DOE/PC/90309--4

DE92 003083

**ANION-EXCHANGE RESIN-BASED
DESULFURIZATION PROCESS**

Received by OSTI

NOV 20 1991

Annual Technical Progress Report

AUGUST 9, 1990 - SEPTEMBER 30, 1991

Prepared by:

Atul C. Sheth
Sterling D. Strevel

The University of Tennessee Space Institute
Tullahoma, Tennessee 37388

DOE Grant No. DE-FG22-90PC90309

"US/DOE Patent Clearance is not required prior to the publication
of this document."

MASTER

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

yes

Table of Contents

OC 1 6 1991

	<u>Page</u>
EXECUTIVE SUMMARY	1
1.0 INTRODUCTION	3
2.0 OBJECTIVES AND PROJECT DESCRIPTION	4
2.1 <u>Task 1.1 Literature Survey, Vendor Contacts and Screening of Resins</u>	6
2.2 <u>Task 1.2 Process Variables Study and Improving Resin Performance</u>	6
2.3 <u>Task 1.3 Optimization of Resin Regeneration Step and Evaluation of Performance Enhancers</u>	7
2.4 <u>Task 1.4 Development of Best-Process Schematic and Related Economics</u>	7
2.5 <u>Task 1.5 Project Management and Reporting</u>	7
3.0 PROJECT STATUS/PROGRESS TO DATE	7
3.1 <u>Task 1.1</u>	10
3.2 <u>Task 1.4</u>	21
3.3 <u>Task 1.5</u>	22
4.0 PLANS FOR NEXT REPORTING PERIOD	23
5.0 SUMMARY	24
6.0 REFERENCES	25

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

List of Figures

	<u>Page</u>
Figure 1. Milestone Schedule and Status Report	8
Figure 2. Milestone Log	9
Figure 3. Schematic of Semi-Automatic Fixed-Bed System	20

List of Tables

	<u>Page</u>
Table 1. Effect of Solution Concentration & Source of K_2SO_4 on Resin Performance	17
Table 2. Effect of Cyclic Operations (Up to 4 Cycles) (K_2SO_4 Solution Concentration = 25,000 ppm)	18
Table 3. Effect of Sulfate Introduced as Sodium Sulfate	19

EXECUTIVE SUMMARY

Under the DOE Grant No. DE-FG22-90PC90309, the University of Tennessee Space Institute (UTSI) has been directed to further develop an anion-exchange, resin-based desulfurization concept that has been developed and tested on a limited scope for feasibility. From environmental as well as the economic viewpoints, it is necessary that the soluble sulfates of alkali metal sorbents be desulfurized (regenerated) and recycled to make regenerative flue gas desulfurization options more attractive. In order to achieve this, a low-temperature, low-cost desulfurization process to reactivate spent alkali metal sorbents is necessary. UTSI's anion-exchange, resin-based concept is believed to satisfy this requirement.

In this DOE-sponsored project, Dr. Atul C. Sheth, an Associate Professor in the Chemical Engineering Department at UTSI, with the aid of a graduate research assistant, Mr. Sterling Strevel, will perform the following investigations:

- screening of commercially available resins
- process variables study and improving resin performance
- optimization of resin-regeneration
- evaluation of performance enhancers
- development of Best-Process Schematic and related economics, and
- planning for proof-of-concept (POC) scale testing

The above activities have been grouped into five major tasks and the entire project is expected to take thirty-six months to complete.

During the first year (August 9, 1990 to September 30, 1991) under this grant, the following progress has been made:

- Performed a computer-based literature search and acquired relevant publications.
- Contacted various resin manufacturers and suppliers and acquired small samples of candidate resins.
- Prepared lab space area.
- A batch mode screening procedure was developed to evaluate performance of candidate resins, relatively easily and quickly.
- Using the developed batch procedure, the screening experiments were carried out for eleven candidate resins. The batch mode evaluation is complete. From the results, IRA-68 (base case), -35, and -93 resins were selected for the process variables study.
- The semi-automated fixed bed experimental setup was designed and assembled. Presently, shakedown experiments are being carried out.
- Attended the conference on projects under the University Coal Research and Historically Black Colleges and University Programs sponsored by DOE/PETC in Pittsburgh during June 25-27, 1991.

The project is on schedule and within budgeted costs.

1.0 INTRODUCTION

Under the current grant (# DE-FG22-90PC90309), the University of Tennessee Space Institute (UTSI) will carry out the bench scale evaluation and further development of the anion-exchange resin-based desulfurization concept to desulfurize alkali metal sulfates. This concept has been developed and patented by UTSI under U.S. Patent No. 4,917,874. The technical feasibility of this concept has been demonstrated and reported in the M.S. theses prepared by Butler⁽¹⁾ and Modeste⁽²⁾. Under the present DOE grant, the commercially available resins were evaluated. From these resins three have been selected for further process variables study. From the process variables study, it is planned to select one resin which we will use in optimizing the resin regeneration step and to evaluate the effect of various performance enhancers. Results of the bench scale study will be incorporated into an improved process concept/schematic, which will then be utilized in developing related process economics. We plan to carry out the bench scale evaluation using reagent grade chemicals as well as representative spent seed (from a coal-fired magnetohydrodynamics-(MHD) system) and/or spent sorbent material (if available from an in-duct sorbent injection system using a sodium based sorbent).

During this reporting year, efforts were made to familiarize the new graduate research assistant with the concepts, chemistry, objectives, and approaches, involved in the project. The graduate student also made an extensive literature search that encompassed the state-of-the-art experimentation, the industrial applications, and the modeling of the ion-exchange process. Various ion-exchange vendors and manufacturers were polled to find suitable candidate resins. The appropriate vendors

and/or manufacturers were asked to send samples of their weak-base anion-exchange resin. The graduate student developed a batch mode evaluation procedure which was used to select three of these resins for the process variables study. The design and construction of the semi-automatic fixed-bed system to be used in the process variables study has been completed. The shakedown experiments for the system were started. The details of these activities are presented below.

2.0 OBJECTIVES AND PROJECT DESCRIPTION

Various energy conversion 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 require complex designs or severe processing conditions. In any case the costs are extremely high. Hence, a wide-spread use of regenerable flue gas desulfurization (FGD) type systems is not possible under the current economic conditions. Therefore, there is a mandate to develop a simple, low-cost and readily acceptable regeneration system to desulfurize alkali metal based spent sorbent material.

Under the present grant from the U.S. Department of Energy's Pittsburgh Energy Technology Center (DOE/PETC), UTSI will develop a low temperature, low cost spent seed/sorbent regeneration (desulfurization) system that uses available

resin-based ion-exchange technology and which can be developed in minimum time and cost. The specific objectives of the present grant are as follows:

- 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 plans to use 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.

The above activities are grouped in the following five tasks for ease of monitoring the progress of the project:

Task 1.1	Literature Survey, Vendor Contacts and Screening of Resins
Task 1.2	Process Variables Study and Improving Resin Performance
Task 1.3	Optimization of Resin Regeneration Step and Evaluation of Performance Enhancers
Task 1.4	Development of Best-Process Schematic and Related Economics
Task 1.5	Project Management and Reporting

The scope of work to be accomplished under the above tasks was discussed in detail in the first quarterly progress report (no. DOE/PC/90309-1) submitted. However, a brief summary of the scope of the work follows:

2.1 Task 1.1 Literature Survey, Vendor Contacts and Screening of Resins

In this task, UTSI will perform a literature search, make contact with ion-exchange resin vendors and/or manufacturers, and modify the existing bench scale fixed-bed system at UTSI. The literature search will provide the information necessary to develop resin screening tests. The contacts with resin vendors and/or manufacturers will provide the means to procure suitable candidate resins. The fixed-bed system will be modified to operate in a semi-automatic, semi-batch mode.

2.2 Task 1.2 Process Variables Study and Improving Resin Performance

From Task 1.1, three candidate resins will be selected for process variables study. The following process variables will be considered:

- solution concentration
- product inhibition
- solution pH
- cycle efficiency (minimum 20 consecutive cycles)
- superficial velocity
- effect of dissolved impurities and other ions
- bed height
- CO₂ pressure
- temperature
- ammonia concentration

The data acquired from the experiments using these parameters will be used in Task 1.4 to validate the math model. The results will also be discussed with the manufacturer to determine possible ways of improving the resins performance.

2.3 Task 1.3 Optimization of Resin Regeneration Step and Evaluation of Performance Enhancers

In this task, means to optimize the resins exhaustion and regeneration efficiency will be studied. Performance enhancers (mild acids) will be added to the eluent to determine if the exhaustion efficiency can be improved. A study of the forms of the functional group during regeneration will hopefully lead to improvements in the regeneration efficiency.

2.4 Task 1.4 Development of Best-Process Schematic and Related Economics

The appropriate modifications will be made to the models used by Butler⁽¹⁾ and Modeste⁽²⁾, and the modified model will be used to test the data collected in Task 1.2.

A schematic of the commercial scale sorbent/seed regeneration process also will be prepared in this task.

2.5 Task 1.5 Project Management and Reporting

This task will provide for overall management of the project by the Principal Investigator. His efforts will be assisted by the Project Support Services group of the Energy Conversion Research and Development Programs (ECP) department. Quarterly and annual reports, along with a final project report will be prepared.

3.0 PROJECT STATUS/PROGRESS TO DATE

The progress made during the period of August 9, 1990 to September 30, 1991 is shown in Figures 1 and 2. Figure 1 shows the proposed schedule and progress to date for each task. Similarly Figure 2 lists the major milestones to be accomplished

Milestone Schedule and Status Report

Contract Identification		ANION - EXCHANGE RESIN - BASED DESULFURIZATION PROCESS		Reporting Period July 1, 1991 - September 30, 1991		Grant Number DE-FG22-90PC90309	
Contractor Name, Address		THE UNIVERSITY OF TENNESSEE SPACE INSTITUTE TULLAHOMA, TENNESSEE 37388		Contract Start Date September 1, 1990		Contract Completion Date August 1993	
ID	Reporting Category - Contract Line Item or Work Breakdown Structure Element	CY 90	I	CY 91	I	CY 92	I
		O	N	D	J	F	M
		A	M	J	J	A	S
		A	S	O	N	D	J
		F	M	A	M	J	J
		J	F	A	M	A	M
		M	A	M	J	J	A
1.0	LITERATURE SURVEY, VENDOR CONTACTS & SCREENING TESTS						
2.0	PROCESS VARIABLE 3 STUDY & IMPROVING RESIN PERFORMANCE						
3.0	OPTIMIZATION OF RESIN REGENERATION STEP AND EVALUATION OF PERFORMANCE ENHANCERS						
4.0	DEVELOPMENT OF BEST PROCESS SCHEMATIC & RELATED ECONOMICS						
5.0	PROJECT MANAGEMENT AND REPORTING						
COMMENTS							
Signature of Contractor's Project Manager & Date							

Figure 1.

[illegible]

9

under each task and their planned and actual completion dates. Activities carried out under each task are as follows:

3.1 Task 1.1

- 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⁽¹⁾ and Modeste's⁽²⁾ theses, additional cross-references were identified. A large volume of relevant publications has now been accumulated and is being reviewed and categorized.
- Telephone contacts with the resin suppliers along with some resins found on-site resulted in the following eleven candidate resins being chosen for the screening tests:

<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)

- To reduce the time required for the selection of three resins for further process variables study, it was decided to carry out initial screening in

the batch mode. 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:

(a) 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 number 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 shown as a function of the ammonia concentration in the following table.

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 SO₄²⁻ recovery, an ammonia concentration of 3.5 wt % was considered sufficient for regenerating exhausted resin in the batch mode screening experiments.

(b) 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 SO₄²⁻ ions removed from a 2.5 wt % K₂SO₄ solution (or exchanged on the resin active sites) as a function of mixing time are as follows:

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 number indicates a better resin performance.

Based on these results, a mixing time of more than 15 minutes does 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.

(c) Selection of Proper Resin Sample Size

Using the desirable mixing time and ammonia solution concentration identified in (a) and (b), 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 reported as follows:

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.

(d) 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 as follows:

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 affects the percent removal. A carbonation time of 30 minutes was selected for the batch mode screening experiments, since beyond 30 minutes, the

improvement in SO_4^{2-} removal by resin (that means the efficiency of resin exhaustion step) was very small.

- Desirable Conditions for Batch Mode Screening Experiments - The results described above were used to develop an experimental procedure to carry out batch mode screening experiments. The following conditions were considered desirable:
 - Mixing time for exhaustion and regeneration steps ~ 15 min.
 - Ammonia solution concentration for regeneration ~ 3.5 wt %.
 - Carbonation time ~ 30 min. (at a CO_2 flow rate of 2 SCF/hr)
 - Resin sample size ~ 25 ml.
 - Solution-to-resin ratio ~ 2:1

Batch Mode Screening Experiments

To select three candidate resins for process variables study, the screening experiments in the batch mode were carried out using the procedure discussed above and varying the following parameters:

- K_2SO_4 solution concentration
 - Spent MHD seed extract
 - Cyclic operation (up to 4 cycles), and
 - Sulfate introduced as sodium sulfate
- (a) Effect of K_2SO_4 Solution Concentration & Source of K_2SO_4 on Resin Performance

Batch mode screening experiments were carried out using K_2SO_4 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 K_2SO_4 . The results, in terms of percent of total SO_4^{2-} removed by the resin (at the end of exhaustion step) as well as percent of total SO_4^{2-} retained on the resin (at the end of resin regeneration step), are reported as functions of solution concentration (varied from 1000 ppm to 50,000 ppm) and source of K_2SO_4 (reagent grade chemical versus MHD spent seed extract) in Table 1. These results indicate that except for IRA-68, -35, and -93, the remainder of the candidate resins demonstrate either low percent SO_4^{2-} removal or high percent SO_4^{2-} retention or both. Therefore, such resins were eliminated from further study. A detailed statistical analysis of the results will be carried out at a later date and will be reported in a future quarterly report. The reason for the greater efficiency of IRA-68, IRA-35, and IRA-93 is believed to be due to their stronger affinity for acidic anions generated by CO_2 .

Table 1. Effect of Solution Concentration & Source of K₂SO₄ on Resin Performance

Resin Identification	1000 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.

(b) Effect of Cyclic Operations (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 2. 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 SO_4^{2-} 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 2. Effect of Cyclic Operations (Up to 4 Cycles)
(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.

(c) 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 25K ppm for K_2SO_4 and 20.4K ppm for Na_2SO_4 . These experiments were performed only on the resins which showed superior performance to date or on those that were reported as not determined in the last quarterly report (no. DOE/PC/90309-3). Table 3 details the results of the experiments. As expected, for the anion-exchange resins, the results indicate that there is no difference between the K and Na systems.

Table 3. Effect of Sulfate Introduced as Sodium Sulfate

Resin Identification	25K ppm K_2SO_4 Solution		20.4K 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

Fixed Bed Setup

A schematic of the semi-automated fixed-bed setup was prepared. (See Figure 3). The system consists of 3 stainless steel tanks for the chosen eluent, for the deionized water, and for the solution of ammonium hydroxide; 2 glass columns of different diameters; 2 timers; and 2 rotameters for splitting the flow (a requirement

Figure 3. Schematic of Semi-Automatic Fixed-Bed System

necessary for the autosampler). The system is designed to use only one glass 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.

The fixed-bed system is now complete. Shakedown runs are being performed to test the basic design for leaks and for performance parameters discussed earlier. The shakedown runs are also being used to develop the experimental procedure for the process variables study.

3.2 Task 1.4

Relevant literature discussing fixed-bed math models for adsorption-desorption and ion-exchange type systems has been acquired as a part of the computer-based search carried out in Task 1.1. This literature, along with the math models used by Butler⁽¹⁾ and Modeste⁽²⁾, are being reviewed to make necessary adjustments in the Antonson's model that was used successfully by Modeste⁽²⁾. We are still carrying out the cursory review of the other reports and articles acquired through the literature search conducted earlier. We have also initiated an effort to evaluate the impact of evaporation and drying costs on the overall economics and to find other alternatives for concentration of aqueous solutions. The reason being that there is a trade-off required between the cost of resin, solution concentration and steam and water requirements. Dilute solutions can offer very high resin efficiency (hence lower resin cost) but high evaporation and drying loads (hence higher cost of steam). On the other hand, concentrated solutions will provide lower resin conversion efficiency (hence

higher resin cost) but reduced evaporation and drying loads (hence lower cost of steam).

3.3 Task 1.5

The following action items required by the DOE contracting office were completed as a part of this task.

- DOE recommended/desired outline/format for the technical quarterly progress report was received from Dr. Soung Kim (PETC technical program officer) and are being followed in the preparation of various quarterly reports.
- Permission to use DOE owned chemistry laboratory equipment (acquired under the existing MHD contract no. DE-AC02-79ET10815) was received from the contracting officer of the DOE/Chicago Operations office. The approval has been granted to use the necessary equipment on a non-interference basis and will expire on September 8, 1993. Mr. John Columbia of DOE/PETC (Acquisition and Assistance Division) has been informed of this approval.
- A negative report on acquisition of any reportable property acquired under this project was filed with Mr. Ralph Bonadio (Property Administrator) of DOE/PETC.
- Similarly, the U.S. Department of Energy's Form 538 (i.e. Notice of R D & D Project) was filed with Ms. Marilyn Keane of DOE/PETC.
- Three quarterly technical progress reports covering the performance periods from August 9, 1990 - June 30, 1991 were issued.

- Participants in the grant attended the DOE sponsored conference on projects under the University Coal Research and Historically Black Colleges and University Programs. This conference was held in Pittsburgh, Pennsylvania from June 25-27, 1991. A 2-page write-up summarizing the accomplishments and providing an abstract was submitted to the DOE/PETC contracting officer (Mr. Robert C. Dolence) for inclusion in the conference proceedings.
- In response to the request from Dr. Lawrence A. Ruth of DOE/PETC to submit a technical paper and present a poster at the Seventh Annual Coal Preparation, Utilization and Environmental Control Contractors' Conference, permission to attend as well as funds to cover the travel expenses were received from the DOE contracting officer. This conference held in Pittsburgh from July 15-18, 1991 was attended by the principal investigator.

To date the project is back on schedule. The reason for the elimination of the four week delay (identified in the last quarterly report no. DOE/PC/90309-3) is that the results for the IRA-68, IRA-35, and IRA-93 resins were significantly better than the other resins. Hence, no further screening experiments are necessary to select three resins for process variables study.

4.0 PLANS FOR NEXT REPORTING PERIOD

By the next reporting period, the shakedown experiments on the semi-automatic fixed-bed system will be completed. Also, the statistical analysis of all the results, both from the batch mode and fixed-bed mode, will be either completed or substantially in

progress. In addition to this experimental work, a review of the literature as well as technical evaluation of the various options for concentrating the aqueous solutions of different strength will be continued.

5.0 SUMMARY

Work performed during this reporting period is summarized as follows:

- Performed a computer-based literature search and acquired relevant publications which are under review.
- Contacted various resin suppliers and acquired small samples of candidate resins that are commercially available.
- Prepared lab space area.
- Evaluated major parameters (such as ammonia and SO_4^{2-} solution concentrations, mixing time, carbonation time and resin sample size) to develop a batch mode screening procedure.
- Using this procedure, evaluated the performance of IRA-68 (as a base case) and the other candidate resins varying SO_4^{2-} solution concentration and source (i.e. reagent grade K_2SO_4 chemical and spent MHD seed extract). Also evaluated the performance of these resins in cyclic operations limited to four(4) consecutive cycles. The results show that IRA-68, IRA-35, and IRA-93 perform better than the other resins.
- A sketch of the proposed modification of the existing setup was prepared and the setup is now ready. At present, we are performing shakedown experiments.

- Attended the conference on projects under the University Coal Research and Historically Black Colleges and University Programs, sponsored by DOE/PETC in Pittsburgh during June 25-27, 1991.
- Submitted three quarterly reports on time.
- Project management related approval to use DOE-owned chemistry laboratory equipment and reporting on the property acquisition and notice of project initiation to various DOE departments/offices have been completed as required.

The project is on schedule and within cost.

6.0 REFERENCES

1. 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 Space Institute, December 1986.
2. 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 Space Institute, December 1988.

END

DATE
FILMED

1/15/92

I