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

Quarterly Technical Progress Report

January 1, 1993 - March 31, 1993

Prepared by:

Atul C. Sheth
Rajeev Dharmapurikar

The University of Tennessee Space Institute
B.H. Goethert Parkway
Tullahoma, Tennessee 37388-8897

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EXECUTIVE SUMMARY

Under DOE Grant No. DE-FG22-90PC90309, the University of Tennessee Space Institute (UTSI) is contracted to further develop its anion-exchange, resin-based desulfurization concept to desulfurize alkali metal sulfates. From environmental as well as economic viewpoints, it is necessary to remove soluble sulfates from the wastes created by flue gas desulfurization systems. In order to do this economically, a low-cost desulfurization process for spent sorbents is necessary. UTSI's anion-exchange resin-based desulfurization concept is believed to satisfy these requirements.

During the reporting period, January 1, 1993 - March 31, 1993, UTSI has completed the batch mode experiments to locate the position of the CO_3^{2-} and SO_4^{2-} ions in the affinity chart. Also, the reviews of the ASPEN Code's capabilities and EPRI-TAG document's methodology are in progress for developing the Best Process Schematic and related economics. The fixed-bed experiments are also in progress to evaluate the cycle efficiency of the candidate resins. So far we have completed ten consecutive cycles of exhaustion/carbonation and regeneration for IRA-35 resin.

Because of the past problems (now resolved) with the fixed-bed system, the addition of batch mode screening experiments, Christmas holidays and spring break, and the moving of UTSI's Chemistry Laboratory to a new location, the program is about 6-8 weeks behind schedule, but well within the budget.

1.0 INTRODUCTION

Under the current grant (# DE-FG22-90PC90309), the University of Tennessee Space Institute (UTSI) will perform 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, January 1, 1993 to March 31, 1993, batch mode experiments to identify the location of the carbonate (CO_3^{2-}) ion in relation to the sulfate (SO_4^{2-}) ion in the affinity chart were completed. The literature on EPRI-TAG methodology is being reviewed for future application in developing the process economics. Also, the fixed-bed experiments are in progress to evaluate cycle efficiency of IRA-35 resin. Similar experiments for the other two candidate resins (IRA-68 and -93) will be performed in the next quarter if it is determined that meaningful data can be obtained in a small bench scale unit.

2.0 OBJECTIVES AND PROJECT DESCRIPTION

Objectives to be satisfied as well as the detailed description of the project tasks and subtasks were described in the Quarterly Technical Progress Report for the period August 9, 1990 - December 31, 1990 (report no. DOE/PC/90309-1).

3.0 PROJECT STATUS/PROGRESS TO DATE

The progress made during the period January 1, 1993 - March 31, 1993 is indicated in Figures 1 and 2. Figure 1 shows the proposed schedule and the progress to date for each task. Figure 2 lists the major milestones to be accomplished under each task and their planned and actual completion dates. Activities performed for 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 reports.

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) is being evaluated under Task 1.3.

Milestone Schedule and Status Report

Contract Identification		ANION - EXCHANGE RESIN - BASED DESULFURIZATION PROCESS		Reporting Period January 1, 1993 - March 31, 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 August 1993		
ID	Reporting Category - Contract Line Item or Work Breakdown Structure Element	CY 90	I	CY 91	I	CY 92	I	CY 93
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MILESTONE LOG

I.D. NO.	DESCRIPTION	ACTUAL COMPLETION DATE	PLANNED COMPLETION DATE	EXPECTED COMPLETION DATE	COMMENTS
1.0A	Complete literature survey, vendor contacts and procure samples of candidate resins	Oct 90	Oct 90		
1.0B	Complete bench scale screening tests and select three resins	Sep 91	Aug 91		
2.0A	Complete bench scale process variables study and select one resin	Aug 92	Apr 92	Jul 92	Delay due to fixed bed and IRA-68 resin related problems (problems now resolved)
3.0A	Complete optimization of resin regeneration step using selected resin	Nov 92	Aug 92	Nov 92	Delay due to 2.0A
3.0B	Complete evaluation of performance enhancers and cycle efficiency for selected resins		Dec 92	Apr 93	Delay due to 2.0A, addition of cycle efficiency evaluation and chem lab moving to new site
4.0A	Validate math model using bench scale process variables study data	Sep 92	Apr 92	Jul 92	Delay due to 2.0A
4.0B	Validate math model using data from optimized resin regeneration step and evaluation of performance enhancers		Jan 93	May 93	Delay due to 2.0A and 3.0B
4.0C	Complete process economics for the Best Process Schematic		Jun 93		
5.0A	Submit quarterly technical reports		(As Indicated)		Tenth quarterly to be submitted in Apr '93
5.0B	Submit annual technical reports		(As Indicated)		
5.0C	Submit final project report		Aug 93		

Figure 2

3.3 Task 1.3

To determine the cycle efficiency, fixed-bed experiments are being carried out with the IRA-68, -35, and -93 resins. In these experiments, the same batch of resin is subjected to repeated cycles involving carbonation/exhaustion, and regeneration steps. In the resin regeneration step, the in-situ regeneration is carried out using a 4 wt % NH_4OH solution. Relatively complete regeneration of the exhausted resin is assumed by performing the regeneration step for a longer time (~60 min) than determined from the batch mode experiments. So far, we have completed ten consecutive cycles for IRA-35 resin. Preliminary results from these experiments are shown in Figure 3, which show that in a small experimental unit it is very difficult to perform the cycle efficiency experiments. Because of the existence of small dead volumes in the system, the sample collected for off-line analysis can be contaminated. Also, it is difficult to assess the effect of such a small level of contamination. However, in a large system this type of problem would not occur or will be insignificant. Butler⁽¹⁾ had carried out similar cycle efficiency experiments using IRA-68 resin in his simple fixed-bed unit; but they were at atmospheric pressure with no CO_2 (hence a 3-step process) and the exhausted resin sample was regenerated externally in a batch mode in the beaker (instead of in-situ as in the present work). Hence, assembling and disassembling was not a major problem to Butler. His results (see Figure 4) showed no degradation in the IRA-68 resin's performance up to 4 consecutive cycles. In comparison to his results, the preliminary results from the present study for IRA-35 resin indicate quite an opposite trend. To confirm whether the IRA-35 resin had really a poor cycle efficiency or the experimental procedure adopted in the present study

- 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.

Figure 4. Cycle Efficiency and Data Reproducibility
(Data taken from Reference 1 for IRA-68 Resin).

cannot meaningfully provide a true evaluation of the cycle efficiency because of its small size and design, we plan to carry out a limited number of cycles with the IRA-68 resin and compare the results with Butler's results. If the results are found satisfactory then we will continue the evaluation for the IRA-93 resin.

Batch mode experiments were also carried out to determine the position of the CO_3^{2-} ion with respect to the SO_4^{2-} ion in the affinity chart. In one series of experiments, this was determined using samples of candidate resins saturated/exhausted with the SO_4^{2-} ions (that means in the $\text{R}_2\bullet\text{SO}_4$ form). Samples of these exhausted resins were then 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 1. 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. We plan to perform additional experiments in which $\text{R}\bullet\text{HCO}_3$ form of resin will be contacted with the 5 wt% K_2CO_3 solution to make sure that all the HCO_3^- ions in the resin are replaced with the CO_3^{2-} ion. The samples of $\text{R}_2\bullet\text{CO}_3$ form of resin will then be contacted with the

solutions containing different concentrations of K_2SO_4 . The amount of SO_4^{2-} picked up by the resin will be measured by the amount of CO_3^{2-} ions found in the filtrate. From this series, we will be able to say whether CO_3^{2-} is to the left or right of the SO_4^{2-} ion in the affinity chart.

Table 1. Determination of Position of CO_3^{2-} Ion in the Affinity Chart

- 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

Results from these batch mode experiments can also be used to infer whether the resin in the bicarbonate (HCO_3^-) form is primarily responsible for the exchange with the SO_4^{2-} ion or not. Knowing that it may be beneficial to have a maximum amount of resin in the bicarbonate form than in the carbonate (CO_3^{2-}) form. This can possibly also explain and justify the observed enhancement in the resin's capacity as the static CO_2 pressure is increased during the resin carbonation/exhaustion step.

3.4 Task 1.4

Under this task, efforts are underway to evaluate the possible effects of the process parameters such as seed solution concentration, regeneration characteristics, type of resin, mode of effluent concentration/evaporation and possible integrated or stand-alone configuration. This evaluation is being carried out to develop the "Best Process Schematic." Possible effects of these parameters on the cost are also being studied, and based on the EPRI-TAG document, a calculation procedure is being developed for the ensuing economic analysis.

3.5 Task 1.5

The following activities were completed under this task.

- The ninth quarterly technical progress report (report no. DOE/PC/90309-9) covering the performance period of October 1, 1992 - December 31, 1992 was issued on January 20, 1993.
- An accepted technical paper entitled, "Spent Seed Regeneration in Coal-Fired MHD System Using Weak-Base, Anion-Exchange Resins," was prepared and submitted for peer review. This paper will be presented and published 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.
- An abstract entitled, "Recent Advances in the UTSI's Anion-Exchange Resin-Based Seed Regeneration Process," was accepted for presentation in the poster session and publication in the proceedings of the 31st Symposium on Engineering Aspects of Magnetohydrodynamics, to be

held from June 29 - July 1, 1993 in Whitefish, Montana. The full technical paper is being prepared for submission prior to May 7, 1993.

At the present time, the project is still about 6 - 8 weeks behind the original schedule (due to earlier equipment related problems (now resolved), increase in work scope due to additional batch mode screening, holidays and UTSI's Chemistry Laboratory moving to a new location). However, it is well within the budget.

4.0 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.

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