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ANION-EXCHANGE RESIN-BASED DESULFURIZATION PROCESS

Quarterly Technical Progress Report

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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 for feasibility on a limited scope. From environmental as well as 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.

During the reporting period, April 1, 1991 - June 30, 1991, the following progress was made:

- Using the developed procedure, the batch mode screening experiments were carried out for all eleven candidate resins. The batch mode evaluation is about 90% complete. From preliminary results, IRA-68, -35, and -93 resins look promising and will be further evaluated in the fixed-bed setup.
- The installation of the fixed-bed setup is about 70% complete.
- 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.

Due to additional work required in the batch mode screening experiments, the project is about four weeks behind schedule but is expected to regain schedule during the next quarter.

1.0 INTRODUCTION

Under the current grant (#DE-FG22-90PC90309), The University of Tennessee Space Institute (UTSI) will carry out the necessary bench scale experiments to further develop its anion-exchange, resin-based desulfurization concept to desulfurize alkali metal sulfates. In particular, it is planned to screen commercially available resins and then carry out process optimization work with three selected resins. Further optimization of the resin regeneration step as well as evaluation of the effect of various performance enhancers will then be carried out with one selected resin. A process schematic, to be developed based on the bench scale results, will be used to estimate the related economics. Some limited scope testing will also be carried out using the spent-seed and sorbent materials obtained from both the coal-fired magnetohydrodynamics (MHD) and the in-duct sorbent injection pilot scale facilities.

During this reporting period, 90% of the planned batch mode screening experiments for the eleven samples of candidate resins were completed. Preliminary evaluation of the resulting data is continuing in order to select a smaller number (3-4) of samples for screening in the fixed-bed setup. The installation of the semi-automated fixed-bed setup is about 70% complete and shakedown experiments will be started in 3-4 weeks. Progress made in relation to these activities is presented below.

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, 1991 - June 30, 1991 is indicated in Figures 1 and 2. Figure 1 shows the proposed schedule and 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

- The automatic sampler for the proposed semi-automated fixed-bed setup was received although some of the fittings and valves, etc. are still on order. The installation of the fixed-bed setup is about 70% complete.
- Using the procedure developed for the batch mode evaluation, (described in the Quarterly Technical Progress Report for the period January 1, 1991 - March 31, 1991, report no. DOE/PC/90309-2), screening experiments were carried out for the following additional resins.

[illegible]

- IRA-93
- IRA-94
- A-7
- A-365
- MWA-1
- WGR-2
- AFP-329
- A-305, and
- Culligan(unknown brand)*

In these experiments, the following variables were evaluated.

- K_2SO_4 solution concentration
- Spent MHD seed extract
- Cyclic operation (up to 4 cycles), and
- Sulfate introduced as sodium sulfate

Because of the unavailability of an autoclave and the complexity of related operations, the effect of CO_2 pressure during the exhaustion cycle will be carried out in the future only on a limited number of resin samples and in the fixed-bed setup. The preliminary results from the above screening experiments are compared with the previously reported results for the IRA-68 and -35 resins as follows:

(a) Effect of K_2SO_4 Solution Concentration and Source of K_2SO_4 on Resin Performance

Batch mode screening experiments were carried out using the developed procedure and K_2SO_4 solutions of different concentrations. Reagent grade chemical as well as spent seed extract obtained from the MHD facility at UTSI were used as two different sources of K_2SO_4 . The

* In our first quarterly report this was inadvertently reported as MSA-1 resin supplied by Dow Chemical.

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 the source of K_2SO_4 (reagent chemical versus MHD spent seed extract) in Table 1. These results indicate, that except for IRA-68, -35, and -93, the rest of the candidate resins demonstrate in the batch mode experiments either low percent SO_4^{2-} removal or high percent SO_4^{2-} retention or both. Therefore, such resins are being eliminated from further study. We are looking into the possible reasons for the observed inferior performance by these resins.

Table 1. Effect of Solution Concentration & Source of K_2SO_4 on Resin Performance

Resin Identification	1000 ppm K_2SO_4 Solution		25,000 ppm K_2SO_4 Solution		50,000 ppm K_2SO_4 Solution		50,000 ppm K_2SO_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	ND	ND	54.5	45.3	ND	ND	ND	ND
AFP-329	ND	ND	32.3	66.9	ND	ND	ND	ND
A-305	ND	ND	48.9	29.6	ND	ND	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)

Batch mode screening experiments were also carried out using the developed procedure and K_2SO_4 solution prepared from the reagent grade chemical with a concentration of 25,000 ppm (on a weight basis). An 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. Within experimental scatter, these results show that except for IRA-68, -35 and -93 resins, the rest of the candidate resins demonstrate, in batch mode experiments either low percent SO_4^{2-} 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 the resin regeneration step. However, whatever such 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 would be acceptable for further development and consideration. The slight variation seen in the performance of each resin is believed to be due to the experimental errors and the

manual way of carrying out these simulated cyclic batch mode experiments. During our proposed experiments in the semi-automated fixed-bed setup, we believe that the results of the cyclic operations (up to 20 cycles), after reaching stable conditions, will show less variation from one cycle to another cycle.

Table 2. Effect of Cyclic Operations (Up to 4 Cycles)
(K₂SO₄ 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 Sodium Sulfate (i.e. Sodium versus Potassium System)

Batch mode screening experiments were also carried out using the developed procedure and K₂SO₄ and Na₂SO₄ solutions prepared from the reagent grade chemicals. The solution concentrations for sodium and potassium sulfate systems were kept at 25,000 ppm (on weight basis). Exhaustion and regeneration conditions were kept the

same for both salts. The resulting performance for each of the eleven candidate resins is given in Table 3. Theoretically, there should be no difference in the performance of each resin for the potassium sulfate and sodium sulfate solutions. The slightly lower efficiency seen for the sodium sulfate solution is believed to be due to the greater number of sulfate ions (i.e. g moles) present in the bulk solution during the resin exhaustion step. At the same concentration on a weight basis, the sodium sulfate solution will have 22.5% more moles of sodium and sulfate ions in the given volume of the bulk solution than the K_2SO_4 solution of equal concentration. Also, in Table 1 it is observed that with increased solution concentration, the resin performance during exhaustion cycle decreases. Hence, based on these two facts, the slight decrease in exhaustion efficiency observed for the sodium sulfate may be explained in terms of having greater sulfate concentration in the solution than the corresponding potassium salt. We plan to carry out additional experiments with the selected candidate resins in which we will keep the molar concentrations of the potassium and sodium sulfate the same. The slight lowering of the percent SO_4^{2-} retention for the sodium sulfate may be due to some cationic influence caused by the smaller sodium ion in comparison to the slightly larger potassium ion. Based on the results given in Table 3, the IRA-68, -35, and -93 resins look promising due to their better performance efficiencies during the exhaustion and regeneration steps.

Table 3. Effect of Sulfate Introduced as Sodium Sulfate
(25,000 ppm Solution Concentration)

Resin Identification	K ₂ SO ₄ Solution		Na ₂ SO ₄ Solution	
	% 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	80.3	13.1
IRA-35	78.3	9.2	67.9	6.8
IRA-93	52.4	25.0	56.6	18.0
IRA-94	51.7	55.0	44.1	50.9
A-7	13.0	30.9	8.8	15.1
A-365	12.9	53.2	3.8	2.8
MWA-1	44.3	54.6	34.2	43.8
WGR-2	60.5	67.3	50.7	61.8
Culligan	54.5	45.3	ND	ND
AFP-329	32.3	66.9	ND	ND
A-305	48.9	29.6	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.
- ND Not determined

3.2 Task 1.4

We are continuing to carry out the cursory review of the 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. 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 higher evaporation and drying loads (hence higher cost of steam). On the other hand, concentrated solutions will provide slightly lower resin conversion efficiency (hence higher resin cost) but reduced evaporation and drying loads (hence lower cost of steam). This trade-off study will use

the preliminary economics developed earlier for UTSI by the Resources Conservation Company for the MHD seed regeneration scheme.

3.3 Task 1.5

The following activities were either completed or are planned under this task.

- The second quarterly technical progress report (report no. DOE/PC/-90309-2) covering the performance period from January 1, 1991 - March 31, 1991, was issued on April 11, 1991. To date we have not received any comments on the first and second quarterly reports from the DOE contracting officer.
- 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. Earlier, a 2-page write-up summarizing the accomplishments and providing an abstract was submitted to the DOE/PETC contracting officer 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 will be held in Pittsburgh from July 15-18, 1991. The manuscript

was mailed to Dr. Ruth on April 29, 1991 and the visual aids for the poster presentation are being prepared.

To date, the project is about four(4) weeks behind schedule. The major reason for this slight delay is the extra work required to screen eleven candidate resins in the batch mode screening experiments, which was not included in our initial project estimate. However, we plan to makeup this slight delay in the next two quarters by cutting down on the fixed-bed screening experiments (if possible) and utilizing our past results on the IRA-68 resin.

4.0 PLANS FOR NEXT REPORTING PERIOD

By the next reporting period the batch mode screening experiments on all eleven resins and setting up of the semi-automated fixed-bed unit are expected to be completed. Based on the work done so far, only 3-4 resins look promising for further development, so we will select only these resins for screening in the fixed-bed unit. IRA-68 resin, one of these 3-4 resins, will utilize our past results to guide our proposed fixed-bed screening experiments. In addition to this experimental work, a review of the literature as well as calculations to evaluate the impact of the evaporation and drying loads on the overall economics will be continued. It is planned to attend the Seventh Annual Coal Preparation, Utilization and Environmental Control Contractors' Conference and make a poster presentation.

5.0 SUMMARY

Work performed during this reporting period is summarized as follows:

- Using the developed batch mode screening procedure, evaluated the effect of major parameters on the performance of eleven candidate resins. This evaluation is about 90% complete. From the results obtained so far, the IRA-68, -35, and -93 samples look promising for further evaluation in the fixed-bed setup.
- In comparison to the potassium sulfate, the sodium sulfate solution of equal concentration (on weight basis) shows a slightly lower performance efficiency during the exhaustion step and higher efficiency during the resin regeneration step. We believe that for equal molar concentration solution this slight difference will not exist and both solutions will demonstrate the similar efficiencies.
- The fixed-bed setup is about 70% ready.
- Submitted second quarterly technical progress report on time.
- 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.

Due to additional work required in the batch mode screening experiments, the project is about four weeks behind schedule but is expected to regain schedule during the next quarter.

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