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DOE/PC/92521--T137

TECHNICAL REPORT
December 1, 1993 through February 28, 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 increasing the strength and durability of zinc titanate 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. A fluidized bed test was completed this quarter on the second promising formulation selected last year. The results showed its chemical reactivity to increase with each of the ten test cycles. While the break-through times were somewhat shorter than for the first formulation tested, the second formulation's attrition resistance was outstanding. On another task in the project, experiments are underway to develop improved sorbent regeneration procedures.

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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.

The second of the planned fluidized bed tests was completed this quarter. The material was prepared from 2 micron TiO_2 and ZnO powders sintered at 1000°C. The composition was Zn_2TiO_4 plus 50% excess TiO_2, which is equivalent to 33.5 wt.% ZnO and 66.5 wt.% TiO_2. The differences between this formulation and the one described last quarter were that coarser oxide particles and a higher sintering temperature were used. The chemical composition was the same.

Results in the form of H_2S breakthrough curves are shown in Figure 1. Breakthrough, defined as 500 ppm H_2S in the gas above the bed, was only 7 minutes for the first cycle, but it improved progressively and the last 3 of the 10 cycles all had breakthrough times in excess of 45 minutes. A similar improvement in breakthrough properties was observed with the first formulation.

Supplementary measurements of sorbent properties showed that the pore structure was finer after than before the test. This change in structure is believed to be responsible for the improvement in breakthrough properties shown in Figure 1. There was a negligible attrition loss of sorbent during the test. A separate attrition test showed the material to be outstanding in this respect., A tentative conclusion drawn for the two fluidizized bed tests completed is that they are on different sides of the optimum in the tradeoff between chemical reactivity and resistance to attrition.

In the task on improving regeneration procedures, laboratory experiments have started, and information on the availability of large quantities of mildly oxidizing gases is being obtained as a part of a senior design project for a group of four engineering students.

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. Current 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 planned for 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 remaining pellets were stored for fixed bed tests to be conducted later in the year.

A fluidized bed test on the second sorbent formulation was completed this quarter. Its composition was 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 coarse (2 micron) ZnO and TiO_2 powders, and its sintering temperature was 1000 °C. This formulation had the highest compressive strength of those evaluated last year, and it also had reasonably good chemical reactivity.

The fluidized bed test was carried out at a pressure of 15 atm. The sulfidation gas mixture was a simulation of product gas from a Texaco gasifier. Its composition is given in Table 1. A temperature of 923K (650°C) was used for sulfidation. Regeneration was carried out at 993K (720° C) in a mixture of 2.5% O_2 in N_2. Characterization of the sample before and after testing was done by sieve analysis, surface area analysis, mercury porosimetry, chemical analysis, thermogravimetric analysis, and x-ray diffraction. A supplementary attrition test was carried out on the sample before and after the fluidized bed test.

Another task in the project concerns the development of improved regeneration procedures. Construction of the fixed bed apparatus for this task is complete. Preliminary experiments on the task are now in progress in the TGA apparatus.

TABLE 1. TEXACO GASIFIER PRODUCT GAS COMPOSITION

Component	Concentration (vol. %)
H_2	27.70
CO	39.44
CO_2	13.10
H_2O	18.64
H_2S	1.12
N_2	0.00
Total	100.00

RESULTS AND DISCUSSION

Last quarter, results were presented for a fluidized bed test on the first of two promising sorbent formulations. Results are now available for the second formulation, which has a coarser structure and a much higher compressive strength (147 versus 56 N/mm or 28 versus 10 MPa). Breakthrough curves for the fluidized bed test are shown in Figure 1 (see Executive Summary). Breakthrough was defined as the time when the H_2S concentration in the exit gas reached 500 ppm. As with the first test, the breakthrough time for the first cycle was poor, then they became progressively better during the ten-cycle test. For the last six cycles, the breakthrough times were all in the range of 40 to 50 minutes. While these results are reasonably good, the first formulation was better, with breakthrough times of 70 to 80 minutes for the last several cycles.

Other data obtained for the second fluidized bed test are summarized in Table 2. It shows the differences in physical properties of the sorbent before and after the test. The first entry shows there was no zinc loss due to vaporization. The next several entries show that some significant changes in structural properties occurred. The x-ray diffraction results show that some of the Zn_2TiO_4 present initially transformed to $ZnTiO_3$ and $Zn_2Ti_3O_8$. Comparing the two tests, the transformation occurred to a greater extent in the first than in the second. These results are rather confusing, and the investigators are not confident of their validity. Checks are being made at other x-ray labs and other checks may be made later with energy dispersive x-ray measurements on a scanning electron microscope.

Returning to Table 2, surface area and mercury porosimetry measurements showed that the pore structure in the sorbent became finer during the test. These data explain the improvement in breakthrough time and chemical reactivity as the number of cycles increased.

CONCLUSIONS AND RECOMMENDATIONS

The project is proceeding on schedule. Fluidized bed tests on two promising sorbent formulations have been completed. Both performed reasonably well; the first was better in chemical reactivity, and the second was better in attrition resistance. It is felt that a little more work is needed to optimize properties. The task on improvement of regeneration procedures was started this quarter and is proceeding smoothly. Fixed bed reactor tests are now being planned.

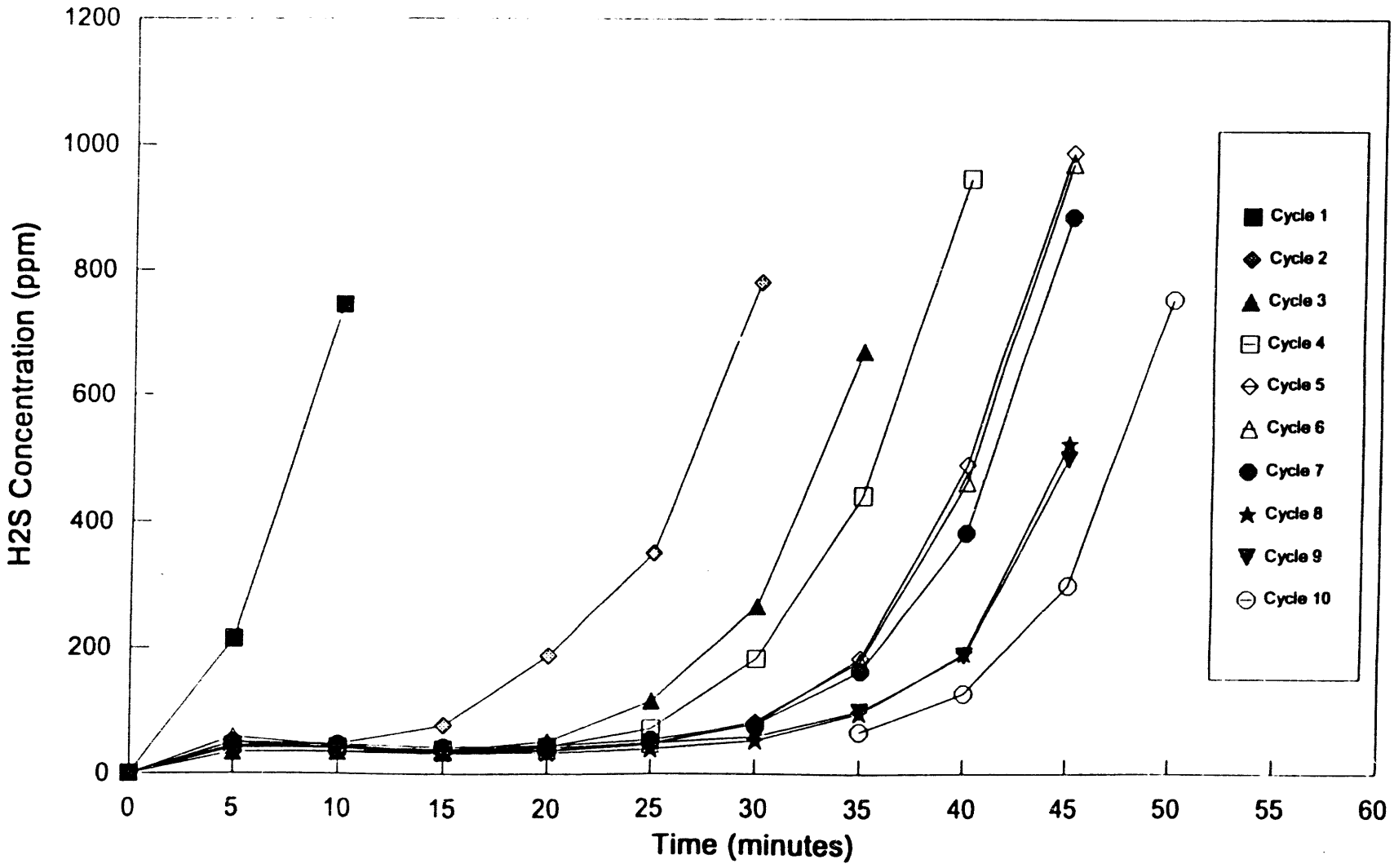

FIGURE 1. BREAKTHROUGH CURVES FROM TEN-CYCLE FLUIDIZED BED TEST OF ZINC TITANATE SORBENT CONTAINING 50% EXCESS TiO_2 MADE FROM 2 MICRON POWDERS AND SINTERED AT 1000°C.

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TABLE 2. CHARACTERIZATION RESULTS ON SORBENT MATERIAL BEFORE AND AFTER FLUIDIZED BED TEST

Method or Property	Fresh	Reacted
Zn Concentration (wt %)	25.3	26.0
X-Ray Diffraction+ (wt %)		
TiO_2	29.9	26.1
Zn_2TiO_4	70.1	56.1
$ZnTiO_3$	0.0	3.2
$Zn_2Ti_3O_8$	0.0	14.6
BET surface area (m^2/g)	0.53	0.90
Mercury porosimetry		
Pore volume (cm^3/g)	0.1269	0.1168
Median pore dia. (Å)	10,419	6,261
Porosity (%)	37.1	34.9
Particle density (g/cm^3)	2.92	2.99
Sieve analysis (wt %)		
-50+60	0.00	0.68
-60+80	60.27	52.88
-80+100	18.15	19.32
-100+120	12.07	15.25
-120+140	8.90	11.86
-140	0.00	0.00
Ave. size (μm)	177.4	171.5

+Provided by West Virginia University

The sieve analysis data are nearly the same for the fresh and reacted sorbent. There was essentially no weight loss of material either. Thus attrition of the sorbent did not occur during the test. A supplementary attrition test was carried out on the material in both the fresh and reacted conditions. Such attrition testing has been done traditionally on catalyst materials to give predictions of durability, and its use has been extended by some investigators to obtain the same information on sulfur sorbents. It is a rather severe test, so there is only a general correspondence to expected performance in fluidized bed reactors. In the tests conducted on the second formulation, the attrition loss of the fresh material was 17.4% after 5 hours and 59.8% after 20 hours. Corresponding values for the reacted material were 9.6% and 39.0%; thus the attrition resistance improved during the test. These losses are very low in comparison to other zinc titanate formulations. The compressive strength, sieve analysis, and attrition test data all indicate the sorbent should be very durable.

Finally, progress was made on the task to improve regeneration procedures from two directions. Initial experiments have been completed using a thermogravimetric analyzer (TGA). It has been determined that zinc sulfate can be produced deliberately if regeneration is carried out at 500° C in slowly flowing pure oxygen. Now various experimental parameters (temperature, gas composition, and system pressure) are being studied to determine which are most effective in preventing sulfate formation. After screening experiments in the TGA have been completed during the third quarter, follow-on experiments well be started in the new fixed bed reactor. Most of these experiments are being done by an exchange student from the Technical University of Clausthal, a German engineering university.

The other aspect of this task is to investigate possibilities for obtaining an inexpensive supply of a mildly oxidizing gas mixture for sorbent regeneration. A group of four undergraduate students are studying this problem as a part of a senior design course at SIUC. Possibilities include the off-gas from an oxygen production plant and exhaust gas from a gas turbine. One or both options would be available at an Integrated Gasification Combined Cycle Power Plant. The students' overall assignment is to design hot gas desulfurization subsystems to the meet the requirements of the Wabash River and Pinon Power IGCC demonstration projects. Several industrial and other contacts have been made in the search for data and advice.

CONCLUSIONS AND RECOMMENDATIONS

The project is proceeding on schedule. Fluidized bed tests on two promising sorbent formulations have been completed. Both performed reasonably well; the first was better in chemical reactivity, and the second was better in attrition resistance. It is felt that a little more work is needed to optimize properties. The task on improvement of regeneration procedures was started this quarter and is proceeding smoothly. Fixed bed reactor tests are now being planned.

PROJECT MANAGEMENT REPORT

December 1, 1993 through February 28, 1994

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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

Two project milestones were completed this quarter. The subcontract from SIUC to RTI was awarded in February, five months later than planned. Fluidized bed testing at RTI was completed in February, as originally scheduled. Completion of this task was accomplished on schedule because of RTI's willingness to work for a period of five months before receipt of the subcontract. It is expected that all of the remaining milestones will be completed on time.

Overall, expenditures to date are close to those planned. However, there is a need to transfer funds between subaccounts because of inaccurate estimates made at the beginning of the contract. The most critical problem is that all of the Materials and Supplies budget has already been committed because of unexpected needs in the setup of the fixed-bed reactor at SIUC. A letter has been prepared to request the needed adjustments.

On February 1, 1994, Dr. Swisher, the PI, became a professor emeritus. University policy does not permit him to continue to have responsibility for fiscal management, so that responsibility has been transferred to Mr. John Mead, Director of the SIUC Coal Research Center. Dr. Swisher is now working essentially full time on research projects, and this project should benefit by his change in status.

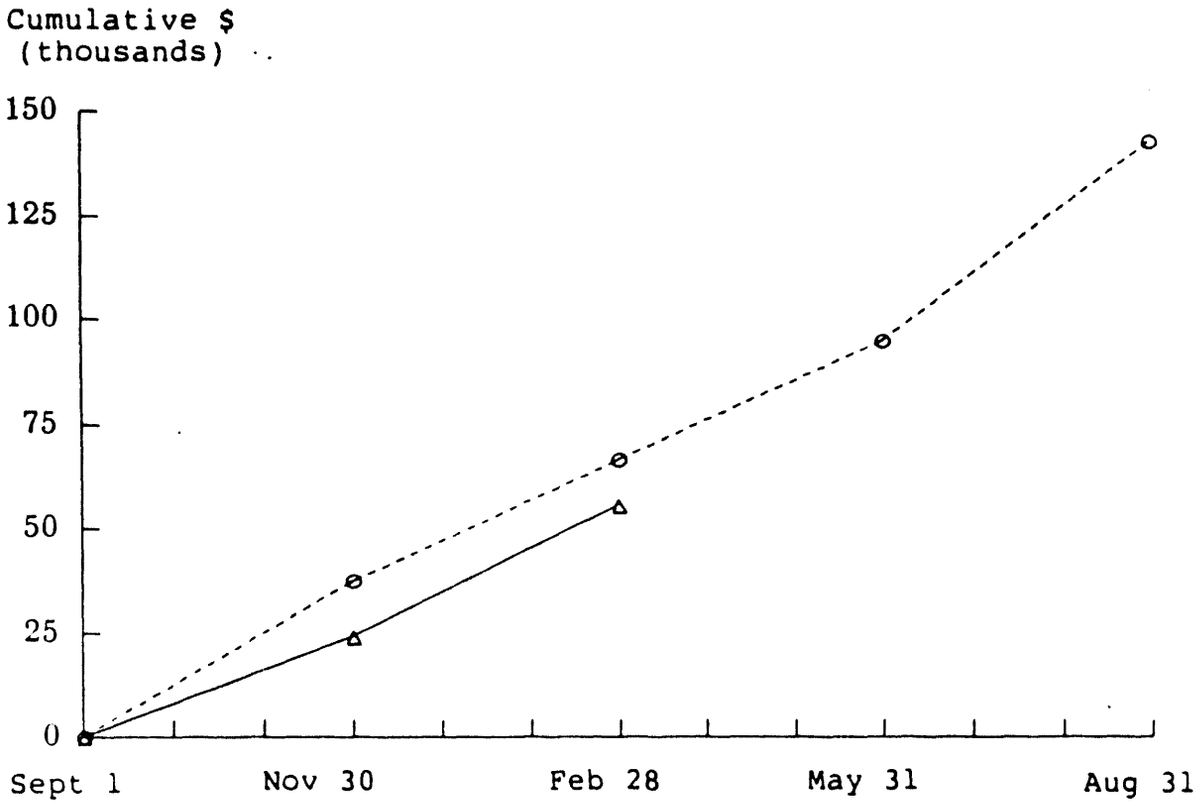
Projected and Estimated Expenditures by Quarter

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								
Sept. 1, 1993 to Aug. 31, 1994	Projected	42,484	9,855	2,100	1,200	7,200	62,024	12,986	142,849
	Estimated								

*Cumulative by Quarter

COSTS BY QUARTER

An Attrition-Resistant Zinc Titanate Sorbent for Sulfur



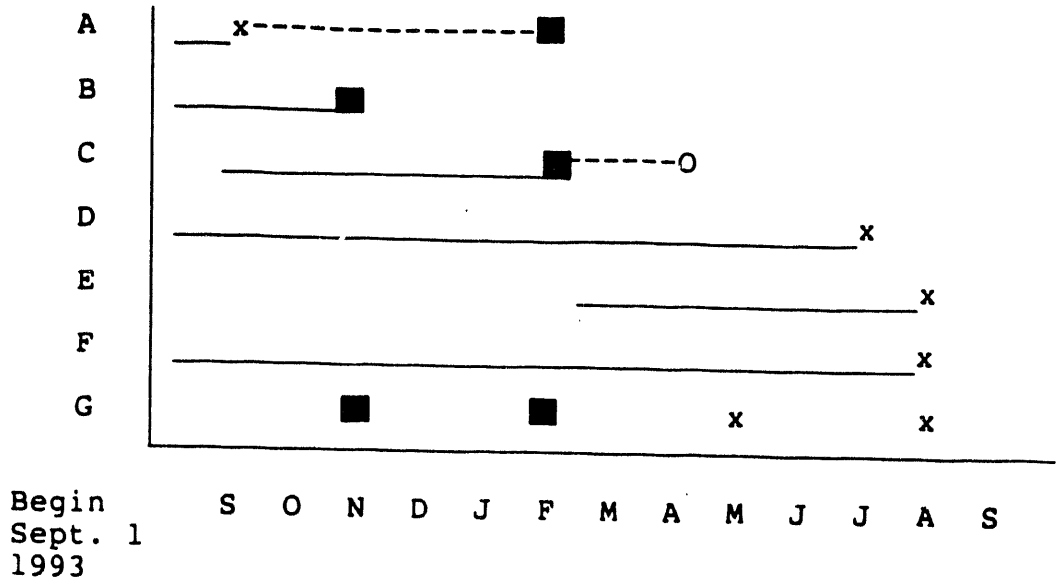
Months and Quarters

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)

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