ANION-EXCHANGE RESIN-BASED DESULFURIZATION PROCESS
Final Report

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January 1994

Work Performed Under Contract No. FG22-90PC90309

For
U.S. Department of Energy
Pittsburgh Energy Technology Center
Pittsburgh, Pennsylvania

By
The University of Tennessee Space Institute
Tullahoma, Tennessee

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January 1994

DOE Grant No. DE-FG22-90PC90309

US/DOE Patent Clearance is not
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1.0 EXECUTIVE SUMMARY

Under DOE Grant No. DE-FG22-90PC90309, the University of Tennessee Space Institute (UTSI) was directed to further develop its weak-base, anion-exchange resin-based desulfurization concept that had been developed and tested earlier for feasibility on a limited scope. From environmental as well as the economic viewpoints, it is necessary that the water-soluble sulfates of alkali metal and alkaline earth metal sorbents be desulfurized (regenerated) and recycled to make regenerative flue gas desulfurization (FGD) and magnetohydrodynamics (MHD) spent seed regeneration options more attractive. In order to achieve this, a low-temperature, low-cost desulfurization process to reactivate spent sorbent materials is necessary. UTSI's anion-exchange, resin-based concept uses the available water-softening (polishing) type technology and is believed to satisfy the desirable attributes required in an ideal desulfurization option.

In this DOE-sponsored project, Dr. Atul C. Sheth, a professor in the Chemical Engineering Department at UTSI, with the aid of graduate research assistants, Mr. Sterling Strevel and Mr. Rajeev Dharmapurikar, performed the following investigations:

- batch mode screening of eleven(11) commercially available resins and selection of three candidate resins for further evaluation in a fixed-bed setup.
- process variables study using three candidate resins in the fixed-bed setup and selection of the "best" resin for process economics development.

- limited optimization of the resin regeneration step under batch mode conditions.
- evaluation of performance enhancement by water-soluble organic acids and relative locations of CO_3^{2-} and SO_4^{2-} ions in the affinity chart from batch mode experiments.
- development of the Best-Process Schematics and related economics for MHD seed regeneration covering low-sulfur and high-sulfur coal-firing situations.
- sensitivity analysis of the process engineering calculations to identify the major parameters affecting the cost of MHD seed regeneration.
- estimation of the cost of spent sorbent reactivation in a sodium-based regenerative FGD option covering low-sulfur and high-sulfur coal-firing situations, and
- recommendation of additional work needed for investigations at the bench scale as well as at pilot/proof-of-concept (POC) scale levels to make the UTSI concept a potentially viable option for commercial applications requiring spent sorbent reactivation/desulfurization/regeneration.

Major conclusions/observations that were drawn as a result of the above successful investigations are as follows:

- Physical and chemical structures of candidate resins appeared to be affecting the exhaustion and regeneration efficiencies in the batch mode experiments.

- **Exhaustion efficiency and solution concentration were found to be inversely related** necessitating a trade-off between the resin cost versus the cost of evaporation/concentration of ensuing effluents.
- Higher concentration of the HCO_3^- form of active sites over less active CO_3^{2-} form of sites in the resin was believed to be the main reason for the observed increase in the equilibrium capacity of the resin at an elevated static CO_2 -pressure. **This increase in capacity was found to level off around 80-120 psig range.** The increase in CO_2 -pressure, however, did not appear to affect the overall ion-exchange kinetics.
- **In the fixed-bed mode, the solution concentration was found to affect the equilibrium capacity of candidate resins.** Their relationship was well satisfied by the Langmuir type non-linear equilibrium isotherm. Alternatively, the effect of solution concentration on overall ion-exchange kinetics varied from resin to resin.
- Product inhibition effect on the resin was observed as an initial increase followed by a significant decrease in the resin's equilibrium capacity for SO_4^{2-} as the $\text{HCO}_3^- / \text{SO}_4^{2-}$ molar ratio in the solution was increased from 0 to 1.0. This ratio, however, did not affect the overall ion-exchange kinetics.
- At low (e.g. < 0.009 cm/s) superficial velocity, the Selke and Bliss' model considering liquid-film mass transfer as the rate-controlling step was considered as an acceptable fixed-bed model. Alternatively, at higher superficial velocity (e.g. > 0.009 cm/s), the Antonson's model including a

non-linear equilibrium at the solid/liquid interface and considering solid phase diffusion as the rate-controlling step was considered as an acceptable fixed-bed model.

- **In the present study, the bed height and low levels of various dissolved impurities did not affect the resin performance significantly.**
- **In as much as ten(10) consecutive cycles of carbonation/exhaustion and regeneration in the fixed-bed mode, the candidate resins showed no significant degradation in their performance.**
- **IRA-68 resin was found to be the best resin based on fixed-bed process variables study results and related statistical analysis. However, the other two resins, IRA-35 and IRA-93, were not significantly inferior and are believed to perform equally well in desulfurizing spent sorbent materials.**
- **By buffering the solution pH to the acidic side (i.e. < 7.0), the small amounts (up to 8 ml. per 100 ml. of 5 wt % K₂SO₄ solution) of concentrated water-soluble organic acids such as formic, acetic and butyric acid were found to increase the candidate resin's equilibrium capacity from 19 to 56%.**
- **In the affinity chart, the CO₃²⁻ ion is most likely located to the left (i.e. OH⁻ side) of the SO₄²⁻ ion. This conclusion also appears to explain the**

observed increase in the resin's capacity as the static CO₂-pressure was increased.

- For concentrating the dilute (e.g. < 5 wt %) solutions, the scheme involving reverse osmosis followed by multiple-effects evaporation was found to be about 20% more expensive than the scheme involving only multiple-effects evaporation. Also, a 5-effects evaporator was found to be economically more attractive than a 3-effects evaporator; and the cost of concentration by mere evaporation was found to decrease asymptotically as the solution concentration increased to 10 wt % level.
- In terms of mid 1992 dollars, the cost of MHD seed regeneration under the "base" case scenario for high sulfur coal was estimated to be about 11.1 mills/Kwh. In comparison, the similar cost using TRW's Econoseed Process has been reported in a recent Westinghouse study⁽⁶⁰⁾ as equal to about 23.1 mills/Kwh. For low-sulfur coal, these costs are estimated as 6.3 mills/Kwh for ion-exchange versus 8.8 mills/Kwh for the Econoseed Process. From additional sensitivity analysis, the sulfur level in coal, plant capacity factor, plant efficiency and sulfate solution concentration were identified as the major parameters affecting the MHD seed regeneration cost.
- For reactivating the spent sodium-based sorbent material received from a regenerable duct-injection type FGD option, the cost of sorbent reactivation for a conventional 1000 MW_t plant burning high sulfur coal was estimated to be about 9.9 mills/Kwh. Also, the corresponding total capital

investment was estimated to be about \$73/Kw. These preliminary estimates compare very well with the similar estimates available for the currently available commercial options such as Wellman Lord and MgO scrubbing processes.

As a result of the present study, some new leads were identified and some additional gaps in the database were found. Hence, to develop this UTSl concept into a viable commercial option, additional work has been recommended. This recommended additional work should include:

- feasibility demonstration and resin life (cycle efficiency) determination at the pilot/proof-of-concept (POC) scale level using representative feed materials.
- development of an analytical technique for on-line measurement of SO_4^{2-} , OH^- , Cl^- , HCO_3^- , and CO_3^{2-} ions in highly alkaline solutions containing potassium, sodium and ammonium type cations.
- optimization of resin regeneration and carbonation steps.
- understanding of the role of organic acid in performance enhancement of a weak-base, anion-exchange resin, and appropriate incorporation into the process concept.
- evaluation of the product inhibition effect as well as impact of other dissolved impurities on the resin performance.

- validation of the relative locations of the CO_3^{2-} and SO_4^{2-} ions in the affinity chart at higher CO_2 -pressures to determine the possible role of carbonation in further improving/maintaining the resin's capacity for SO_4^{2-} ions.
- system analysis of schemes integrating MHD power plant operations with MHD seed regeneration; and spent sorbent reactivation operations with the SO_2 -removal step in a regenerative sodium-based duct-injection type FGD system.
- evaluation of the advanced and upcoming processing mode that would involve a continuous operation of the ion-exchange columns in a carousel type configuration. (This type of configuration is considered ideal for commercial applications involving very short cycle times and is being used successfully in South America).

In summary, the UTSI's weak-base, anion-exchange resin-based desulfurization concept is shown in this study to be capable of becoming an attractive option warranting appropriate considerations for the spent sorbent reactivation in conventional power plants and waste incineration as well as for spent seed regeneration in the MHD-based advanced energy conversion technology. With successful completion of the recommended work above, it can provide an excellent potential for applications in a variety of energy conversion and chemical waste destruction areas.

2.0 INTRODUCTION

Chemical reactions between SO_2 and alkali metal salts, such as Na_2CO_3 , NaHCO_3 , KOH , and K_2CO_3 , proceed to completion under relatively moderate conditions. The products that are formed usually contain primarily sulfates, with smaller amounts of sulfites and other forms of sulfur compounds. Currently, the following technologies use this type of chemical reaction to control the emission of SO_2 and other sulfur-containing gaseous species:

- flue gas desulfurization (FGD)
- coal-fired magnetohydrodynamics (MHD) power systems
- catalytic coal/biomass gasification
- waste incineration

2.1 Importance of Spent Sorbent Desulfurization

From an environmental standpoint, the waste material coming from the above applications cannot be acceptably and easily disposed of in conventional landfills. Alkali metal sulfates and other salts are water soluble and would pose a problem of leaching into the groundwater. Surface run-offs from such disposal sites can also alter the soil pH, which is not allowed under current regulations. Because of the Resource Conservation and Recovery Act and the Toxic Substance Control Act, the problems and costs associated with the disposal of such waste material have greatly increased. Also, the use of such waste material as fertilizer may not be viable because of the low demand and possible presence of trace elements, such as cadmium, vanadium, and zinc. The economics of such sulfur-emission control applications are highly sensitive to the amount of fresh sorbent required, since the cost of replacement material to

control the emission of sulfur-containing species is quite significant. From the economic as well as environmental point of view, it becomes desirable that alkali metal sulfates be converted to sulfur-free form, so that they can be reused.

2.2 Desirable Attributes of An Ideal Desulfurization System

Researchers working in the fields of flue gas desulfurization (FGD), pulp and paper production, catalytic coal gasification, and MHD power generation have investigated various options to achieve desulfurization of alkali metal sulfates. Under the U.S. Department of Energy (DOE) sponsored programs, several processes capable of separating sulfur from alkali metal sulfates have been identified and process evaluation studies have been conducted⁽¹⁻⁵⁾. All of these studies have identified significant needs for technology advancement necessary to design and develop an acceptable, economical regeneration system. An ideal desulfurization concept should have the following attributes:

- easy operation at low operating temperature and pressure
- low cost and no significant environmental problems
- use of available technology (hence reduced development time and cost)
- high recovery and recycle of alkali metal reagent

The ability to remove simultaneously other anions such as Cl^- , F^- , and NO_3^- is considered an added advantage. Since the presently considered options for seed and spent sorbent regeneration do not meet all or most of the above criteria, a need exists to develop a simple and readily acceptable option.

3.0 PROCESS DESCRIPTION AND STATUS

The options available to desulfurize alkali metal based spent sorbents require either complex designs or severe processing conditions. In any case, the costs of desulfurizing the spent sorbents for recycle in the process are extremely high. Hence, a wide-spread use of a regenerable FGD type system is not possible under the current economic conditions. Therefore, there is a mandate to develop a simple, low-cost and readily acceptable desulfurization system to desulfurize alkali metal based spent sorbent material.

3.1 Anion-Exchange Resin-Based Desulfurization Chemistry & Concept

A concept has been developed and tested at the University of Tennessee Space Institute (UTSI) which employs a commercially available weak-base, anion-exchange resin to remove sulfur from alkali metal sulfates.

One of the characteristics of anion-exchange resins is their varying affinities for certain anions. As reported in the literature⁽⁶⁾, the affinity of a weak-base, anion-exchange resin for various anions decreases in the following order.

A weak-base anion-exchange resin is commercially supplied in a hydroxide form by the supplier. Based on the above mentioned selective affinity for specific anions, the active sites in the fresh resin must be converted to the bicarbonate form before its first time exhaustion or replacement with SO_4^{2-} ions. This is accomplished by treating the resin with carbonated water (water saturated with CO_2) to produce active bicarbonate groups according to the following reaction:

(Here R represents the complex cation groups present in the resin). The resin is then exhausted by an aqueous solution of alkali metal (M) sulfate as follows:

The bicarbonate containing solution is then converted to a corresponding carbonate and/or bicarbonate during the evaporation/concentration steps, before it is recycled to the process, as a dry powder or concentrated solution. Carbon dioxide released during this conversion can be reused in carbonating the hydroxide form of the resin in Reaction 2. The exhausted resin is then regenerated to the hydroxide form using an NH_4OH solution.

The ammonium sulfate, $(NH_4)_2SO_4$, produced can then be concentrated (if necessary) and sold as fertilizer or processed for recovery and recycle of the NH_3 using the following optional step (see equation (5)). In this step, an aqueous solution of $(NH_4)_2SO_4$ when heated in a batch reactor to about 473 - 523 K (200-250°C) temperatures, would decompose into ammonia (boiling point of ~ 240 K) and water vapors (boiling point of 373 K). The remaining liquid fraction thus becomes concentrated in sulfuric acid, H_2SO_4 (decomposition temperature of 613 K). On controlled cooling, the ammonia vapors can be separated from the water condensate. The recovered ammonia can then be recycled to the resin regeneration step.

The free base resin thus formed is then treated with carbonated water for reuse in the next cycle.

3.1.1 Earlier Version

The three steps of resin exhaustion, regeneration, and carbonation are schematically shown in Figure 1 as an earlier version of UTSI's concept. It involved two separate steps for regenerating the exhausted resin. Butler⁽⁷⁾ demonstrated the technical feasibility of the UTSI process using this 3-step version of the concept.

3.1.2 Improved Version

Modeste⁽⁸⁾ improved upon Butler's concept by combining the carbonation and exhaustion into one step that was carried out under 50-100 psig (static) pressure of CO₂. Modeste's improved concept is also shown in Figure 1. This improvement in the process concept achieved the following:

- Simplified the concept and reduced the number of processing steps from three to two.
- Increased the resin capacity for SO₄²⁻ by about 50 percent.
- Reduced the resin inventory by 33 percent.

3.2 Status of UTSI's Anion-Exchange Resin-Based Desulfurization Process (Prior to Current Project)

Using the 3-step process and reagent grade chemicals, Butler⁽⁷⁾ demonstrated the technical feasibility of UTSI's concept by performing fixed-bed experiments at the bench scale level. In doing so, he showed that a particular resin (Amberlite IRA-68) maintained a capacity for SO₄²⁻ for at least four consecutive cycles of exhaustion and

Figure 1. Schematic of Ion-Exchange Resin-Based Desulfurization Concept.

IL-1506

regeneration, and that the solution concentration and bed height did not affect the ion-exchange kinetics significantly. However, from Butler's work, the product inhibition effect caused by the presence of KHCO_3 in the initial sulfate containing solution was noted (above certain molar ratios of $\text{KHCO}_3/\text{K}_2\text{SO}_4$) as an apparent reduction in the resin's capacity for the SO_4^{2-} ions.

Using the 2-step process (where exhaustion and carbonation steps were combined), Modeste⁽⁸⁾ demonstrated that by increasing the static CO_2 pressure from 0 psig to 40 psig, the equilibrium capacity of the Amberlite IRA-68 resin could be increased by about 50%. His work also showed that the fixed-bed kinetics data can be better satisfied by the math model that incorporates a non-linear equilibrium at the solid/liquid interface and a solid-phase diffusion as the overall mass transfer controlling step. Such a model was found to resolve the problem faced by Butler in satisfying his bench scale data with the math model incorporating the liquid-film mass transfer as the overall rate controlling step.

4.0 UCR PROJECT OBJECTIVES AND DESCRIPTION

As mentioned earlier, the various energy conversion and pollution control technologies use chemical reactions between SO_2 and alkali metal salts to comply with the sulfur oxides emission standards. Cost and availability of fresh sorbents, scarcity of landfill area, and difficulties in disposing spent sorbent material necessitate the desulfurization and recycling of these alkali metal based sorbents. The options available at present to desulfurize such spent sorbent material do not satisfy all or

most of the attributes identified earlier for an ideal desulfurization system. As a result, the wide-spread use of regenerable FGD type systems is not possible under the current economic conditions. **Therefore, there is a need to develop a simple, low-cost and readily acceptable regeneration system to desulfurize alkali metal based spent sorbent material.**

Under a University Coal Research (UCR) program grant from the U.S. Department of Energy's Pittsburgh Energy Technology Center (DOE/PETC), UTSI was asked to develop a low temperature, low cost spent sorbent regeneration (desulfurization) system that would use available resin-based ion-exchange technology and which could be developed in minimum time and cost. **The specific objectives of this UCR grant were:**

- **To further Improve the UTSI concept by identifying the best available resin and to optimize the resin exhaustion, regeneration and carbonation conditions.**
- **To develop Best-Process Schematic and related economics.**

To accomplish the above objectives, UTSI developed the following approach:

- **Perform a screening of the commercially available candidate resins,**
- **Perform process variables study and improve resin performance,**
- **Optimize resin regeneration step,**
- **Evaluate effect of potential performance enhancers,**
- **Develop Best-Process Schematic and related economics, and**
- **Develop plans for proof-of-concept (POC) scale testing.**

Also, the above activities were grouped in the following five tasks for ease of monitoring the progress of the UCR project:

- Task 1 Literature Survey, Vendor Contacts and Screening of Resins
- Task 2 Process Variables Study and Improving Resin Performance
- Task 3 Optimization of Resin Regeneration Step and Evaluation of Performance Enhancers
- Task 4 Development of Best-Process Schematic and Related Economics
- Task 5 Project Management and Reporting

The major activities that were carried out under each of these tasks are as follows:

4.1 Task 1 Literature Survey, Vendor Contacts and Screening of Resins

In this task, UTSI performed a literature search, made contact with ion-exchange resin vendors and/or manufacturers, and modified the existing bench scale fixed-bed system at UTSI. The literature search was carried out to provide the information necessary to develop the resin screening tests. The contacts with resin vendors and/or manufacturers were made to procure samples of suitable candidate resins. The fixed-bed system was modified to facilitate semi-automatic and semi-batch mode operations of the fixed-bed.

4.2 Task 2 Process Variables Study and Improving Resin Performance

From Task 1, three candidate resins were selected for process variables study. Initially, the following process variables were considered for evaluation:

- solution concentration • product inhibition
- solution pH • cycle efficiency

- superficial velocity
- effect of dissolved impurities and/or other ions
- bed height
- CO₂ pressure
- ammonia concentration

The data acquired from these experiments were used in Task 4 to validate the fixed-bed math model.

4.3 Task 3 Optimization of Resin Regeneration Step and Evaluation of Performance Enhancers

In this task, means to optimize the resin's exhaustion and regeneration efficiency were studied. Performance enhancers (mild acids) were added to the eluent in small quantities to determine if the resin exhaustion efficiency can be improved. A study of the forms of the functional groups during regeneration/carbonation steps was also carried out to improve the resin efficiency.

4.4 Task 4 Development of Best-Process Schematic and Related Economics

In this task, the fixed-bed math models used by Butler⁽⁷⁾ and Modeste⁽⁸⁾ were used to test the data collected in Task 2. Schematics of the commercial scale spent sorbent/seed regeneration processes were developed and the related economics were determined.

4.5 Task 5 Project Management and Reporting

This task provided for the overall management of the project by the principal investigator. His efforts were assisted by the Project Support Services group of the Energy Conversion Research and Development Programs (ECP) department at UTSI.

Also, quarterly and annual progress reports, along with a final project report were prepared and submitted to the DOE/PETC office.

5.0 LITERATURE SURVEY AND RESULTS FROM VENDOR CONTACTS

Under Task 1 activities, the relevant literature on ion-exchange resin-based technologies was collected and reviewed as well as contacts were made with the resin suppliers and manufacturers.

5.1 Status of Related Ion-Exchange Resin-Based Technologies

Using the UTSI library, a computer based literature search was carried out to identify relevant publications that are included in the Dialog's Engineering Index. Using these references as well as Butler⁽⁷⁾ and Modeste's⁽⁸⁾ theses, additional cross-references were identified. A large volume of relevant publications was accumulated, reviewed and categorized. To assess the status of the related ion-exchange resin-based technologies, the collected and reviewed literature was categorized into various topics such as fixed-bed mathematical models, testing of resin and industrial applications. Assessments made in each of these areas are as follows:

5.1.1 Mathematical Models

The kinetic theories of Fick and Nernst-Planck represent models for ideal systems. These models use curve fitting to interpret the kinetics of an ion-exchange system. The resulting conclusions are sometimes misleading because the applied model is usually not case-specific. Hence, these models should be considered only as approximations to the physico-chemical systems being investigated⁽⁹⁾. The Nernst-Planck model has been used to analyze intraparticle mass transfer in ternary systems

with constant self-diffusivities and particle diameter⁽¹⁰⁾. The Nernst-Planck non-linear equations of ionic motion are used to calculate the ideal limiting laws for the kinetics of particle diffusion in batch experiments with uniform bead size and ions of different mobilities⁽¹¹⁾. Other case-specific models found in the literature are as follows:

- multicomponent model of mass-action equilibria which discusses the inversion of resin affinities⁽¹²⁾
- thermodynamic model which defines surface excess as the separative characteristics of ion exchangers⁽¹³⁾
- dimensionless numerical model for the constant-pattern pore- and solid-diffusion mechanisms which includes external mass transfer for irreversible equilibrium⁽¹⁴⁾
- zone height model based on a counter-current system with infinite bed height⁽¹⁵⁾
- linear mass transfer model for cyclic operation and co-current regeneration⁽¹⁶⁾
- simple physical model of coherent waves that defines their interference on multicomponent adsorption⁽¹⁷⁾
- ideal solid-solution model which considers the ionic interaction in calculating the thermodynamic equilibrium constants for the batch experimental model⁽¹⁸⁾
- multicomponent model which predicts the ion-exchange equilibria from a binary system data⁽¹⁹⁾

- pore diffusion model based on the orthogonal collocation method which utilizes both batch and fixed-bed data⁽²⁰⁾
- shrinking core model for batch experiments with Ligand exchange⁽²¹⁾
- model for cyclic systems with concave Langmuir isotherms⁽²²⁾, and
- shell progressive, shrinking core, model with changing concentration and column volume⁽²³⁾.

5.1.2 Resin Testing

In the literature resin testing is exhaustively described. Resin is tested for quality and deterioration by analyzing for total chemical capacity and physical strength⁽²⁴⁾. Testing of gel type resins have shown that the particle size affects uptake rate and electrolyte invasion depends strongly on counter-ion valence which also governs the uptake rate⁽²⁵⁾. Anion resin was tested for sulfate leakage by McNulty⁽²⁶⁾, who showed that the leakage was directly related to the harmonic mean particle size of the anion resin in the mixed bed. Macroreticular resin structure with pore diameters between 10-100 Å and 100-10,000 Å were shown to enhance the chemical accessibility and mass transfer of ions and/or molecules by Lee⁽²⁷⁾. The effect of cross-linking was evaluated by Glueckauf⁽²⁸⁾, who showed that the low cross-linking in the resins used in his experiments resulted in faster equilibrium. Equilibrium testing for a porous exchanger batch system was performed by Patell⁽²⁹⁾.

Anion-exchange resins were tested for stability and regenerant efficiency by Calmon⁽³⁰⁾. These resins are distinguished by their functional groups: trimethyl groups (Type I) and dimethyl-ethanol groups (Type II). Type II resins were found to be less stable but they had higher regenerant efficiency than Type I resins. Tertiary

amine oxide groups were found to give greater physical stability and to have less volume change during acid-base cycling than the aromatic tertiary amine group⁽³¹⁾.

Glueckauf⁽²⁸⁾ found that the ion-exchange operations can be optimized by using small particle size, large ratios of distribution coefficients, sufficiently small EHTP (Effective Height of the Theoretical Plate), a sufficiently large number of theoretical plates, the optimum solution concentration, and a displacing mixture with stronger ionic species.

5.1.3 Industrial Applications of Resin-Based Technologies

Major applications of the weak electrolyte resins are found in the DESAL process or a modification of the DESAL process and in the SUL-BI-SUL process. The DESAL process was developed by Rohm & Haas Company for use with the 500-3,000 ppm salinity brackish waters--acid mine drainage and sewage plants. The DESAL process consist of an anion-, a cation- and an anion-exchange resin columns in series. The anion columns contain weak-base resins (IRA-68). The cation column contains weak-acid resin (IRC-84). The procedure in this process is to (1) convert the weak-base resin to a bicarbonate salt, (2) convert the bicarbonate salt to an alkali metal salt, and (3) convert the weak-acid free-base form to a sodium form. The chemical reactions involved are:

where R is the resin's non-exchangeable functional groups. The regeneration of the resins in this process can be described by the following equations:

Modifications to the DESAL process consisted of combining the carbonation and alkalization steps, increasing CO₂ pressure, and regenerating the resin with lime instead of ammonia⁽³¹⁾. Additional modifications were later on implemented by Popper⁽³²⁾. The DESAL process concept has also been used in the work of other investigators, including Wilmoth⁽³³⁾ and Popper⁽³²⁾. Wilmoth used 2000-3000 ppm sulfate concentrations in his work while Popper used 2000-10000 ppm salt concentrations in his work.

The SUL-BI-SUL process consists of replacing the sulfate ion on an anion-exchange resin with a bisulfate ion and the anion to be removed. The advantage of this process was claimed to be its use of a hydrated lime slurry for resin regeneration as the lime slurry is less expensive than the sodium hydroxide. The SUL-BI-SUL process has also been used in the treatment of acid mine drainage⁽³⁴⁾.

Other applications of ion-exchange resin-based technologies have been found in scale prevention in process units^(35,36), removal of organics^(37,38,39), removal of nitrates⁽⁴⁰⁾, removal of ammonia⁽⁴¹⁾, removal of sulfates⁽⁴²⁾, removal of decontaminated solvents⁽⁴³⁾, potassium recovery from potash⁽⁴⁴⁾, and removal of boron⁽⁴⁵⁾.

5.2 Results from Vendor Contacts

Telephone contacts were made with the representatives of various suppliers and manufacturers of commercially available resins. Successful contacts were established with the appropriate staff personnel of Rohm & Haas, Biorad, Culligan,

Dow Chemicals, and Sybron. Representative quantities of the following (eleven) candidate resins were collected as a result of these contacts.

<u>Company Name</u>	<u>Commercial Name</u>
Rohm & Haas	Amberlite IRA-68 Amberlite IRA-35 Amberlite IRA-93 Amberlite IRA-94 Duolite A-7
Dow Chemicals	MWA-1 WGR-2
Sybron	Ionac AFP-329 Ionac A-365 Ionac A-305
Culligan	(Unknown)

6.0 BATCH MODE SCREENING EXPERIMENTS AND RESULTS

In the program that was originally proposed to the DOE/PETC office, there was no plan to carry out screening experiments on the candidate resins in the batch mode. All the candidate resins were to be evaluated in the fixed-bed mode experiments. However, from contacts with the resin suppliers, eleven candidate resins were identified. Evaluations of so many resins in the fixed-bed mode would take an exceptionally long time, so a decision was made to evaluate them first in the batch mode experiments.

6.1 Development of Batch Mode Screening Procedure

The experimental procedure for these batch mode screening experiments was developed by testing reagent grade K_2SO_4 solutions with IRA-68 resin and varying major parameters as follows:

6.1.1 Selection of Proper Ammonia Concentration for Resin Regeneration

To recover most of the SO_4^{2-} ions from the exhausted resin, the ammonia concentration must be optimized. To find the optimum ammonia concentration during the resin regeneration step, batch mode screening experiments were carried out in which exhaustion conditions (i.e. K_2SO_4 solution concentration, carbonation rate and time, exhaustion and regeneration time, resin sample size and solution-to-resin ratio) were kept constant. The concentration of ammonia in aqueous solution was varied from 0.58 - 4.64 wt %. The amount of SO_4^{2-} ions remaining on the resin at the end of the regeneration step (which indicates the regeneration efficiency) is expressed as "percent retained" and is shown as a function of the ammonia concentration in Table 1.

**Table 1. Effect of Ammonia Concentration on Regeneration
of IRA-68 Resin
(Batch Mode Screening Experiments)**

NH ₃ Solution Concentration (wt %)	Percent SO_4^{2-} Retained on Resin*
0.58	77.7
1.16	44.4
1.74	29.2
2.90	13.4
3.84	11.2
4.35	11.6
4.64	8.5

* Values reported as percent of total sulfate ions present at the beginning of the regeneration step (i.e. end of the exhaustion step). Lower number indicates better resin regeneration efficiency.

Considering experimental errors, cost of ammonia and incremental improvement in SO_4^{2-} recovery, an ammonia concentration of 3.5 wt % was considered

sufficient for regenerating exhausted resin in the batch mode screening experiments.

6.1.2 Selection of Proper Mixing Time for Exhaustion & Regeneration Cycles

Assuming that the mass transfer rates and steps would be similar, the mixing time for both cycles was selected from the exhaustion experiments carried out with samples of IRA-68 resin in which all other parameters except the exhaustion mixing time were kept constant. The exhaustion mixing time was varied from 15 to 60 minutes. The results, reported as percent of the total SO_4^{2-} ions removed from a 2.5 wt % K_2SO_4 solution (or exchanged on the resin's active sites) as a function of mixing time are shown in Table 2.

**Table 2. Effect of Mixing Time on Exhaustion by IRA-68 Resin
(Batch Mode Screening Experiments)**

Exhaustion Cycle Mixing Time (minutes)	Percent SO_4^{2-} Removed by Resin*
15	88.0
30	85.4
60	85.8

* Values reported as percent of total sulfate ions present in the bulk solution which is removed by the active resin sites. Higher numbers indicates a better resin performance.

Based on these results, a mixing time of more than 15 minutes did not appear to affect the percent SO_4^{2-} removed, and therefore, for the exhaustion and regeneration cycles, 15-minutes was considered sufficient for batch mode screening experiments.

6.1.3 Selection of Proper Resin Sample Size

Using the desirable mixing time and ammonia solution concentration identified in 6.1.1 and 6.1.2, the resin sample size was varied from 10 to 100 ml. This was

necessary because some of the vendor supplied resin samples were very small. The percent SO_4^{2-} removed from the bulk solution by the resin at the end of the exhaustion cycle and the percent SO_4^{2-} retained on the resin at the end of the regeneration cycle were calculated and are given in Table 3.

Table 3. Effect of Sample Size on Exhaustion and Regeneration Efficiencies of IRA-68 Resin (Batch Mode Screening Experiments)

Resin Sample Size (mL)	Percent SO_4^{2-} Removed by Resin(a)	Percent SO_4^{2-} Retained on Resin(b)
10	82.3	9.6
50	86.2	10.0
100	87.0	9.7

(a) Indication for efficiency of resin exhaustion step.

(b) Indication for efficiency of resin regeneration step.

These results show that resin sample size did not affect the percent removed or retained. Hence, a sample size of 25 ml. was selected for batch mode screening experiments.

6.1.4 Selection of Proper Carbonation Time

Using the desirable values for the other parameters discussed above, the carbonation time was varied from 15 to 60 minutes at a CO_2 flow rate of 2 SCF/hr. Again, the percent SO_4^{2-} removed by the resin from the bulk solution at the end of the exhaustion cycle was calculated as a function of carbonation time and is reported in Table 4.

Table 4. Effect of Carbonation Time on Exhaustion Efficiency of IRA-68 Resin (Batch Mode Screening Experiments)

Carbonation Time @ CO ₂ Rate of 2 SCF/hr (minutes)	Percent SO ₄ ²⁻ Removed by Resin
15	65.1
30	83.6
60	86.7

These results indicate that carbonation time do affect the percent removal. A carbonation time of 30 minutes was selected for the batch mode screening experiments, since beyond 30 minutes, the improvement in SO₄²⁻ removal by the IRA-68 resin (that means the efficiency of resin exhaustion step) was very small.

Based on the results described above, the following conditions were considered desirable for the batch mode screening experiments:

- Mixing time for exhaustion and regeneration steps ~ 15 min.
- Ammonia solution concentration for regeneration ~ 3.5 wt %.
- Carbonation time ~ 30 min. (at a CO₂ flow rate of 2 SCF/hr).
- Resin sample size ~ 25 ml.
- Solution-to-resin ratio ~ 2:1.

6.2 Results From Batch Mode Evaluation of Major Parameters

To select the best three candidate resins for process variables study in the fixed-bed mode, the batch mode screening experiments were carried out first using the procedure described above and varying the following parameters:

- K₂SO₄ solution concentration

- Spent MHD seed extract
- Cyclic operation (up to 4 cycles), and
- Sulfate introduced as sodium sulfate

6.2.1 Effect of K₂SO₄ Solution Concentration & Source of K₂SO₄ on Resin Performance

Batch mode screening experiments were carried out using K₂SO₄ solutions of different concentrations. Reagent grade chemical as well as spent seed extract obtained from the magnetohydrodynamics (MHD) facility at UTSI were used as two different sources of K₂SO₄. The results, in terms of percent of total SO₄²⁻ removed by the candidate resin (at the end of exhaustion step) as well as percent of total SO₄²⁻ retained on the same resin (at the end of resin regeneration step), are reported as functions of solution concentration (varied from 1,000 ppm to 50,000 ppm) and source of K₂SO₄ (reagent grade chemical versus MHD spent seed extract) in Table 5. These results indicate that, except for IRA-68, -35, and -93, the remainder of the candidate resins demonstrate either low percent SO₄²⁻ removal or high percent SO₄²⁻ retention, or both. Therefore, such resins were eliminated from further study. Later in the report a detailed statistical analysis of the results is provided to support this conclusion. The reason for the greater efficiency of IRA-68, IRA-35, and IRA-93 is believed to be due to their stronger affinity for the acidic anions generated by CO₂.

Table 5. Effect of Solution Concentration & Source of K₂SO₄ on Resin Performance (Batch Mode Screening Experiments)

Resin Identification	1,000 ppm K ₂ SO ₄ Solution		25,000 ppm K ₂ SO ₄ Solution		50,000 ppm K ₂ SO ₄ Solution		50,000 ppm K ₂ SO ₄ -MHD Seed Extract (c)	
	% SO ₄ ²⁻ Removed by Resin ^(a)	% SO ₄ ²⁻ Retained on Resin ^(b)	% SO ₄ ²⁻ Removed by Resin ^(a)	% SO ₄ ²⁻ Retained on Resin ^(b)	% SO ₄ ²⁻ Removed by Resin ^(a)	% SO ₄ ²⁻ Retained on Resin ^(b)	% SO ₄ ²⁻ Removed by Resin ^(a)	% SO ₄ ²⁻ Retained on Resin ^(b)
IRA-68	100	9.9	85.9	11.9	60.2	13.9	66.1	21.3
IRA-35	100	8.8	78.3	9.2	55.4	14.2	56.2	12.6
IRA-93	100	28.2	52.4	25.0	42.3	19.3	40.5	10.4
IRA-94	100	55.9	51.7	55.0	30.9	56.7	28.9	43.4
A-7	74.4	7.1	13.0	30.9	9.7	32.3	9.3	42.0
A-365	63.9	27.1	12.9	53.2	7.8	29.2	8.2	66.4
MWA-1	98.5	45.0	44.3	54.6	23.6	41.4	28.6	43.3
WGR-2	99.2	54.5	60.5	67.3	36.4	63.2	40.5	63.3
Culligan	98.5	52.0	54.5	45.3	29.1	36.1	ND	ND
AFP-329	97.7	67.7	32.3	66.9	ND	ND	ND	ND
A-305	98.5	6.3	48.9	29.6	26.3	30.8	ND	ND

- (a) Indicates efficiency of resin exhaustion step. Higher number means better resin performance.
- (b) Indicates efficiency of resin regeneration step. Lower number means better efficiency of resin regeneration step.
- (c) Obtained from MHD spent seed in the aqueous extract form.
- ND Not determined.

6.2.2 Effect of Cyclic Operation (up to 4 cycles)

To evaluate the effect of cyclic operations, experiments were carried out using a 25,000 ppm (on a weight basis) K₂SO₄ solution prepared from the reagent grade chemical, in which exhaustion, regeneration and carbonation sequence was applied to each of the candidate resins to simulate four consecutive cyclic operations. The resulting performance for each of the eleven candidate resins is given in Table 6. These results (based on magnitude) show that except for IRA-68, -35 and -93 resins, the rest of the candidate resins demonstrate in batch mode experiments, either low percent SO₄²⁻ removal or high percent SO₄²⁻ retention or both. Also, certain resins (e.g. IRA-94, A-365, MWA-1, WGR-2 Culligan's Unknown, and AFP-329) demonstrate some

kind of conditioning effect indicated by the progressive improvement in the percent SO_4^{2-} retention at the end of resin regeneration step. However, whatever the conditioning effect may be, it does not appear to progressively improve the resin's exhaustion efficiency. Based on the results from these (limited) cyclic operations, only IRA-68, -35, and -93 resins were considered acceptable for further development and considerations.

Table 6. Effect of Cyclic Operations (Up to 4 Cycles in Batch Mode Screening Experiments)

Basis: K_2SO_4 Solution Concentration = 25,000 ppm

Resin Identification	Cycle 1		Cycle 2		Cycle 3		Cycle 4	
	% SO_4^{2-} Removed by Resin ^(a)	% SO_4^{2-} Retained on Resin ^(b)	% SO_4^{2-} Removed by Resin ^(a)	% SO_4^{2-} Retained on Resin ^(b)	% SO_4^{2-} Removed by Resin ^(a)	% SO_4^{2-} Retained on Resin ^(b)	% SO_4^{2-} Removed by Resin ^(a)	% SO_4^{2-} Retained on Resin ^(b)
IRA-68	85.9	11.9	84.4	7.9	84.4	7.9	83.4	6.6
IRA-35	78.3	9.2	78.4	4.8	78.9	8.2	79.2	8.9
IRA-93	52.4	25.0	67.9	7.2	67.7	4.1	68.1	7.8
IRA-94	51.7	55.0	42.7	31.1	42.0	21.6	42.1	17.7
A-7	13.0	30.9	13.2	21.4	15.6	34.1	16.0	31.9
A-365	12.9	53.2	16.2	44.0	22.5	31.2	22.4	24.6
MWA-1	44.3	54.6	44.5	34.1	43.7	30.7	43.4	26.6
WGR-2	60.5	67.3	48.4	42.1	44.1	34.4	35.6	14.7
Culligan	54.5	45.3	51.5	20.8	47.5	13.3	56.2	20.0
AFP-329	32.3	66.9	28.7	38.6	24.6	20.3	28.7	19.8
A-305	48.9	29.6	48.3	22.1	51.7	19.6	48.4	20.1

- (a) Indicates efficiency of resin exhaustion step. Higher number means better resin performance.
- (b) Indicates efficiency of resin regeneration step. Lower number means better efficiency of resin regeneration step.

6.2.3 Effect of Sulfate Introduced as Sodium Sulfate

To evaluate the effect of a sodium versus potassium system, experiments were carried out using K_2SO_4 and Na_2SO_4 solutions prepared from the reagent grade chemicals. The molar concentrations of SO_4^{2-} were kept the same. The resulting concentrations (on a weight basis) were 25,000 ppm for K_2SO_4 and 20,400 ppm for

Na_2SO_4 . These experiments were performed only on the selected resins whose performances in the evaluation of the other parameters were found to be acceptable. Table 7 provides the results of these experiments. As expected, for the anion-exchange resins, the results indicate that there is no difference between the K and Na systems.

Table 7. Effect of Sulfate Introduced as Sodium Sulfate

Resin Identification	25,000 ppm K_2SO_4 Solution		20,400 ppm Na_2SO_4	
	% SO_4^{2-} Removed by Resin(a)	% SO_4^{2-} Retained on Resin(b)	% SO_4^{2-} Removed by Resin(a)	% SO_4^{2-} Retained on Resin(b)
IRA-68	85.9	11.9	83.7	8.6
IRA-35	78.3	9.2	75.6	10.1
IRA-93	52.4	25.0	53.6	29.2
Culligan	54.5	45.3	51.8	44.7
AFP-329	32.3	66.9	ND	ND
A-305	48.9	29.6	45.9	39.3

- (a) Indicates efficiency of resin exhaustion step. Higher number means better resin performance.
 (b) Indicates efficiency of resin regeneration step. Lower number means better efficiency of resin regeneration step.
 ND Not determined.

6.3 Statistical Analysis of Batch Mode Screening Results & Selection of Three Resins

As described above, the test parameters for the batch mode evaluations included cation (different alkali metals), cycle efficiency, solution concentration and dissolved impurities (e.g. spent MHD seed material). The results from these screening experiments were analyzed by the analysis of variance, two-way fixed-effects model and a multiattribute technique.

6.3.1 Statistical Analysis

The analysis of variance, two-way fixed-effects model was used to determine the effects of resin type, solution concentration, cyclic operations, and cations on the resin's removal and regeneration efficiencies. The values used in these calculations were the first observations taken for each resin and test condition. The batch experimental procedure was developed before the first observation was made. Therefore, there was no learning curve associated with the results, freeing the data of any bias. Due to time constraints, only one observation was taken. This weakened the statistical results and combined the interaction (C-N-R) and error terms. Therefore, no interaction effect or error could be determined from the data. The test statistic is f_o , defined as the mean square (MS) resin and/or concentration divided by the mean square interaction. This test statistic was assumed to follow the F-distribution. The f_o 's were compared with the appropriate values from a F-distribution table for a 95% confidence level that the null hypothesis was true, when it was true. In this analysis the null hypothesis was that none of the above factors affected the exhaustion or regeneration efficiency. When the f_o and the F-distribution table values are relatively close in magnitude, the conclusions drawn from the analysis are considered conditional⁽⁴⁶⁾. The terms, SS and DF used in this analysis represent the sum of square and the degrees of freedom respectively. In Table 8, the comparison of the test statistic with the appropriate value from a F-distribution table shows that the resin type and solution concentration definitely affect the SO_4^{2-} removal efficiency. Later on this conclusion is further supported by the fact that the equilibrium resin capacities determined from the

fixed-bed experiments were satisfactorily correlated with the respective solution concentrations by the non-linear Langmuir type isotherm.

Table 8. Resin and Concentration Effects on Exhaustion Efficiency

Source	SS	DF	MS	t_0	$F_{0.05, 9, 18}$ $F_{0.05, 2, 18}$	Effect
Resin	8100.6	9	900.1	11.91	2.46	Yes
Conc.	19603.4	2	9801.7	129.7	3.55	Yes
C-N-R	1360.1	18	76.6	0.0		
Error	0.0	0	0.0			
Total	29064.2	29				

Table 9 deals with the effect of resin type and solution concentration on the regeneration step of the batch procedure. The percent retained is 100 minus the regeneration efficiency. In Table 9, the only effect on the regeneration efficiency is found to be due to the resin type.

Table 9. Resin and Concentration Effects on Regeneration Efficiency

Source	SS	DF	MS	t_0	$F_{0.05, 9, 18}$ $F_{0.05, 2, 18}$	Effect
Resin	8953.1	9	994.8	15.24	2.46	Yes
Conc.	396.9	2	198.4	3.04	3.55	No
C-N-R	1175.2	18	65.3	0.0		
Error	0.0	0	0.0			
Total	10525.1	29				

Tables 10 and 11 deal with the effect of resin type and cyclic operation (4 cycles) on the exhaustion and regeneration efficiency. The solution concentration used was 25,000 ppm K_2SO_4 . Table 10 shows that there is definitely an effect due to resin type on exhaustion efficiency. Also in Table 10 the analysis leads to the

conclusion that 4 consecutive cycles of exhaustion and regeneration do not affect the exhaustion efficiency which is expected for a good commercial resin.

Table 10. Resin and Cycle Effects on Exhaustion Efficiency

Source	SS	DF	MS	t_0	$F_{0.05, 10, 30}$ $F_{0.05, 3, 30}$	Effect
Resin	20055.3	10	2005.5	82.38	2.16	Yes
Cycle	17.8	3	5.9	0.24	2.92	No
C-N-R	730.3	30	24.3	0.0		
Error	0.0	0	0.0			
Total	20803.5	43				

Table 11 deals with the effect of resin type and cyclic operation on the regeneration efficiency. Also in Table 11 the results from the fixed-effects calculations imply that both the resin type and exhaustion-regeneration cycles affect the regeneration efficiency. In some resins this means that the resin regeneration performance improves. In other cases the regeneration performance deteriorates or is erratic. Theoretically, the regeneration efficiency for 4 consecutive cycles on a relatively new resin sample should either improve or remain constant. This observed inconsistent behavior is probably due to the lack of multiple observations and few number of cycles.

Table 11. Resin and Cycle Effects on Regeneration Efficiency

Source	SS	DF	MS	t_0	$F_{0.05, 10, 30}$ $F_{0.05, 3, 30}$	Effect
Resin	5850.8	10	585.1	7.68	2.16	Yes
Cycle	3466.5	3	1155.5	15.27	2.92	Yes
C-N-R	2285.1	30	76.2	0.0		
Error	0.0	0	0.0			
Total	11602.4	43				

Tables 12 and 13 deal with the effects of resin type and cation (sodium versus potassium sulfate) on the exhaustion and regeneration efficiency. The solutions used were 25,000 ppm K_2SO_4 and 20,400 ppm Na_2SO_4 . These solutions contain the same molar concentration of sulfate ion. Table 12 shows that there is only an effect of resin type on percent removal. Similarly, the resin type definitely has an effect on the regeneration efficiency. The cations, however, have no effect on the percent removed or retained, because no cations are involved in the exhaustion and regeneration steps.

Table 12. Resin and Cation Effects on Exhaustion Efficiency

Source	SS	DF	MS	f_0	$F_{0.05, 4, 4}$ $F_{0.05, 1, 4}$	Effect
Resin	2350.0	4	587.5	255.0	6.39	Yes
Cation	16.6	1	16.6	7.22	7.71	No
C-N-R	9.2	4	2.3	0.0		
Error	0.0	0	0.0			
Total	2375.9	9				

Table 13. Resin and Cation Effects on Regeneration Efficiency

Source	SS	DF	MS	f_0	$F_{0.05, 4, 4}$ $F_{0.05, 1, 4}$	Effect
Resin	1898.0	4	474.5	40.72	6.39	Yes
Cation	10.8	1	10.8	0.93	7.71	No
C-N-R	46.6	4	11.6	0.0		
Error	0.0	0	0.0			
Total	1955.4	9				

In Tables 14 and 15, the effect of sulfate source (i.e. pure reagent grade K_2SO_4 versus spent seed extract from the MHD Baghouse/ESP material) and resin type on the exhaustion and regeneration efficiencies are determined. In addition to potassium

and sulfate, the spent seed extract also contains small quantities of other dissolved impurities. Table 14 shows that there is definitely an effect due to resin type. However, there is no effect due to small levels of the dissolved impurities. In Table 15, the similar analysis was performed to determine the effect on resin regeneration efficiency or the percent retained. Again, as shown in Table 15, the only parameter that affects the percent retained is the resin type, and the small levels of the dissolved impurities have no effect.

Table 14. Resin and Seed Effect on Exhaustion Efficiency

Source	SS	DF	MS	f_0	$F_{0.05, 4, 4}$ $F_{0.05, 1, 4}$	Effect
Resin	2110.6	4	527.6	81.57	6.39	Yes
Seed*	2.4	1	2.4	0.37	7.71	No
C-N-R	25.9	4	6.5	0.0		
Error	0.0	0	0.0			
Total	2138.9	9				

* Seed extract from MHD spent seed

Table 15. Resin and Seed Effect on Regeneration Efficiency

Source	SS	DF	MS	f_0	$F_{0.05, 4, 4}$ $F_{0.05, 1, 4}$	Effect
Resin	1388.1	4	347.0	12.09	6.39	Yes
Seed*	38.0	1	38.0	1.32	7.71	No
C-N-R	114.8	4	28.7	0.0		
Error	0.0	0	0.0			
Total	1541.0	9				

* Seed extract from MHD spent seed

Thus based on the statistical analysis of the batch mode screening experiments, the exhaustion and regeneration efficiencies were found to be affected by different parameters. The only exception to this statement is the resin type, which strongly

seemed to affect both the exhaustion and regeneration efficiencies. The exhaustion efficiencies were found to be affected by the resin type and the solution concentration, whereas the regeneration efficiency was found to be affected by the resin type and the cycling between the exhaustion and regeneration steps. Table 16 summarizes the major findings from the statistical analysis of the batch mode screening experiments.

**Table 16. Parameter Effects on Exhaustion and Regeneration Efficiencies
(From Batch Mode Screening Experiments)**

Parameter	Effect on	
	Exhaustion Efficiency	Regeneration Efficiency
Resin Type	Significant	Significant
Solution Concentration	Varies inversely	No effect
Cyclic Operation	No effect	Significant
Cation (Na vs. K)	No effect	No effect
Dissolved Impurities (spent seed)	No effect	No effect

6.3.2 Multiattribute Analysis

Multiattribute analysis involves the use of an importance rating and a utility scheme to determine the best of several alternatives⁽⁴⁷⁾. For the data from the batch mode screening experiments, the scheme developed considered the percent removal as the most important result. The importance of the resin's performance for each test condition were also established. Table 17 lists the importance ratings in two columns. The first column lists the importance of each parameter. The second column lists the importance of the attributes contained within each parameter. These ratings were arbitrarily chosen to reflect the results of the previous section, which means that the

high solution concentration and cyclic operations were given the most importance. The percent removal was given slightly more importance than the percent retained.

Table 17. Parameter Importance Ratings

Parameter Rating (k_p)		Attribute Rating (k_A)	
Solution Concentration	0.3	Percent Removal	0.6
Cyclic Operation	0.3	Percent Retained	0.4
Cation (Na vs. K)	0.2		
Seed (Dissolved impurities)	0.2		
Total		1.0	

Results from the batch mode screening experiments were used in the weighting calculations. These calculations consisted of averaging the removal and retained percentages to reflect the resin's ability to handle concentration changes, repeated cycles of exhaustion and regeneration, and possible cation interference. The values associated with the spent MHD seed extract were used as the weights corresponding to the resins tendency to be fouled by the dissolved impurities.

For each of the parameters listed in Table 17, their individual utilities were calculated using the additive utility model,

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

where U_p is the utility of the parameter, k_A is the importance rating for the attributes, and U_A is the utility of the attributes. The attribute's utility function for the interval between 0 and 1 is given by:

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

where

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

X_A is either the percent removal or retained, X_i is the beginning of the interval, and X_f is the end of the interval. For the percent removal X_i and X_f are 0 and 100, respectively. These values are reversed for the percent retained. This type of utility function gives more weight to those removal or retained percentages that are closer to their ideal values (that is 100% for removal and 0% for retained) than to those less than 10 points of their ideal value (e.g. 90% for removal and 10% for retained). The utility for each resin was then calculated using

$$U_R = \sum_{p=1}^4 k_p U_p \quad (13)$$

where U_R is the utility of the resin and k_p is the importance rating of the parameter(47). For a resin to achieve a utility of 1.0, all of the percent removal and retained values must be ideal and equal to 1.0. The calculated resin utilities are given in Table 18. The best resins from the statistical analysis were found to be the IRA-35, IRA-68, and IRA-93, and therefore, were used for the process variables study discussed later on.

Table 18. The Calculated Resin Utilities

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

7.0 FIXED-BED PROCESS VARIABLES STUDY AND RESULTS

To carry out the process variables study using the three best resins identified from the batch mode screening experiments, a fixed-bed rig was designed and constructed.

7.1 Description of Fixed-Bed Setup & Experimental Procedure

Initial design of the fixed-bed system included provisions for a semi-automatic and long-time unsupervised operation. Problems occurred, however, during the shakedown experiments that prompted a re-design of the system. These problems included unstable system flow-rates, high initial concentrations of sulfate, and unstable sampler flow-rates. The unstable system flow-rates had to be dealt with procedurally. In the re-designed system, six of the manually operated valves and three of the solenoid valves (present in the original design) were replaced with three two-way valves and a four-way valve, respectively, to reduce/remove the dead-spaces in the system (suspected of contributing to the high initial sulfate concentrations). Due to the

removal of most of the solenoids one of the timers present in the original design was deleted from the system. Two isolation valves were added to the eluent and regenerant tanks to aid in the post-run system flush. The flush was also added to reduce the initial high sulfate concentrations. In the revised system, the full flow-rate through the column could be directed to the sampler, thereby eliminating the unstable sampler flow-rates caused by the flow-splitting sampling system. The schematic of the re-designed fixed-bed system is presented in Figure 2.

As shown in this schematic, the final design of the fixed-bed setup included three stainless steel tanks for the chosen eluent, for the deionized water, and for the solution of ammonium hydroxide; two glass columns of different diameters; and necessary timer, solenoid valves, rotameters, and other accessories. This system was designed to use one column at a time, to sustain pressures up to 180 psi at ambient temperature, to tolerate temperatures up to 77°C at 50 psi, and to be capable of being operated in a semi-automatic mode.

After the shakedown of the original and re-designed fixed-bed systems, the development of experimental procedure included measures of prevention and constant monitoring. The preventive measures that were necessary to provide a good run were primarily associated with the filling and flushing of the eluent and regenerant tanks. These tanks were found on-site and were modified by removing their internal baffles. The subsequent welding with a copper based welding rod caused the production of copper sulfate/hydroxide when the weld was exposed to the ammonium hydroxide (regenerant) or the potassium sulfate (eluent) solution. Therefore, these tanks could not be filled to the weld line. Another problem caused by the scavenged

Figure 2. Fixed-Bed Schematic

eluent and regenerant tanks was that of low final sulfate concentration due to a dead space in the tanks themselves. This problem could be solved by either initiating a sulfate solution rinse of the eluent tank or by using a more concentrated eluent. But due to the time required to make adjustments in sulfate solution, the former method was used. The bulk sulfate concentration of the eluent was determined by taking a few extra samples at the end of a run.

The eluent tank was flushed because of the tendency of the sulfate to precipitate out from concentrated solution when the room temperature dropped below 20°C. Therefore, the eluent tank and its associated tubing were flushed with hot tap and deionized water, respectively. The high initial sulfate concentration was thus reduced by a factor of ten (from 50 ppm to 4 ppm SO_4^{2-}). An additional preventive measure concerned the resin's ionic form. This preventive measure consisted of performing an initial regeneration on the fresh resin sample to ensure that it was in the free base form. The 4.0 wt % ammonia solution was used in batch mode with a mixing time of approximately 24 hours. The unstable system flow-rates persisted throughout the experimental runs and could only be controlled through constant monitoring.

The valve line-ups for the regeneration, rinse, and exhaustion steps are outlined in Table 19. Even though the in-column resin regeneration and subsequent rinse step were not used in the present investigation, Table 19 includes their line-ups for future applications.

For an experiment run these steps were followed:

- (1) remove exhausted column from its mount, (2) remove top flange from column, (3) remove glass wool plug, (4) use deionized water pump to drive the resin from the

column and into an appropriate container, (5) remove bottom glass wool plug, (6) rinse column with hot tap and then with deionized water, (7) insert fresh plug of glass wool, (8) add a measured amount of settled fresh resin and water slurry to column, (9) tap column on table to settle resin, (10) insert another glass wool plug, (11) replace the column's top flange, (12) remount column, (13) rinse column using the line-up from Table 19, (14) estimate flow-rate and adjust with rotameter, (15) rinse eluent tank with an appropriate volume of the sulfate solution, (16) fill tank with the sulfate solution, (17) reconnect the tubing to the eluent tank and to the four-way valve, (18) fill this tubing with the sulfate solution, (19) place the column under 50 psig of carbon dioxide for 20 minutes, (20) bleed system pressure off, (21) line-up all the valves except the column solenoid (closed) as indicated in Table 19, (22) pressurize the system to the appropriate pressure, (23) close the appropriate static pressure column valve, (24) create an approximately one psig positive pressure differential between the regulator's pressure and the system's pressure gauge, (25) open the column solenoid, (26) adjust the flow-rate with the rotameter and start the auto-sampler, (27) store the samples appropriately, (28) analyze samples for sulfate, and (29) flush system with deionized water.

Table 19. Valve Line-ups for the Fixed-Bed System

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

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

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

³ Flow Splitting valve used in open position to aid in rinsing.

The breakthrough curves obtained from the procedure described above showed good reproducibility and compared well with the Modeste's results. Figure 3 is a comparison of a typical breakthrough curve from Modeste's work⁽⁸⁾ with a similar one from the present study. The test conditions for this comparison are listed in Table 20. Although the pressure, flow-rate, and bed height were slightly different, the breakthrough curve from this study compared well with the Modeste's curve. A check for the reproducibility was also performed. The results, in the form of breakthrough curves, are shown in Figure 4. From these curves, it was concluded that the revised

Figure 3. Comparison of Strevel's and Modeste's Breakthrough Curves.

Figure 4. Reproducibility Check for IRA-35 at 10 psig, 0.014 gm SO_4^{2-} /ml, 20.3 cm Bed Height, and 10.8 cc/min.

fixed-bed system and procedure would provide the necessary reliability to ensure an adequate run reproducibility.

Table 20. Test Conditions for IRA-68 Breakthrough Curve Comparison

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

Test Conditions	Present Study	Modeste's Study ⁽⁸⁾
CO ₂ -Pressure (psig)	10	5
Solution Flow-rate (cm ³ /min)	11	10
Resin Bed Height (in.)	16	18

Using this rig and three candidate resins (IRA-68, -35, and -93), the following process variables were evaluated.

- CO₂-pressure
- solution concentration
- product inhibition
- bed height
- dissolved impurities
- superficial velocity
- solution pH

Results from this process variables study are discussed in the following sections.

7.2 Equilibrium Capacity and Its Relationships with CO₂-Pressure and Solution Concentration

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

written as:

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

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

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

where q_{∞} is the equilibrium capacity (gm SO_4^{2-} / ml resin) and A is the area under the $(1-C/C_0)$ vs. time curve. The area under the curve was determined using a modified version of Modeste's numerical integration program⁽⁸⁾, which used the method of trapezoids.

The experimentally determined values of the equilibrium capacities for each resin are tabulated versus CO_2 -pressure in Table 21. Table 21 also includes the equilibrium capacities for IRA-68 that were determined by Butler⁽⁷⁾ and Modeste⁽⁸⁾.

Table 21. Effect of CO₂-Pressure on Equilibrium Loading

Basis: 0.028 gm SO₄²⁻ / ml solution

CO ₂ -Pressure (psig)	IRA-35 (g SO ₄ ²⁻ / ml _R)	IRA-68 (g SO ₄ ²⁻ / ml _R)	IRA-68 (g SO ₄ ²⁻ / ml _R)
0	-	0.068 ^a	-
10	0.073	0.065	0.074
20	-	0.087 ^b	-
40	0.098	0.124 ^b	0.096
80	0.130	-	0.164
120	0.126	0.136	0.168

^a Butler(7)

^b Modeste(8) with 0.039 gm SO₄²⁻ / ml solution

R is for resin

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

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

The kinetic rate of reversible adsorption can be written as

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

where k_1 is the forward ion-exchange reaction (adsorption) rate constant, k_2 is the backward ion-exchange reaction (desorption) rate constant, and C_T is the total concentration of available ion-exchange (adsorption) sites. When the ion-exchange system is at equilibrium, equation (17) is equal to zero and q is maximum and equal to

q_{∞} . Hence, by comparing equations (16) and (17), the Langmuir constants, a_1 and a_2 , can be defined in terms of the rate constants, k_1 and k_2 , and the concentration of available exchange sites, C_T as:

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

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

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

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

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

Using the fitted data from Butler⁽⁷⁾, Modeste⁽⁸⁾ and the present investigation, a maximum experimental C_T -value, (defined as $\overline{C_T}$), can be determined for IRA-68.

These $\overline{C_T}$ -values and their corresponding Langmuir constants are presented in Table

22. The pre-run CO_2 -pressure is the static CO_2 -pressure applied to the system prior to the exhaustion/carbonation step. The $\overline{C_T}$ -values seem to be dependent on the static CO_2 -pressure during the pre-run and the carbonation/exhaustion step. It is believed that the higher static CO_2 -pressures would create more bicarbonate ions on the resin.

Since the bicarbonate ions can be easily replaced on the resin by the sulfate ions, the maximum concentration of sulfate ions that can be removed by the resin is approached as the CO₂-pressure is increased. The CO₂-pressure effect on the resin sites can be represented by the following reaction:

where R is the complex cation group on the resin.

Table 22. $\overline{C}_T$ Values for IRA-68

Study	a_1 (g SO ₄ ²⁻ /ml)	a_2 (dimension less)	$\overline{C}_T$ (g SO ₄ ²⁻ /ml)	CO ₂ - Pressure (psig)	Pre-Run CO ₂ - Pressure (psig)
Butler	24.23	318.7	0.076	0	None*
Modeste	74.07	830.2	0.089	20	20 (5 min)
	42.73	322.2	0.133	40	40 (5 min)
Present	3.13	19.0	0.165	10	50 (20 min)

* Butler carbonated the resin at atmospheric pressure with a CO₂ bubbling apparatus.

In other words the capacity of the resin for sulfate would increase with CO₂-pressure. This conjecture is supported by the results in Table 21, which shows the equilibrium loading increasing as the static CO₂-pressure is increased.

From Table 21 the resin's equilibrium loading seems to level-out around 80 psig. Therefore, the $\overline{C}_T$ -values should also level-out at the same pre-run CO₂-pressure. This means that the $\overline{C}_T$ -value for IRA-68 would approach a constant value at higher CO₂-pressures. Based on this, the highest experimental $\overline{C}_T$ -value of 0.165 g SO₄²⁻/ml resin was used to calculate the Langmuir constants for IRA-68 at higher static

CO₂-pressures. These calculations used the following linearized form of the Langmuir isotherm,

$$\frac{1}{a_1} = \frac{C_o}{q_{\infty}} - \frac{1}{C_T} C_o, \quad (22)$$

and the experimental values of C_o and q_{∞} . Calculated values of a_1 and a_2 using this procedure are presented in Table 23.

Table 23. Calculated Langmuir Constants for IRA-68

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

The $\frac{1}{C_T}$ -values and respective Langmuir constants for IRA-35 and IRA-93 were obtained from fitting the experimental data at 10 psig. The same Langmuir constants were used for the higher CO₂-pressures because the actual experimental data were limited and the results from equation (22) would give a negative intercept. The $\frac{1}{C_T}$ -values and the Langmuir constant used for the IRA-35 and IRA-93 resins are presented in Table 24.

Table 24. Calculated Langmuir Constants for IRA-35 and IRA-93

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

Equation (22) when solved for the C_o / q_∞ gives

$$\frac{C_o}{q_\infty} = \frac{1}{a_1} + \frac{1}{\overline{C_T}} C_o. \quad (23)$$

These linearized Langmuir equilibrium isotherms for IRA-35, IRA-68, and IRA-93 are provided in Figures 5-7. These plots represent the least squares fits to the concentration and equilibrium loading data at various static CO₂-pressures. The calculated regression coefficients are $1/a_1$ (intercept) and $1 / \overline{C_T}$ (slope) of equation (23). From these coefficients the second Langmuir constant, a_2 , was determined. The regressed values of $\overline{C_T}$ for IRA-68 resin are compared with the similar values reported by Butler⁽⁷⁾ and Modeste⁽⁸⁾ in Table 22. $\overline{C_T}$ values in the present study are found to be slightly higher than the earlier investigations. This difference is believed to be caused by the different pre-run CO₂-pressures used in each investigation. Also, the difference seems to be reduced as the pre-run CO₂-pressure is increased. The calculated values of q_∞ at various solution concentrations for IRA-35, IRA-68, and IRA-93 at a CO₂-pressure of 10 psig are shown in Figure 8. IRA-93 seems to have the highest equilibrium loading at a given solution concentration.

7.3 Fixed-Bed Mathematical Model

The bench scale fixed-bed data collected by Butler⁽⁷⁾ were compared to the Selke and Bliss⁽⁴⁸⁾ model. This model is simple, neglects the importance of solid pore diffusion, and assumes that the overall mass transfer to and from the solid resin phase is controlled by liquid film diffusion. To compare the experimental data with the Selke and Bliss model prediction, the data are expressed in the form of

Figure 5. Plot of Fitted Linearized Langmuir Isotherm for IRA-35

Figure 6. Plot of Fitted Linearized Langmuir Isotherm for IRA-68.

Figure 7. Plot of Fitted Linearized Langmuir Isotherm for IRA-93.

Figure 8. Langmuir Isotherms for IRA-35, IRA-68, and IRA-93 at 10 psig CO_2 -Pressure

$$\ln \frac{C}{C_0} = \frac{k_L S C_0}{q_{\infty} V_s} y - \frac{k_L S x}{V_s} - 1 \quad (24)$$

where C is the concentration of SO_4^{2-} in effluent solution, C_0 is the concentration of SO_4^{2-} in initial solution, k_L is the liquid-film mass transfer coefficient, S is the effective surface area of resin, q_{∞} is the concentration of SO_4^{2-} ion on resin in equilibrium with C_0 , V_s is the volumetric flow rate of solution, x is the weight of resin traversed in the bed, and y is the volume of the collected effluent after correction for the fluid in bed voids.

Butler's data and predicted data from the above model did not match at $C/C_0 \geq 0.8$. This divergence at the tail end of the breakthrough curve was attributed to intraparticle diffusion in resin becoming more significant at close to saturation level.

Because of this mismatch at the tail end of the breakthrough curves, Modeste⁽⁸⁾ used the fixed-bed model proposed by Antonson⁽⁴⁹⁾. Antonson's model is more complex and incorporates solid phase diffusion control for a system exhibiting Langmuir type non-linear equilibrium isotherm. Antonson's model can be summarized by the following set of equations.

$$\frac{\partial C}{\partial x} + \frac{1}{m} \frac{\partial q}{\partial \theta} = 0 \quad (25)$$

$$\frac{\partial q_i}{\partial \theta} = \frac{D}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial q_i}{\partial r} \right) \quad (26)$$

$$q(x, \theta) = \frac{3}{r^3} \int_0^R q_i(r, x, \theta) r^2 dr \quad (27)$$

$$q_i(R, x, \theta) = \frac{a_1 C_s}{1 + a_2 C_s} \quad (28)$$

with the initial and boundary conditions given by

$$q(\theta=0) = 0 \quad (29)$$

$$C(x=0) = C_o \quad (30)$$

$$\frac{\partial q_i}{\partial r}(r=0) = 0 \quad (31)$$

where

- C = concentration of sorbate in solution phase
- q = concentration of sorbate in resin phase
- $x = \frac{z}{mv}$
- $\theta = t - \frac{z}{v}$
- m = ratio of void fraction to particle fraction in packed bed
- z = height of the bed
- v = superficial velocity
- t = time
- q_i = local concentration of sorbate in resin phase
- r = radial coordinate
- D = intraparticle diffusion coefficient
- R = radius of resin particle
- C_s = sorbate concentration at the surface of the resin particle
- C_o = sorbate concentration at the inlet to the bed

Antonson⁽⁴⁹⁾ solved the above set of equations to give final solution in the form of

$$\frac{\partial \theta}{\partial X^*} = -2 \cdot \sum_{n=1}^{\infty} \int_0^{\theta^*} \frac{\partial (\theta/(1 + a_3 \Phi))}{\partial \lambda} \exp\left(-\frac{1}{2} n^2 \pi^2 (\theta^* - \lambda)\right) d\lambda \quad (32)$$

where,

$$\Phi = C/C_o$$

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

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

$$a_3 = a_2 C_o$$

Modeste's data were very well matched by the Antonson's model predicted data at the tail end portion. However, slight deviation was seen in the early portion

(e.g. $C/C_o \leq 0.1$). This slight deviation was attributed by Modeste to possible non-equilibrium conditions existing at the beginning of the exhaustion cycle as well as to the influence of liquid film transfer.

In the present study, the decision was made to use the Antonson's model based on Modeste's results. This model requires two inputs. These are a_2C_o and X^* , the dimensionless column length ($X^*=3Da_1Z/mR^2v$). With these inputs, the model will generate a breakthrough curve which can be fitted to an experimental curve. Examples of the effect of X^* on C/C_o at a fixed a_2C_o and of a_2C_o on C/C_o at a fixed X^* are shown in Figures 9 and 10, respectively. In Figure 9 the increase in dimensionless column length, X^* , can be interpreted as the effect of increasing diffusion parameter, D/R^2 (or rate of intraparticle diffusion), or an increase in resin bed height, z , or a decrease in linear velocity, on C/C_o values for a given resin. The model responds by shifting the curve's origin to the right and by changing their slopes from very small to large positive values. In Figure 10 the effect of decreasing a_2C_o on the model's C/C_o values represents the change from a highly non-linear equilibrium to a more linear equilibrium. Correspondingly, the curve's slopes change from very large values for large a_2C_o to small values for small a_2C_o . An example of the typical best fit for a run is shown in Figure 11.

To determine diffusion coefficient, the experimental breakthrough data were plotted as a semi-log plot of C/C_o versus θ and then compared to a similar semi-log plot of model calculated values of C/C_o versus θ^* . The use of semi-log plot in the

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Figure 9. Effect of X^* on C/C_0 at $a_2C_0 = 1.0$.

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Figure 10. Effect of $a_2 C_0$ on C/C_0 at $X^* = 1.0$.

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Figure 11. Typical Best Fit: Run 59 (IRA-68, 10 psig, 0.004 g SO_4^{2-} /ml, 20.3 cm Bed Height, 4.96 cm^2 Column Area, and 11.0 cc/min)

curve matching process makes the relationship between θ and θ^* of just a displacement along the X-axis since the dimensionless time, θ^* is related to the actual time by

$$\ln(\theta^*) = \ln(\theta) + \ln\left(\frac{2D}{R^2}\right) \quad (33)$$

where $\theta = t - \frac{Z}{V}$.

In this study, the a_2C_0 value for the given run was calculated from the regressed value of a_2 and corresponding solution concentration, C_0 . For this value of a_2C_0 , a set of theoretical curves was generated using Antonson's model/program for different values of X^* . The best matching X^* value was then used to determine the diffusion coefficient by the relationship

$$X^* = \frac{3D a_1 z}{m R^2 v} \quad (34)$$

In the present work no attempts were made to isolate micropore diffusion from macropore diffusion. Hence, to facilitate comparison with other literature reported values, the calculated diffusion coefficients are presented as D/R^2 where R is the radius of the resin particle.

The calculated diffusion parameters for IRA-35, IRA-68 and IRA-93 are given in Table 25. When dissolved impurities (as in spent seed) are present in the test solution, the diffusion parameters are roughly the same for IRA-35 and IRA-93. However IRA-68's diffusion parameter for dissolved impurities is approximately half that of the parameter for the pure K_2SO_4 solution. The probable cause for this effect could be the temporary fouling of the pores caused by the large ions or non-ionic

impurities present in the spent seed extract. IRA-35 and IRA-93 have a polymer matrix that possibly prevents large ions or particles from entering the porous resin bead by reducing the size of the pores. In Table 26 the range of diffusion parameters for this investigation are compared with those found in the literature. The D/R^2 range found by Modeste⁽⁸⁾ for IRA-68 compares well with the values found in the present investigation.

The diffusion parameters for each resin are plotted against CO_2 -pressure and solution concentration in Figures 12 and 13, respectively. In Figure 12 the general trend of the diffusion coefficients with increasing CO_2 -pressure is downward. Above 40 psig all the resins show roughly the similar downward trend of decreasing D/R^2 values. In Figure 13, as the solution concentration increases, the diffusion parameters also increase in value. The diffusion parameters for IRA-68 at 10 psig CO_2 -pressure from this study compare well with those found by Modeste⁽⁸⁾ at 20 psig and 40 psig CO_2 -pressure, and in general, show a higher average value than for the other two resins. IRA-35 and IRA-93 have average diffusion parameters that are very similar. The effective diffusion parameters seems to decrease in value as the superficial velocity increases. These observations are discussed in greater detail in the following sections.

**Table 25. Calculated Diffusion Parameters for IRA-35, IRA-68
and IRA-93**

C_o (g SO_4^{2-} /ml)	a_2C_o	CO_2 - Pressure (psig)	Column no.	X^* (dimension less)	D/R^2 (S-1) $\times 10^{-3}$
• IRA-35					
0.005	0.930	10	I	1.0	0.017
0.013	2.188	10	I	2.5	0.043
0.026	4.411	10	I	3.0	0.054
0.024	4.210	40	I	1.5	0.026
0.027	4.567	80	I	2.0	0.034
0.026	4.548	120	I	0.9	0.016
0.021*	3.531	10	I	3.0	0.052
0.026	4.504	10	II	2.0	0.008
• IRA-68					
0.004	0.076	10	I	2.0	0.143
0.012	0.228	10	I	0.6	0.043
0.025	0.475	10	I	3.0	0.215
0.024	0.610	40	I	2.0	0.018
0.021	0.534	80	I	2.5	0.022
0.026	4.757	120	I	0.8	0.006
0.021*	0.399	10	I	1.5	0.108
0.027	0.513	10	II	2.0	0.034
• IRA-93					
0.005	1.293	10	I	2.0	0.024
0.013	3.108	10	I	2.0	0.024
0.025	6.116	10	I	4.0	0.048
0.026	6.470	40	I	5.0	0.060
0.027	6.657	80	I	3.0	0.036
0.028	6.955	120	I	4.0	0.048
0.021*	5.145	10	I	5.0	0.060
0.027	6.537	10	II	4.0	0.011

* Spent Seed extract

Table 26. Comparison of the Diffusion Parameters with the Literature

System	Reference	Temperature (°C)	D/R ² (S ⁻¹) x 10 ³
SO ₄ ²⁻ / IRA-35	Present	21	0.005-0.054
SO ₄ ²⁻ / IRA-68	(8)	20	0.050-0.083
SO ₄ ²⁻ / IRA-68	Present	21	0.006-0.215
SO ₄ ²⁻ / IRA-93	Present	21	0.011-0.060

7.4 Effects of Major Process Variables

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

7.4.1 Effect of Static CO₂-Pressure

The effect of static CO₂-pressure during the combined exhaustion/carbonation step on the equilibrium capacity of the three candidate resins is shown in Table 21. As seen from this table, the equilibrium loading increases with the CO₂-pressure and appears to level off at around 80-120 psig. Based on these results, it is believed that the higher static CO₂-pressures would create more bicarbonate ions on the resin sites, which are then substituted by sulfate ions in the solution resulting in an increased capacity. This possibility can be represented by the following reaction:

where R is the complex cation group on the resin.

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Figure 12. Effect of Static CO₂-Pressure on Diffusion Parameter

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Figure 13. Effect of Solution Concentration on Diffusion Parameter

IRA-93 resin seems to have the highest equilibrium loading at a given solution concentration and CO₂-pressure.

The typical effect of CO₂-pressure on the ion-exchange kinetics can be seen in Figure 14 for IRA-93. Figure 14 shows that the increased static CO₂-pressure slightly alters the shape of the breakthrough curve. The curve's shape changes from a somewhat steep S-curve at 10 psig and 40 psig CO₂-pressure to a slightly more linear (less steep) curve at 80 and 120 psig CO₂-pressure. This CO₂-pressure effect was further evaluated in terms of the diffusion parameter, (D/R^2) , derived by matching the experimental and theoretically generated model breakthrough curves. As shown in Figure 12 and Table 25, the D/R^2 values for candidate resins changed very little with the CO₂-pressure indicating that the kinetics did not change significantly.

7.4.2 Effect of Solution Concentration

As discussed earlier the experimental results on equilibrium capacities of each resin at different solution concentrations and CO₂-pressures were fitted to the non-linear Langmuir isotherm given by equation (16). The typical fitted isotherms for the three candidate resins at a CO₂-pressure of 10 psig are shown in Figure 8. As shown in this figure, at a given solution concentration the IRA-93 resin seemed to provide a slightly greater loading than the other two resins.

The solution concentration affects the ion-exchange kinetics of IRA-93 resin very little as shown by the shapes of the experimental breakthrough curves in Figure 15. To accommodate variation in sulfate input rate at a fixed volumetric flow rate but different input solution concentration, the x-axis is expressed in terms of total sulfate

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Figure 14. Effect of Static CO_2 -Pressure on IRA-93

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Figure 15. Effect of Solution Concentration on IRA-93

introduced at various times instead of time itself. The breakthrough curves shown in this figure, indicate only a slight effect of the solution concentration. This is further supported by the D/R^2 values listed in Table 25 and also shown in Figure 12

Similarly determined values of D/R^2 for IRA-35 and IRA-68 resins are also shown in Table 25 and Figure 13. Based on these results, the effect of solution concentration on the ion-exchange kinetics of IRA-35 resin also seems to be very slight when allowing for the experimental scatter. However, the effect of concentration on the IRA-68 resin seems to be significant. For IRA-68 resin, the D/R^2 value is found to increase with the solution concentration. The increase in D/R^2 means corresponding increase in the X^* values. As shown in Figure 9, at increased value of X^* , the breakthrough curves become more and more steep. Hence in case of IRA-68 resin the shape of the breakthrough curves would change significantly as the solution concentration changes. This particular behavior of the IRA-68 resin could be caused by its gel-type matrix; because the gel-type resins usually have larger pores and, therefore, possibly better (or faster) intraparticle diffusion.

7.4.3 Effect of Product Inhibition

Product inhibition (PI) is defined as the interference caused by the product, KHCO_3 , to the operation of the ion-exchange resin. By retarding the transfer of HCO_3^- ions from the resin, the KHCO_3 present in the bulk solution can affect the transfer of SO_4^{2-} ions from the bulk solution to the resin sites, and thereby, can reduce the resin's

capacity for sulfates. The magnitude of the PI effect in the experiments was determined by using bulk solutions containing initially known molar ratios of KHCO_3 / K_2SO_4 . Resulting equilibrium capacities of the candidate resins for SO_4^{2-} are compared with the results reported by Butler(7) in Table 27. Within experimental scatter, there seems to be no effect of PI on the loading of IRA-35. However, for IRA-68 and -93, the loadings increase for molar ratios up to 0.1 and then show a significant decrease at a molar ratio of 1.0 and higher. For IRA-68 Butler(7) saw a similar effect of increase in equilibrium loading at the 0.1 molar ratio, followed by a significant decrease at a molar ratio of 1.0 and higher. The possible reasons for such behavior are not known at present but can be studied in the future program.

Table 27. Effect of Product Inhibition (PI) on Equilibrium Loading

Basis: 0.028 gm SO_4^{2-} / ml solution and 10 psig CO_2 -pressure

Molar Ratio (PI)	IRA-35 (g SO_4^{2-} / ml _R)	IRA-68 (g SO_4^{2-} / ml _R)	IRA-93 (g SO_4^{2-} / ml _R)
0.0	0.073	0.065	0.063 _B
0.1	0.068	0.095	0.087 _B
1.0	0.072	0.061	0.047 _B

B is for Butler's(7) runs at atmospheric pressure
ml_R - represents volume of resin in cm³

In Figure 16, the effect of PI on ion-exchange kinetics is shown. This is shown in terms of the experimental breakthrough curves determined at different initial molar ratios of KHCO_3 / K_2SO_4 . As shown in this figure, the shape of the breakthrough curve does not seem to change with the increasing ratio of the product (KHCO_3) in the initial bulk solution. However, the volume of sulfate-containing solution needed to exhaust

Figure 16. Effect of Product Inhibition on IRA-68

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the resin (that means resin's equilibrium capacity) increases for the 0.1 molar ratio of $\text{KHCO}_3 / \text{K}_2\text{SO}_4$ and then drops back for the higher ratio case. Butler(7) also saw a similar effect of PI on the ion-exchange kinetics of IRA-68.

7.4.4 Effect of Resin Bed Height

Height of the resin bed should not affect the equilibrium loading of the resin measured in terms of $\text{gm SO}_4^{2-} / \text{ml of resin}$. Hence only the kinetic effect was evaluated. The resin bed height affects the ion-exchange kinetics only slightly, if at all, when considering experimental error. The typical breakthrough curves presented in Figure 17 for IRA-93 as the fraction of sulfate removed versus the number of bed volumes shows this result. Here, bed volume is defined as the cumulative volume of the bulk solution introduced at any time divided by the volume of resin bed. The fact that the curves for two different bed heights overlap within experimental error proves that no channeling occurred. Channeling would result in not all of the resin bed being utilized and would show a steadily rising curve rather than a typical S-shaped curve. Butler(7) saw a similar effect of bed height on the ion-exchange kinetics for IRA-68.

7.4.5 Effect of Dissolved Impurities

The effect of dissolved impurities on equilibrium loading and ion-exchange kinetics was evaluated using the MHD spent seed extract. This extract was prepared by treating a representative spent seed/fly ash sample from UTSI's MHD facility (e.g. Coal-Fired Flow Facility, CFFF) with appropriate amounts of deionized water and filtering several times the resulting mixture to remove most of the insoluble fly ash material. The major soluble cations and anions present in the resulting extract

Figure 17. Effect of Resin Bed Height on IRA-93

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included: K^+ , Na^+ , Ca^{++} , Mg^{++} , SO_4^{2-} , Cl^- and F^- . There were also trace levels of silicon and aluminum in the extract. Besides SO_4^{2-} the major anion present was Cl^- at about 588 ppm level. In Table 28, the effect of the dissolved impurities on the resin's equilibrium loading is shown. There seems to be a slight effect on IRA-35; however, this could be the result of experimental error. On IRA-68 and IRA-93 resin, no change in equilibrium loading values is observed suggesting that low levels of dissolved impurities possibly did not change the capacity of these two resins.

Table 28. Effect of Dissolved Impurities on Equilibrium Loading

Basis: 10.0 psig CO_2 and 0.028 gm SO_4^{2-} / ml

SO_4^{2-} Source	IRA-35 (g SO_4^{2-} / ml _R)	IRA-68 (g SO_4^{2-} / ml _R)	IRA-93 (g SO_4^{2-} / ml _R)
Reagent	0.073	0.065	0.074
Spent Seed	0.058	0.060	0.076

R is for resin.

Using spent seed extract from a different MHD test, Butler(7) had noticed a slight decrease in the capacity of IRA-68 under similar experimental conditions. However, the chloride level in his extract was only 55 ppm. Hence it is believed that depending upon the MHD spent seed material, the concentrations of dissolved impurities (major as well as minor species) could change significantly and possibly could cause a significant change in the resin's capacity for the sulfate ions. For the spent seed taken from the UTSI's MHD facility, the composition of the spent seed could change from test to test, as this facility in its proof-of-concept (POC) mode of testing program tests different parameters, such as K_2/S ratio and coal type, etc.; and it never reaches

theoretically considered steady state conditions. Hence, in a future study, the effect of dissolved impurities on the resin's equilibrium capacity needs to be evaluated using carefully prepared reagent grade chemicals.

The typical effect of dissolved impurities on the ion-exchange kinetics is shown in Figure 18. This figure shows the breakthrough curves for the runs using a reagent grade potassium sulfate solution and a spent seed extract. Within the experimental error, the shape of the curves are approximately the same. Therefore, no change in the ion-exchange kinetics can be detected. From the batch mode screening results discussed earlier in Section 6, the diffusion parameters given in Table 25, and the Figure 18, there seems to be a little or no effect of dissolved impurities on the ion-exchange kinetics of the three candidate resins. Butler(7) also showed a similar slight to no kinetic effect due to dissolved impurities.

Besides possibly affecting the equilibrium capacity of the candidate resin and corresponding ion-exchange kinetics, some of the dissolved anions such as Cl^- and F^- were also found to be removed by the resin from the bulk solution. This simultaneous removal of SO_4^{2-} , Cl^- , NO_3^- , F^- , etc. by the UTSI's concept was not evaluated in the present study. However, under a separate DOE sponsored Small Business Innovative Research Phase I and II programs, a team consisting of HMJ, Incorporated and UTSI is studying the simultaneous SO_4^{2-} and Cl^- removal by the ion-exchange resin-based concept.

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Figure 18. Effect of Dissolved Impurities on IRA-68

7.4.6 Effect of Superficial Velocity

In general, unless a very high superficial velocity is employed, the equilibrium loading of the given resin should not vary with the velocity. At very high velocities there exists a potential of bulk solution by-passing the resin bed material completely or partially, and thereby, resulting in low values for the observed equilibrium capacity. Since very high velocity was not used in this study and all resins were believed to behave similarly, only the effect on the ion-exchange kinetics of the IRA-35 resin was evaluated.

Experiments were carried out for the IRA-35 resin using similar volumetric flow rate and a nominal 5 wt % K_2SO_4 solution in two columns of different diameter (which provided different superficial velocities). The resulting curves, $\left(\frac{C}{C_0}\right)$, when plotted against the grams of sulfate introduced per unit volume of resin (i.e. $gm\ SO_4^{2-} / ml_{resin}$), showed a finite displacement (see Figure 19). If there was no difference in the rate controlling mass transfer step at these two velocities, the two curves should overlap or be close to each other within experimental scatter. The fact that the curve for lower velocity (e.g., 0.009 cm/s) broke through earlier, indicated that most likely the mass transfer across the liquid film surrounding the resin particle controlled the rate. As a result, less SO_4^{2-} was being removed by the resin particles, and therefore, more SO_4^{2-} showed up in the effluent as unexchanged.

On the other hand, as shown in Figure 11, most of the experimental breakthrough curves generated in the present study at higher velocities (e.g. higher than 0.009 cm/s) were well satisfied by the Antonson's⁽⁴⁹⁾ fixed-bed model that considers

Figure 19. Effect of Superficial Velocity on IRA-35

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solid-phase (intraparticle) diffusion as the rate controlling step. Hence, it is believed that for experiments carried out at lower velocities (e.g., at 0.009 cm/s and lower), one should use the Selke and Bliss model⁽⁴⁸⁾ that considers liquid-film transfer as the rate controlling mass transfer step. Butler⁽⁷⁾, using the Selke and Bliss model also saw a significant effect of superficial velocity on the ion-exchange kinetics of IRA-68 resin. He measured this effect in terms of the parameter $K_L S$, (that is the product of liquid-film mass transfer coefficient (K_L) and the resin's effective surface area (S)). From his observations, Butler provided the following empirical relationships between the superficial velocity, u and $K_L S$ ⁽⁵⁰⁾. Reynolds number, Re , in these relationships is calculated based on the particle diameter.

$$\text{for } u \leq 0.02 \text{ cm/s (or } Re \leq 0.09) \\ K_L S = 0.00367 \left(\frac{u}{0.0065} \right)^{0.99} \text{ (in cm}^3 \text{/g resin}\cdot\text{s)} \quad (35)$$

$$\text{for } u > 0.02 \text{ cm/s (or } Re > 0.09) \\ K_L S = 0.011 \text{ (in cm}^3 \text{/g resin}\cdot\text{s)} \quad (36)$$

Thus, the superficial velocity was found to significantly affect the mass transfer coefficient as well as the overall rate-controlling step. Based on these findings, it is recommended to take appropriate care in selecting the fixed-bed model for data analysis.

7.4.7 Effect of Solution pH

The effect of initial solution pH on the resin's performance was evaluated by carrying out fixed-bed experiments using 50,000 ppm K_2SO_4 solution (pH = 7.5), and a mixture of 50,000 ppm K_2SO_4 solution with a small amount of acetic acid solution (pH = 4.25). For all three resins, the effect was similar in the sense that the breakthrough

curves for pH = 4.25 moved slightly to the right of the curves for pH = 7.5. However, the shape of the curves remained the same. A typical set of experimental breakthrough curves for IRA-68 resin is shown in Figure 20. These results can be interpreted as slightly acidic solutions at the bed inlet either helping in maintaining the acidic to neutral conditions (as recommended by the manufacturers) in the entire bed, and thereby, improving the resin capacity or helping in improving the ionic mobility of the sulfate ions. From the similar shapes of the breakthrough curves it can be stated that the solution pH did not change the ion-exchange kinetics significantly, and therefore, the diffusion parameter D/R^2 . Later on, under the section dealing with the resin's performance enhancement by small doses of organic acids, this potential effect of solution pH on improving the equilibrium capacity of resin is discussed further.

7.5 Determination of Cycle Efficiency

For industrial applications, some of the desired attributes of an ion-exchange resin include its high equilibrium capacity, high resistance to fouling by the dissolved/undissolved impurities and, of course, the high diffusion coefficients. In addition, the long term resin life and/or acceptable performance for large numbers of cyclic operations without significant degradation in efficiency are also equally important. This is true because the cost of resin replacement can be a significant factor in the economics (operating cost) of the resin-based applications.

To determine the cycle efficiency, fixed-bed experiments were carried out with the samples of IRA-68, -35 and -93 resins. In these experiments, the same batch/sample of resin was subjected to repeated cycles involving carbonation/exhaustion, and

Figure 20. Effect of Solution pH on Breakthrough Curve for IRA-68.

regeneration steps. During the resin regeneration step, the in-situ regeneration was carried out using a 4 wt % NH_3 solution and a flow rate of 10 cc/min. Relatively complete regeneration of the exhausted resin was assumed to be achieved by performing the regeneration step for a longer time (~ 30 minutes) than determined from the earlier batch mode experiments. Using this procedure 10 consecutive cycles were completed for IRA-35 resin. Results from these experiments are shown in Figure 21 and indicate a progressive deterioration (determined based on curves moving to left and breakthrough occurring early) in the resin's performance. However, earlier in a smaller fixed-bed unit, Butler⁽⁷⁾ had carried out similar cycle efficiency experiments using IRA-68 resin without noticing any performance degradation up to four(4) cycles. Hence, it was believed that the observed degradation in the performance could be related to the experimental procedure (inadequate regeneration of resin) or equipment (dead volumes in the system).

The dead volumes in the fixed-bed set-up could not be reduced anymore beyond what was achieved during our initial shakedown experiments. Hence to correct the problem due to possible incomplete regeneration of the exhausted resin, the experimental procedure was slightly modified by increasing the NH_4OH solution concentration to 13.4 wt % (equivalent to 6.5 wt % as NH_3) and regeneration time to 90 minutes at the 25 cm^3/min flow rate. In the future, however, this step needs to be studied in detail to identify the optimum in-situ regeneration conditions for the fixed-bed operations. This revised procedure was then used to determine the cycle efficiency of the candidate resins. During exhaustion/carbonation step, the samples of

- Flow Rate of K_2SO_4 Solution = 11 cc/min
- Resin volume = 100 cc
- 5 wt% K_2SO_4 solution

Figure 21. Preliminary Data from Cycle Efficiency Experiments for IRA-35 Resin.

the column effluent were taken at regular time intervals to determine an experimental breakthrough curve and the resin's capacity for that particular cycle. However, similar samples during the resin regeneration step were not taken, as analytical technique to measure SO_4^{2-} ion in highly alkaline ammonia-containing solution is not available at present and the in-situ regeneration conditions for the fixed-bed operations need to be further optimized in a separate study anyhow.

The experimentally determined breakthrough curves at cycle #1, 5, and 10 for candidate resins are shown in Figures 22-24. From these three figures, it can be seen that within the experimental errors the candidate resins showed no degradation in performance. This conclusion was reached based on the closeness of the breakthrough curves for various carbonation/exhaustion cycles.

To further confirm the above conclusion, candidate resin's capacity for each cycle was calculated following the approach described in Section 7.2. The resin's calculated capacities as a function of corresponding cycle number for candidate resins are shown in Figures 25-27. From these figures, it is evident that the variations in the calculated resin's capacities were within $\pm 10\%$. Also, there was no trend showing either a continuous decline or improvement in the resin's capacity. The observed variations in the resin's capacity could be attributed to possible experimental scatter.

Experimentally determined breakthrough curves were then compared with the Antonson's model-based theoretically generated breakthrough curves to determine diffusion parameter, D/R^2 . This matching technique has been described earlier in the Section 7.3. The calculated values of D/R^2 as a function of corresponding cycle

- 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 22. Cycle Efficiency Experiments For IRA-68 Resin

- Flow Rate of K₂SO₄ Solution = 11 cc/min
- Resin volume = 100 cc
- 5 wt% K₂SO₄ solution
- CO₂ Pressure = 10 psig.

Figure 23. 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 24. Cycle Efficiency Experiments For IRA-35 Resin

Figure 25. Calculated Equilibrium Capacity of IRA-68 Resin As a Function of Cycle Number

**Figure 26. Calculated Equilibrium Capacity of IRA-93 Resin
As a Function of Cycle Number**

Figure 27. Calculated Equilibrium Capacity of IRA-35 Resin As a Function of Cycle Number

number for candidate resins are shown in Figure 28. From this figure, it is evident that even the variations in the calculated values of D/R^2 were within $\pm 10\%$. Also, there was no trend showing either a continuous decline or increase in the D/R^2 value, which proved that the resin's micro and macro porous structure more or less remained the same and no fouling had taken place.

Thus, based on Figures 22-28, one can say that the performance as well as overall structure of the candidate resins remained the same for up to ten(10) consecutive cycles.

To confirm that the resin has very high life expectancy and is suitable for repeated use in industrial applications, one needs to carry out hundreds and thousands of consecutive cycles. However, this can only be demonstrated at a bigger pilot scale (prototypical units) since the small size of a bench scale unit and the limited degree of automation would make it very difficult. This is an important parameter to be addressed in the future study, as high resin life expectancy means low replacement (operating) cost, and, therefore, improved process economics.

7.6 Multiattribute Analysis of Fixed-Bed Results & Selection of "Best" Resin

Multiattribute analysis method is described in Section 6.3, and it was used to select three candidate resins for the fixed-bed process variables study. The same method was used again to select the "Best" resin based on the results from the fixed-bed process variables study. As described earlier, this multiattribute analysis uses importance ratings for the various attributes to determine the utility of a particular alternative. The best alternative is the one with the highest calculated utility. The

Figure 28. Variation in Diffusion Parameter as a Function of Cycle Number.

major parameters/variables considered this time include: resin's equilibrium capacity, cycle efficiency, resin cost, solution concentration, dissolved impurities and cation effect. From preliminary evaluation of the results, certain parameters were found to have no or very little effect on the resin's performance, therefore, these parameters were removed from any further consideration. The list of selected parameters/variables with their impact on resin selection and the arbitrarily assigned attribute values (required for multiattribute analysis), all are given in Table 29. Using these arbitrarily assigned attribute values for the major parameters and the approach described earlier, the utilities of the three resins were calculated which are reported in Table 30. Based on these calculated utilities the IRA-68 resin was selected as the "best" resin for further work to develop Best-Process Schematic and related process economics. However, IRA-35 and -93 resins were not too far behind in the utility values. Hence, it is believed that all the three candidate resins would perform well in desulfurizing alkali metal sulfates.

Table 29. Effect of Various Parameters on Resin's Fixed-Bed Performance

Parameter	Contribution in Resin Selection/Performance	Value Assigned to the Attribute
Resin Capacity	Significant	0.30
Cycle Efficiency	Significant	0.25
Cost of Resin	Significant	0.30
Solution Concentration	Small Effect	0.15
Dissolved Impurities	No Effect	-
Cation	No Effect	-

Table 30. Calculated Resin Utilities from Process Variables Study

<u>Resin Type</u>	<u>Utility (U_B)</u>
IRA-68	0.48
IRA-35	0.44
IRA-93	0.40

8.0 PERFORMANCE ENHANCEMENT & RELATIVE LOCATION OF CO_3^{2-} AND SO_4^{2-} IONS IN AFFINITY CHART

As part of the proposed program, simple batch mode experiments were also carried out to explore possible ways of enhancing the resin's capacity for SO_4^{2-} ions. Based on the fixed-bed results on the effects of solution pH and static CO_2 -pressure on candidate resin's equilibrium capacity and related ion-exchange kinetics, the efforts were focused on:

- Evaluating the effect of organic acids in enhancing the resin's equilibrium capacity for SO_4^{2-} , and
- Establishing the relative position of SO_4^{2-} and CO_3^{2-} ions in the affinity chart (to demonstrate beneficial results of higher CO_2 -pressure).

8.1 Effect of Performance Enhancers

The effect of performance enhancers (e.g. low-molecular weight, saturated, aliphatic carboxylic acids) on the exhaustion efficiency of all the three candidate resins was evaluated using small amounts of concentrated solutions of various organic acids. The main reason for using concentrated acids rather than dilute acids, was to avoid unnecessary dilution of the 5 wt % K_2SO_4 solution. Four different organic acids in their

reagent grade chemicals form were used. They are: formic acid (number of carbon atoms = 1), acetic acid (number of carbon atoms = 2), butyric acid (number of carbon atoms = 4) and palmitic acid (number of carbon atoms = 16). The first three acids are water soluble, and therefore, were used in 50 vol % solution form. Palmitic acid is insoluble in water, and therefore, a solution in warm alcohol was prepared. As a result, the behavior of the first three acids was found to be different from that of the palmitic acid.

In Tables 31 - 34, the observed enhancements in the candidate resin's capacity (measured in terms of exhaustion efficiency) as a fraction of different dosages of the various organic acids are given. For all three water-soluble organic acids, a significant improvement in the candidate resin's exhaustion efficiency was observed as the dosage of the acid solution under investigation was increased. Palmitic acid being insoluble in water and used as a mixture with warm alcohol seemed to be ineffective. According to the resin manufacturers, the weak-base, anion-exchange resins are recommended for use in the medium pH of ≤ 7.0 . However, although the starting pH of K_2SO_4 solution is 7.0, as more and more ion-exchange takes place, more and more HCO_3^- ions accumulate in the bulk solution. Because HCO_3^- ions produce alkaline solution with pH ranging from 8.5 - 10, the solution containing mixture of SO_4^{2-} and HCO_3^- ions does not remain neutral. As a result, the exhaustion efficiency may be slightly reduced. By adding small amounts of mild but concentrated and water-soluble organic acids, the H^+ ions provided by the acid would keep the initial solution pH way below 7.0 (probably around 4.5) without unduly diluting K_2SO_4 . With further addition

of the HCO_3^- ions (as a result of the ion-exchange), the overall pH of the bulk solution containing the mixture of the SO_4^{2-} , and HCO_3^- ions would still remain below or at 7.0. As a result, the exhaustion efficiency of the candidate resin would improve significantly. Thus, the water-soluble organic acids are believed to be behaving more like a pH buffering agent. Palmitic acid being insoluble in water is not able to provide necessary H^+ ions to keep the pH of the mixture below 7.0; and therefore, is not able to improve the resin's exhaustion efficiency.

Table 31. Performance Enhancement by Addition of Formic Acid Solution (50 vol. %)

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

<u>Resin Type</u>	<u>Amount of Added Acid Solution (ml/100 ml. resin)</u>	<u>% SO_4^{2-} Removed during Exhaustion</u>	<u>% Improvement</u>
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 32. Performance Enhancement by Addition of Acetic Acid Solution (50 vol. %)

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

<u>Resin Type</u>	<u>Amount of Added Acid Solution (ml/100 ml. resin)</u>	<u>% SO_4^{2-} Removed during Exhaustion</u>	<u>% Improvement</u>
IRA-35	0	51.2	-
	2	52.6	2.3
	4	55.8	9.3
	6	58.1	13.7
	8	67.0	31.3
IRA-93	0	50.0	-
	2	51.7	3.3
	4	57.8	15.7
	6	62.2	24.4
	8	70.4	40.9
IRA-68	0	53.6	-
	2	63.5	18.4
	4	65.7	22.5
	6	70.6	31.6
	8	72.9	35.9

Table 33. Performance Enhancement by Addition of Butyric Acid Solution (50 vol. %)

- 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

Amount of Added Acid Solution (ml/100 ml resin)	% Sulfate Removed during Exhaustion	% 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 34. Performance Enhancement by Addition of Palmitic Acid Solution (50 vol. % 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

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

The observed results on enhancement were further correlated with the respective organic acid's strength (e.g. pKa value) and molecular weight. This correlation is shown in Table 35.

Table 35. Relationship Between Performance Enhancement & pKa Value and Molecular Weight of Organic Acids

Basis: • Performance enhancement by 8 ml of acid (50% v/v) per 50 ml. of resin
• IRA-68 Resin

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

Going from formic acid to butyric acid the pKa value as well as number of carbon atoms (and therefore molecular weight) increase. However, higher pKa value means a weaker organic acid. Hence, from the results given in Table 35, it is seen that for stronger organic acid (e.g. formic acid) the extent of enhancement is lower than that observed for slightly weaker acid (e.g. butyric acid). One would expect this to be the other way that is a stronger organic acid like formic acid to be having a greater influence on the resin's exhaustion efficiency than the weaker butyric acid. It is possible that the anions of the respective organic acids are also occupying some of the active sites on the resin, and that the anions of the lower molecular weight acids such as formic acid would occupy relatively more sites (because of their smaller size) than the bigger anions of the heavier molecular weight acids such as butyric acid. This simultaneous exchange of SO_4^{2-} and organic acid anions would cause less sites to be available for SO_4^{2-} ions in case of the enhancement by the formic acid than in the case with the enhancement by the butyric acid. In the future, this possible role of the

organic acid's anions on the improvement of the resin's exhaustion efficiency need to be evaluated by conducting a well-planned study.

8.2 Relative Location of CO_3^{2-} and SO_4^{2-} Ions in Affinity Chart

Information regarding location of CO_3^{2-} ion with respect to the SO_4^{2-} ion in the affinity chart is important as it can determine whether the carbonate form of resin ($\text{R}_2\cdot\text{CO}_3$) can also exchange the anions with the K_2SO_4 solution as the bicarbonate form of resin ($\text{R}\cdot\text{HCO}_3$) does normally.

In one series of experiments, samples of the candidate resins saturated/exhausted with the SO_4^{2-} ions (that means in the $\text{R}_2\cdot\text{SO}_4$ form), were contacted with the K_2CO_3 solutions of different concentrations. After mixing for a certain time the solution-resin mixture was filtered and the filtrate was analyzed for SO_4^{2-} ion. The amount of SO_4^{2-} present in the filtrate determined the amount of SO_4^{2-} replaced from the exhausted resin by the CO_3^{2-} ions. The results from this series of experiments are given in Table 36. From these results, it is observed that the CO_3^{2-} ion from the solution can replace SO_4^{2-} ion present in the resin. However, the extent of exchange depends on the concentration of the CO_3^{2-} ions in the bulk solution. As the bulk solution concentration increases the extent of SO_4^{2-} ion replacement by the CO_3^{2-} ion also increases. Hence, based on these results, one can only say that the position of the CO_3^{2-} ion in the affinity chart would be very close to the SO_4^{2-} ion.

Table 36. Exchange of CO_3^{2-} Ions with $\text{R}_2\cdot\text{SO}_4$ Form of Resin

Basis: • Resin exhausted using 5 wt % K_2SO_4 solution
• Solution-to-resin ratio = 2
• Mixing time = 30 min.

Type of Resin	Concentration of K_2CO_3 Solution (ppm)	Percentage SO_4^{2-} Exchanged
IRA-68	5,000	9.1
	10,000	24.0
	50,000	68.1
IRA-93	5,000	12.3
	10,000	31.1
	50,000	70.2
IRA-35	5,000	8.7
	10,000	22.0
	50,000	67.6

To confirm whether CO_3^{2-} ion is located to the left or right of the SO_4^{2-} ion in the affinity chart, additional experiments were carried out. In these additional experiments, the candidate resin (available in $\text{R}\cdot\text{OH}$ form) was first converted to $\text{R}\cdot\text{HCO}_3$ form by carbonation. This $\text{R}\cdot\text{HCO}_3$ form of resin was then treated with a 5 wt % K_2CO_3 solution for sufficient time (45 minutes) to convert some or all of the HCO_3^- ions on the resin into the CO_3^{2-} ions form. The resulting mixture was assumed to contain $\text{R}\cdot\text{HCO}_3$ and $\text{R}_2\cdot\text{CO}_3$ forms of resin and was then filtered and washed with de-ionized water and treated with a 5 wt % K_2SO_4 solution. By measuring the SO_4^{2-} ion concentration in the initial and final solution, the percent SO_4^{2-} removal by the candidate resin (in

$R \cdot HCO_3 + R_2 \cdot CO_3$ form) was calculated. The results from these additional experiments are given in Table 37. From this table, it can be seen that the SO_4^{2-} removal efficiencies for candidate resins varied from 31 to 33%.

Table 37. Exchange of SO_4^{2-} Ions with Mixture of $R \cdot HCO_3$ & $R_2 \cdot CO_3$ Forms of Resin

- Basis:
- Some $R \cdot HCO_3$ converted to $R_2 \cdot CO_3$ using 5 wt % K_2CO_3 solution
 - $R \cdot HCO_3 + R_2 \cdot CO_3$ forms of resin exhausted using 5 wt % K_2SO_4 solution
 - Solution-to-resin ratio=2

Type of Resin	Initial SO_4^{2-} Concentration (ppm)	Final SO_4^{2-} Concentration (ppm)	% SO_4^{2-} 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

Under the identical conditions, but with resin being only in $R \cdot HCO_3$ form (see Table 5), the SO_4^{2-} removal efficiencies for candidate resins were:

<u>Resin Type</u>	<u>% SO_4^{2-} Exchanged</u>
IRA-68	60.2
IRA-35	55.4
IRA-93	42.3

Hence, the removal efficiency of the candidate resins decreased as follows:

<u>Resin Type</u>	<u>Decrease in SO_4^{2-} Removal Percentages</u>
IRA-68	27.6
IRA-35	22.5
IRA-93	11.2

Or, the relative decrease in SO_4^{2-} removal efficiency for each of the candidate resins between its ($\text{R}_2 \cdot \text{CO}_3 + \text{R} \cdot \text{HCO}_3$) form and $\text{R} \cdot \text{HCO}_3$ form were:

<u>Resin Type</u>	<u>Relative Decrease in SO_4^{2-} Removal Efficiency</u>
IRA-68	45.8%
IRA-35	40.6%
IRA-93	26.5%

These observed decreases in the SO_4^{2-} removal efficiencies of candidate resins in the mixture containing $\text{R} \cdot \text{HCO}_3$ and $\text{R}_2 \cdot \text{CO}_3$ forms can be attributed to the CO_3^{2-} ions on the resin which possibly is unable to exchange with the SO_4^{2-} ions in the bulk solution.

From the first set of experiments, it was shown that CO_3^{2-} ions from bulk solution exchange with the $\text{R}_2 \cdot \text{SO}_4$ form depending upon the K_2CO_3 solution concentration. Hence, most likely the CO_3^{2-} would be to the left of SO_4^{2-} . The 2nd set of experiments confirmed that SO_4^{2-} ions from the bulk solution would not exchange (at all or easily) with the $\text{R}_2 \cdot \text{CO}_3$ form of resin.

Hence, by combining the results of the two series of experiments, one can say that most likely the CO_3^{2-} ion is present to the left of the SO_4^{2-} ion in the affinity chart as shown below:

This conclusion would also explain the observed increase in the resin's capacity for the SO_4^{2-} ions during the exhaustion/carbonation cycle, as the CO_2 -pressure is increased. Because at higher CO_2 pressure, the $\text{R}_2 \cdot \text{CO}_3$ form is significantly reduced in comparison to $\text{R} \cdot \text{HCO}_3$ form as per the following reaction:

In the future, careful study needs to be carried out to provide direct (rather than an indirect one offered here) evidences of the presence of $R_2 \cdot CO_3$ and $R \cdot HCO_3$ forms of resin under various CO_2 pressure to show their relative preference towards SO_4^{2-} ions.

Based on the fixed-bed study, IRA-68 resin was selected for developing the appropriate process flow schemes and related economics for various desulfurization applications. The major applications that were considered in this study include:

- **Reactivation/desulfurization of spent sorbent material derived from sodium-based induct sorbent injection type flue gas desulfurization (FGD) option.**

Other possible applications such as in the pulp and paper industries, waste incineration and catalytic coal/biomass gasification can be easily developed from the process engineering information for the two major applications that were considered in this study. Hence, efforts in the present study were spent mainly towards developing the applications for the MHD seed regeneration and for reactivation of FGD spent sorbent.

9.1 Trade-Off Between Solution Concentration and Evaporation/Concentration Load

In order to develop the Best Process Schematic, it was necessary to determine the trade-off between the solution concentration used during the resin exhaustion step and the subsequent evaporation/concentration load for the effluent stream. Dilute feed solutions (concentration less than 1 wt %) would give a sulfate removal efficiency approaching 100%. On the other hand, the resin efficiency would drop to the 50-60% range for concentrated feed solutions (concentration ≥ 10 wt %). This would then necessitate the use of significantly more resin than predicted based on the observed equilibrium capacity. Thus, in general, the dilute solution would require lower resin cost than the concentrated solution. Consequently, the dilute solution would require a significantly greater evaporation/concentration of the effluent stream than the concentrated solution. Assuming that the initial sulfate and resulting bicarbonate solutions have nearly similar concentrations, for a 1 wt % solution, 99 lbs of water will need to be

from a 10 wt % solution, one will need to remove only 9 lbs of water per pound of dry salt. Hence, a trade-off study was considered necessary to determine the optimum solution concentration and the related evaporation/concentration load.

Evaporation alone may not be economical in this type of application and might be used in combination with other unit operations. Reverse osmosis (RO) can be used as an initial concentration step for dilute solution which can then be further concentrated by multiple-effect evaporation. Madsen and co-workers⁽⁵¹⁾ have discussed their experience with RO in concentrating industrial solutions. In their work, they have presented membrane data and case specific studies for different solutions. Their work was mostly concerned with the organic solutions containing species such as enzymes, lactose and whey proteins. Wowk and Suffet⁽⁵²⁾ evaluated the RO system for brackish water concentration. Weily and co-workers⁽⁵³⁾ considered an RO system for concentrating the dilute wastewaters from pulp and paper industries. The major species in these wastewaters included mostly sulfates in the range of 1-2 wt %. A detailed comparison of the concentration of sugar solution by RO and evaporation has been presented by Blomgren⁽⁵⁴⁾. He showed that the RO system would be more expensive in comparison to evaporation for sugar solution concentration. Sambrilo and co-workers⁽⁵⁵⁾, Friedlander and co-workers⁽⁵⁶⁾, and Miller⁽⁵⁷⁾, all have presented design procedures and economic analysis for desalting (desalination) by RO. Their procedure and approach was followed in the present work. Thus, based on the review of the available literature, RO was considered appropriate for the initial concentration step for a dilute solution.

To carry out the trade-off study, two alternative schemes were considered for the concentration of dilute effluents from the exhaustion step. They are:

- 1) Process schematic using Reverse Osmosis (RO) in combination with the subsequent evaporation in multiple-effect evaporator, (see Figure 29) and
- 2) Total concentration using evaporation in multiple-effect evaporator (see Figure 30).

In the first schematic the initial concentration was assumed to be carried out by using RO from 1 wt % to 5 wt %. The solution was then assumed to be further concentrated to 47 wt % by using multiple-effect evaporation. 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 for comparison. 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 31. It is 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 would not be very high and will be compensated by the corresponding higher capital costs. Thus a 5 to 6-effect evaporator with steam economies between 3 to 3.5 is considered 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

CG-2461

Figure 29. Process Schematic for Dilute Effluents

CG-2462

Figure 30. Process Schematic for Concentrated Effluents

CG-2544

Figure 31. Effect of Solution Concentration and Number of Evaporator Effects on Relative Cost of Concentration

evaporator was calculated for the ($\text{KHCO}_3/\text{K}_2\text{CO}_3$) system for various inlet concentrations by following the available procedure for evaporator design⁽⁵⁸⁾. The calculated results are presented in Table 38. These results were then correlated to find the steam economy as a function of initial solution concentration. From linear regression this relationship was obtained as:

$$\text{Economy} = 3.144 - 0.107\log(c) \quad (38)$$

where the concentration c is expressed as weight fraction and steam economy is in lb of water/lb of steam. This correlation is considered valid in the concentration range of 1 to 25 wt %. Preliminary calculations for the concentration of 1000 m³/hr of dilute solution were also performed using RO scheme. The calculated costs for concentration by RO are presented against the costs of evaporation by conventional evaporation in Table 39. While performing these calculations, a feed concentration of 10,000 ppm (1 wt %) 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 membranes were considered. Membrane life was assumed to be one year in these calculations. The membrane price was taken at \$200/m² 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 the similar analyses but for different applications, reported in references 54, 56, and 57. Based on these calculations, as shown in Table 39, the Reverse Osmosis proved to be about 20% more expensive compared to the evaporation alone. This RO-based alternative would become unattractive anyhow as the

sensitivity analysis presented later on suggests that the operation of the resin-based desulfurization plant at higher concentrations ($\geq 10\%$) would be more economical. The higher cost in the RO scheme can be attributed to the high cost of replacement of RO membranes. Development and availability of a cheaper membrane would perhaps make this scheme more competitive in the future. In RO, the best possible rejection ratio that can be realized at present is around 97% to 98%. Thus, there will also be a loss of 2 to 3% of incoming carbonate/bicarbonate solution. This factor would also need to be considered while deciding to concentrate the effluents by this scheme.

Table 38. Steam Economies for 6-Effect Evaporator

Basis: • Concentration of 1000 gal/min of $K_2CO_3/KHCO_3$ solution

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

Table 39. Preliminary Costs of Concentration by Evaporation and Reverse Osmosis

Basis: • Costs for 1000 m³/hr of concentration capacity

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

Thus, evaporation in multiple-effect evaporator was judged as the most suitable scheme for concentrating the bicarbonate/carbonate containing effluents. The availability of low pressure steam at lower costs in the sorbent desulfurization system integrated with the corresponding power plant would probably make it still more attractive. Next, to develop the optimum evaporator design, calculations were also performed to find out the optimum number of evaporator effects. Addition of an effect would improve the steam economy but in turn would also add to the fixed cost of the equipment. It was found from simplified calculations that the relative cost of evaporation per 1000 lbs of potassium salt purified would go down from a triple effect to a five effect evaporator (see Figure 31). This analysis of calculating the relative cost of

evaporation was then extended to various inlet solution concentrations. It was found from these additional calculations that the cost of evaporation for the 4-effects evaporator went down as the inlet concentration of the solution increased. (See Figure 32).

9.2 Application to MHD Seed Regeneration

As described earlier, the spent seed material from the coal-fired MHD combined cycle system contains mostly K_2SO_4 with some K_2CO_3 , and coal-ash related minerals. For economic and environmental reasons, this spent seed needs to be desulfurized/regenerated and recycled to the MHD combustor with > 95% recovery efficiency. At present, under DOE sponsorship, the TRW Company is developing a seed regeneration option called the "Econoseed Process" which is based on the old "Formate Process." The major chemical reactions involved in this process and the related operating conditions are as follows:

Ca-formate production:

K-formate production:

The major differences between the Ion-Exchange Resin-Based option and the Econoseed Process-Based option are described in Table 40⁽⁵⁹⁾. As discussed in this table, the Econoseed Process may not be attractive enough for incorporation into the future commercial MHD-based power plants, and therefore, a need exists to develop other simple and low-cost option(s). It is believed that the ion-exchange resin-based

CG-2545

Figure 32. Effect of Solution Concentration on Relative Cost of Concentration for 4-Effects Evaporator

option can satisfy such needs. Hence, the efforts in the present project were geared towards addressing the needs of MHD seed regeneration for the low and high sulfur coals.

Table 40. Major Differences Between Ion-Exchange and Econoseed Process Based MHD Seed Regeneration Options*

PARAMETER	ION-EXCHANGE OPTION	ECONOSEED OPTION
• MAJOR REACTIONS	carbonation/exhaustion and resin-regeneration	$\text{Ca}(\text{COOH})_2$ production and K_2SO_4 conversion to KCOOH
• REACTOR OPERATING CONDITIONS		
- Temperature	ambient to $< 70^\circ\text{C}$	$> 200^\circ\text{C}$
- Pressure	60 - 120 psig of CO_2	1200 - 1300 psig of CO
- Type of Reactor	unconventional packed bed configuration	unproven multi-nozzle, multistage column reactor for $\text{Ca}(\text{COOH})_2$ production
- Automation	easily automated	highly labor intensive
• DEVELOPMENT RISK	very low because commercially used	very high
• MAJOR CHEMICAL CONSUMABLES	CO_2 (NH_3 for resin regeneration is recovered and recycled)	CO and lime
• BY-PRODUCTS/WASTE STREAMS	can give H_2SO_4 , $(\text{NH}_4)_2\text{SO}_4$ or MgSO_4 depending upon local demand	CaSO_4 requires landfilling as no chemical value
• CHLORIDE CONTROL	high chloride removal from product streams	no chloride removal mechanism other than to discard portion of seed
• POTASSIUM LOSS	low	can be high if discarding seed for chloride control
• IMPURITIES IN RECYCLED SEED	can be controlled to any desired low level	low levels of Cl species not possible
• POTENTIAL WASTE DISPOSAL PROBLEM	none	high due to CaSO_4 as well as purged unprocessed spent seed

* Taken from Reference No. 59.

9.2.1 Computer Program for MHD Plant Simulation

Based on the available literature on MHD technology, for regeneration/desulfurization of the spent seed material, the process stream coming out from a wet

electrostatic precipitator (WESP) was considered as an input to the ion-exchange resin-based system. Two separate process flow schemes were developed; one for low sulfur coal (that means high K_2/S ratio case) and another one for the high sulfur coal (that means low K_2/S ratio case). These two flow schemes are shown in Figures 33 and 34 respectively. Based on the trade-off calculations described in Section 9.1, the concentration/evaporation of the resulting bicarbonate/carbonate-containing solution was assumed to be carried out in a multi-effects evaporator system followed by a dryer. The sulfate-containing solution concentration going to the ion-exchange resin column for carbonation/exhaustion step was assumed to be greater than 5 wt %.

As shown in Figures 33 and 34, the composition as well as flow rate of the spent seed material coming to the desulfurization scheme would change depending upon the operating parameters of the MHD power plant. Hence a simple computer program was developed that would calculate the spent seed flow rate and composition under different input conditions to a 300 MW_t MHD power plant. The major variables included in this computer program are shown in Figure 35, and the related information flow chart for calculating the spent seed flow rate and composition is shown in Figure 36.

In an MHD plant it is necessary to have about 1 - 1.5 wt % potassium in plasma, in order to achieve the desired electrical conductivity. The material and energy balance computations suggest that, for a low sulfur coal, the amount of seed required as K_2CO_3 for sulfur removal would not make up this percentage, and therefore, some potassium in the form of K_2SO_4 will also be needed to achieve this potassium level in the plasma. It would thus be more economical to recycle some of the spent seed in the

**Figure 33. Process Schematic For Ion - Exchange Resin - Based Seed
Regeneration Process for Low-Sulfur Coal (High K_2/S Ratio)**

Resin Exhaustion/Carbonation Step

Resin Regeneration Step

**Figure 34. Process Schematic For Ion - Exchange Resin - Based Seed
Regeneration Process for High-Sulfur Coal (Low K_2/S Ratio)**

Figure 35. Major Variables Included in Calculations of Spent Seed Flow Rate and Composition.

Figure 36. Information Flow Chart for Calculating Spent Seed Flow Rate and Composition.

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. Thus it will be necessary to regenerate all or most of the seed in this case. Because there are small amounts of sodium-containing species present in the coal and seed material, instead of K₂/S ratio, a carbonate-to-sulfur (e.g. CO_3/S) molar ratio is considered more appropriate to characterize seed's sulfur removal capability. Based on the recent Westinghouse study⁽⁶⁰⁾, this ratio was assumed to be 1.2 for complete SO_x removal in this study.

Based on the Westinghouse study⁽⁶⁰⁾, the operating conditions of a "base" case 300 MW_t coal-fired MHD plant were fixed as follows:

- * Combustor thermal input = 300 MW_t
- * Ash rejection = 70%
- * Moisture in prepared coal = 2 wt %
- * CO_3/S molar ratio = 1.2
- * Desired potassium level in channel = 1.5 wt %
- * Sulfur removal efficiency = 100%
- * Molar ratio of Na/K in recycled seed = 0.1667
- * Oxygen in the primary air = 35 vol. %
- * Amount of primary air supplied = 95% of stoichiometric requirement

The details about the computer program are available in Reference 61. In brief, this program uses the coal analysis, plant efficiency and plant capacity factor as input parameters to carry out material and energy balance computations. Other major variables that are considered at different stages in the MHD combined cycle plant are

plant are shown in Figure 35. This program was used to calculate the overall material balance for low sulfur coal (Montana Rosebud coal with 1.28 wt % S) and high sulfur coal (Illinois No. 6 coal with 4.29 wt % S) cases. The results in terms of the mass flow rates of major sodium, potassium and sulfur-containing species are given in Table 41. These results compare very well with the similar results reported in the Westinghouse report⁽⁶⁰⁾.

Table 41. Material Balance for a 300 MW_e Coal-Fired MHD Plant

Component	Flow Rate (lb/hr)	
	4.29 wt % S Case	1.28 wt % 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 Remainder Coal	3,441	1,140
Total Sulfur (from Coal + Ash)	3,474	1,321
Sodium Carbonate in Seed	1,972	751.9
Potassium Carbonate in Seed	15,403	5,862
Sulfur Removed by Carbonate	3,472	1,321
Unused Sodium Carbonate	394	150.4
Unused Potassium Carbonate	3,080	1,172
Potassium Tied-up in Slag	120.0	27.6
Potassium Tied-up in Ash	68.8	59.8
Total Potassium Tied-up	188.8	88.0
Potassium from Coal	151.4	78.6
Sodium Sulfate in Spent Seed	2,183	1,169
Potassium Sulfate in Spent Seed	16,069	8,608
Makeup Seed (as K ₂ SO ₄)	2,363	1,265

9.2.2 Computer Program for Seed Regeneration Plant Simulation

A similar material balance program was also prepared to calculate the mass flow rates around major components in the resin-based desulfurization scheme. Appropriate parts of the process flow schemes for low and high sulfur coal cases are shown in Figures 33 and 34 respectively. The major variables to be considered for each important component/operation are shown in Figure 37.

For this computer program, an estimate needs to be made about resin's useable capacity for sulfate ions under desirable operating conditions (CO_2 -pressure ~ 100 psig and superficial velocity ≥ 0.03 cm/s). To determine this, a least square fit was developed between the experimentally determined equilibrium resin capacity at higher CO_2 -pressure (≥ 40 psig) and respective sulfate concentration in the bulk solution. Since from a seed regeneration plant, relatively S-free form of regenerated seed will be required, the column effluent from resin beds cannot afford to have significant concentration of sulfate in $\text{KHCO}_3/\text{K}_2\text{CO}_3$ solution. As a result, the carbonation/ exhaustion cycle needs to be terminated when $C/C_o \leq 0.05$. This means that less than 100% of the experimentally determined resin capacity would be utilized. This value of actual (useable) capacity of IRA-68 resin was calculated by terminating the numerical integration procedure before the breakthrough point (e.g. at which $C/C_o \leq 0.05$). Four separate experimental runs were utilized in this determination and the results are shown in Table 42. Based on these results, the useable capacity of IRA-68 was taken as 80% of the equilibrium value under desirable operating conditions.

To determine the cycle time for switching from carbonation/exhaustion to regeneration step, fixed-bed results were used. This cycle time was found to be

Resin Carbonation / Exhaustion

Resin Regeneration

Figure 37. Major Variables Included in Simulation of Spent Seed Regeneration Based on Ion-Exchange Resin Concept.

inversely proportional to the sulfate concentration in the solution and to the square root of the superficial velocity. In terms of a best fit equation, this relationship was found to be satisfied by:

$$t = \{ 2.0 q / (0.136 c) \} \{ (0.009/v)^{0.5} \} \quad (41)$$

where t is the cycle time in minutes, q is the useable 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 equation was used in the material balance calculations as well as process design calculations for the seed regeneration part. This equation should be used for situations in which c varies from 5 to 10 wt %. Extrapolation beyond that may give erroneous cycle time.

Table 42. Useable Resin Capacity for IRA-68

• Numerical integration terminated at $C/C_0 = 0.05$

Run Number	q/q_{∞}
1	0.798
2	0.813
3	0.821
4	0.791

Average = $\overline{0.806}$

The information flow chart for the computer program simulating the seed regeneration plant operations is shown in Figure 38. The details about the computer program that follows this information flow chart are available in Reference 61. In brief, the program calculates the useable resin capacity based on the input sulfate solution

Figure 38. Information Flow Chart to Perform Process Engineering & Economic Calculations for Resin-Based Desulfurization System.

concentration. The above correlation for cycle time is then used in conjunction with an initial guess of the superficial velocity in the resin bed 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 the two successive iterations is less than the tolerance which was set at 10%.

9.2.3 "Base" Case Calculations

Using the "base" case conditions listed earlier for a 300 MW_t MHD plant, burning Illinois No. 6 coal, calculations were carried out for the flow scheme represented by Figure 34. Coal composition for these calculations was used from the Westinghouse report⁽⁶⁰⁾ for the Scholz plant design. Input spent seed was assumed to be in the form of solution of 10 wt % concentration. (For low sulfur coal as shown in Figure 33, the spent seed will be obtained in the form of a wet cake which then would need 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 five ion exchangers operating in parallel. A simultaneous carbonation was assumed to be going on during this operation at 100 psig. The cycle time for the carbonation/exhaustion process was estimated to be 2.23 minutes under these conditions.

The regenerated solution was then assumed to be concentrated using a 6-effects evaporator to 47 wt % strength. The evaporator was considered to be a long tube evaporator with countercurrent operation. Steam of 150 psig pressure was

considered for evaporation. At 47 wt % concentration a solution of potassium carbonate/potassium bicarbonate will be near its saturation point at a temperature of 98°C. The concentrated solution was then led through a spray dryer to obtain dry potassium carbonate. The spray dryer in consideration was a natural gas operated unit. The carbon-dioxide released during the evaporation and drying steps was assumed to be collected, compressed and recycled to the carbonation step.

The exhausted resin was regenerated 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 in the ammonia recovery unit. Ammonia recovery was assumed to be carried out by flashing the solution at 200 to 250°C. The recovered ammonia was then cooled and recycled. This thermal decomposition of ammonium salts gives sulfuric acid as a by-product, which can be sold after proper concentration if adequate demand exists. However, the present study did not assume any credit from any such sales or debit from additional processing. The design calculations used 10% excess of CO_2 over stoichiometric requirement and ammonia makeup requirements of 20%.

Table 43 gives the equipment sizing for this "base" case. These estimated specifications were then used to calculate the various cost components and to perform economic and sensitivity analysis.

Table 43. Equipment Specifications for MHD Seed Regeneration Plant (Base Case)

Equipment	Design Conditions	Material of Construction	Remarks
Seed Dissolver	-	C.S.	For use with Low Sulfur Coal only
Rotary Drum Filter	-		For use with Low Sulfur Coal only
Spent Seed Receiver	Atmospheric Pressure, 3,000,000 gallons	C.S.	Cone roof tank
CO ₂ Receiver	Design Pressure 400 Psig, Capacity 50 tons	C.S.	
CO ₂ Blower	Design Pressure 150 Psig, Capacity 800 ft ³ /min.	S.S.	Purchased Unit Two Stage
Ion-Exchange Columns	Design Pressure 150 Psig, 5.8' Dia., 8.6' Ht.	C.S.	10 units
Regenerated Seed Tank	Atmospheric Pressure, 2,750,000 gallons	C.S.	Cone roof tank
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 fired
Water Tanks	Atmospheric Pressure, Capacity 4,000,000 gallons	C.S.	2 units
Regenerated Seed Solution Tanks	Capacity 3,000,000 gallons	C.S.	2 units
Ammonia Recovery System	Flash Distillation Unit, Capacity 1300 lb/hr, Includes Condenser, Buffer Tank, etc.	C.S.	Purchased As a Package
CO ₂ Cooler/ Condenser	Water Cooled, Capacity 500 lb/hr.	C.S.	
Sulfuric Acid Tank	Capacity 50,000 gallons	Glass lined	
Ammonia Tank	Capacity 20 tons	C.S.	

9.2.4 Process Economics for "Base" Case

Based on the process design described above, the cost estimation was carried out for a "base" case MHD seed regeneration plant receiving spent seed from a 300 MW_t plant burning Illinois No. 6 high sulfur coal. The guidelines provided by EPRI⁽⁶²⁾, 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:

9.2.4.1 Total Plant Cost

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

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

Process capital was calculated by considering the 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 of inflation, wherever necessary. 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 expenditures 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. Similarly, the project contingency is a capital cost contingency factor that covers the cost of additional equipment 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 about 15% of the total process capital, engineering and home office fees and process contingency. Hence a value of 15% was used in the present study.

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 the 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 44. The components of total plant cost are listed in Table 45. Table 46 lists the components of total plant investment.

Table 44. 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 45. 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 46. Components of Total Plant Investment (Base Case)

Component	Cost (Mid. 92 \$)
Total Plant Capital	11,006,218
Total Prepaid Royalty	33,854
Preproduction Costs	230,931
Land Costs	272,000
Initial Resin Costs	268,309
Initial Inventory Cost	97,315
<u>Total Capital Investment</u>	<u>11,908,627</u>

9.2.4.2 Operating Costs

The operating costs consist 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 need was determined using the per equipment labor requirement given in Peters and Timmerhaus⁽⁵⁸⁾. The present process concept would require about 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 as 1% of the total plant capital cost.

The costs of consumables such as steam, electricity, CO₂, 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⁽⁶²⁾, were used with proper allowance for inflation. The breakup of the variable operating costs is given in Table 47. Components of the fixed operating costs are given in Table 48. To calculate the

annualized fixed cost, factors such as depreciation, interest, taxes and insurance were considered. The breakdown of these fixed charge rates is given in Table 49.

Table 47. 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 ₂ SO ₄)	529,998
<u>Total Variable Operating Cost</u>	<u>3,880,647</u>

Table 48. Components of Fixed Operating Cost (Base Case)

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

Table 49. 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
<u>Total Fixed Charge Rate</u>	<u>12.1</u>

9.2.4.3 Cost of MHD Seed Regeneration ("Base" Case)

Based on the estimated costs given above for the "base" case, the total cost of seed regeneration (TCSR) is given by:

$$\begin{aligned}\text{TCSR} &= \text{Annualized Fixed Cost} + \text{Annual Operating Cost} \\ &= 0.121 (11,908,627) + 3,880,647 + 1,012,176 \\ &= \$6,333,766\end{aligned}$$

Total electricity generated (TEG) from this "base" case plant in Kwh is given by:

$$\begin{aligned}\text{TEG} &= \text{Plant Rating} \times \text{Plant Efficiency} \times \text{Plant Capacity Factor} \times (\text{hrs/year}) \\ &= 300,000 \times 0.333 \times 0.65 \times 8760 \\ &= 569,400,000 \text{ Kwh}\end{aligned}$$

Hence, the cost of seed regeneration in mills/Kwh is given by:

$$\begin{aligned}\text{Cost of seed regeneration (mills/Kwh)} &= \frac{1000 \times \text{TCSR}}{\text{TEG}} \\ &= \frac{1000 \times 6,333,766}{569,400,000} \\ &= \underline{11.1 \text{ mills/Kwh}}\end{aligned}$$

Thus, for the high sulfur coal under the “base” case conditions, the cost of MHD seed regeneration was estimated to be about 11.1 mills/Kwh of power generated. This estimated cost figure would further go down in the absence of the high values of the project and process contingencies and other add-ons suggested by the EPRI methodology 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 seed regeneration in this case was found to be about 9.9 mills/Kwh. It is believed that this cost would go down further if the observed higher resin capacity due to performance enhancement by the organic acids, and/or the regeneration plant integrated with the main MHD power plant, and/or the optimized conditions for the resin regeneration and ammonia recovery are included in the process design and economics.

9.2.5 Cost Comparison with Econoseed Process

Three different levels of sulfur in coal were used to develop cost of seed regeneration using ion-exchange resin-based concept under “base” case conditions. The coal compositions for these three sulfur levels were obtained from the Westinghouse Study⁽⁶⁰⁾ that were corresponding with the Corette plant design (e.g. 1.28 wt % sulfur in Western Montana Rosebud type coal), hypothetical (e.g. 3 wt % sulfur in coal similar to Illinois No. 6 coal), and Scholz plant design (e.g. 4.29 wt % sulfur in Eastern Illinois No. 6 type coal). Costs of seed regeneration for these three levels of coal sulfur using ion-exchange resin-based concept and TRW’s Econoseed Process are given in Table 50. It is evident from this table that the ion-exchange resin-based seed regeneration scheme tends to be cheaper than the Econoseed Process at all sulfur levels. In particular, this cost advantage seems to be a lot higher for the high sulfur coals.

Table 50. Comparison of Cost of MHD Seed Regeneration Based on Ion-Exchange and Econoseed Processes

- Basis:**
- 300 MW_t MHD plant
 - Plant Efficiency = 33.33%
 - Plant Capacity Factor = 65%
 - Complete Sulfur Removal

% Sulfur in Coal	Total Cost of Seed Regeneration in mills/Kwh ^(a)	
	by Ion-Exchange Process	by Econoseed Process ^(b)
1.28% (Corette Plant Design)	6.3 ^(c)	8.8
3.0% (Hypothetical)	9.01	16.8
4.29% (Scholz Plant Design)	11.1	23.1

(a) - Includes capital and operating costs.

(b) - Reported by Westinghouse Corporation(60) for 100% SO₂-removal.

(c) - Also includes concentration/drying of > 35 wt % K₂CO₃ solution taken out as a slip stream from the wet ESP/rotary drum filter system and bypassing most of the seed regeneration plant components (see Figure 33).

9.2.6 Sensitivity Analysis

In order to determine the effect of various parameters such as % sulfur in coal, plant capacity factor 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 computer code ECONO described in Reference 61.

While determining the equipment costs for evaporator, dryer and some other important equipment, installed costs of the equipment were correlated to the respective capacities by using the data from literature^(58,63). For other equipment, appropriate scaling 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 39 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 Corette plant design, %S from Econoseed plant design and %S from Scholz plant design. Compositions for these three coals were obtained from the Westinghouse Study⁽⁶⁰⁾. It is obvious from this plot that the cost of regeneration does not go 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. Besides, for low sulfur coal, the K_2CO_3 -containing process stream separated in the MHD's wet ESP/rotary drum filter set up (see Figure 33) although does not need desulfurization/regeneration still needs concentration and drying before being recycled to the MHD combustor. Hence based on the estimates given in Table 50 and Figure 39, the ion-exchange resin-based process will be more attractive for the high sulfur coals.

The variation in the cost of seed regeneration with the plant capacity factor is shown in Figure 40. In developing data for this figure, the availability of the MHD plant and seed regeneration plant were assumed to be the same. As the capacity factor increases, the variable operating cost components increase. However, the total electricity generated (TEG) also increases. As a result, the total cost of seed regeneration decreases with the increase in the plant capacity factor. By having the same capacity factor for the seed regeneration plant as for the MHD power plant, one needs to design the seed regeneration plant with much higher capacity than necessary. Usually, the availability of the chemical processing plant such as seed regeneration

Figure 39. Cost of MHD Seed Regeneration vs. Sulfur Level in Coal

Figure 40. Cost of MHD Seed Regeneration vs. Plant Capacity Factor

plant here, should be higher than 90% of the total possible time. Hence, it would be more advisable to provide a buffer storage capacity for the spent seed and recycled seed material between the two plants and then carry out the seed regeneration plant operations in a smaller plant independent of the capacity factor of the MHD power plant.

Next, the cost of seed regeneration was evaluated as a function of the MHD plant's overall efficiency in producing electrical energy from coal's thermal energy. The results are shown in Figure 41 and indicate that the cost of seed regeneration goes down as the overall energy conversion efficiency increases. This is due to the reduced coal and seed consumption, and therefore, lower spent seed flow rates to be processed for a specific electrical output.

The sensitivity of the cost to the seed solution concentration is shown in Figure 42. For low solution concentrations, the evaporation load is very high, and the resin capacity (q_m) is relatively lower. Combined effect of these two factors makes the cost of regeneration very high at low solution concentrations. As the solution concentration increases, the cost goes down initially with a very high rate. However, at concentrations of about 10 wt %, the curve flattens suggesting only marginal decrease. Resin performance data at high solution concentrations will be necessary to throw more light on this option. Because beyond ~ 10 wt % K_2SO_4 solution concentration, one may have to operate the resin columns at higher temperatures to keep the potassium sulfate in solution. However, it is possible that the resin's capacity and efficiency may be reduced at high temperature operations. All these may slightly raise the plant

Figure 41. Cost of MHD Seed Regeneration vs. Plant Efficiency

Figure 42. Cost of MHD Seed Regeneration vs. Effluent Solution Concentration

operating costs which may offset the anticipated advantages from the reduced evaporation costs and slightly lower equipment costs.

Thus, based on the sensitivity analysis carried out in this study, the sulfur level in coal, the plant capacity factor and efficiency, and solution concentration, all are found to be the important parameters.

9.3 Application to Desulfurization of Sodium-Based Spent FGD Sorbent

The ion-exchange resin-based desulfurization process can also be utilized for reactivation/desulfurization of the sodium-based FGD sorbent. The exhausted sorbent in this case will be in the form of sodium sulfate which has to be converted to active form consisting of sodium bicarbonate/sodium carbonate. The activated sorbent is then reutilized to remove sulfur as SO_2 from the flue gases in a conventional coal-fired power plant. A simple material balance was carried out for a 1000 MW_t power plant for low (sulfur level < 1 wt %) as well as high (sulfur level > 3 wt %) sulfur coal. A schematic of the SO_2 -removal step integrated with the sorbent reactivation/regeneration step is shown in Figure 43. In the simple material balance calculations, stoichiometric amount of sodium was considered for SO_2 removal and the removal of sulfur oxides was assumed to be complete. Recycled sorbent was assumed to be as dry Na_2CO_3 powder. The plant capacity factor was assumed to be 65% for both, the power plant as well as the sorbent regeneration plant. Similarly, the overall energy conversion efficiency of the conventional power plant was assumed to be 33.3%.

Using the process design and economic calculations carried out for the MHD seed regeneration application, and appropriate scale up procedures, the equipment size and various fixed and variable cost components were calculated. For the high

Figure 43. Process Schematic For Ion - Exchange Resin - Based Desulfurization of Sodium - Based FGD Sorbent

SO₂ - Removal & Resin Exhaustion/ Carbonation Step

Resin Regeneration Step

sulfur coal case, these estimated cost components are given in Tables 51-54. From these calculations, the cost of sorbent reactivation (in mills/Kwh) and total capital investment (in \$/Kw) were calculated for low and high sulfur coal cases. These results are given in Table 55.

Table 51. Components of Total Plant Capital for Spent Sorbent Reactivation Plant

Basis: 1000 MW_t conventional plant burning high sulfur coal.

Component	Cost (Mid. 92 \$)
Process Capital	13,811,446
General Facilities Capital	697,184
Engineering & Home Office Fees	976,042
Project Contingency	2,865,432
Processs Contingency	4,183,118
<u>Total Plant Capital</u>	<u>22,533,222</u>

Table 52. Components of Total Plant Investment for Spent Sorbent Reactivation Plant

Basis: 1000 MW_t conventional plant burning high sulfur coal.

Component	Cost (Mid. 92 \$)
Total Plant Capital	22,533,222
Total Prepaid Royalty	69,716
Preproduction Costs	475,564
Land Costs	560,139
Initial Resin Costs	552,538
Initial Inventory Cost	200,404
<u>Total Capital Investment</u>	<u>24,391,583</u>

**Table 53. Components of Variable Operating Cost for Spent Sorbent
Reactivation Plant**

Basis: 1000 MW_t conventional plant burning high sulfur coal.

Component	Cost (Mid. 92 \$)
Steam (150 psig)	3,250,453
Process water	754,125
Ammonia (Make-Up)	377,958
CO ₂ (Make-Up)	4,044,186
Natural gas	1,009,497
Cooling water	188,531
Resin replacement (20% per Year)	178,691
Make-up seed (As Na ₂ SO ₄)	794,997
<u>Total Variable Operating Cost</u>	<u>10,598,438</u>

**Table 54. Components of Fixed Operating Cost for Spent Sorbent
Reactivation Plant**

Basis: 1000 MW_t conventional plant burning high sulfur coal.

Component	Cost (Mid. 92 \$)
Operating Labor	2,775,699
Maintenance & Overhead Charges	2,464,680
<u>Total Fixed Operating Cost</u>	<u>5,240,379</u>

Table 55. Preliminary Costs for Spent Sorbent Reactivation in Sodium-Based FGD System

- Basis: • 1000 MW₁ conventional coal-fired power plant
 • 65% Plant Capacity Factor
 • 33.3% Overall energy conversion efficiency

% Sulfur in Coal	Total Capital Investment (\$/Kw)	Total Cost of Spent Sorbent Reactivation (mills/Kwh)*
4.29	73.2	9.9
1.28	39.9	5.5

* Includes capital and operating costs.

Next, the ion-exchange resin-based sorbent reactivation system was integrated conceptually with the SO₂-removal step using in-duct injection of the sodium-based sorbent. The process schematic of this integrated concept is shown in Figure 44. The SO₂-removal step in this schematic was assumed to include, operations such as sodium-based sorbent injection in the duct, spent sorbent collection with fly-ash in the baghouse or electrostatic precipitator and any required flue gas conditioning before releasing via the stack. The spent sorbent reactivation part included operations such as dissolution of the spent sorbent/fly-ash mixture, separation of insoluble fly-ash material, desulfurization of SO₄²⁻ containing solution in ion-exchange resin columns, concentration/drying of HCO₃⁻/CO₃²⁻ containing effluent, resin regeneration and ammonia recovery/recycle. Using available EPRI report⁽⁶⁴⁾, the total capital investments for the low-sulfur case (e.g. sulfur level < 1 wt %) and high sulfur case (e.g. sulfur level ≥ 3 wt %) were estimated. The total capital investments for the sorbent reactivation/regeneration part were used from the present study. The total capital

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Figure 44. Process Schematic for Anion-Exchange Resin-Based Desulfurization of Sodium-Based Spent FGD Sorbent

investments for the proposed scheme are compared with the EPRI reported similar capital investments for the commercially available regenerable FGD options such as Wellman Lord and MgO scrubbing processes in Table 56.

Table 56. Preliminary Capital Cost Estimate for Regenerable Sodium-Based FGD System

Basis: 1000 MW₁ conventional coal-fired power plant

OPTION	← Total Capital Investment →	
	Low-Sulfur Coal (\$/kw)	High-Sulfur Coal (\$/kw)
● Ion-Exchange Resin-Based Concept		
- Cost of Sorbent Reactivation	40	73
- Cost of SO ₂ -Removal*	25	50
- Total	65	123
● Wellman Lord & MgO Scrubbing Process**	-	275

* Estimated based on information in Reference 64.

** From Reference 65.

The Wellman-Lord process is a high temperature process and the MgO scrubbing process has significant operating problems. The preliminary capital cost estimates shown in Table 56 indicate that the FGD system, based on in-duct sorbent injection of sodium carbonate/bicarbonate coupled with the resin-based regeneration will be cheaper and probably easier to operate than these commercially available options. Hence, these preliminary estimates do warrant further analysis and development of the proposed concept.

10.0 CONCLUSIONS

Most of the workscope that was proposed to DOE/PETC was accomplished in the present study. Optimization of the resin regeneration step was not carried out because the analytical techniques to measure ions such as SO_4^{2-} and OH^- , in the presence of highly alkaline NH_4^+ ion-containing solutions are not currently available. Similarly, the simultaneous removal of Cl^- and SO_4^{2-} ions, as well as ammonia recovery/recycle step by thermal decomposition of the resulting ammonium salts, will be evaluated under an ongoing separate DOE program. Results from this separate study are not yet available. In absence of this critical information about resin regeneration and ammonia recovery, conservative assumptions were made in carrying out the cycle efficiency experiments, developing the process economics and determining the cycle time for process engineering related calculations. In spite of these limitations, the present DOE/PETC sponsored project at UTSI was quite successful and has identified an attractive option for desulfurizing the alkali metal sulfates containing spent sorbent materials. The major conclusions/observations derived from this study are as follows:

- Efficiencies of resin exhaustion step and regeneration step differed from resin to resin. This implied that physical and chemical structures of candidate resins must play a role as to the accessibility of the active sites in the resin interior and the affinity with which the various ions would be held or can be exchanged from these sites.

- The efficiency of exhaustion step decreased with an increase in the solution concentration. This implied that for commercial applications a trade-off will be required to optimize the resin cost versus the cost of evaporation and concentration load for the ensuing effluents.
- Based on the statistical analysis of the batch mode screening results, the IRA-68, -35 and -93 performed better than the rest of the candidate resins.
- Under the static CO₂ atmosphere, the equilibrium capacity of IRA-68, -35 and -93 resins increased as the CO₂-pressure increased and then leveled off around 80-120 psig range. However, the CO₂-pressure did not affect the overall ion-exchange kinetics.
- The solution concentration affected the resin performance in two ways. First, the equilibrium capacity of resin increased with the solution concentration and then leveled off (hence satisfied by the Langmuir isotherm type relationship). Second, the diffusion parameter, D/R^2 either increased (for IRA-68) or remained constant (for IRA-35 and -93) with the increase in the solution concentration.
- Product inhibition effect caused by different amounts of KHCO₃ in the initial solutions indicated that up to a molar ratio of KHCO₃/K₂SO₄ equal to 0.1 there was a positive effect on the resin's capacity. However, beyond 0.1, the capacity decreased significantly with the further increase in the molar ratio. This ratio, however, did not affect the overall ion-exchange kinetics.

- Superficial velocity seemed to affect the rate controlling step. At low velocity (e.g. < 0.009 cm/s), most likely the liquid-film diffusion controlled the overall mass transfer rate that could be satisfied by the Selke and Bliss type model. At higher velocity (e.g. > 0.009 cm/s), the solid-phase diffusion seemed to control the overall rate and could be satisfied by the Antonson's model.
- Within the range of values tried, the bed height and dissolved impurities did not significantly affect the performance of the three candidate resins. On the other hand, a slightly acidic pH of the initial solution seemed to improve the equilibrium capacity of the resin.
- Within the experimental scatter, the IRA-68, -35, and -93 resins showed no significant degradation in their performance up to ten(10) consecutive cycles of carbonation/exhaustion, and regeneration in the fixed-bed mode. This conclusion is supported by the following observations:
 - closeness of the experimentally determined breakthrough curves for carbonation/exhaustion cycles,
 - calculated equilibrium capacity of candidate resins varying randomly within $\pm 10\%$, and
 - calculated diffusion parameter, D/R^2 , for candidate resins varying randomly within $\pm 10\%$.

- Based on the multiattribute analysis of the fixed-bed process variables study results, the IRA-68 resin was found to be the “best” resin. However, IRA-35 and -93 resins were not too far behind and are believed to perform equally well in desulfurizing alkali metal sulfates.
- Small amounts (up to 8 ml per 100 ml. of 5 wt % K_2SO_4 solution) of concentrated water-soluble organic acids such as formic, acetic and butyric acids were found to increase the resin's equilibrium capacity significantly (e.g. from 19 to 56%). However, in case of water-insoluble palmitic acid, such enhancement was found to be negligible or absent. The major reason behind the increase in the resin's capacity is believed to be due to the pH buffering action provided by the organic acid in maintaining the mixture/solution pH below 7.0.
- From a limited number of experiments, it was found that in the affinity chart for the weak-base, anion-exchange resins, the CO_3^{2-} and SO_4^{2-} ions would be very close to each other. Most likely the CO_3^{2-} ion will be slightly to the left (that means on the OH^- side) of the SO_4^{2-} ion. This conclusion/observation also seems to explain the observed increase in the resin's capacity for SO_4^{2-} ions during the carbonation/exhaustion cycle, as the CO_2 -pressure was increased.
- From simple calculations, it was demonstrated that the solution concentration scheme making use of reverse osmosis to concentrate very dilute (i.e. < 5 wt % solution) carbonate/bicarbonate containing solution will be

about 20% more expensive than the scheme involving only multi-effects evaporation. Also, showed that a 5-effects evaporator would be economically better than a 3-effects evaporator and that the relative cost of concentration by mere evaporation would asymptotically decrease as the solution concentration increases to about 10 wt % strength.

- In terms of mid 1992 dollars, the cost of MHD seed regeneration for a "base" case situation (e.g. 300 MW_t plant burning high sulfur Illinois No. 6 coal, plant efficiency = 33.3% and plant capacity factor = 65%), was estimated to be about 11.1 mills/Kwh. In comparison, the cost of seed regeneration by the presently considered Econoseed Process for 100% SO₂-removal has been reported by the Westinghouse study as equal to 23.1 mills/Kwh. For low-sulfur coal (e.g. for 1.28 wt % S used in the Corette plant design) the costs of seed regeneration were estimated as 6.3 mills/Kwh for the ion-exchange option and 8.8 mills/Kwh for the Econoseed Process. From sensitivity study, the sulfur level in the coal, plant capacity factor and efficiency, and sulfate solution concentration were identified as the major parameters affecting the regeneration cost.
- For reactivating the spent, sodium-based sorbent material received from a regenerable duct-injection type FGD option, the cost of reactivation for a conventional 1000 MW_t plant burning high sulfur coal (e.g. ≥ 3 wt % sulfur level), was estimated to be about 9.9 mills/Kwh. The corresponding total capital investment was estimated to be about \$73/Kw. This preliminary estimate compares very well with the similar estimates for the

currently available but less desirable options such as the Wellman Lord (requires high temperature operations) and MgO Scrubbing Processes (has various operational problems).

In summary, the weak-base, anion-exchange resin-based desulfurization concept evaluated under this DOE/PETC program, has been shown to be an attractive option for MHD seed regeneration, and for reactivating the spent sorbent materials from the sodium-based FGD systems and from scrubbers in waste incinerators.

11.0 RECOMMENDED FUTURE WORK

It is successfully demonstrated in the previous sections that from process complexity and severity as well as other technical, economic and environmental considerations, the ion-exchange, resin-based desulfurization process offers an attractive option for MHD seed regeneration and spent sorbent reactivation. Also, as a result of the present program some new leads have been identified and some additional gaps in the data have been found. Hence, to develop this resin-based desulfurization concept into a viable commercial option, an additional development program is required. This program at the least should address the following important issues/concerns and valuable leads:

- Demonstrate the technical feasibility of the concept at the pilot plant scale and evaluate effects of major process parameters including long-term cycle efficiency (i.e. resin's life), high temperature operations, > 10 wt % solution concentration, etc. using representative feed materials.

- Develop an analytical technique that has a very fast response to measure on-line, anions such as SO_4^{2-} , OH^- , Cl^- , HCO_3^- , and CO_3^{2-} in the highly alkaline solutions containing potassium, sodium and ammonium type cations.
- Optimize processing steps such as resin regeneration and carbonation that are not yet fully developed or evaluated in detail. (The thermal decomposition of ammonium salts for recovery/recycle of ammonia, and simultaneous removal of SO_4^{2-} , and Cl^- are planned for evaluation in the separate DOE/HMJ Inc. sponsored Phase II SBIR program at UTSI).
- Evaluate the role of water-soluble organic acid in improving the performance of the weak-base, anion-exchange resin and determine the optimum conditions for successful incorporation of this performance enhancement idea into the overall process concept.
- Evaluate in detail the product-inhibition (PI) effect caused by the HCO_3^- -containing product material in the exchange of the SO_4^{2-} ions from the feed materials; and identify conditions/options to minimize/eliminate any possible adverse impacts. Similarly, evaluate using well-characterized samples of feed materials, the effects of low levels of dissolved impurities on the resin's performance.

- Validate the relative locations of the CO_3^{2-} and SO_4^{2-} ions in the affinity chart by carrying out additional experiments under different CO_2 pressures and determine the role of carbonation in improving/maintaining the resin's capacity for SO_4^{2-} ions.
- Carry out detailed system analysis for an integrated MHD and seed regeneration plant as well as integrated in-duct sorbent injection system and spent sorbent reactivation plant. From such system analysis, identify optimum conditions.
- Lastly, operate such integrated SO_2 -removal step and seed/sorbent reactivation step to develop information on impurities build-up, acceptable levels of impurities in various process streams and verification of the optimum conditions identified from the above-mentioned system analysis. As a part of this test program, it is recommended to test an advanced upcoming process concept involving continuous operation of the resin-filled column. (A presently available continuous ion-exchange system, marketed by the Advanced Separation Technologies, Incorporated in the U.S.A. and commercially used in Bogota, Colombia for manufacture of KNO_3 from KCl , is shown in Figure 45). Use of this type of continuous system is believed to work fine for systems involving short cycle times and to further reduce the cost of desulfurization significantly.

Figure 45. Commercially Available Typical Continuous Ion-Exchange System
(Taken from the Technical Brochure provided by Advanced Separation Technologies, Inc.)

In summary, the ion-exchange resin-based desulfurization concept can be equally well applied to sodium, potassium or any soluble alkaline earth metal salts. A successful development program as outlined above can provide an attractive, low-cost, low-temperature, regenerative FGD system for conventional plants and scrubber technology for waste incineration as well as efficient second generation seed regeneration option for the MHD-based advanced energy conversion technology. At UTSI, we continue to have confidence that a resin-based desulfurization system has an excellent potential for successful applications in a variety of energy conversion and chemical waste destruction areas.

12.0 REFERENCES

1. Sheth, A. C. and T. R. Johnson, "Evaluation of Available MHD Seed Regeneration Processes on the Basis of Energy Consideration," ANL/MHD-78-4, a report prepared by Argonne National Laboratory for DOE under contract no. W-31-109-Eng-38, September 1978.
2. Sheth, A. C., et al., "Seed Recovery and Regeneration in Coal-Fired, Open-Cycle Magnetohydrodynamic Systems," Proceedings of the 9th Annual Energy-Sources Technology Conference and Exhibition, New Orleans, February 23-27, 1986. Published in Technical Economics, SynFuels and Coal Energy-1986, PD-Vol. 5, edited by J. B. Dicks, sponsored by ASME, February 1986.
3. Matty, R. E., "Evaluation of Alternative Seed Regeneration Processes Applicable to Coal-Fired MHD Power Plant," FE-1760-33, a report prepared by The University of Tennessee Space Institute for DOE under contract no. EX-76-C-01-1760, January 1979.
4. Krumreich, B. M., "Seed Regeneration Processes for Coal-Fired MHD Power Plants," DOE/CH-10018-14, a report prepared by The Babcock and Wilcox Company for DOE under contract no. DE-AC02-79CH10018, May 1985.
5. Jackson, D. M., "Evaluation of Seed Regeneration Processes for Coal-Fired MHD Power Plants," FE-1760-36, a report prepared by The University of Tennessee Space Institute for DOE under contract no. DE-AC02-79ET10815, July 1985.

6. "Application of Ion-Exchange Technique in Seed Regeneration Experiments for MHD Power Generation," an internal document, Chong Sho Chemical Fraternity, Su Chow Area Chemical Institute, China, 1980.
7. Butler, W. A., "Bench Scale Evaluation of Anion-Exchange Resin-Based Seed Regeneration Concept for Coal-Fired Magnetohydrodynamics Power System," a thesis presented for M.S. degree, The University of Tennessee, Knoxville, Tennessee, December 1986.
8. Modeste, D. C., "Evaluation of Improved Anion-Exchange Resin-Based Seed Regeneration Concept for Coal-Fired MHD Power System," a thesis presented for M.S. degree, The University of Tennessee, Knoxville, Tennessee, December 1988.
9. Liberti, L., D. Petruzzelli, G. Boghetich, R. Passino, "A New Approach to Ion Exchange Kinetics," In: Naden, D., M. Streat, Ion Exchange Technology, N. Y., Halsted Press, p. 201, 1984.
10. Yoshida, Hiroyuki, Takeshi Kataoka, "Intraparticle Ion-Exchange Mass Transfer in Ternary Systems: Theoretical Analysis of Concentration Profiles," The Chemical Engineering Journal, 39, p. 55, 1988.
11. Helfferich, F., M. S. Plesset, "Ion Exchange Kinetics. A Nonlinear Diffusion Problem," The Journal of Chemical Physics, 28 (3), p. 418, March 1958.
12. Tondeur, D., "Theory of Ion Exchange Column," Chemical Engineering Journal, 1, p. 337, 1970.

13. Novosad, J., A. L. Myers, "Thermodynamics of Ion Exchange as an Adsorption Process," The Canadian Journal of Chemical Engineering, 60, p. 500, August 1982.
14. Hall, Kenneth R., Lee C. Eagleton, Andreas Acrivos, Theodore Vermeulen, "Pore- and Solid-Diffusion Kinetics in Fixed-Bed Adsorption under Constant-Pattern Conditions," I&EC Fundamentals, 5 (2), p. 212, May 1966.
15. Michaels, Alan S., "Simplified Method of Interpreting Kinetic Data in Fixed-Bed Ion Exchange," Industrial and Engineering Chemistry, 44 (8), p. 1922, August 1952.
16. Tan, K. S., I. H. Spinner, "Dynamic of Cyclic Fixed Bed Ion Exchange: An Analysis Based on a Linear Mass Transfer Model," The Canadian Journal of Chemical Engineering, 49, p. 105, February 1971.
17. Helfferich, Fredrich G., "Conceptual View of Column Behavior in Multicomponent Adsorption or Ion-Exchange Systems," In: Sherman, John D., Adsorption and Ion Exchange, American Institute of Chemical Engineers, New York, p. 1, 1984.
18. Pal, G. C., A. K. Chakravarti, M. Sengupta, "Studies in Ion Exchange Equilibria II: Some Cation and Anion Exchange Selectivities in Amberlite Resins," Ion Exchange and Membranes, 2, p 21, 1974.
19. Smith, Robert P., Edward T. Woodburn, "Prediction of Multicomponent Ion Exchange Equilibria for the Ternary System SO_4^{2-} , NO_3^- , Cl^- from Data of Binary Systems," AIChE Journal, 4 (4), p. 577, July 1978.

20. Bolden, Wayne B., Frank R. Groves, Jr., "Amine Recovery by Ligand Exchange: Pore Diffusion Model," Industrial and Engineering Chemistry Research, 29 (1), p. 116, January 1990.
21. Bolden, Wayne B., Ted White, Frank R. Groves, Jr., "Continuous Fixed-bed Ligand Exchange: The Shrinking-Core Model," AIChE Journal, 35 (5), p. 849, May 1989.
22. Bunke, G., D. Gelbin, "Breakthrough Curves in the Cyclic Steady State for Adsorption Systems with Concave Isotherms," Chemical Engineering Science, 33, p. 101, 1978.
23. Zuyi, Tao, Niu Jinlong, "Shell-Progressive Model with Changing Bulk Concentration and Exchanger Volume in Ion Exchange," Solvent Extraction and Ion Exchange, 8 (1), p. 99, February 1990.
24. Ball, M., N. J. Ray, "An Ion-Exchange Resin Testing Service-- Methods and Findings," Effluent and Water Treatment Journal, 16, p. 73, February 1976.
25. Adams, G., P. M. Jones, J.R. Miller, "Kinetics of Uptake by Weak-Base Anion Exchangers," Journal of the Chemistry Society, London, p. 2543, 1969.
26. McNulty, James T., "Anion Exchange Resin Kinetics in Mixed Bed Condensate Polishing," In: Naden, D., M. Streat, Ion Exchange Technology, N. Y., Halsted Press, p. 50, 1984.
27. Lee, S. C., C. C. Hsiang, H. Huang, G. Ting, "A Comparative Study of Gel-Type and Macroreticular Exchange Resins for the Separation of Rare Earth Elements," Separation Science and Technology, 25 (13-15), p. 1857, 1990.

28. Glueckauf, E., "Principles of Operation of Ion-Exchange Columns," Ion Exchange and Its Applications, London, Society of Chemical Industry, 1955.
29. Patell, S., J. C. R. Turner, "The Equilibrium and Sorption Properties of some Porous Ion-Exchangers," Journal of Separation Process Technology, 1 (1), p. 42, 1979.
30. Calmon, C., "Impact of Improved Ion-Exchange Materials and New Techniques on Separation Performance," In: Sherman, John D., Adsorption and Ion Exchange, American Institute of Chemical Engineers, New York, p. 84, 1984.
31. Kunin, Robert, "Further Studies on the Weak Electrolyte Ion Exchange Resin Desalination Process (DESAL Process)," Desalination, 4, p. 38, 1968.
32. Popper, Karel, Robert J. Bouthilet, Vladimir Slamecka, "Ion-Exchange Removal of Sodium Chloride from Water with Calcium Hydroxide As Recoverable Regenerant," Science, 141, p. 1038, 1963.
33. Wilmoth, Roger C., Robert B. Scott, James L. Kennedy, "Investigation of Ion Exchange Treatment of Acid Mine Drainage," Kennedy Symposium on Coal Mine Drainage Research, 7th, Louisville, Kentucky, 1977.
34. Zabban, Walter, Theodore Fithian, "Converting AMD to Potable Water by Ion Exchange Treatment," Coal Age, 77 (7), p. 107, July 1972.
35. Sturla, Piero, "Demineralization of Brackish Waters by Means of Ion-Exchange," Proceedings of the First International Symposium on Water Desalination, Washington, D.C., October 1965.

36. Vermeulen, Theodore, Badawi W. Tleimat, Gerhard Klien, "Ion-Exchange Pretreatment for Scale Prevention in Desalting Systems," Desalination, 47, p. 149, 1983.
37. Evans, Sheldon, Theo F. J. Maalman, "Removal of Organic Acids from Rhine River Water with Weak Base Resins," American Chemical Society, 13 (6), p. 741, June 1979.
38. Naumczyk, J., L. Szpyrkowicz, F. Zilio Grandi, "Organics Isolation from Fresh and Drinking Waters by Macroporous Anion-Exchange Resins," Water Research, 23 (12), p. 1593, December 1989.
39. Rook, John J., Sheldon Evans, "Removal of Trihalomethane Precursors from Surface Waters Using Weak Base Resins," Journal American Water Works Association, 71 (9), p. 520, 1979.
40. Korngold, E., "Removal of Nitrates from Potable Water by Ion Exchange," Water, Air, and Soil Pollution, 2, p. 15, 1973.
41. Liberti, L., "Ion Exchange Advanced Treatment to Remove Nutrients from Sewage," Physicochemical Methods for Water and Wastewater Treatment, New York Elsevier Scientific, p. 225, 1982.
42. George, D'Arcy R., J. M. Riley, Laird Crocker, "Preliminary Process Development Studies for Desulfating Great Lake Salt Brines and Sea Water," Report of Investigations 6928, U.S. Dept. of the Interior, Bureau of Mines, 1967.
43. Velmurugan, Sankaralingam, et al., "Behaviour of Ion Exchange Resins and Corrosion Inhibitors in Dilute Chemical Decontamination," Journal of Nuclear Science and Technology, 28 (6), p. 517, June 1991.

44. Kapor, J. N., "Recovery of Potassium from Distillery Slop by Ion-Exchange Technique," Fertilizer Technology, 16 (1), p. 57, 1979.
45. Tsuboi, Izumi, Eiichi Kunugita, Isao Komasaawa, "Recovery and Purification of Boron from Coal Fly Ash," Journal of Chemical Engineering of Japan, 23 (4), p. 480, August 1990.
46. Hines, William W. and Montgomery, Douglas C., "Probability and Statistics in Engineering and Management Science," Wiley, New York, 1990.
47. Canada, John R. and Sullivan, W. C., "Economic and Multiattribute Evaluation of Advanced Manufacturing System," Prentice Hall, New Jersey, 1989.
48. Selke, W. A. and H. Bliss, "Application of Ion-Exchange, Copper-Amberlite IR-120 in Fixed Beds," Chemical Engineering Progress, 46 : p. 509, 1950.
49. Antonson, C. R., "Adsorption of Ethane in Molecular Sieve Particles," a Ph.D. dissertation submitted to Northwestern University, Evanston, Illinois, 1968.
50. Sheth, A.C., et al., "Desulfurization of Alkali Metal Sulfates Using Anion-Exchange Resins," AIChE Journal, v. 35, no. 3, p. 519-522, March 1989.
51. Madsen, R. Frik, "Experience with Concentration and Separation of Industrial Solutions with Reverse Osmosis and Ultrafiltration," Filtration and Separation, v. 9, no. 5, p. 567, September/October 1972.
52. Wowk, A. M. and I. H. Suffett, "Concentration of Organic and Inorganic Solutes in Aqueous Solution by Reverse Osmosis and Ultrafiltration," 188th National Meeting of American Chemical Society, Division of Environmental Chemistry, v. 24, no. 2, Philadelphia, Pennsylvania, August 26-31, 1984.

53. Weiley, A. J., G. A. Dubey, J. M. Holderby and A. C. F. Ammerlaan, "Concentration of Dilute Pulping Wastes by Reverse Osmosis and Ultra Filtration," Journal WPCF, v. 42, no. 8, August 1970.
54. Blomgren, Y., Joensson, A. S. and R. Wimmerstedt, "Concentration of Acid Hydrolyzate by Reverse Osmosis and Mechanical Vapor Recompression Evaporation," Journal of Wood Chemistry and Technology. Industrial and Engineering Chemistry, v. 11, no. 1, March 1991.
55. Sambrillo, D. and B. Kunst, "On the Calculation of the Stream Concentrations in Reverse Osmosis Processes," Desalination, Elsevier Science Publishers B. V., Amsterdam, 1986.
56. Friedlander, H. Z. and Robert N. Rickles, "Desalting by Reverse Osmosis," Chemical Engineering, p. 145, June 6, 1966.
57. Miller, E. F., "Reverse Osmosis Desalting," Chemical Engineering, p. 153, November 18, 1968.
58. Peters, Max S. and Timmerhaus, K. D., Plant Design and Economics for Chemical Engineers, 4th ed. McGraw-Hill, Inc., New York, 1991.
59. Sheth, A. C., et al., "Recent Advances in Anion-Exchange Resin-Based Seed Regeneration Process," Proceedings of the 31st Symposium on Engineering Aspects of Magnetohydrodynamics, Whitefish, Montana, June 19 - July 1, 1993.
60. Lance, J. R., "Conceptual Design of a Coal-Fired MHD Retrofit Plant, Seed Regeneration System Study (II)," a topical report no. 93-9TKO-MHDCR-R1 prepared by the Westinghouse Electric Corporation for the U.S. DOE/PETC under contract no. DE-AC22-87PC79668, November 1992.

61. Dharmapurikar, R. S., "The Anion-Exchange Resin-Based Desulfurization Process for Spent Seed Regeneration in an MHD Power Plant," a thesis presented for M.S. degree, The University of Tennessee, Knoxville, Tennessee, May 1994.
62. "Technical Assessment Guide," v. 1, Electric Power Research Institute, Palo Alto, California, 1986.
63. Perry, R., Don Green, eds. Chemical Engineer's Handbook, Sixth Edition, McGraw-Hill, Inc., New York, 1991.
64. Moore, T., "Dry Capture of SO₂," EPRI Journal, p. 20, March 1984.
65. "Economic Evaluation of FGD Systems: Regenerable FGD Processes, High-Sulfur Coal., CS-3342, volume 2, a report prepared by the Stearns-Roger Engineering Corporation, Denver, Colorado for Electric Power Research Institute under the Research Project No. 1610-1, December 1983.