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DOE/PC/92521--T175

TECHNICAL REPORT
March 1 through May 31, 1994

Project Title: **AN ATTRITION-RESISTANT ZINC TITANATE SORBENT FOR SULFUR**

DOE Grant Number: DE-FC22-92PC92521 (Year 2)
ICCI Project Number: 93-1/3.2A-3M
Principal Investigator: James H. Swisher, Southern Illinois University at Carbondale
Other Investigators: William S. O'Brien, Southern Illinois University at Carbondale
Raghubir P. Gupta, Research Triangle Institute
Project Manager: Franklin Honea, Illinois Clean Coal Institute

ABSTRACT

In the continuing search for good sorbent materials to remove sulfur from hot, coal-derived gases, zinc titanate sorbents have shown great promise. The objective of this project is to extend the effort started last year on sorbents with little or no loss in chemical reactivity. The principle is to contain Zn_2TiO_4 in a structural matrix of excess TiO_2. Progress on several tasks was made during the third quarter. The new fixed bed apparatus at SIUC was made operational, and experiments in it have started. The feasibility of using turbine exhaust gas diluted with N_2 for sorbent regeneration was demonstrated through experiments at both SIUC and RTI. The third of four ten-cycle tests was completed at RTI. It was a fixed bed test on one to two promising formulations developed last year. The results followed the pattern of the fluidized bed tests completed earlier in that the chemical reactivity was good, except for the first few cycles. Lastly the undergraduate student design project on hot gas desulfurization hardware was completed this quarter.

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EXECUTIVE SUMMARY

For hot-gas cleanup, zinc titanate sorbents are now receiving more attention than any other class of materials. They undergo fewer phase transformations during sulfidation-regeneration cycles than zinc ferrite and are less susceptible to zinc loss by evaporation. A major objective of this project is to develop a zinc titanate sorbent that is stronger than previous formulations, with little or no loss in chemical reactivity. The higher strength should provide more resistance to attrition in fluidized bed reactors and more resistance to decrepitation in fixed bed reactors. The approach being taken is to incorporate a zinc titanate compound in a structural matrix of TiO_2. A second objective of the project is to develop an improved method for sorbent regeneration. The impetus for this task is an unsolved problem with sulfate formation in fixed bed applications.

The project is an extension of research completed last year. Fifteen sorbent formulations were evaluated using thermogravimetric analysis as the method for evaluating chemical reactivity. Crush strength measurements were also made to obtain a good compromise between strength and reactivity. The two best formulations are being evaluated this year in fluidized and fixed bed tests.

During the third quarter, the effort was divided between several tasks. The construction and checkout of the fixed bed apparatus at SIUC was completed. It will be used primarily for research on improved regeneration procedures, and these experiments have begun. To guide this task, thermodynamic calculations were carried out and a phase stability diagram was constructed. The main feature of importance is the region of stability of Zn sulfate compounds, which are undesirable products of regeneration reactions.

In one set of experiments, the feasibility of using turbine exhaust gas diluted with N_2 for regeneration was studied. The benefits of this approach are to take advantage of sensible heat in the gas and to reduce the amount of N_2 required for producing a mildly oxidizing gas mixture for regeneration. An example is shown in Fig. 1. When a simple 5% O_2 in N_2 mixture was used, the SO_2 evolution from the fixed bed was somewhat irregular, and the SO_2 concentration was still measurable after 2.2 h. When simulated turbine exhaust gas was diluted with N_2 until the O_2 concentration was again 5%, a smooth, symmetrical curve was obtained, and the SO_2 concentration fell to virtually zero in less that 1.5 h.

The same idea was explored further as a part of a ten-cycle fixed bed test at RTI. The sorbent material was the same as that tested in a fluidized bed reactor and described in the

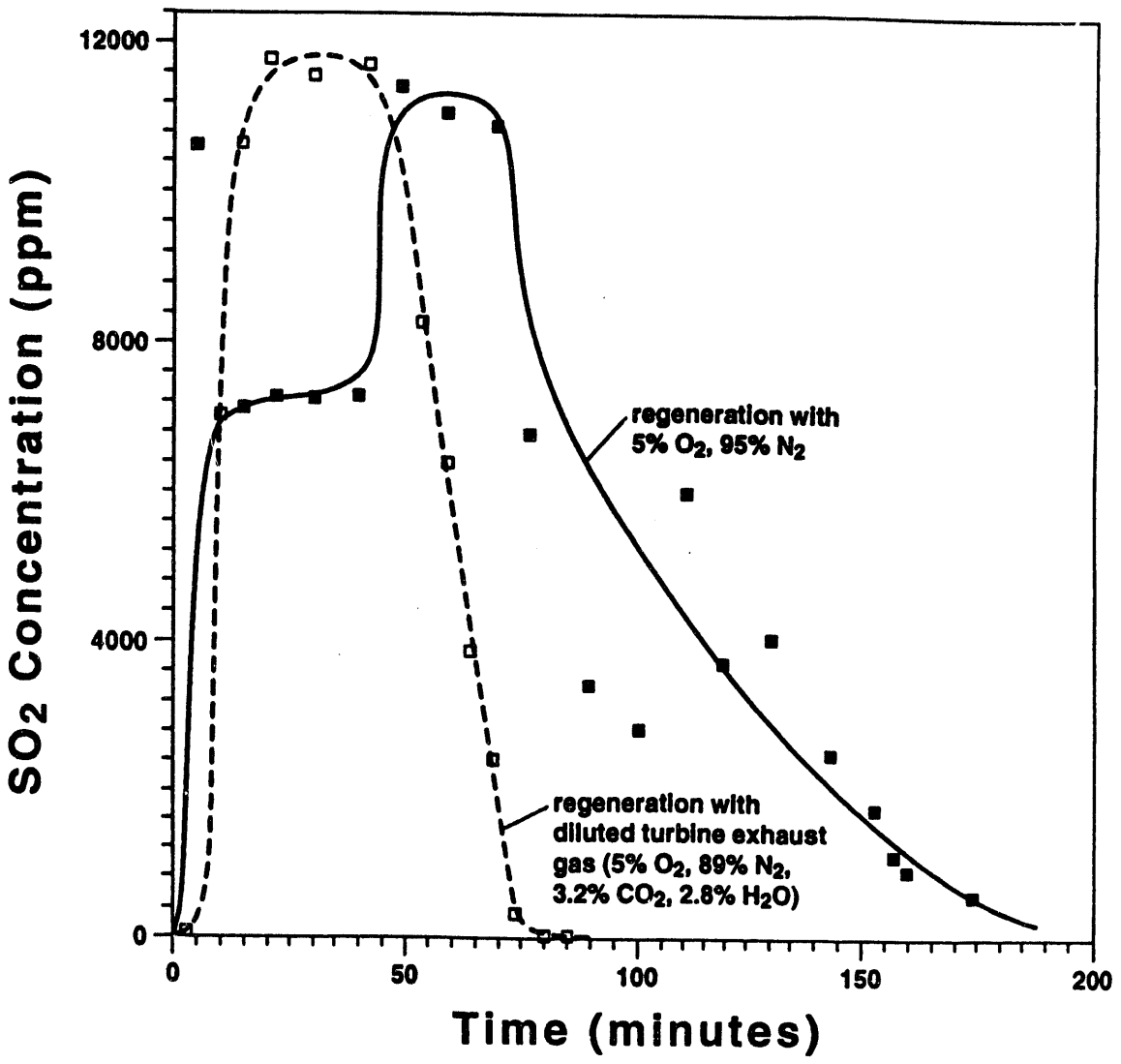


Figure 1. Evolution of SO_2 During Regeneration of Zinc Titanate Sorbent at 650°C.

first quarterly progress report (33.5% ZnO, 0.3 micron powders, sintered at 900°C). The regeneration gas used for the first 5 cycles was a mixture of 2.5% O_2 in N_2. For the last 5 cycles, diluted turbine exhaust gas was used. The test data showed no apparent difference between the two regeneration methods. Thus the feasibility of the idea was demonstrated.

In the same test, H_2S breakthrough curves showed good chemical reactivity in the sorbent, except for the first few cycles. In all three of the ten-cycle tests completed to date, the initial cycles had relatively short breakthrough times. Since the sorbents are expected to last for hundreds or even thousands of cycles, reactivity during the first few cycles is not critical. However, experiments are planned to study simple pretreatments that might be used to activate the sorbent. The post-test sorbent characterization work has not been completed. Some breakage and cracking of the pellets occurred, which is a common observation in fixed bed tests on zinc-based sorbents.

The student design study on hot gas desulfurization hardware was completed this quarter. Emphasis was placed on a retrofit design for the Wabash River IGCC Demonstration Project. The students recommended that an elutriated bed be used in the desulfurization reactor. However, the particle retention time was rather short, so a circulating fluidized bed would probably be better . For regeneration, a bubbling fluidized bed reactor was specified. Regeneration gas was to be obtained by adding air to the off gas from the O_2 plant adjacent to the gasifier. A lesser amount of time was spent on hardware for the Piñon Pine project.

Finally, interactions have started with the Eagle Zinc Company in Hillsboro, IL. They produce both pigment and ceramic grades of ZnO powders. A representative of their company visited SIUC and provided a sample for evaluation.

OBJECTIVES

One objective of the project is to carry out ten-cycle fluidized bed and fixed bed tests on the two best zinc titanate formulations developed during the past year. Of special interest are the chemical reactivity and durability of the sorbents. A second objective is to develop an improved regeneration procedure for fixed bed processes. Currently, there are problems with sulfate formation and decrepitation during sorbent regeneration.

INTRODUCTION AND BACKGROUND

Modern methods of burning high-sulfur coal and converting high-sulfur coal to fuel gas all incorporate a provision for gas desulfurization. Integrated gasification combined cycle (IGCC) systems employing hot gas cleanup are very promising for electric power generation from coal. The thermal efficiency of such systems can approach 50%, compared to 30 to 35% for conventional coal-fired power plants. These IGCC systems with hot gas cleanup have the potential to remove more than 90% of the sulfur and other pollutants from the coal. This subject has been a priority research area for the Illinois Clean Coal Institute (ICCI) and the Morgantown Energy Technology Center (METC) for several years.

The emphasis in research on sulfur sorbents for hot gas cleanup has been on mixed oxide compounds since the early 1980's. Currently sorbents containing zinc titanate compounds are believed to have the most promise and are receiving the most attention. They have the ability to reduce H_2S and COS concentrations in hot gas streams to very low levels. Provided that they are regenerated and reused many times, their cost is not prohibitive. The remaining interrelated concerns are with form stability and durability over many sulfidation-regeneration cycles and with undesirable sulfate formation during regeneration.

This project is a continuation of research performed last year on attrition-resistant zinc titanate sorbents. The principle behind the project is to add excess TiO_2 to Zn_2TiO_4 to form a strong structural skeleton and thereby improve sorbent durability. Fifteen formulations were evaluated for chemical reactivity, crush strength, and other properties. All of the experiments were done on individual particles; thermogravimetric analysis (TGA) was used to study chemical reactivity. Two of the fifteen formulations were selected at the end of the study with the best combination of properties. It is these two formulations that are being tested this year on a larger scale in fluidized bed and fixed bed reactors.

The problem of mechanical degradation of sorbents due to sulfate formation is most serious with fixed bed processes, where the retention time of SO_2 near the particle surfaces is longer. Therefore, there is a need to develop regeneration procedures that reduce or eliminate sulfate formation. Effort to solve this problem is also being done this year.

EXPERIMENTAL PROCEDURES

Two 1.5kg batches of sorbents were prepared for evaluation in fluidized bed and fixed bed reactor tests. The preparation procedures were similar to those used last year with a few differences. Roughly spherical pellets approximately 5mm in diameter were hand rolled to shape. A starch binder was used. After sintering, 400 to 500 grams from each batch of material was crushed and ground to a particle size range of 100 to 250μm for fluidized bed tests. The results of the two fluidized bed tests were discussed in prior quarterly reports. The remaining pellets are now being evaluated, along with new regeneration procedures, in fixed bed tests. The preliminary tests are being conducted in a TGA apparatus and a new fixed bed apparatus at SIUC. The ten-cycle tests are being conducted at RTI.

RESULTS AND DISCUSSION

The fixed bed apparatus at SIUC was made fully operational during this quarter. The associated gas chromatograph was calibrated for the measurement of various concentrations of H_2S and SO_2 exiting the fixed bed. In the initial experiments, emphasis was placed on evaluating an idea for reducing the cost of sorbent regeneration in a mildly oxidizing gas mixture. In the laboratory, mixtures of 2 to 5% O_2 in N_2 work well. Air is not satisfactory because the regeneration reaction is strongly exothermic, and overheating of the sorbent causes pore closure and sintering.

The idea evaluated was to dilute turbine exhaust gas with nitrogen until the resulting oxygen concentration is 2 to 5%. With this procedure, one can take advantage of sensible heat in the exhaust gas and reduce the amount of N_2 that must be used. It is an alternative to using off gas from an O_2 plant, which may be available near O_2-blown gasifiers but not air-blown gasifiers.

The turbine exhaust gas at the Piñon Pine Power Plant is expected to have the composition listed in Table 1*. Also listed is the composition of the gas mixture used in the SIUC experiments to evaluate the idea. In the latter, the O_2 was diluted with N_2 from 11.5 to 5.0%, which caused

(Footnote: *Data provided by W. M. Cambell, M. W. Kellogg Co., Houston, TX, February, 1994.)

TABLE 1. Example Gas Turbine Exhaust Composition and Composition of Gas Used for SIUC Regeneration Tests.

Component	Piñon Pine Power System (%)	SIUC Test Composition (%)
O_2	11.5	5.0
H_2O	6.4	2.8
CO_2	7.3	3.2
N_2	74.0	89.0
Ar	0.8	—
TOTALS	100.0	100.0

corresponding reductions in the concentrations of H_2O and CO_2. For convenience, an equal amount of N_2 was substituted for Ar. The idea was tried first with single particles in the TGA apparatus. The results showed no appreciable difference between regeneration in the simulated turbine exhaust gas diluted with N_2 and a simple mixture of 5% O_2 in N_2.

Fixed bed experiments were then conducted using the same approach. The zinc titanate formulation used contained Zn_2TiO_4 plus 50% excess TiO_2, which is equivalent to 33.5 wt.% ZnO and 66.5 wt.% TiO_2. It was prepared from fine (0.3 micron) powders and sintered at 900°C. Sulfidation was carried out at 400°C in an H_2-H_2S gas mixture. During regeneration at 650°C, the SO_2 concentration was measured as a function of time. The results are plotted in Fig. 1. (See Executive Summary Section.) For the diluted turbine exhaust gas, a smooth bell-shaped curve was obtained, and the SO_2 concentration fell to virtually zero in less than 1.5 h. For the simple 5% O_2 in N_2 gas mixture, the SO_2 evolution curve was more complex, and the SO_2 concentration was still measurable after 2.2 h. The data point corresponding to a time of 5 min. and indicating a high SO_2 concentration was probably influenced by residual sulfur in the apparatus. Therefore it was ignored in drawing the curve through the other data points. Also, most of the data points for both curves in the vicinity of 11000 to 12000 ppm SO_2 are artificially low because of flooding of the gas chromatograph detector. The test for 5% O_2 in N_2 will be repeated to determine if the results are reproducible. If the results are correct, it means that low concentrations of CO_2 and H_2O have a beneficial effect on reaction kinetics. One must use caution with this interpretation because large concentrations of H_2O have been found by others to increase the tendency toward decrepitation. In the RTI fixed bed test to be discussed later, additional results on this subject will be presented.

Considering the topic of regeneration reactions in a broader sense, thermodynamic calculations were carried out to guide experiments on the tendency toward sulfate formation. The results of some of these calculations are shown as a phase stability diagram in Fig. 2. Results are shown for the upper limit (1100K) and lower limit (700K) of the temperature range of practical interest. One important feature is that the O_2 pressure at which sulfate phases form shifts to higher values at higher temperatures. Thus, as others have determined also, regeneration at high temperature reduces the tendency toward sulfate formation. The disadvantage of high temperature is that additional sintering and pore closure will occur if the temperature is too high. It can also be seen from the diagram that there is a strong tendency for sulfate to form at any temperature if regeneration is carried out in an air atmosphere.

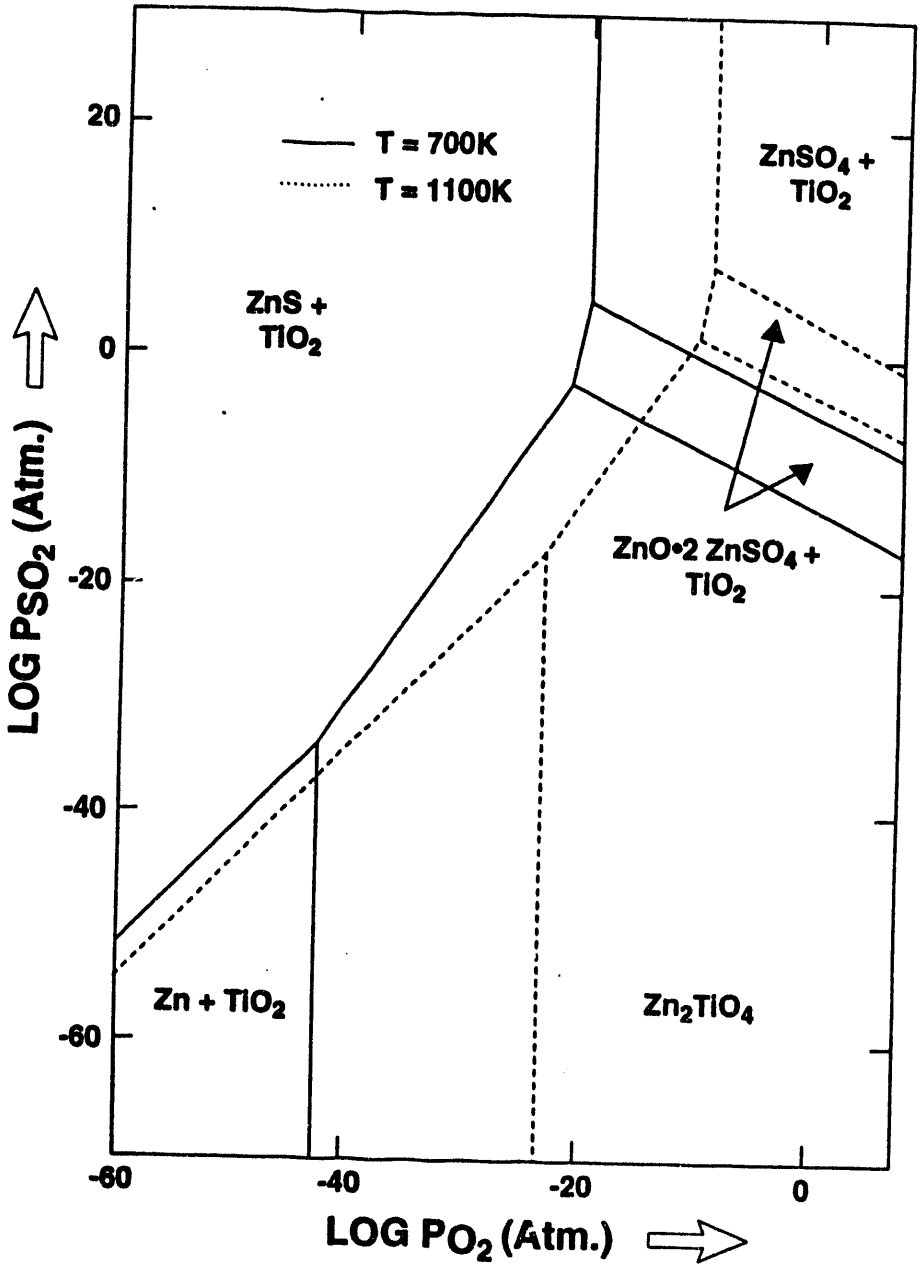


Figure 2. Phase Stability Diagram to Guide Experiments on Zinc Titanate Sorbent Regeneration

Another factor which could be important in analyzing sorbent properties is the tendency for reduction of Zn_2TiO_4 to Zn + TiO_2 at low O_2 pressures. Most coal gasification product gases are sufficiently reducing at these temperatures that Zn metal can be produced. Observations have been made during desulfurization measurements which indicate that at least some Zn forms as an intermediate step in the conversion of Zn_2TiO_4 to ZnS + TiO_2. Zn formation, particularly if it occurs above the melting point of Zn (692K or 419°C), could cause changes in pore structure and vaporization losses.

In using the diagram in Fig. 2 to design regeneration experiments, several ideas were investigated. The first was to try to form Zn sulfate deliberately through regeneration in 100% O_2 at 773K (500°C). When the reaction was carried out in the TGA apparatus, it appeared from the weight gain that only a small amount of sulfate formed. The same conclusion resulted from a fixed bed experiment. Based on gas analysis data, it was estimated that 3% of the Zn was converted to sulfate during regeneration. An attempt is now being made to identify sulfate in the sample by x-ray diffraction analysis. Thus, even though thermodynamic calculations indicated that sulfate should form readily under these conditions, it did not occur to a significant extent. One is tempted to draw the conclusion that high pressure conditions, which also favor sulfate formation, must be present for sulfate formation to be a problem.

Another experiment tried was to regenerate in a CO_2-H_2O gas mixture that gave an O_2 pressure comparable to the stability limits of $ZnSO_4$ and $ZnO \cdot 2ZnSO_4$. The result was that the regeneration reaction was too slow to be of practical interest.

Discussion of some other experiments in progress to develop a better understanding of regeneration reactions will be covered in the next progress report.

Results of the first ten-cycle fixed bed test at RTI will now be presented. The sorbent formulation was the same as for the first fluidized bed test at RTI and for the experiment described in Fig. 1 (pellets prepared from fine TiO_2 and ZnO powders sintered at 900°C). The test conditions are summarized in Table 2. Note in particular that the first 5 regeneration steps were conducted in a simple mixture of 2.5% O_2 in N_2. In the next 3 cycles, the gas simulated the dilution of turbine exhaust gas with N_2, but assuming the H_2O was removed. Removal of H_2O could lessen the tendencies toward decrepitation and deposition of elemental sulfur. The last 2 cycles were carried out assuming H_2O from the turbine exhaust gas was not removed.

Table 2. Experimental Conditions for Ten-Cycle Fixed Bed Test

Parameter	Value
Reactor Pressure	20 atm. (294 psi)
Gas Space Velocity	3000 h^{-1} (35 l/min)
Sulfidation Temperature	550°C
Sulfidation Gas	Simulated Shell Gasifier
Regeneration Temperature	Start: 600 - 640°C Final: 680 - 730°C
Regeneration Gas	
Cycles 1-5	2.5%O_2, 97.5%N_2
Cycles 6-8	2.5%O_2, 1.6%CO_2, 95.9% N_2
Cycles 9-10	2.5%O_2, 1.6%CO_2, 1.4%H_2O, 94.5%N_2

A portion of the results from this test is shown in Fig. 3. Some of the other results were not available in time to meet the progress report schedule. Fig. 3 shows H_2S breakthrough curves for the sulfidation steps. For a breakthrough concentration of 500 ppm, the breakthrough time for the first cycle was 125 min., and, for the other 9 cycles, it exceeded 145 min. The shorter breakthrough time for the first cycle was observed also for the ten-cycle fluidized bed tests described in previous reports. Apparently there is a beneficial change in pore characteristics as Zn in the sorbent is chemically transformed to sulfide, then back to oxide. There could be a simpler way to accomplish the same effect. For example, reduction of Zn to the metallic state in H_2, followed by reoxidation might be used as a pretreatment. Experiments along these lines are planned.

In conducting the ten-cycle test, some Zn vaporization occurred at the 550°C sulfidation temperature. A minor problem occurred as a result; the test had to be interrupted after the 3rd cycle when a filter clogged. This problem may have had an impact on the validity of the data for Cycle 4, where an abnormally long breakthrough time is shown.

Another important result from the test was that the diluted turbine exhaust gas seemed to work as well for regeneration as the simple 2.5% O_2 in N_2 gas mixture. A final conclusion on this point should be deferred until the remainder of the results are available. As with zinc titanate sorbents developed by others, the fixed bed environment resulted in some cracking and breakage of pellets.

It was mentioned in prior quarterly reports that the principal investigator has been supervising a group of undergraduate students who met a course requirement by designing equipment for hot gas desulfurization. Their assignment was to design a retrofit subsystem for the Wabash River IGCC Demonstration Project and to outline modifications of their design to match requirements for the Piñon Pine Project. The former will use an oxygen-blown gasifier and the latter an air-blown gasifier. The students were encouraged but not required to use fluidized bed technology, and zinc titanate was to be the sulfur sorbent. Interfaces were set up with several companies, so that the students could obtain information and advice. The companies included three DOE/METC contractors: Destec, Kellogg, and Gilbert Commonwealth, who were all cooperative and helpful.

For the Wabash River Project, it was decided to specify an elutriated bed in a vessel with an OD of 4.7 ft. and a height of 161 ft. Even with these dimensions, the calculated average retention time of the sorbent was only about 10 min. This feature of the design is probably unsatisfactory, and the students probably should have specified a circulating fluidized bed with a mechanism for continuously

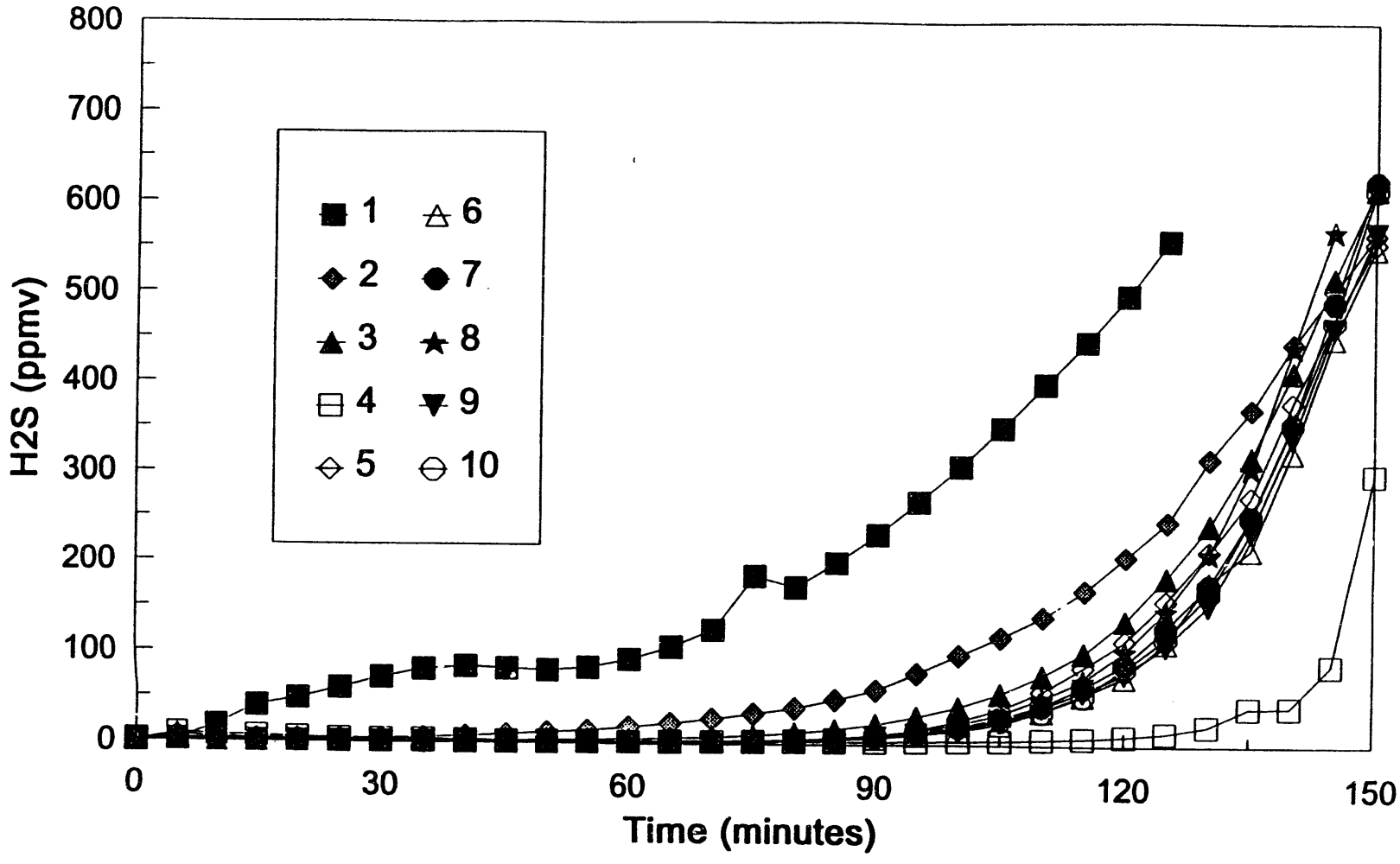


Figure 3. H_2S Breakthrough Curves from Ten-Cycle Test in Fixed Bed Reactor

extracting a smaller amount of the sorbent (compared to the elutriated bed).

A cyclone was specified to separate sorbent exiting the vessel from the clean fuel gas. The regeneration vessel was designed as a bubbling fluidized bed. Its dimensions were 17 ft. OD by 46 ft. high. Circulation of sorbent back to the desulfurization vessel was to occur by positioning the regeneration vessel high enough that gravity flow of solids would occur. The regeneration gas was to be 3 to 5% O_2 in N_2, prepared by blending off gas from the O_2 plant (virtually pure N_2) with air. The estimated costs of compressing and heating this gas were found to be quite high.

Concerning materials of construction, refractory-lined steel was specified for both vessels. Piping in the high temperature portions of the system was to be made from a 300-series stainless steel. Cast iron was specified for low temperature piping.

The students did not leave enough time available to address many of the differences between the Wabash River and Piñon Pine designs. Hardware for the Piñon Pine plant was to be 40 to 50% smaller, which is consistent with the lower estimated power rating of the plant. It was found that the nearest large O_2 plant is in Sacramento, CA, 125 miles away. However, there is an existing distribution system by truck to supply small users in the Reno area with O_2. Whether or not a similar distribution system or pipeline for the N_2 off gas is feasible was not analyzed.

The design study was certainly beneficial for the students and their instructor. Hopefully others will find some aspects of the study useful as well.

A final item of interest is that a representative of the Eagle Zinc Company of Hillsboro, Illinois, visited SIUC in April. It was an outcome of an attempt to identify a commercial supplier of ZnO powders with a particle size of approximately 2 microns. Eagle Zinc is the only U.S. company that currently can produce such material, which is called ceramic grade rather than pigment grade. A sample of their material was donated for experimental evaluation.

CONCLUSIONS AND RECOMMENDATIONS

All planned tasks on the project are proceeding on schedule. During this quarter, the feasibility of using turbine exhaust gas diluted with N_2 for sorbent regeneration was demonstrated. A phase stability diagram was constructed to aid in the design of experiments to study sulfate formation during regeneration. The third of four ten-cycle tests was completed at RTI. It was a fixed bed test in which good

sorbent reactivity after the first cycle was demonstrated. The student design study on hot gas desulfurization hardware was completed. The major conclusions were that an elutriated bed reactor should be used for desulfurization and that a bubbling bed should be used for regeneration.

Plans for the last quarter include additional experiments on improved regeneration procedures, experiments on initial activation of the sorbents, and the fourth reactor test at RTI for sorbent evaluation.

PROJECT MANAGEMENT REPORT
March 1, 1994 through May 31, 1994

Project Title: **AN ATTRITION-RESISTANT ZINC TITANATE SORBENT FOR SULFUR**

DOE Grant Number:	DE-FC22-92PC92521 (Year 2)
ICCI Project Number:	93-1/3.2A-3M
Principal Investigator:	J. H. Swisher Department of Mechanical Engineering and Energy Processes Southern Illinois University at Carbondale
Other Investigators:	W. S. O'Brien Southern Illinois University at Carbondale R. Gupta Research Triangle Institute
Project Manager:	F. I. Honea, Illinois Clean Coal Institute

COMMENTS

No new project milestones were scheduled for completion this quarter, except for progress report submissions. Three of the four reactor tests at RTI are complete, and all tasks in the project are on schedule. An unscheduled supplementary task, the student design study, was completed in May.

On fiscal management, the SIUC Vice President for Administration gave special permission for fiscal authority for the project to be returned to the PI. Normally, emeritus professors are not permitted to be fiscal officers by the University. A rebudgeting request was approved by the ICCI in March to cover certain costs which exceeded expectations, mainly in the Materials and Supplies category. Now there should be no difficulty in completing the project with the allocated budget. To date, spending is somewhat below projected expenditures. The difference is due largely to the lag time in processing vouchers from RTI under the subcontract.

Projected and Estimated Expenditures by Quarter

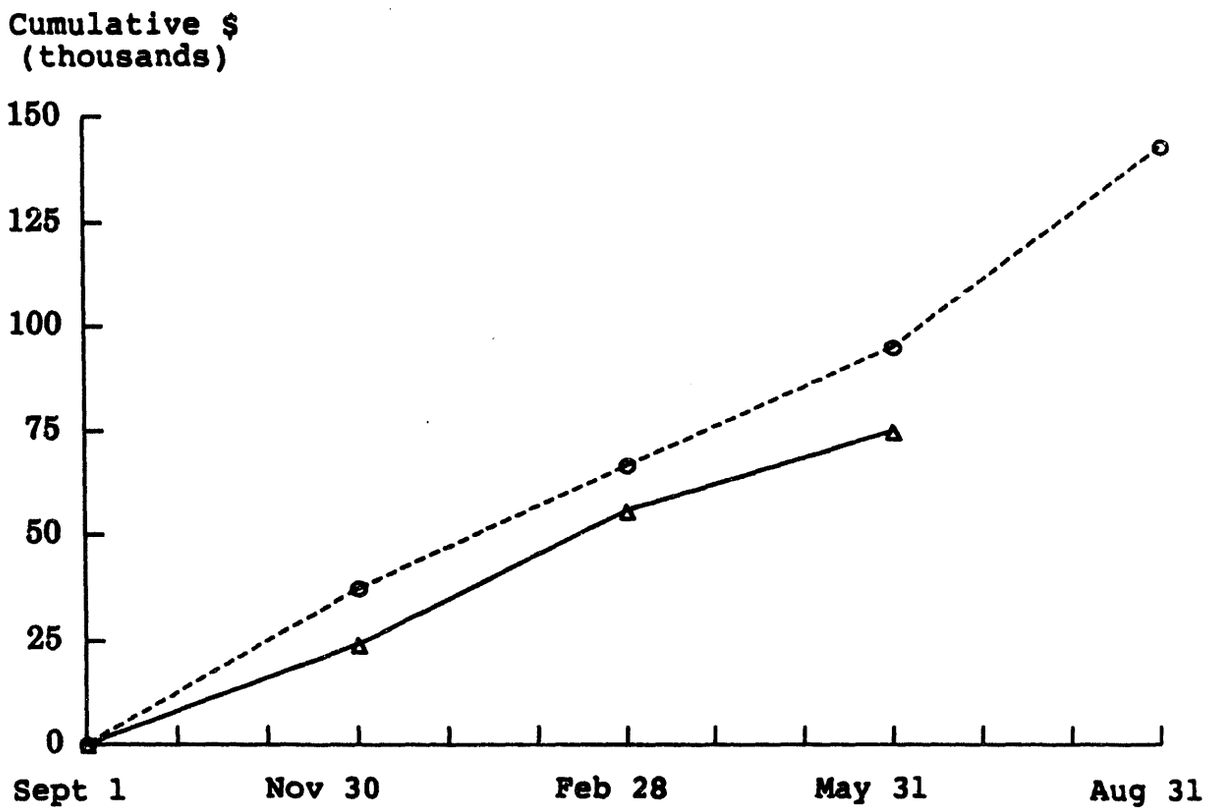
Quarter*	Types of Cost	Direct Labor	Fringe Benefits	Materials & Supplies	Travel	Major Equipment	Other Direct Costs	Indirect Costs	Total
Sept. 1, 1993 to Nov. 30, 1993	Projected	7,158	1,827	800	0	7,200	16,750	3,374	37,115
	Estimated	11,416	1,224	1,025	350	7,200	550	2,177	23,942
Sept. 1, 1993 to Feb. 28, 1994	Projected	14,316	3,654	1,400	500	7,200	33,512	6,058	66,640
	Estimated	15,499	1,647	2,208	985	7,200	23,925	4,426	55,890
Sept. 1, 1993 to May 31, 1994	Projected	21,474	5,481	1,700	500	7,200	50,012	8,637	95,004
	Estimated	25,148	1,413	4,107	800	7,200	29,029	6,770	74,467
Sept. 1, 1993 to Aug. 31, 1994	Projected†	45,984	2,655	4,500	1,500	7,200	68,024	12,986	142,849
	Estimated								

*Cumulative by Quarter

†Reflects internal budget transfers approved on March 8, 1994

COSTS BY QUARTER

An Attrition-Resistant Zinc Titanate Sorbent for Sulfur



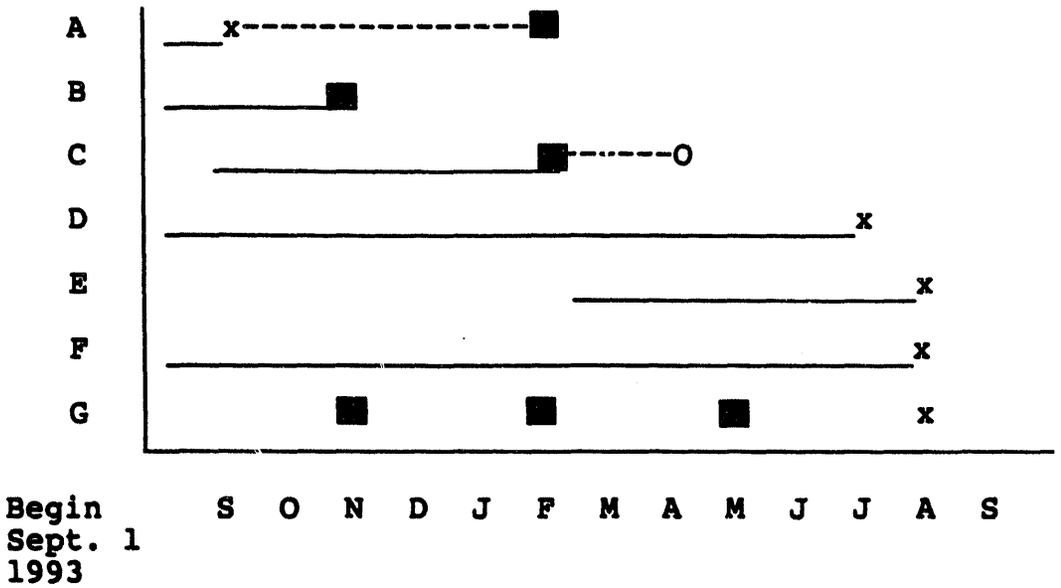
Months and Quarters

O = Projected Expenditures ---------

Δ = Estimated Actual Expenditures _____

Total Illinois Clean Coal Institute Award $142,849

SCHEDULE OF PROJECT MILESTONES



Milestones:

A. Issue subcontract (SIUC)
B. Prepare sorbent materials (SIUC)
C. Fluidized bed testing (RTI)
D. Develop improved regeneration procedures (SIUC)
E. Fixed bed testing (RTI)
F. Materials characterization (SIUC, RTI)
G. Technical and project management reports (SIUC, RTI)

DATE
FILMED
10/19/94

END