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ANION-EXCHANGE RESIN-BASED DESULFURIZATION PROCESS

Annual Technical Progress Report

October 1, 1992 - September 30, 1993

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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 and MHD spent seed regeneration 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 uses the available technology and is believed to satisfy this requirement.

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, will perform the following investigations:

- screening of commercially available resins
- process variables study and improving resin performance
- optimization of resin-regeneration step
- 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 third year (October 1, 1992 to September 30, 1993) under this grant the following progress has been made:

- Small amounts (up to 8 ml. per 100 ml. of 5 wt % K_2SO_4 solution) of concentrated organic acids such as formic and acetic acid are found to increase the resin's equilibrium capacity from 19 to 41%. Additional experiments with the butyric acid and palmitic acid will be carried out to determine the possible correlation between the percent improvement in resin's capacity and the organic acid's strength (or number of carbon atoms in its molecular structure).
- From a limited number of experiments, it can be inferred that in the affinity chart, CO_3^{2-} and SO_4^{2-} ions are very close to each other. Most likely the CO_3^{2-} ion seems to be slightly to the left (that means on the OH^- side) of the SO_4^{2-} ion. This conclusion can 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.
- From ten consecutive cycles carried out using the revised experimental procedure, no significant degradation was found in the performance of the three candidate resins. This conclusion was further validated by calculating the equilibrium capacity of resin for various cycles. The calculated capacities for each of the candidate resins varied within $\pm 10\%$ indicating no decline or improvement in the resin's capacity for ten consecutive cycles.

- From multi-attribute analysis of the process variables study results, the IRA-68 resin was judged to be the best resin for the desulfurization of alkali metal sulfates. However, the IRA-35 and IRA-93 resins were not too far behind in the overall performance.
- A computer program to calculate spent seed flow rate and composition for different input conditions to the MHD power plant has been prepared and validated against the published results of Westinghouse. Another computer program to simulate the spent seed regeneration/desulfurization based on the ion-exchange resin-based concept is under development.
- A technical paper entitled, "Spent Seed Regeneration in Coal-Fired MHD System Using Weak-Base, Anion-Exchange Resins" has been accepted for presentation and publication in the Proceedings of the 5th International Conference on Processing and Utilization of High Sulfur Coals, to be held from October 24-28, 1993 in Lexington, Kentucky.
- Another technical paper entitled, "Recent Advances in the UTSI's Anion-Exchange Resin-Based Seed Regeneration Process" was presented and published in the Proceedings of the 31st Symposium on Engineering Aspects of Magnetohydrodynamics, held from June 29 - July 1, 1993 in Whitefish, Montana.
- Attended the Contractors' Review Meeting from June 23-25, 1993 and made a poster presentation of the work done so far.

- Received a no-cost extension from DOE to extend the completion date of our project to December 31, 1993.

At present, the project is on schedule to complete the proposed work scope by December 31, 1993 and within the 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⁾. The developmental program proposed under this DOE grant includes screening of commercially available resins to select three candidate resins for further study. These three resins will undergo a series of experiments designed to test the resins' performance under different process conditions (including the use of spent MHD seed material). The best of these resins will be used in optimizing the regeneration step and in testing the effects of performance enhancers. The process schematic developed from the results will be used to estimate the related economics.

During this reporting period, October 1, 1992 to September 30, 1993, bench scale experiments were carried out to evaluate the effects of various organic acids in enhancing the performance of the candidate resins, and to determine the relative locations of the CO_3^{2-} and SO_4^{2-} ions in the affinity chart. Also, the fixed-bed operation was modified slightly to accommodate in-situ resin regeneration, and using this revised procedure, cycle efficiencies of candidate resins were tested up to 10 consecutive cycles of exhaustion/carbonation and regeneration. Also, during this time period, the process flow sheets for the regeneration of spent magnetohydrodynamics (MHD) seed material under low and high K_2/S ratio cases as well as for reactivation of the

spent sorbent material from the in-duct sorbent injection type flue gas desulfurization (FGD) system were developed. A computer program has been developed to calculate the spent seed flow rate and composition under different input conditions to the integrated MHD system and the results have been verified with the similar results reported by Westinghouse⁽³⁾ for low and high sulfur coal cases. Efforts are now underway to simulate the ion-exchange resin-based desulfurization system via a computer program to calculate process economics under different conditions and for different applications represented by the above mentioned process flow sheets.

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 1.4 Project Management and Reporting

The scope of work to be accomplished under the above tasks has been discussed in detail in the first quarterly progress report (no. DOE/PC/90309-1), and the first annual technical progress report (no. DOE/PC/90309-4) submitted earlier.

3.0 PROJECT STATUS/PROGRESS TO DATE

The progress made during the period of October 1, 1992 to September 30, 1993 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 under each task and their planned and actual completion dates.

Activities carried out under each task are as follows:

3.1 Task 1.1

This task was completed in September 1991 and the results were reported in prior quarterly and annual reports. (Report nos. DOE/PC/90309-1 to 4).

3.2 Task 1.2

This task was completed in August 1992 and the results were reported in the Annual Technical Progress Report for the period October 1, 1991 - September 30, 1992 (Report no. DOE/PC/90309-8). The cycle efficiency of the selected three resins (IRA-68, -35, and -93) was evaluated under Task 1.3.

3.3 Task 1.3

Activities under this task were mainly divided in the areas of evaluating the effect of performance enhancers (e.g. effect of organic acids), determining the cycle efficiencies of candidate resins, and determining the relative locations of CO_3^{2-} and SO_4^{2-} ions in the affinity chart.

3.3.1 Effect of Performance Enhancers

The effect of performance enhancers on the exhaustion efficiency of the candidate resins was evaluated using small amounts of concentrated organic acids. A

Milestone Schedule and Status Report

Contract Identification ANION - EXCHANGE RESIN - BASED DESULFURIZATION PROCESS		Reporting Period October 1, 1992 - September 30, 1993		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 December 1993												
ID	Reporting Category - Contract Line Item or Work Breakdown Structure Element	CY 90	CY 91	CY 92	CY 93											
		O	N	D	J	F	M	A	M	J	J	A	S	O	N	D
1.1	LITERATURE SURVEY, VENDOR CONTACTS & SCREENING TESTS															
1.2	PROCESS VARIABLES STUDY & IMPROVING RESIN PERFORMANCE															
1.3	OPTIMIZATION OF RESIN REGENERATION STEP AND EVALUATION OF PERFORMANCE ENHANCERS															
1.4	DEVELOPMENT OF BEST PROCESS SCHEMATIC & RELATED ECONOMICS															
1.5	PROJECT MANAGEMENT AND REPORTING															
COMMENTS																
Signature of Contractor's Project Manager & Date		10/13/93														

Figure 1.

MILESTONE LOG

I.D. NO.	DESCRIPTION	ACTUAL COMPLETION DATE	PLANNED COMPLETION DATE	EXPECTED COMPLETION DATE	COMMENTS
1.1 A	Complete literature survey, vendor contacts and procure samples of candidate resins	Oct 90	Oct 90		
1.1 B	Complete bench scale screening tests and select three resins	Sep 91	Aug 91		
1.2 A	Complete bench scale process variables study and select one resin	Aug 92	Apr 92		
1.3 A	Complete optimization of resin regeneration step using selected resin	Nov 92	Aug 92		
1.3 B	Complete evaluation of performance enhancers and cycle efficiency for selected resins	Jun 93	Dec 92		
1.4 A	Validate math model using bench scale process variables study data	Sep 92	Apr 92		
1.4 B	Validate math model using data from optimized resin regeneration step and evaluation of performance enhancers		Jan 93	Oct 93	Delay due to delays in 2.0A and 3.0B
1.4 C	Complete process economics for the Best Process Schematic		Jun 93	Oct 93	Delay due to delays in 2.0A, 3.0B, and 4.0B
1.5 A	Submit quarterly technical reports		(As indicated)		
1.5 B	Submit annual technical reports		(As indicated)		Third annual report to be submitted in Oct '93
1.5 C	Submit final project report		Aug 93	Dec 93	Because of no-cost extension

Figure 2

significant improvement in the candidate resin's exhaustion efficiency was observed as the dosage of the organic acid solution was increased. The results using acetic and formic acids are presented in Tables 1 and 2. From comparison of the results in Tables 1 and 2, it is evident that the acetic acid (no. of carbon atoms =2) solution is more effective (especially at higher dosages) than the formic acid (no. of carbon atoms =1) solution. 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 organic acids (such as acetic acid or formic acid), the initial solution pH is kept below 7.0 (probably around 4.5) without unduly diluting K_2SO_4 solution, and 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 still remains below or at pH=7.0. As a result, the resin's exhaustion efficiency improves significantly. Thus, the organic acids most likely are behaving more like a pH buffering agent.

Similar additional experiments with the butyric acid (no. of carbon atoms=4) and palmitic acid (no. of carbon atoms=16) are planned for the next quarter to correlate the extent of the enhancement in the resin's performance with the organic acid's strength and/or number of carbon atoms in the molecule.

Table 1. Performance Enhancement by Addition of Formic Acid Solution (50 vol. %)

- Basis:
- 5 wt % of K₂SO₄ 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>% SO₄²⁻ 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 2. Performance Enhancement by Addition of Acetic 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

<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

3.3.2 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 (R_2CO_3) can also exchange the anions with the K_2SO_4 solution as the bicarbonate form of resin ($R \cdot HCO_3$) does normally.

In one series of experiments, samples of the candidate resins saturated/exhausted with the SO_4^{2-} ions (that means in the R_2SO_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. The results from this series of experiments are given in Table 3. 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-} ion in the bulk solution. As the bulk solution concentration increases the extent of SO_4^{2-} replacement by the CO_3^{2-} ion also increases. Hence, based on these results, one can say that the position of the CO_3^{2-} ion in the affinity chart is very close to the SO_4^{2-} ion. However, it does not clearly indicate whether it is to the left or right of the SO_4^{2-} ion. Hence, additional experiments were carried out to shed further light on this matter. 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 containing $\text{R}\cdot\text{HCO}_3$ and $\text{R}_2\cdot\text{CO}_3$ forms of resin 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 was calculated. The results from these additional experiments are given in Table 4. From this table, it can be seen that the SO_4^{2-} removal efficiencies for candidate resins varied

from 31 to 33%. In comparison, for the all $R\cdot HCO_3$ form of resin when exhausted with a 5 wt % K_2SO_4 solution, the SO_4^{2-} removal efficiencies under similar conditions were found to vary from 42 to 60% (see report no. DOE/PC/90309-4). Hence, the removal efficiency of the candidate resins seems to decrease by about 46% for IRA-68 resin to about 73% for IRA-93 resin. These observed decreases in the SO_4^{2-} removal efficiencies of candidate resins in a mixture containing $R\cdot HCO_3$ and $R_2\cdot CO_3$ forms can be attributed to the inability of the CO_3^{2-} ions on the resin from being exchanged by the SO_4^{2-} ions in the bulk solution.

Table 3. Exchange of CO_3^{2-} Ions with $R_2\cdot SO_4$ 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

Table 4. Exchange of SO_4^{2-} Ions with Mixture of $\text{R}\cdot\text{HCO}_3$ & $\text{R}_2\cdot\text{CO}_3$ Forms of Resin

- Basis:**
- Some $\text{R}\cdot\text{HCO}_3$ converted to $\text{R}_2\cdot\text{CO}_3$ using 5 wt % K_2CO_3 solution
 - $\text{R}\cdot\text{HCO}_3$ + $\text{R}_2\cdot\text{CO}_3$ 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

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:

3.3.3 Determination of Cycle Efficiency

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 regeneration steps. During the resin regeneration step, the in-situ regeneration was carried out using a 4 wt % NH_4OH solution. Relatively complete regeneration of the exhausted resin was assumed to be achieved by performing the regeneration step for a longer time (~ 60 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 3 and indicate a progressive deterioration in the resin's performance. However, earlier in a smaller fixed-bed unit, Butler⁽¹⁾ 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 recent problems could be related to the experimental procedure (inadequate regeneration of resin) or equipment (dead volumes in the system).

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 % 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 regeneration conditions for the fixed-bed operations. This revised procedure was used to determine the cycle efficiency of candidate resins. During exhaustion/carbonation step, the samples of the column effluent were taken at regular

- Flow Rate of K₂SO₄ Solution = 11 cc/min
- Resin volume = 100 cc
- 5 wt% K₂SO₄ solution

Figure 3. Preliminary Data from Cycle Efficiency Experiments for IRA-35 Resin.

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 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 4 - 6. From these three figures, it can be seen that within the experimental errors the candidate resins showed no degradation in performance. This conclusion is reached based on the closeness of the breakthrough curves for various exhaustion/carbonation cycles.

To further confirm the above conclusion, using numerical integration, the resin's capacity for each cycle was calculated following the approach used in the past UTSI studies. The calculated resin's capacities as a function of corresponding cycle number for candidate resins are shown in Figures 7 - 9. From these figures, it is evident that the variations in the calculated resin's capacities are within $\pm 10\%$. Also, there is no trend showing either a continuous decline or improvement in the resin's capacity. Therefore, the observed variations in the resin's capacity can be attributed to possible experimental errors. Thus, based on Figures 4 - 9, one can say that the performance of candidate resins remained the same for up to ten(10) consecutive cycles.

- 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 4. Cycle Efficiency Experiments For IRA-68 Resin

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

Figure 5. Cycle Efficiency Experiments For IRA-93 Resin

CG-3013 1093

- 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 6. Cycle Efficiency Experiments For IRA-35 Resin

CG-3062

**Figure 7. Calculated Equilibrium Capacity of IRA-68 Resin
As a Function of Cycle Number**

CG-3014

**Figure 8. Calculated Equilibrium Capacity of IRA-93 Resin
As a Function of Cycle Number**

CG-3015

Figure 9. Calculated Equilibrium Capacity of IRA-35 Resin As a Function of Cycle Number

CG-3058

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 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.

3.4 Task 1.4

Two major activities were carried out under this task in the reporting period. They are: multi-attribute analysis of the process variables study results developed from fixed-bed experiments, and the development of process flow sheets and process economics for various desulfurization applications.

3.4.1 Multi-Attribute Analysis of Fixed-Bed Results

Using the approach similar to the one used by Strevel(4), a multi-attribute analysis was carried out for the process variables study results obtained for the three candidate resins. This multi-attribute 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 major parameters variables considered in this analysis include: resin's equilibrium capacity, cycle efficiency, resin cost, solution concentration, dissolved impurities and cation effect. From the evaluation of the preliminary results, certain parameters were found to have no or very little effect on the resin's performance, and therefore, these parameters were removed from any further

consideration. The list of such parameters/variables with their impact on resin selection and the arbitrarily assigned attribute values (required for multi-attribute analysis) are given in Table 5. Using these arbitrarily assigned attribute values to the major parameters and the approach similar to the one used by Strevel⁽⁴⁾, the utilities of the three resins were calculated which are reported in Table 6. Based on these calculated utilities the IRA-68 resin was selected as a "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 5. Effect of Various Parameters on Resin's 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 6. 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

3.4.2 Development of Process Flow Sheets & Economics

To evaluate the possible effects of the process parameters such as sulfate solution concentration, regeneration characteristics, type of resin, mode of effluent concentration/evaporation and possible integrated versus stand-alone configuration, preliminary process flow sheets were developed to apply for MHD spent seed regeneration (e.g. desulfurization of K_2SO_4 -rich material) and for spent sorbent reactivation in FGD (e.g. desulfurization of Na_2SO_4 -rich material). For regeneration/desulfurization of the MHD spent seed, the process stream coming out from a wet electrostatic precipitator (WESP) was considered as an input to ion-exchange resin-based system. For spent sorbent reactivation in FGD applications, the mixture of spent sorbent and fly-ash material captured in the baghouse/electrostatic precipitator type control device was considered as an input to the sorbent desulfurization system. These process flow schematics for a low K_2/S ratio (that means high sulfur coal) and a high K_2/S ratio (that means low sulfur coal) are shown in Figures 10 and 11 respectively. A similar schematic for the desulfurization of the spent sodium-based flue gas desulfurization (FGD) sorbent obtained from an in-duct sorbent injection type of SO_2 -removal option is shown in . These three schemes will be further analyzed in our future efforts to compare the major similarities and differences and to develop related process economics based on EPRI-TAG document.

As shown in Figures 10 and 11, the spent seed composition as well as flow rate would change depending upon the operating parameters of the MHD power plant. Hence a general computer program was developed that would calculate spent seed

Figure 10. Process Schematic For Ion - Exchange Resin - Based Seed Regeneration Process (Low K_2/S Ratio)

Figure 11. Process Schematic For Ion - Exchange Resin - Based Seed Regeneration Process (High K_2S Ratio)

Resin Exhaustion/Carbonation Step

Resin Regeneration Step

Figure 12. Process Schematic For Ion - Exchange Resin - Based Desulfurization of Sodium - Based FGD Sorbent

SO₂ - Removal & Resin Exhaustion/ Carbonation Step

Resin Regeneration Step

flow rate and composition under different input conditions to the 300 MW_i MHD power plant. The major variables included in this computational scheme are shown in Figure 13. The information flow chart for calculating the spent seed flow rate and composition is shown in Figure 14. The results for the low and high sulfur coal cases were compared with the similar results reported in the recent Westinghouse report⁽³⁾, and were found to agree very well.

Another computer program is now being developed to simulate the resin-based desulfurization concept. The process flow schemes shown in Figures 10 and 11 as well as the spent seed compositions and flow rates calculated from the above-mentioned computer program (following Figures 13 and 14) are utilized in this second program. The major variables included in this second program are shown in Figure 15. Using these two computer programs, we plan to evaluate the sensitivity of the calculated results to various major variables and then determine the Best-Process Schematic and the lowest seed regeneration cost for the high as well as low sulfur coals.

3.5 Task 1.5

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

- The 2nd annual technical progress report (report no. DOE/PC/90309-8) covering the performance period from October 1, 1991 - September 30, 1992, as well as three quarterly technical progress reports covering the

Figure 13. Major Variables Included in Calculations of Spent Seed Flow Rate and Composition.

Figure 14. Information Flow Chart for Calculating Spent Seed Flow Rate and Composition. CG-3061

Resin Carbonation / Exhaustion

Resin Regeneration

Figure 15. Major Variables Included in Simulation of Spent Seed Regeneration Based on Ion-Exchange Resin Concept.

CG-3060

performance periods from October 1, 1992 - June 30, 1993 were issued.

- A technical paper entitled, "Spent Seed Regeneration in Coal-Fired MHD System Using Weak-Base, Anion-Exchange Resins," has been accepted for presentation and publication in the Proceedings of the 5th International Conference on Processing and Utilization of High Sulfur Coals, to be held from October 24-28, 1993 in Lexington, Kentucky. A final draft of this paper was submitted to the Elsevier Science Publishers who is putting together the conference proceedings.
- Graduate student, Sterling Strevel completed his M.S. thesis based on the work done on this grant in the first two years. He received his M.S. degree in Engineering Science & Mechanics (E.S.&M) from the University of Tennessee (UT). His M.S. thesis is now available for anyone's use from UT/UTSI libraries.
- A technical paper entitled, "Recent Advances in the UTSI's Anion-Exchange Resin-Based Seed Regeneration Process" was presented in the poster session and published in the Proceedings of the 31st Symposium on Engineering Aspects of Magnetohydrodynamics, held from June 29 - July 1, 1993 in Whitefish, Montana.
- A two-page write-up describing the abstract and highlighting the accomplishments of our research project along with a completed technical subject index were submitted to the DOE/PETC office on May

3, 1993, for inclusion in the report assembled by DOE on the various University Coal Research (UCR) projects. This report was distributed at the 1993 UCR Contractors' Review meeting scheduled by DOE in Pittsburgh. Rajeev Dharmapurikar (a graduate student) and Atul Sheth (a principal investigator) attended this DOE/PETC sponsored UCR Contractors' Review meeting held in Pittsburgh from June 23-25, 1993 and made a poster presentation of the work done so far.

- A no-cost extension was requested from DOE via a letter dated June 17, 1993. In this letter, a request was made to DOE to extend the completion date of our project to December 31, 1993 so that the proposed program can be successfully completed and documented in a final project report. We received DOE approval on July 2, 1993 to our no-cost extension request.

At present, the project is on schedule to complete the proposed work scope by December 31, 1993 and well within the budget.

4.0 REFERENCES

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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, Knoxville, December 1988.
3. 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.
4. Strevel, S.D., "The Anion-Exchange Resin-Based Desulfurization Concept," a thesis presented for M.S. degree, The University of Tennessee, Knoxville, December 1992.

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