ANION-EXCHANGE RESIN-BASED DESULFURIZATION PROCESS

Quarterly Technical Progress Report

April 1, 1992 - June 30, 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, April 1, 1992 - June 30, 1992, we have nearly completed the process variables study in which we have evaluated the effects of seven major process variables. At present, we are analyzing the data using the fixed bed math model used in our earlier study. We have also initiated the batch mode resin regeneration experiments to identify optimum conditions for the fixed bed regeneration. Similarly, we are also continuing with our efforts to determine the trade-off between the solution concentration and the evaporation/concentration load.

The earlier problems with the fixed bed system had put us behind schedule; and we are recovering. At present, we are still about 4 - 6 weeks behind schedule, but well within the budget.
1.0 INTRODUCTION

The University of Tennessee Space Institute (UTSI) has a U.S. 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, April 1, 1992 - June 30, 1992, process variables studies using the three candidate resins (i.e. IRA-68, -35, and -93) were performed. So far, we have evaluated the effects of solution concentration, solution pH, superficial velocity, bed height, product inhibition, dissolved impurities and CO2-pressure. The analysis of the experimental results has started. We have also started simple process engineering type calculations to determine the trade-off between the solution concentration and the resulting evaporation/concentration load.

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 April 1, 1992 - June 30, 1992 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 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

The problems related to the fixed bed unit that had shown up during the shakedown experiments were successfully resolved and the experimental procedure was finalized. Using this procedure, so far we have evaluated the effects of the following major process variables on the performance of three candidate resins.

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

Until the resin regeneration step is optimized in Task 1.3, we cannot evaluate the cycle efficiency. Similarly, all the candidate resins cannot be procured in different
Milestone Schedule and Status Report

Contract Identification: ANION - EXCHANGE RESIN - BASED
DESULFURIZATION PROCESS

Contractor: THE UNIVERSITY OF TENNESSEE SPACE INSTITUTE
TULLAHOMA, TENNESSEE 37388

Reporting Period: April 1, 1992 - June 30, 1992
Grant Number: DE-FG22-90PC90309

Contract Start Date: September 1, 1990
Contract Completion Date: August 1993

<table>
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<th>CY 91</th>
<th>CY 92</th>
<th>CY 93</th>
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<td>▼</td>
<td>▼</td>
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<td>2.0</td>
<td>PROCESS VARIABLES STUDY &amp; IMPROVING RESIN PERFORMANCE</td>
<td></td>
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<td>▼</td>
<td>▼</td>
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<td>3.0</td>
<td>OPTIMIZATION OF RESIN REGENERATION STEP AND EVALUATION OF PERFORMANCE ENHANCERS</td>
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<td></td>
<td>▼</td>
<td>▼</td>
</tr>
<tr>
<td>4.0</td>
<td>DEVELOPMENT OF BEST PROCESS SCHEMATIC &amp; RELATED ECONOMICS</td>
<td>▼</td>
<td>▼</td>
<td>▼</td>
<td>▼</td>
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<tr>
<td>5.0</td>
<td>PROJECT MANAGEMENT AND REPORTING</td>
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COMMENTS

Signature of Contractor's Project Manager & Date: 7/16/92

Figure 1.
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<th>I.D. NO.</th>
<th>DESCRIPTION</th>
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<th>PLANNED COMPLETION DATE</th>
<th>EXPECTED COMPLETION DATE</th>
<th>COMMENTS</th>
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<tr>
<td>1.0A</td>
<td>Complete literature survey, vendor contacts and procure samples of</td>
<td>Oct 90</td>
<td>Oct 90</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>candidate resins</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.0B</td>
<td>Complete bench scale screening tests and select three resins</td>
<td>Sep 91</td>
<td>Aug 91</td>
<td></td>
<td>Delay due to fixed bed and IRA-68 resin related problems</td>
</tr>
<tr>
<td>2.0A</td>
<td>Complete bench scale process variables study and select one resin</td>
<td></td>
<td>Apr 92</td>
<td>Jul 92</td>
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<td>3.0A</td>
<td>Complete optimization of resin regeneration step using selected resin</td>
<td>Aug 92</td>
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<td>Sep 92</td>
<td>Delay due to 2.0A</td>
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<tr>
<td>3.0B</td>
<td>Complete evaluation of performance enhancers using selected resin</td>
<td>Dec 92</td>
<td>Jan 93</td>
<td></td>
<td>Delay due to 2.0A</td>
</tr>
<tr>
<td>4.0A</td>
<td>Validate math model using bench scale process variables study data</td>
<td>Apr 92</td>
<td>Jul 92</td>
<td></td>
<td>Delay due to 2.0A</td>
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<tr>
<td>4.0B</td>
<td>Validate math model using data from optimized resin regeneration step and</td>
<td>Jan 93</td>
<td></td>
<td></td>
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<tr>
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<tr>
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<td>Complete process economics for the Best Process Schematic</td>
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<td>5.0A</td>
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<td>Submit final project report</td>
<td>Aug 93</td>
<td></td>
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**Figure 2**
but similar particle size fractions and with different porosity. Also, the working temperature range for most of the candidate resins is about 20 - 70°C, and we do not expect the temperature to be a significant variable in this range. Hence, under Task 1.2, we do not plan to evaluate the effects of temperature, cycle efficiency and resin particle size/or porosity. Later on under Task 1.3 when the optimum resin regeneration conditions are identified, we will use those conditions to carry out the cycle efficiency experiments for the "best" resin identified from the present three candidates. Some of the gaps in the data for the variables already studied, are at present being filled and we plan to complete this task (except cycle efficiency) by the end of July 1992.

The results obtained from the process variables studies are still being analyzed. The results from our preliminary analysis are as follows:

**Effect of CO₂ Pressure**

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 CO₂ pressure, we have carried out fixed bed experiments using K₂SO₄ solution (concentration = 50,000 ppm or 0.028 gm SO₄²⁻/ml. of solution) and static CO₂ pressures varying from 10 to 120 psig. The results in terms of effects of CO₂ pressure on the equilibrium loading and on ion-exchange kinetics are given in Table 1 and Figure 3 respectively. As shown in Table 1, the equilibrium loading seems to level off at about 80 psig and there is a significant increase in the loading values for all the three resins for CO₂ pressure varying from 10 - 80 psig. At higher CO₂ pressure the breakthrough
Effect of CO$_2$ Pressure on Equilibrium Loading

Basis: 0.028 gm SO$_4^{2-}$/ml solution

<table>
<thead>
<tr>
<th>CO$_2$ Pressure psig</th>
<th>Equilibrium Loading (gm SO$_4^{2-}$/ml resin)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>IRA-68</td>
</tr>
<tr>
<td>0</td>
<td>0.068 (a)</td>
</tr>
<tr>
<td>10</td>
<td>0.065</td>
</tr>
<tr>
<td>20</td>
<td>0.087 (b)</td>
</tr>
<tr>
<td>40</td>
<td>0.124 (b)</td>
</tr>
<tr>
<td>80</td>
<td>-</td>
</tr>
<tr>
<td>120</td>
<td>0.136</td>
</tr>
</tbody>
</table>

(a) from Bulter's Thesis
(b) From Modesta's Thesis with 0.039 gm SO$_4^{2-}$/ml solution

Table 1.
Effect of CO\textsubscript{2} Pressure on Performance of IRA-93 Resin

![Graph showing the effect of CO\textsubscript{2} pressure on the performance of IRA-93 resin. The graph plots eluent concentration (C/C\textsubscript{0}) against time (min). The graph includes data points for 10 psig, 40 psig, 80 psig, and 120 psig. The conclusions drawn from the graph are not explicitly stated.]

Figure 3.
curves show a different shape which indicates that there may be some effect of CO₂ pressure on the ion-exchange kinetics. We will explore this in our planned data analysis.

Effect of Bed Height

Two different bed heights of 8 and 16 inches were tried. The resulting breakthrough curves for IRA-93 resin are shown in Figure 4, which indicate that there is no effect of the bed height. This can also be interpreted as absence of any possible channeling or short-circuiting in the shorter bed.

Effect of Dissolved Impurities

Sulfate solutions prepared from the reagent grade K₂SO₄ and MHD spent seed material (with equal sulfate concentration of ~0.024 gm SO₄²⁻/ml of solution) were used in evaluating the effect of other dissolved impurities. According to analysis provided by Butler(2), the MHD spent seed extract would also contain the dissolved impurities such as species containing Cl⁻, F⁻, calcium, sodium, magnesium and of course the potassium. The results in terms of effects on equilibrium loading and breakthrough curves are shown in Table 2 and Figure 5 respectively. Within experimental error, the small levels of dissolved impurities do not seem to affect the loadings on these three candidate resins. As shown by the similar shapes of breakthrough curves in Figure 5, the small levels of dissolved impurities also did not affect the kinetics for IRA-35 resin. Similarly, Butler(2) also did not see any difference in the shape (i.e. ion-exchange kinetics) for the IRA-68 resin.
Effect of Resin Bed Height on Performance of IRA-93 Resin

Figure 4.
Effect of Dissolved Impurities on Equilibrium Loading

Basis: 0.024 gm $\text{SO}_4^{2-}$/ml solution

<table>
<thead>
<tr>
<th>Source</th>
<th>IRA-63</th>
<th>IRA-35</th>
<th>IRA-93</th>
</tr>
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<tbody>
<tr>
<td>Regent Grade $\text{K}_2\text{SO}_4$</td>
<td>0.065</td>
<td>0.073</td>
<td>0.074</td>
</tr>
<tr>
<td>MHD Spent Seed (a)</td>
<td>0.060</td>
<td>0.058</td>
<td>0.076</td>
</tr>
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</table>

(a) Also contained 588 ppm of chloride, and trace levels of coal-derived mineral matter.

Table 2.
Effect of Dissolved Impurities on Performance of IRA-35 Resin

![Graph showing the effect of dissolved impurities on the performance of IRA-35 resin. The x-axis represents time in minutes (0 to 60), and the y-axis represents eluent concentration (C/C₀). The graph includes data points for 0.028 gm SO₄²⁻/ml as K₂SO₄ and 0.022 gm SO₄²⁻/ml as MHD Spent Seed.]

Figure 5.
Effect of Superficial Velocity

Typical breakthrough curves for the IRA-35 resin at superficial velocities of 0.036 cm/sec and 0.009 cm/sec are shown in Figure 6. As shown in this Figure, there is a significant slow down in the kinetics at lower superficial velocity. This is possible if the mass transfer controlling steps are different at higher and lower velocities. Sheth, Prasad and Butler(3) observed the similar results and have developed empirical relationships between the liquid film mass transfer coefficient and the superficial velocity. These expressions are based on the Selke and Bliss' liquid film mass transfer controlling model and are given as:

for \( u \leq 0.02 \text{ cms (or Reynolds number} \leq 0.09) \)

\[
k_L S = 0.00367 \left( \frac{u}{0.0065} \right)^{0.99} \text{ (in cm}^3/\text{g resin} \cdot \text{s)}
\]  

(1)

for \( u > 0.02 \text{ cms (or Reynolds number} > 0.09) \)

\[
k_L S = 0.011 \text{ (in cm}^3/\text{g resin} \cdot \text{s)}
\]  

(2)

Effect of Solution Concentration

Preliminary results for the IRA-35 and -93 resins, showing the effect of solution concentration on the ion-exchange kinetics (i.e. on breakthrough curves) were discussed in the previous quarterly progress report. For both resins, the shape of the curves seemed to remain the same except the curve for higher concentrations had shifted slightly to the left. This shift was explained in terms of resin particles having a finite number of active sites. In line with such explanation we have tried now plotting
Effect of Superficial Velocity on Performance of IRA-35 Resin

Figure 6.
the same breakthrough curves as functions of total sulfate introduced into the column (i.e. a product of solution concentration, flow rate and time) to eliminate the variable parameter of sulfate concentration in the solution. The results are shown in Figure 7, which indicate that all the points should have fallen on the same curve if concentration did not affect the kinetics (or mass transfer coefficient). There seems to be a progressive shift to the right as concentration increases which indicates that there is possibly some effect of the solution concentration on the ion-exchange kinetics. We are looking into this further.

We are still analyzing the experimental results obtained from runs varying solution pH, and molar ratios of K₂SO₄-to-KHCO₃ (i.e. product inhibition effect). These results will be presented in our next quarterly report.

3.3 Task 1.3

To optimize the resin regeneration step, we plan to first carry out simple batch mode experiments. In these experiments, small aliquots of the exhausted resins with known sulfate loadings will be treated to evaluate effects of major parameters such as ammonia concentration, ratio of \((\text{NH}_4)\text{SO}_4\)-to-\(\text{NH}_4\text{OH}\) in the initial solution, and mixing time. In separate efforts, we will use different organic acids such as acetic acid to evaluate their effects on the performance enhancement of the respective resin. We also plan to perform some simple batch mode experiments to understand the effect of carbonation on the hydroxide form of the resin to identify conditions under which one can minimize the formation of \(R_2\cdot\text{CO}_3\) type undesirable form and maximize the formation of \(R\cdot\text{HCO}_3\) type desirable form. The work under this task has just been started.
Effect of Solution Concentration on Performance of IRA-93 Resin

Figure 7.
3.4 **Task 1.4**

Development of "Best Process Schematic" necessitates the determination of the trade-off between the solution concentration used during resin exhaustion step and the subsequent evaporation/concentration load. As presented in the previous quarterly report, two alternative schemes were considered for the concentration of dilute seed solution. They are:

1) Process schematic using Reverse Osmosis (R.O.) in combination with the subsequent evaporation in multiple-effect evaporator, and

2) Total concentration using evaporation in multiple-effect evaporator.

In the first schematic the initial concentration was carried out by using R.O. from 1 wt% to 5 wt%. The solution was further concentrated to 47 wt% by using multiple-effect evaporation. Our preliminary results show that for this scheme, the annualized cost per 1000 lbs of seed concentrated will be higher by about 12% over the evaporation alone. The higher cost can be attributed to the high cost of replacement of membranes. Development and availability of a cheaper membrane would perhaps make this scheme more competitive. In R.O., the best possible rejection ratio realized is around 97% to 98%. Thus, there is also a loss of 2 to 3% of incoming seed solution. This factor would also contribute to the higher costs.

Thus, evaporation in multiple-effect evaporator still remains the most suitable scheme. The availability of low pressure steam at lower costs in the system integrated with the power plant would make it still more attractive. To develop the optimum evaporator design, calculations were also performed to find out the optimum number of effects. Addition of an effect would improve the steam economy but in turn would
also add to the fixed cost of the equipment. It was found from our preliminary calcula-
tions that the relative cost of evaporation per 1000 lbs of seed purified goes down from
a triple effect to a five effect evaporator. (See Figure 8). The analysis of the relative
cost of evaporation was then extended to various inlet seed concentrations. It was
found that the cost of evaporation would go down as the concentration increases.
(See Figure 9). Results of these preliminary calculations will be further refined when
we have optimized all the processing steps and developed the "Best Process
Schematic."

3.5 Task 1.5

The following activities were completed under this task.

- The quarterly technical progress report (report no. DOE/PC/90309-6)
  covering performance period of January 1, 1992 - March 31, 1992 was
  issued on April 21, 1992.

- Two of the program participants (Sheth and Strevel), attended the
  contractors' review meeting organized by DOE/PETC during June 15-17,
  1992 in Pittsburgh and presented the work done so far to the meeting
  attendees.

- On June 17, 1992, the program participants (Sheth and Strevel) pre-
sented the mid-way progress of the project to the technical program
  officer (Dr. Soung Kim) and DOE/MHD contract management personnel
  at the DOE/PETC office.
Effect of Solution Concentration on Relative Cost of Concentration for 4-Effect Evaporator

Figure 9.

Relative Annualized Cost of Concentration

Solution Concentration (wt %)
To date, the project is about 4 - 6 weeks behind schedule. By readjusting the priorities and putting an additional graduate student to work on the process engineering part of the project, we plan to get back on schedule as soon as possible.

4.0 PLANS FOR THE NEXT REPORTING PERIOD

During the next reporting period, we plan to complete the process variables study including analysis of the derived fixed bed data using the math model used by Modeste(1). By the end of the next reporting period, Sterling Strevell expects to complete his M.S. thesis for a degree in Engineering Science and Mechanics. We also plan to continue with our resin regeneration experiments in the batch mode and complete the trade-off study to determine the optimum solution concentration and respective evaporation/concentration load.

5.0 SUMMARY

The work performed during this period is summarized as follows:

- Process variables study on the three candidate resins is nearly complete and at present we are analyzing the fixed bed data using the model/approach used by Modeste(1). Thus far we have evaluated the effects of solution concentration, bed height, CO2-pressure, superficial velocity, solution pH, dissolved impurities and product inhibition. Evaluation of cycle efficiency on the “best” resin will be carried out later when the resin regeneration step is optimized.
• From preliminary analysis of the results, the CO₂ pressure, superficial velocity and solution concentration seem to have significant effect on the equilibrium loading and/or ion-exchange kinetics.

• From our preliminary calculations, the solution concentration scheme making use of reverse osmosis to concentrate very dilute feed solution (i.e. < 5 wt% solution) is found to be more expensive than a multi-effect evaporator scheme. Also, 5-effects evaporator is found to be better than a 3-effects evaporator and the relative cost of concentration by mere evaporation seems to asymptotically fall as the solution concentration increases to about 10 wt% strength.

At the present time, the project is about 4 - 6 weeks behind schedule but still well within the budget.

6.0 REFERENCES

