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TECHNICAL REPORT
March 1 through May 31, 1995

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Project Title: **COMPOSITION MODIFICATION OF ZINC TITANATE
SORBENTS FOR HOT GAS DESULFURIZATION**

DOE Cooperative Agreement Number: DE-FC22-92PC92521 (Year 3)
ICCI Project Number: 94-1/2.2A-2M
Principal Investigator: James H. Swisher, Southern Illinois University
at Carbondale
Other Investigator: Ranajit K. Datta, Virginia Polytechnic Institute
and State University
Project Manager: Franklin I. Honea, Illinois Clean Coal Institute

ABSTRACT

For new coal gasification systems, zinc titanate sorbents are being developed to remove sulfur from the hot product gas prior to its use in combined cycle turbines and high temperature fuel cells. Although most of the properties of these sorbents are very attractive, there are still concerns about durability over many sulfidation-regeneration cycles and zinc losses due to vaporization. Doping the zinc titanate with other metal ions could alleviate both concerns, which are the objectives of this project. After a screening study was completed, it was decided that Cr offered more promise as a dopant than Ni, Cu, Mg, and Al. Therefore six new sorbent formulations containing Cr were prepared, and they are now being evaluated with a series of bulk density, x-ray diffraction, crush strength, and thermogravimetric analysis (TGA) measurements. Results to date suggest that, while Zn vaporization losses can be reduced with Cr additions, a penalty in chemical reactivity occurs. A fixed bed test was also completed this quarter on a Cr- containing formulation. The H₂S breakthrough time was about 11 hours, and utilization of Zn in the sorbent was 60.5%.

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EXECUTIVE SUMMARY

Sulfur sorbents which contain zinc as the primary desulfurizing agent continue to show promise for coal gasification applications. Scale-up tests are now in progress for Integrated Gasification Combined Cycle (IGCC) systems. There are still concerns, however with sorbent durability over many sulfidation-regeneration cycles and with vaporization losses of zinc. Therefore research and development directed at these potential problems is continuing. Zinc titanate sorbents are among the few that have reached the stage of large scale testing.

An approach that has received little attention to date for improving the properties of zinc titanate is to dope the material with other metal ions. In principle, it should be possible to both strengthen the material and reduce zinc vaporization losses in this way. Based on ceramic crystal chemistry principles, it was decided to study the possible beneficial effects of Ni, Cr, Cu, Mg, and Al as dopants in zinc titanate. During the first half of the contract period, a screening study was conducted to determine which of the dopants offered the most promise. Bulk density, crush strength, x-ray diffraction, and thermogravimetric analysis (TGA) measurements were made. It was decided, primarily on the basis of TGA results of chemical reactivity, that emphasis in subsequent research should be placed on sorbent formulations containing Cr.

During the third quarter, six new formulations were prepared for evaluation. One of the formulations, which had an intermediate Cr content was sintered at three different temperatures: 900, 950, and 1000° C. The others had higher and lower Cr contents, all sintered at 900° C. When the materials were sulfidized in a simple mixture of 0.9% H₂S, 92.4% H₂, and 6.7% N₂, both Zn and Cr reacted to form sulfides. When simulated coal gas was used, only the Zn sulfidized. A thermodynamic calculation was carried out to explain this difference.

It was found generally that Cr additions had a retarding effect on reaction kinetics. This result is not surprising because the thermodynamic activity of Zn in the titanate spinel compound is reduced when Cr dissolves as a dopant. The same thermodynamic effect also reduces the vapor pressure of Zn, thereby reducing the susceptibility to vaporization losses. Thus there is a tradeoff between two important properties when Cr is added to the material. Experiments designed to measure Zn vaporization loss tendency are planned for the next quarter.

The first fixed bed test was conducted during the past month. The material tested was from the formulation prepared last fall, which had a 4:1 ratio of Zn to Cr. Its chemical reactivity in TGA experiments was as good or better than that of the formulations just prepared. Three sulfidation-regeneration cycles were carried out at a temperature of 650° C. The pre-breakthrough concentration of H₂S in the gas exiting the bed was less than 1 ppmv. Breakthrough occurred suddenly at a reaction time of approximately 11 hours. At breakthrough, a mass balance calculation showed that 60.5% of the Zn in the sorbent was converted to ZnS. Regeneration in an O₂-N₂ mixture was complete in 2 to 3 hours. The next fixed bed test will probably be conducted at a higher temperature, since Cr doping may offer advantages over undoped zinc titanate only at temperatures above 650° C.

OBJECTIVES

The general objective of the project is to improve the engineering properties of zinc titanate sorbents for the removal of H_2S from coal gasification product gases. These improvements will be made by systematically adding dopants, such as Ni, Cu, Cr, Mg, and Al, to zinc titanate formulations. The main tasks designed to meet the objectives are sorbent preparation, solubility measurements, and bench-scale testing of sorbent pellets. Expected results include both engineering property characterization and an understanding of the crystal chemistry of the doped sorbents.

INTRODUCTION AND BACKGROUND

All modern coal combustion and coal conversion processes must have provisions to meet strict specifications on emissions of H_2S and SO . For many systems, removal of sulfur-bearing species from hot gases is also needed to prevent corrosive damage to materials and components. Both requirements apply to Integrated Gasification Combined Cycle (IGCC) and Molten Carbonate Fuel Cell (MCFC) systems. An important milestone in the development of IGCC systems was successful completion of the Cool Water Coal Gasification Program (Douglas, 1990). In this program, the fuel gas was cooled down for H_2S removal, then reheated before injection into the turbine combustor. To avoid the associated efficiency loss with cooling of the fuel gas, most of the active development projects now include hot gas desulfurization with regenerable sorbents.

Many metals, oxides, and other compounds have been evaluated for their ability to remove H_2S from hot, coal-derived gases. In recent years, one of the classes of compounds that has been studied extensively and continues to show promise is zinc titanate (Swisher, O'Brien, and Gupta, 1994; Gupta, Gangwal and Jain, 1993; Gupta and Gangwal, 1993; Datta, 1994; Mei, et al., 1993; Ayala, et al., 1993; and Grindley, 1990). The status of the technology has matured to the point where large scale testing in process development units and pilot plants is in progress (Bevan, et al., 1994; Kontinen, et al., 1994).

There are still a few concerns with zinc titanate sorbents which are being investigated in current projects. The most important of these is durability over many sulfidation cycles in fixed and fluidized bed reactors. There is a lesser concern with vaporization losses of zinc. In this regard, current sorbent formulations are adequate unless the sulfidation reaction is carried out above a temperature of approximately $600^\circ C$.

In the project described here, the research is directed toward both problem areas. By the incorporation of a third metal ion into the zinc titanate crystal structure, the thermodynamic activity and vapor pressure of zinc can be reduced. Also, the dopant may improve the strength and durability of the sorbents. Scanty information has been found in the literature on this subject, so the present work is pioneering in nature.

EXPERIMENTAL PROCEDURES

The procedure used for sorbent preparation was the same as that used in prior ICCI projects. Reagent-grade oxide powders were blended in a dilute solution of starch in water. Excess water was removed until the material had a consistency like toothpaste, then it was extruded through a 1 cm dia. metal tube and cut to lengths of approximately 1.5 cm. After drying further, the green pellets were sintered for three hours at various temperatures. The graduate assistant at VPI spent three days at SIUC in March to obtain training on these procedures, and she will carry out this task for the remainder of the project. Six new formulations containing Cr were prepared this quarter.

Characterization of the as-sintered pellets consisted of compressive strength, x-ray diffraction, and bulk density measurements. Porosity values were calculated from the x-ray diffraction and bulk density data. Thermogravimetric analysis (TGA) experiments were carried out on all the new formulations to evaluate their chemical reactivities.

The first fixed bed test was conducted this quarter. The material tested was the formulation prepared during the first quarter because its reactivity in TGA experiments was better than that of the new formulations. For the fixed bed test, pellets were crushed to a particle size range of -6 to +30 mesh size (0.6 to 3.4 mm.). The reactor was made from 3 cm ID quartz tubing, and a Hewlett Packard gas chromatograph was used to analyze gas mixtures exiting the bed for H₂S and SO₂.

A calculation was carried out to select a composition of simulated coal gas that approximated Texaco Gasifier conditions but did not cause an extensive amount of carbon deposition in the apparatus. Table 1 shows the initial composition of the mixture, fixed by metering the flow rates of individual gases, and the equilibrium composition at 650° C, as determined by computer calculation. A mixture of 5% O₂ in N₂ was used for regeneration.

TABLE 1. Composition of Simulated Coal Gas

| Component | Starting Composition | Equilibrium Composition (650° C) |
|------------------|----------------------|----------------------------------|
| H ₂ | 49.5% | 33.8% |
| H ₂ O | 1.0% | 14.4% |
| CO | 17.0% | 26.0% |
| CO ₂ | 32.0% | 22.7% |
| CH ₄ | ----- | 2.6% |
| H ₂ S | 0.5% | 0.5% |
| O ₂ | ----- | 1x10 ⁻²³ atm |
| S ₂ | ----- | 2x10 ⁻⁹ atm |

RESULTS AND DISCUSSION

A summary of the physical properties obtained to date on the new sorbent formulations containing Cr is given in Table 2. For one of the compositions, the material was sintered at three different temperatures. For others, the Cr concentration was varied, and the sintering temperature was held constant at 900° C. Crush strength data for three of the formulations have yet to be determined (TBD) because of repairs being made on the mechanical testing equipment.

TABLE 2. Physical Properties of New Sorbent Formulations Containing Chromium

| Composition | Sintering Temp. (° C) | Bulk Density (g/cm ³) | Estimated Porosity (%) | Crush Strength (N/mm) |
|---|-----------------------|-----------------------------------|------------------------|-----------------------|
| Zn _{1.9} Ti _{0.9} Cr _{0.2} O ₄ | 900 | 2.62 | 51.9 | 113 |
| Zn _{1.9} Ti _{0.9} Cr _{0.2} O ₄ | 950 | 2.68 | 49.9 | 120 |
| Zn _{1.9} Ti _{0.9} Cr _{0.2} O ₄ | 1000 | 2.93 | 45.3 | 163 |
| Zn _{1.95} Ti _{0.9} Cr _{0.1} O ₄ | 900 | 2.89 | 46.2 | TBD |
| Zn _{1.8} Ti _{0.8} Cr _{0.4} O ₄ | 900 | 2.41 | 55.2 | TBD |
| Zn _{1.5} Ti _{0.5} Cr _{1.0} O ₄ | 900 | 2.28 | 58.1 | TBD |

For the first three entries in Table 2, the porosity decreases and the crush strength increases with increasing sintering temperature, as one would expect. In comparing the properties with different Cr concentrations sintered at 900° C, the bulk density decreases and the porosity increases with increasing Cr concentration. Thus Cr has a hindering effect on sintering kinetics. This effect is not viewed as a problem because a higher temperature could be used without difficulty if it were desired to increase the density and reduce the porosity. The variation of crush strength with Cr concentration will be discussed in our final technical report.

It was reported last quarter, based on x-ray diffraction data, that all of the compositions listed in Table 2 form spinel solid solutions at temperatures of 1000 and 1100° C. There was a concern that the solid solutions might be unstable at 650° C, the temperature at which TGA and fixed bed experiments were planned. Therefore, a series of tests were carried out to check this possibility. Samples with various Cr concentrations, denoted by x in the formula Zn_{2-x}Ti_{1-x}Cr_{2x}O₄, were prepared at 1100° C. Then they were held for times of 1.5, 3, and 5 days at 650° C in air. The stability was studied by determining the lattice parameter of the spinel compound by x-ray diffraction measurements before and after the 650° C treatments. The results are given in Table 3. It can be seen that no changes in lattice parameter occurred with prolonged heating at 650° C. Also, there were no other phases detected which could

have been spinel decomposition products. Additional checks on phase stability will be made in connection with fixed bed tests.

TABLE 3. Lattice Parameter Data for $Zn_{2-x}Ti_{1-x}Cr_{2x}O_4$ Samples Prepared at 1100° C and Held for Various Times at 650° C.

| X | Average a_0 (Å) | | | |
|------|-------------------|-------|-------|-------|
| | 1100° C | R1* | R2* | R3* |
| 0.10 | 8.437 | 8.436 | 8.433 | 8.437 |
| 0.20 | 8.412 | 8.413 | 8.411 | 8.412 |
| 0.25 | 8.398 | 8.397 | 8.397 | ----- |
| 0.30 | 8.363 | 8.363 | 8.366 | 8.366 |
| 0.40 | 8.390 | 8.386 | ----- | 8.387 |
| 0.50 | 8.347 | 8.347 | 8.349 | 8.346 |

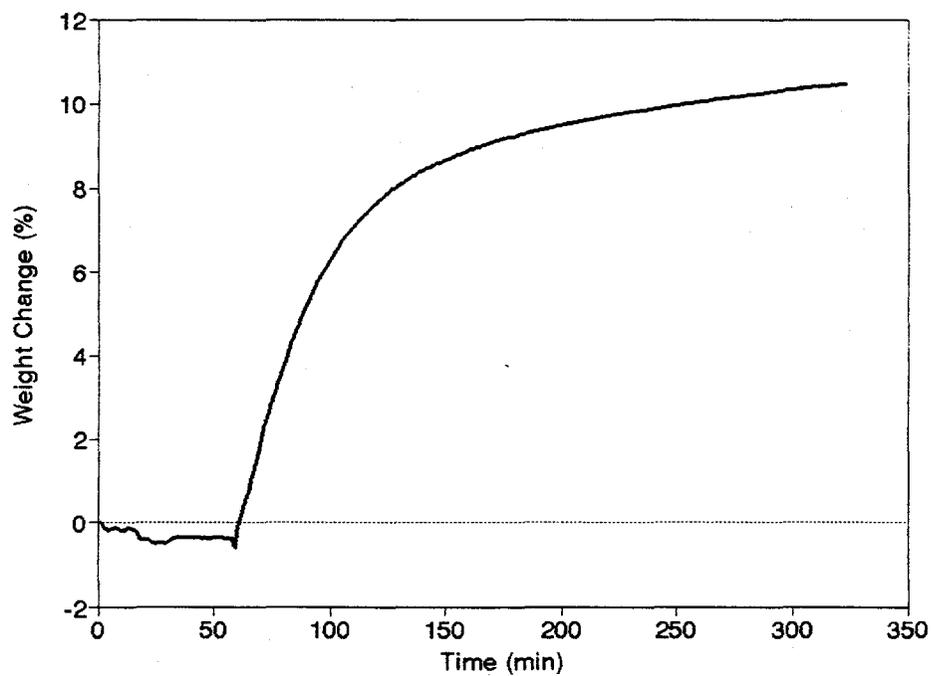
1100° C = prereacted for 24 hours

* specimens reheated to 650° C for 1.5 days (R1), 3 days (R2), and 5 days (R3)

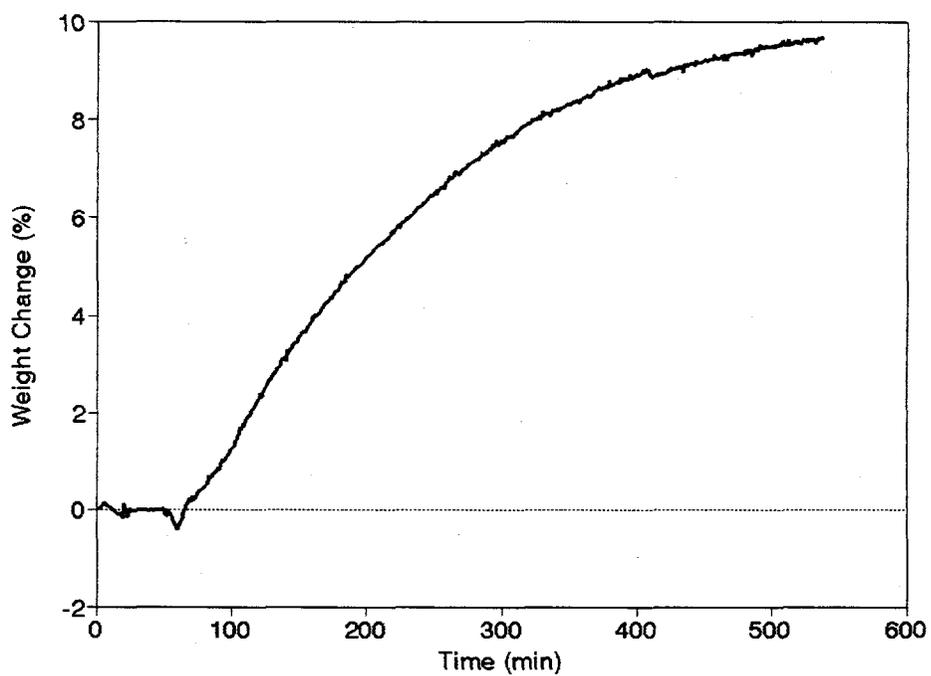
Thermogravimetric analysis (TGA) experiments were carried out on all the new sorbent formulations. In some of these, a mixture of 0.9% H_2S , 92.4% H_2 , and 6.7% N_2 was used for sulfidation as a screening method to judge chemical reactivity. Some of the formulations were also tested in simulated coal gas. Only a few of the results will be presented because the new formulations were found to be similar to or worse than the reactivity of the formulation prepared last fall and discussed in the September-November, 1994, quarterly report. The new results do, however, contribute greatly to an understanding of how chromium additions alter the properties of zinc titanate sorbents.

The TGA results to be discussed in detail appear in Figures 1 and 2. The specimens were from the formulation of the composition $Zn_{1.9}Ti_{0.9}Cr_{0.2}O_4$ sintered for 3 hours at 900° C. Data in the top part of Figure 1 show the sulfidation rate in the mixture of 0.9% H_2S , 92.4% H_2 and 6.7% N_2 at 650° C. After introducing the sulfidizing gas at a time of 60 minutes, the weight gain was fast for the next 60 minutes, then became much slower. The total weight gain was 10.5%, and the specimen color changed from pastel green to dark gray during sulfidation. In the bottom part of Figure 1, data are given for a similar specimen sulfidized in simulated coal gas. The rate was generally lower, mainly a consequence of the lower H_2S content of the gas (0.5 vs. 0.9%). The total weight gain was 9.7%, and the specimen color remained pastel green. As will be discussed in connection with Figure 3, it is believed that both Zn and Cr sulfidized under the conditions of Figure 1 (a), but only Zn sulfidized under the conditions of Figure 1 (b).

Figure 2 shows regeneration data for the same specimens. The weight losses match the weight gains from Figure 1, and the regeneration rate was somewhat faster for the specimen sulfidized in simulated coal gas. This faster rate would be expected if the pores were larger as a result of a smaller amount of sulfide in the material.

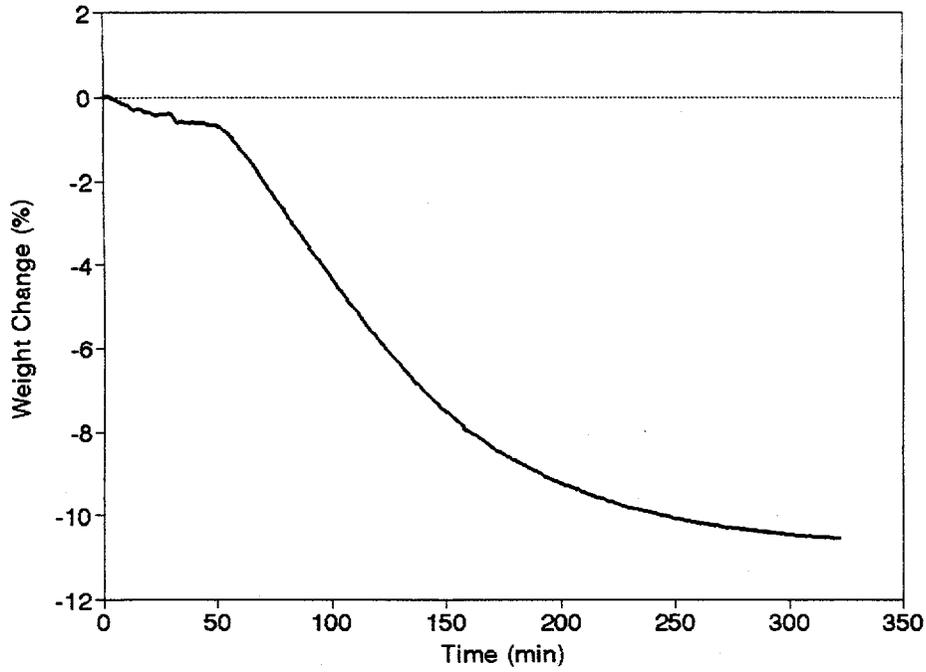


(a)

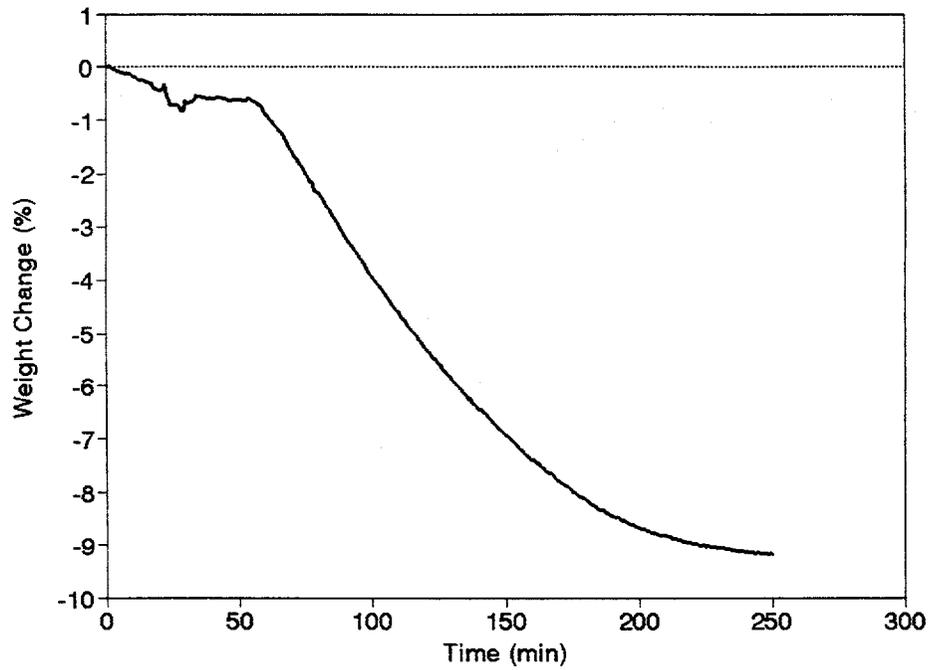


(b)

Figure 1. Sulfidation of $Zn_{1.9}Ti_{0.9}Cr_{0.2}O_4$ (sintered at $900^\circ C$) at $650^\circ C$ (a) in 0.9% H_2S , 92.4% H_2 , and 6.7% N_2 (b) in simulated coal gas.



(a)



(b)

Figure 2. Regeneration of specimens from Figure 1 in 5% O₂ and 95% N₂ at 650° C
(a) sulfidized in 0.9% H₂S (b) sulfidized in coal gas.

A computer calculation was carried out to analyze the tendency of Cr in the material to sulfidize under the experimental conditions. The results are shown as a phase stability diagram in Figure 3. Some caution should be used in drawing conclusions from the diagram in that it ignores the fact that Cr is present at reduced thermodynamic activity in compounds with Zn. In plotting the point labelled 0.9% H₂S, it was assumed that the impurity level of H₂O in the gas mixture was 10 ppmv. It can be seen that Cr should convert to a sulfide under these conditions. For the point on the diagram corresponding to the simulated coal gas composition used, it can be seen that Cr should remain in oxidized form. The results of this calculation support the explanation of Figure 1 given previously. In the future, most or all of the TGA experiments will be done in simulated coal gas to avoid the complication of producing different reaction products with different experimental gas mixtures.

The results of TGA tests on the other four sorbent formulations prepared this quarter were similar in that the rates of the sulfidation and regeneration reactions were slow compared to results of prior investigations on undoped zinc titanate formulations. The general picture that appears to be emerging is the following:

- Cr dissolves readily in zinc titanate to form a mixed spinel.
- Solution of Cr in the spinel reduces the thermodynamic activity of Zn, which should suppress Zn vaporization losses at high temperature.
- The same thermodynamic effect has a deleterious effect on sorbent reactivity.

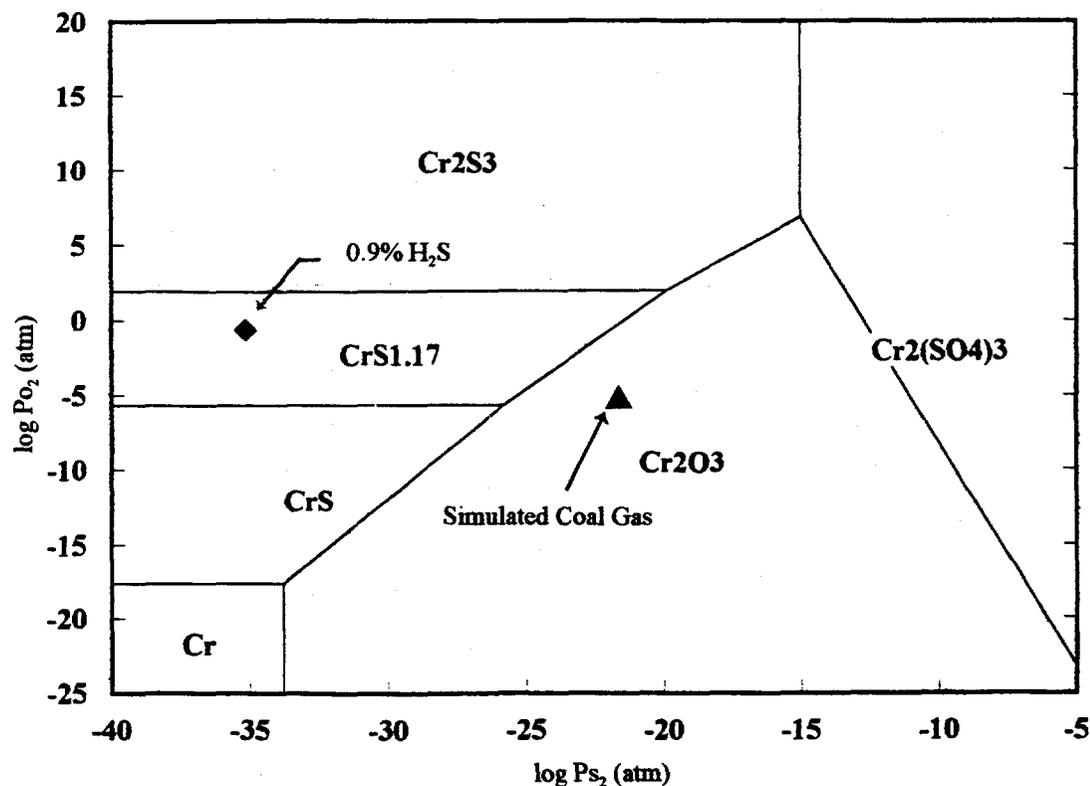


Figure 3. Phase stability diagram for Cr-O-S system at 650° C with points corresponding to experimental gas compositions.

Thus it is believed that a clear tradeoff exists between Zn vaporization tendency and chemical reactivity. The advantages of Cr doping probably outweigh the disadvantages at high ($>650^{\circ}\text{C}$) but not low operating temperatures.

The last task for which results were obtained this quarter is the fixed bed test. The formulation tested was described in preceding reports as having the composition, $\text{Zn}_{1.6}\text{Cr}_{0.4}\text{TiO}_4$, which assumed Cr substituted for Zn as a divalent ion. Now it is believed that Cr substitutes for both Zn and Ti and that it is present in the spinel primarily as a trivalent ion. The evidence is that no weight loss occurs when sorbents are prepared with Cr_2O_3 as an ingredient, and the sorbents after sintering have the green color characteristic of Cr^{3+} . Therefore, it is more appropriate to specify its composition as $\text{Zn}_{1.6}\text{Cr}_{0.4}\text{TiO}_{4+x}$. X-ray diffraction results showed it to be primarily a spinel solid solution, but with small amounts of Cr_2TiO_5 and ZnTiO_3 present.

In the fixed bed test, three sulfidation-regeneration cycles were conducted at 650°C . For sulfidation, the simulated coal gas described in Table 1 was passed upward through the bed at a space velocity of 2000 h^{-1} . For regeneration, the gas mixture used was 5% O_2 in N_2 , flowing upward at the same space velocity of 2000 h^{-1} . The sulfidation data are given in Figure 4 in the form of H_2S breakthrough curves. For the first several hours, there was no detectable amount of H_2S in the exit gas. Approximately 1 ppmv of H_2S was detected in all three cycles at a reaction time of 600 minutes or 10 hours. In the first, but not the second and third cycles, the test was shut down after 684 minutes and continued the following day. After restarting the test, there was a period of about 60 minutes before the gas chromatograph

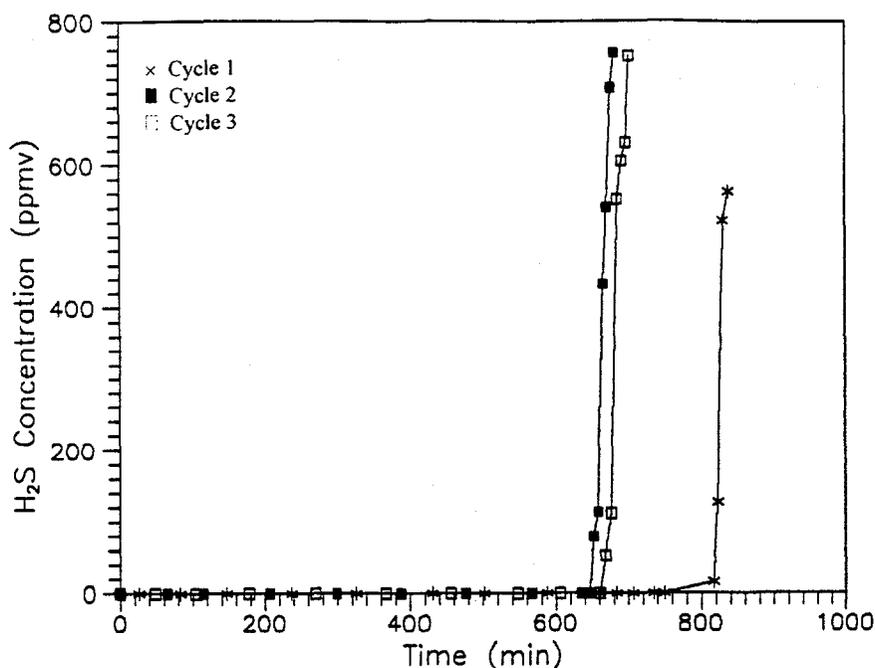


Figure 4. H_2S breakthrough curves for three-cycle fixed bed test at 650°C for sorbent of composition $\text{Zn}_{1.6}\text{Cr}_{0.4}\text{Ti}_{4+x}$.

reached stable operation. Therefore, the time of the breakthrough event for the first cycle is probably not as accurate as for the other cycles. Note that breakthrough occurred over a very short time period. It was more sudden than in any prior investigation known to the authors.

A sulfur mass balance calculation was carried out to analyze the sorbent's capacity. The ideal sulfur uptake of the bed was 0.21g S/g sorbent or 7.67g in the 36.0g bed. The amount of sulfur supplied by the gas train was 4.64g for a reaction time of 650 minutes. These data correspond to 60.5% utilization of Zn in the sorbent. During regeneration, rapid evolution of SO₂ occurred during the first 15 minutes, and regeneration was complete in 2 to 3 hours. The next bed test will probably be carried out at a higher temperature, where the reactivity and Zn utilization of the sorbent should be higher.

CONCLUSIONS AND RECOMMENDATIONS

Six new zinc titanate formulations containing chromium were prepared. In the evaluations completed to date on these formulations, it appears that the main advantage of chromium doping is to reduce vaporization losses of zinc in the high temperature region of potential operating conditions for hot gas cleanup. Specific data on zinc vaporization tendency will be obtained next quarter. The compromise that is made in achieving this benefit is slower sulfidation kinetics. Both effects can be explained by a reduction of the thermodynamic activity of zinc in the mixed titanate compound.

The formulation prepared last fall and having the composition Zn_{1.6}Cr_{0.4}TiO_{4+x} appears to have the best combination of properties, so a fixed bed test was carried out on this material. H₂S breakthrough occurred suddenly at a reaction time of about 650 minutes or 11 hours. Zinc utilization of the bed was 60.5%. The next bed test will be carried out at a higher temperature to check of vaporization loss of zinc and to obtain a higher sorbent reactivity.

DISCLAIMER STATEMENTS

This report was prepared by James H. Swisher of Southern Illinois University at Carbondale with support, in part by grants made possible by the U.S. Department of Energy Cooperative Agreement Number DE-FC22-92PC92521 and the Illinois Department of Energy through the Illinois Coal Development Board and the Illinois Clean Coal Institute. Neither James Swisher of Southern Illinois University at Carbondale nor any of its subcontractors nor the U.S. Department of Energy, Illinois Department of Energy and Natural Resources, Illinois Coal Development Board, Illinois Clean Coal Institute, nor any person acting on behalf of either:

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PROJECT MANAGEMENT REPORT
March 1 through May 31, 1995

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Other Investigator: Ranajit K. Datta, Virginia Polytechnic Institute and
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Project Manager: Franklin I. Hoena, Illinois Clean Coal Institute

COMMENTS

On the project milestone chart, one technical item is specified for this quarter, sorbent preparation. The graduate assistant at VPI spent three days at SIUC to obtain training on the preparation of sorbent pellets. Six formulations containing chromium were prepared during March, thus satisfying the intent of the milestone. TGA results on these formulations fell short of expectations, so some additional formulations are being prepared for evaluation. A bench-scale fixed bed test was completed on the original formulation prepared last fall; it was found to have a better combination of properties than the five formulations prepared in March.

A budget adjustment request was submitted and approved on April 21, 1995. The adjustment was a consequence of a reduction in the amount of work subcontracted from SIUC to VPI, due in part to the involvement of one rather than two VPI students in the project. Overall spending is lower than planned.

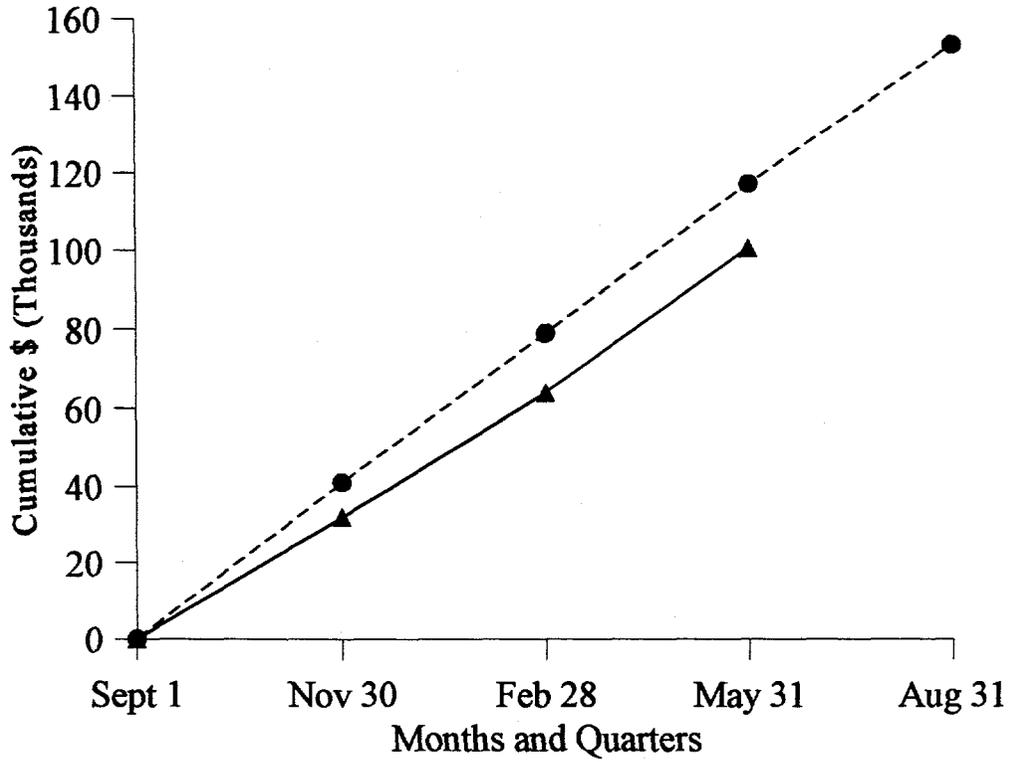
PROJECTED AND ESTIMATED EXPENDITURES BY QUARTER

| Quarter* | Types of Cost | Direct Labor | Fringe Benefits | Materials and Supplies | Travel | Major Equipment | Other Direct Costs | Indirect Cost | Total |
|--------------------------------------|---------------|--------------|-----------------|------------------------|--------|-----------------|--------------------|---------------|---------|
| Sept. 1, 1994 to Nov. 30, 1994 | Projected | 8,064 | 63 | 775 | 2,350 | 300 | 25,858 | 3,711 | 41,121 |
| | Estimated | 4,307 | 25 | 1,000 | 1,100 | 0 | 22,924 | 2,936 | 32,292 |
| Sept. 1, 1994 to Feb. 28, 1995 | Projected | 16,128 | 126 | 1,550 | 2,350 | 300 | 51,715 | 7,187 | 79,356 |
| | Estimated | 10,708 | 87 | 1,778 | 1,481 | 0 | 43,551 | 5,823 | 64,048 |
| Sept. 1, 1994 to May 31, 1995 | Projected | 24,192 | 189 | 2,325 | 2,350 | 300 | 77,573 | 10,663 | 117,592 |
| | Estimated | 19,733 | 122 | 3,085 | 1,219 | 0 | 67,250 | 9,141 | 100,540 |
| Sept. 1, 1994 to Aug. 31, 1995 | Projected | 32,256 | 252 | 3,100 | 2,700 | 300 | 100,820 | 13,943 | 153,371 |
| | Estimated | | | | | | | | |

*Cumulative by Quarter

COSTS BY QUARTER

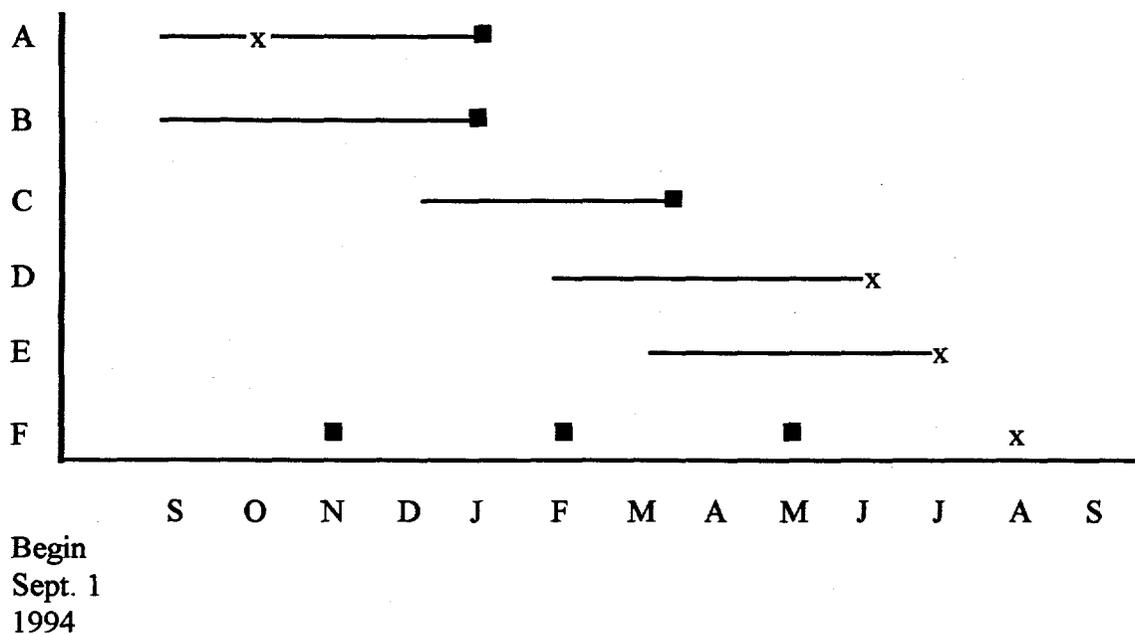
Composition Modification of Zinc Titanate Sorbents for Hot Gas Desulfurization



● = Projected Expenditures - - - - -
▲ = Actual Expenditures _____

Total Illinois Clean Coal Institute Award \$153,371

SCHEDULE OF PROJECT MILESTONES



Hypothetical Milestones:

- A: Literature search; materials and equipment procurement (SIUC and VPI)
- B: $\text{ZnTiO}_4\text{-MO}_x$ solubility experiments (VPI)
- C: Sorbent preparation (VPI)
- D: Bench-scale testing (SIUC)
- E: Characterization of bench-scale samples (SIUC and VPI)
- F: Reporting (SIUC)

