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ANION-EXCHANGE RESIN-BASED DESULFURIZATION PROCESS

Quarterly Technical Progress Report

January 1, 1992 - March 31, 1992

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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, 1992 - March 31, 1992, a major problem was found in the fixed-bed setup and corrective actions taken. The sulfate precipitation in dead spaces contaminated the rinse water which was reducing the efficiency of the activated resin. We have identified the necessary modifications and the required valves and fittings are on order. We also modified our procedure to alleviate such problems from reoccurring in the future. The experiments carried out to date appear to agree well with the past UTSI bench scale work. We also initiated a study to determine the trade-off between solution concentration and the evaporation/concentration load.

The fixed-bed problem put us about eight weeks behind schedule. However, by including a second graduate research assistant (GRA) to work on Tasks 1.3 and 1.4, we plan to regain the lost time and return to the schedule shortly.

1.0 INTRODUCTION

The University of Tennessee Space Institute (UTSI) has a Department of Energy grant to further develop the Institute's anion-exchange resin-based desulfurization concept. The developmental program proposed 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, 1992 - March 31, 1992, the shakedown experiments on the fixed-bed setup were carried out, and, based on the results necessary modifications to the experimental setup and to the procedure were made. Process variables studies using the three candidate resins (i.e., IRA-68, -35, and -93) were initiated and preliminary results compare well with the past UTSI bench scale results.

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, 1992 - March 31, 1992 is indicated in Figures 1 and 2. Figure 1 shows the proposed schedule and the progress

Milestone Schedule and Status Report

Contract Identification		ANION - EXCHANGE RESIN - BASED DESULFURIZATION PROCESS		Reporting Period January 1, 1992 - March 31, 1992		Grant Number DE-FG22-90PC00309	
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	J	CY 91	J	CY 92	CY 93
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MILESTONE LOG

[illegible]

Figure 2

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 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 reports.

3.2 Task 1.2

During the shakedown experiments and the procedure development work with the modified fixed-bed unit, several additional problems were experienced. The major one was the contamination of activated resin during the rinse cycle that preceded the exhaustion run by sulfate crystallized-out in the lines and dead spaces. This problem has now been solved by removing the solenoids from the lines and replacing them with a 5-way manually operated valve. Also, additional check valves have been installed and the procedure has been modified to drain the sulfate solution tank at the end of the day and wash the lines with hot water, so that during the overnight period the sulfate would not crystallize out and be deposited in dead spaces and joints. Similar precautions have been taken to prevent contamination of NH_4OH solution from the potassium sulfate solution.

The experimental procedure is still in the evolution stage and will be finalized as soon as some of the ordered fittings are received and the modified experimental setup is ready. During this phase of the fixed-bed study, experiments were carried out in which the concentration of the sulfate solution was varied from 1,000 ppm to 50,000 ppm as K_2SO_4 .

Reproducibility of the experimental procedure and subsequent analysis of the samples is demonstrated in Figure 3. Two different runs carried out with two different samples of the IRA-35 resin and 25,000 ppm K_2SO_4 solution showed reproducibility that can be accepted within possible experimental errors.

Based on the success of Modeste⁽¹⁾ in combining the exhaustion and carbonation cycles together by carrying out the exhaustion run under a moderate static CO_2 pressure, the fixed-bed system built by UTSI has such a provision. To test the validity of results obtained from the UTSI system, Table 1 gives a comparison of the equilibrium capacity of IRA-68 resin determined at 10 psig CO_2 pressure with the similar results reported by Modeste⁽¹⁾ and Butler⁽²⁾. Although there is a slight difference in the solution concentration, the results obtained from the present study fits very well with the trend established by the work of Butler and Modeste. The increase in equilibrium capacity of resin observed as a function of increasing CO_2 pressure will be further validated in the process variables study for IRA-35 and -93 resins.

Table 1. Equilibrium Capacity of IRA-68 Resin as a Function of CO_2 Pressure

Solution Concentration (gm SO_4^{2-} /ml sol'n)	CO_2 Pressure (psig)	Equilibrium Capacity (gm SO_4^{2-} /ml resin)	Reference
0.039	40	0.124	(1)
0.039	20	0.087	(1)
0.028	10	0.072	Present*
0.028	0	0.066	(2)*

* Averaged results

Reproducibility Check for IRA-93 Resin at CO₂ Pressure of 10 psig and 25K ppm K₂ SO₄ Solution

FIGURE 3.

To evaluate the effect of solution concentration on the shape and location of the breakthrough curves (that means to understand the ion-exchange kinetics), preliminary results for the IRA-35 resin (at 1,000 ppm and 50,000 ppm level of K_2SO_4 solution) and for IRA-93 resin (at 10,000 ppm and 50,000 ppm level of K_2SO_4 solution) are shown in Figures 4 and 5 respectively. Within experimental scatter, the shapes of the breakthrough curves are considered similar which indicates that the underlying ion-exchange kinetics does not change significantly as the solution concentration changes. This can be further extrapolated to conclude that the effective diffusion coefficient can be considered to be independent of the solution concentration. In future experiments, this conclusion will be further tested and verified.

Each resin particle has a finite number of active sites. Hence, at higher solution concentrations these sites are being used-up at a faster rate than at a lower solution concentration. Because of the faster rate of consumption, the breakthrough (i.e. time at which $C/C_0 \geq 0.05$) occurs earlier at higher solution concentration resulting in the breakthrough curve for concentrated solution being more towards the left on the time axis. This particular behavior is seen in both Figures 4 and 5. Equilibrium capacities of both of the resins calculated from these breakthrough curves are given in Tables 2 and 3 and appear to compare satisfactorily with the values reported by the resin supplier.

Breakthrough Curves for IRA-35 Resin at CO₂ Pressure of 10 psig

FIGURE 4.

Breakthrough Curves for IRA-93 Resin at CO₂ Pressure of 10 psig

FIGURE 5.

Table 2. Equilibrium Capacity of IRA-35 Resin at CO₂ Pressure of 10 psig

Solution Concentration (gm SO ₄ ²⁻ /ml sol'n)	Equilibrium Capacity (gm SO ₄ ²⁻ /ml resin)
0.001	0.068
0.028	0.067

Table 3. Equilibrium Capacity of IRA-93 Resin at CO₂ Pressure of 10 psig

Solution Concentration (gm SO ₄ ²⁻ /ml sol'n)	Equilibrium Capacity (gm SO ₄ ²⁻ /ml resin)
0.006	0.058
0.028	0.080

Based on the satisfactory agreement between the preliminary results derived to date and the earlier bench scale work carried out at UTSI, we believe that our experimental setup and the procedure are capable of providing comparable results. Hence, as soon as the modifications to the fixed-bed unit are made to avoid sulfate contamination in the rinse water, the scheduled process variables study will be started.

3.3 Task 1.4

In order to develop the Best Process Schematic, it will be necessary to determine the trade-off between the solution concentration used during the resin exhaustion step and the subsequent evaporation/concentration load. Dilute solutions (concentration less than 1 wt %) gives a sulfate removal efficiency that approaches

100%. On the other hand, the resin efficiency drops to the 50-60% range for concentrated solutions (concentration ≥ 10 wt %). This would necessitate the use of significantly more resin than predicted by the theoretical equilibrium capacity. Thus, in general, the dilute solution would require lower resin cost than concentrated solution. Consequently, the dilute solution would require a significantly greater evaporation/concentration than the concentrated solution. For example, for a 1 wt % solution, 99 lbs of water will need to be removed by evaporation or other schemes per pound of dry salt. Compared to this, 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 needs to be carried out to determine optimum solution concentration and the related evaporation/concentration load.

Evaporation alone cannot be economical in this case and must be used in combination with other unit operations. Reverse Osmosis (RO) can be used as an initial concentration step for dilute solution which can be further concentrated by multiple-effect evaporation. RO is considered suitable because it has proven to be economical and energy efficient for salt solutions in desalination industries and is finding more and more applications in the concentration of similar solutions in the paper and pulp industries.

To carry out this trade-off study, the process schematics shown in Figures 6 and 7 will be used. In Figure 6, the dilute solution is first concentrated using RO to a 10 wt % level, after which it is concentrated to a 47 wt % level using a multiple-effect evaporator. Effluent from the last effect of the evaporator can be dried in a spray dryer to provide desulfurized sorbent in a dry powder form. In Figure 7, the concentrated

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Process Schematic for Dilute Effluents

FIGURE 6.

Process Schematic for Concentrated Effluents

FIGURE 7.

solution (> 10 wt % level) can be treated directly using a multiple-effect evaporator-dryer setup to the desired form.

Using the above two schemes, we plan to develop an appropriate material and energy balance around the major components which will then be used to estimate capital and operating costs for these components. All of the costs will then be adjusted on a uniform basis (i.e. annualized cost) and compared as a function of inlet solution concentration. The minimum annualized cost will provide the optimum solution concentration to be used in the development of the Best Process Schematic.

We have started developing a computer program that will carry out the above calculations for different inlet solution concentrations. From our preliminary analysis, we have found that a triple-effect evaporator will be sufficient for evaporation. Addition of another effect will improve the steam economy only slightly but will add significantly to the equipment cost. Similar analysis of the scheme with the reverse osmosis unit is also underway.

3.4 Task 1.5

The following activities were completed under this task.

- The quarterly technical progress report (report no. DOE/PC/90309-5) covering the performance period from October 1, 1991 - December 31, 1991 was issued on January 15, 1992.
- We have received a letter from Mr. Robert C. Dolence, Acting Program Coordinator for the University Coal Research program, requesting a two-page abstract summarizing the project's accomplishments and plan by April 10, 1992. He also requested us to make an oral presentation at the

contractors' review meeting to be held in Pittsburgh, Pennsylvania from June 15-17, 1992.

- Via a telephone call, Dr. Soung Kim (PETC Technical Program Officer) asked us to brief her in an informal presentation about the halfway progress during our planned visit to Pittsburgh in June 1992. This briefing schedule replaces her earlier request to do the same thing in May 1992 .

To date, the project is about eight(8) weeks behind schedule. The major reason is the unexpected contamination of the activated resin caused by the rinse water which picked up crystallized sulfate from dead spaces in lines and fittings. Because of this unexpected contamination, it is necessary to repeat some of the experiments that were already completed to evaluate effect of solution concentration on the performance of IRA-68, -35, and -93 resins. To avoid this problem from reoccurring, we have modified the fixed-bed setup and our experimental procedure. Also, we have now included the help of a second graduate research assistant. With the two students' efforts and hopefully no future equipment related problems, we should be able to overcome this slippage.

4.0 PLANS FOR THE NEXT REPORTING PERIOD

During the next reporting period, we plan to complete the process variables study using a modified fixed-bed setup and the analysis of the resulting data using a math model used by Modeste⁽¹⁾. By the end of the next reporting period, Sterling Strevel expects to complete his M.S. thesis for a degree in Engineering Science and

Mechanics. The trade-off study, to determine optimum solution concentration and respective evaporation/concentration load, will also be completed.

5.0 SUMMARY

The work performed during this period is summarized as follows:

- Necessary modifications to the fixed-bed setup to avoid contamination of the rinse water by sulfate deposited in lines or dead spaces were identified and the required valves and fittings have been ordered.
- Experimental procedure for fixed-bed system is finalized and the preliminary results from the few runs carried out with the IRA-68, -35, and -93 resins agree satisfactorily with the earlier UTSI work.
- The reproducibility of the procedure and resin performance were checked for the IRA-35 resin and were found to be satisfactory.
- Trade-off studies to determine optimum solution concentration and related evaporation/concentration load has been initiated.

At the present time, the project is about eight weeks behind schedule but still well within the budget.

6.0 REFERENCES

1. 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.

2. 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.

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8/27/92