSTPR+COSTR+COSTLN
*       ROYALTIES
        RYL=.005*COSTI
```

```
*       PREPRODUCTION COSTS
        PRECOS=.02*CAPT
*       INVENTORIES FOR 60 DAYS OF CONSUMABLES ONE YEAR FOR RESIN
        RIN= COSTR*.2
        AMMN=405.65*RM
        TIN=RIN+AMMN
*       COMPONENTS OF TOTAL PLANT INVESTMENT
        WRITE(3,*)' COMPONENTS OF TOTAL INVESTMENT'
        WRITE(3,*)CAPT,COSTLN,RYL,PRECOS,TIN
*       TOTAL PLANT CAPITAL
        TPC=CAPT +PRECOS+RYL+RIN +AMMN
        WRITE(3,*)'TOTAL PLANT CAPITAL'
        WRITE (3,*)TPC
        ANFC=.121*TPC
        WRITE(3,*)' '
        WRITE(3,*)' OPERATING COSTS'
*       OPERATING COSTS
*       ********************************************
        READ (2,*)A,EFF
*       RESIN REPLACEMENT
        CS(1)=COSTR*.2
*       STEAM COST
        CS(2)= STEAM*24.*A*365.*4.71/1000.
*       CO2 COST
        CS(3)=1.1*RM*24.*A*365.*44.*.05
*       MAKE UP AMMONIA COST
        CS(4)=.2*RM*2.0*24.*A*365.*17.*.06*.454
*       DRYER OPERATING COST
        CS(5)=DRYRL*24*A*365.*895.*3.5/1000000.
*       PROCESS WATER
        CS(6)=.1*FR*A*24*365*.454*.006
*       MAKEUP SEED
        CS(7)=.075*WT*A*8760.*.068
*       MAINTENANCE
        CS(10)=.015*TPC
        cs(8)=0.
        DO 41 I=1,7
        CS(8)=CS(8)+CS(I)
  41    CONTINUE
*       LABOR
        CS(9)=40.*3*365*19.*(FACT**.6)
        DO 45 I=1,10
        WRITE(3,*)CS(I)
  45    CONTINUE
*       TOTAL OPERATING COST
        CSTOP=CS(8)+CS(9)+cs(10)
        WRITE(3,*)' '
        WRITE(3,*)' TOTAL OPERATING COST'
        WRITE(3,*)CSTOP
*       TOTAL COST
        TOTAL=CSTOP+ANFC
        WRITE(3,*)' '
        WRITE(3,*)'TOTAL ANNUALIZED COST'
        WRITE(3,*)TOTAL
*       TOTAL ELECTRICITY GENERATED
        GEN=300.*EFF*A*24.*365.*1000.
        CSTRG=TOTAL*1000/GEN
        WRITE(3,*)'COST OF REGENERATION MILS/KWHR'
        WRITE(3,*)CSTR
        STOP
        END
```

```
13170,1789,.1,3.29
.65,.33333333
```

COST OF RESIN
268311.4

EQIPMENT COSTS
1220868.
6544420.
43879.29
150231.0
100154.0
91145.04
100154.0
150231.0
71109.33
57087.77
110184.3
210187.2
801231.9

TOTAL PLANT CAPITAL
1.3656665E+07

OPERATING COSTS
53662.28
615240.2
1348079.
113503.4
239417.1
566168.9
204850.0
3140922.
833548.9

TOTAL OPERATING COST
3974471.

TOTAL ANNUALIZED COST
5736181.

COST OF REGENERATION MILS/KWHR
10.07418

APPENDIX B

Experimental Fixed Bed Data

- "pH data"

time (min)	c/co (pH=7)	c/c0 (pH=4.25)
0.0000	0.0000	0.0000
5.0000	0.0000	0.0000
10.000	0.00060000	0.0000
15.000	0.20000	0.0070000
20.000	0.81000	0.21000
25.000	0.89000	0.78000
30.000	0.91000	0.88000
35.000	0.94500	0.91000
50.000	0.96500	0.94000
70.000	0.99100	0.98700

- "Cycle Efficiency Data IRA-68"

TIME(min)	CYCLE 1	CYCLE 2	CYCLE 3	CYCLE 4
0.0000	0.0000	0.0000	0.0000	0.0000
5.0000	0.00060000	0.00090000	0.0020000	0.00030000
10.000	0.12000	0.21000	0.12700	0.11900
15.000	0.45000	0.75000	0.45500	0.64000
20.000	0.80000	0.82000	0.80800	0.79000
25.000	0.84900	0.85900	0.85000	0.82200
30.000	0.93500	0.86000	0.94500	0.84500
35.000	0.96800	0.91000	0.94800	0.87500
40.000	0.97300	0.93000	0.97300	0.93500
45.000	0.97500	0.95800	0.98100	0.97500
50.000	0.98000	0.98100	0.98000	0.98000
55.000	1.0000	1.0000	1.0000	1.0000

CYCLE 5	CYCLE 6	CYCLE7	CYCLE 8	CYCLE 9
0.0000	0.0000	0.0000	0.0000	0.0000
0.0050000	0.049000	0.0039200	0.019000	0.18270
0.14210	0.15670	0.18790	0.46904	0.52760
0.71000	0.72320	0.53110	0.66744	0.68692
0.80000	0.81904	0.79780	0.78344	0.71704
0.92000	0.95840	0.88664	0.85752	0.79320
0.97900	0.95670	0.94030	0.94120	0.88610
0.98000	0.96072	0.94024	0.97096	0.96220
0.98100	0.98148	0.98628	0.98983	0.97096
0.98500	0.98700	0.98900	0.98824	0.99000
0.98800	0.98890	0.99100	0.98876	0.99100
1.0000	1.0000	1.0000	1.0000	1.0000

CYCLE 10
0.0000
0.21000
0.56000
0.71230
0.82420
0.84640
0.91230
0.97840
0.98260
0.98870
0.99200
1.0000

- "CYCLE EFFICIENCY IRA-93"

TIME (min)/ C/	CYCLE 1	CYCLE 2	CYCLE 3	CYCLE 4
0.0000	0.0000	0.0000	0.0000	0.0000
5.0000	0.0031000	0.00090000	0.019000	0.0020000
10.000	0.014000	0.075000	0.021000	0.014000
15.000	0.27000	0.17500	0.26440	0.13750
20.000	0.84000	0.93000	0.82690	0.71080
25.000	1.0000	1.0000	1.0000	1.0000

CYCLE 5	CYCLE 6	CYCLE 7	CYCLE 8	CYCLE 9
0.0000	0.0000	0.0000	0.0000	0.0000
0.0040000	0.0080000	0.0078000	0.0090000	0.0067000
0.037000	0.043000	0.051000	0.049400	0.052000
0.20900	0.19850	0.21000	0.20000	0.22000
0.75610	0.89760	0.87900	0.91000	0.92000
1.0000	1.0000	1.0000	1.0000	1.0000

CYCLE 10
0.0000
0.0024000
0.061000
0.24000
0.91000
1.0000

- "CYCLE EFFICIENCY IRA-35"

Time (min)/ C/C0	cycle 1	cycle2	cycle 3
5.0000	0.00044000	0.00039000	0.00021200
10.000	0.011690	0.012000	0.0068900
15.000	0.061440	0.071000	0.097000
20.000	0.69670	0.56790	0.78700
25.000	0.91490	0.87610	0.97580
30.000	0.99000	0.95170	1.0000
35.000	1.0000	1.0000	1.0000

cycle 4	cycle 5	cycle 6	cycle 7
0.00059200	0.00018000	0.00010500	0.00011000
0.014700	0.0010000	0.0012000	0.0016000
0.24070	0.077000	0.079000	0.082000
0.76700	0.53570	0.74000	0.73100
0.94940	0.90280	0.92000	0.93000
0.99690	0.98950	0.97800	0.98100
1.0000	1.0000	1.0000	1.0000

cycle 8	cycle 9	cycle 10
0.00036000	0.00018500	0.00012000
0.0042000	0.0036000	0.0048000
0.078000	0.098000	0.079000
0.69100	0.74620	0.76400
0.94000	0.93000	0.94300
0.98000	0.97900	0.99100
1.0000	1.0000	1.0000

VITA

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