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TECHNICAL REPORT

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Project Title: **TESTING AND TECHNOLOGY TRANSFER FOR ZINC TITANATE  
SORBENT IN A TITANIA MATRIX**

DOE Cooperative Agreement Number: DE-FC22-92PC92521 (Year 4)  
ICCI Project Number: 95-1/2.2A-1M  
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Other Investigator: Raghbir P. Gupta, Research Triangle Institute  
Project Manager: Franklin I. Honea, ICCI

ABSTRACT

For new coal gasification systems, zinc-based sorbents are being developed to remove sulfur from the hot product gas prior to its use in combined-cycle gas turbines and high-temperature fuel cells. In general, the properties of these sorbents are considered to be very attractive, but there are still concerns about degradation of mechanical properties and sulfur capacity over many sulfidation-regeneration cycles. It is believed that containing zinc titanate in a matrix of excess titania could solve both problems, which is the objective of this project. During this quarter, plans were made for United Catalysts, Inc. to produce two batches of the sorbent using a commercial extrusion process. A subcontract was just issued to the Research Triangle Institute for sorbent characterization and for a 50-cycle performance test designed to simulate the General Electric Company's moving-bed reactor conditions. In a parallel effort, numerous contacts were made on the technology transfer task.

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## EXECUTIVE SUMMARY

The timing on availability of hot-gas cleanup technology for two Integrated Gasification Combined Cycle (IGCC) plants scheduled to start up next year is now critical. Unfortunately, some nagging problems remain with both sulfur sorbent and particle filter technology that may result in the use of cold rather than hot-gas cleanup in these plants. With sulfur sorbents, the main problems are with mechanical property degradation and/or loss of sulfur capacity over many sulfidation-regeneration cycles. The sorbents receiving the most attention are all zinc-based and include various zinc titanate formulations and a proprietary material, called Z-Sorb, developed by the Phillips Petroleum Company.

The most important outcome of research done by the principal investigator and co-workers on zinc titanate sorbents (now in its fourth year) was the development of a super-strong formulation that contained zinc titanate in a structural skeleton of excess titania. Its starting composition was 33.5 wt.% ZnO and 66.5 wt.% TiO<sub>2</sub>, and it was prepared from 2- $\mu$ m powders fired for 3 hours at 1,000 °C. The resulting crush strength of 224 N/mm was more than six times that of zinc titanate sorbents prepared by other investigators. In 10-cycle fixed- and fluidized-bed tests, its chemical reactivity was good after the first few cycles. An activation pretreatment was developed to improve initial performance.

This year's project is a continuation of work on the same sorbent. The material is being prepared by United Catalysts, Inc. (UCI), using a proprietary process for extrusion and rounding of pellets. A 50-cycle fixed-bed test will be carried out at the Research Triangle Institute (RTI). The activation pretreatment will be used, and test conditions will be selected to mimic conditions in the General Electric's (GE's) moving-bed hot-gas desulfurization system to be used in the TECO Clean Coal Technology Demonstration Project. RTI will also carry out physical and chemical characterization of the sorbent before, at the midpoint, and after the 50-cycle test.

The status of the sorbent preparation task is that a confidentiality agreement and request for quote (RFQ) were prepared by E&A Associates and were sent to UCI. The former was signed and a preliminary response to the RFQ was received. UCI plans to begin the fabrication work in December. The status of the characterization and 50-cycle test tasks is that a subcontract between E&A Associates and RTI is currently being negotiated, and RTI will start work as soon as UCI supplies the sorbent material to RTI.

Another task in the project entails information dissemination and technology transfer. This task was started early because of the timing of receipt of the ICCI contract and late start on sorbent preparation by UCI. Organizations that have been contacted thus far include Destec, GE, Norton, Argonne, Degussa, Johnson Matthey, the Electric Power Research Institute (EPRI), and the U.S. Department of Energy (U.S. DOE). In what might also be classified as technology transfer, former Ph.D. student, Dr. J. Yang, has joined the staff of TDA Research, Inc. He is partially supported by a U.S. DOE/small business innovative research (SBIR) contract on zinc titanate sorbents.

## OBJECTIVES

The project is designed to extend prior work on the development of a zinc titanate sorbent containing excess titania for high strength and decrepitation resistance. The specific objectives are:

- Contract with a catalyst manufacturing company to produce cylindrical pellets by extrusion.
- Carry out a 50-cycle test with a reduction-oxidation pretreatment and related sorbent characterization.
- Initiate technology transfer activities to acquaint potential manufacturers and users of the sorbent with its properties and potential.

## INTRODUCTION AND BACKGROUND

Integrated gasification Combined Cycle (IGCC) systems with cold-gas cleanup have now reached the early stages of commercialization. The foundation for this was successful completion of the Cool Water Coal Gasification Program several years ago.<sup>1</sup> Destec Energy, Inc., a subsidiary of Dow Chemical Company, has a plant in operation in Louisiana, and the Wabash River Plant in Indiana is now starting up.<sup>2</sup> A similar plant based on the Shell gasification technology is operating in the Netherlands.

There are two plants in the United States scheduled for startup in 1996—the Tampa Electric Plant in Florida and the Sierra Pacific Power Plant in Nevada. There is a desire to incorporate hot-gas cleanup technology in both of these plants. Interest in IGCC plants is also strong in Europe and Asia. The rate at which new plants are built depends to a large extent on the need for new electric power generation capacity. For example, Bailey et al.<sup>3</sup> report that in certain southern and midwestern states this need will not be significant until after the year 2004.

Whether or not hot-gas cleanup is used in new plants depends on several interrelated factors. The overall efficiency increase with hot compared to cold-gas cleanup is estimated to be 2 to 3 percent, which may not be a large enough increase to satisfy all decision makers. There are also unsolved problems with both desulfurization and particle filter technology that require more research and development. A report published by the NOVEM group in the Netherlands in 1991<sup>4</sup> has caused an upheaval in the thinking of IGCC designers and analysts. The main conclusion of the NOVEM Report was that nearly all of the efficiency gain is obtained between wet gas cleaning at low temperature and dry gas cleaning at 350 °C. Raising the gas cleaning temperature to 500 or 600 °C produced minuscule benefits because the increase in gas turbine power is almost offset by a decline of steam turbine power. It would seem appropriate because of the importance of this information that an independent study be carried out in the United

States to verify the conclusions of the NOVEM Report. Operation of gas cleanup systems at 350 °C instead of 600 °C would make it easier to qualify materials of construction, valves, and particle filters. It is too early to tell if it would be easier or more difficult to find an acceptable sulfur sorbent. It is clear, however, that this technology needs to be improved quickly if it is to be used in the IGCC plants now in design and construction.

The best current information on hot-gas cleanup R&D is disseminated in the annual U.S. Department of Energy/Morgantown Energy Technology Center (DOE/METC) contractor review meetings on this subject and the published proceedings of those meetings. Some, but not all, relevant citations from the June 1995 meeting are mentioned here. Nearly all of the research in progress is on zinc-based sorbents, and they are being evaluated for applications in fluidized beds, moving beds, and transport reactors. The General Electric (GE) Company is the prime contractor for a moving-bed hot-gas desulfurization system for the Tampa Electric Power Company Clean Coal Technology Demonstration Program.<sup>5,6</sup> The current emphasis in this program is to evaluate various zinc titanate sorbent formulations and Z-Sorb, a sorbent developed by the Phillips Petroleum Company. Problems remain with decrepitation of zinc titanate and loss of capacity with Z-Sorb with multiple sulfidation-regeneration cycles.

Zinc titanate sorbents are also being evaluated for fluidized-bed and transport reactor applications.<sup>7,8</sup> Due in part to the use of small particles (50 to 300  $\mu\text{m}$ ), mechanical properties and attrition resistance appear to be adequate. Maintaining good chemical reactivity over long-term use (>100 sulfidation-regeneration cycles) has yet to be demonstrated. Furthermore, attrition resistance of the current sorbents needs to be improved for them to be commercially viable.

The question of availability of sorbents that perform well at lower temperatures (343 to 538 °C) is being addressed in two projects.<sup>9,10</sup> Both projects started shortly before the contractors meeting was held.

The last of this set of projects to be discussed is the Enviropower IGCC project.<sup>11,12</sup> It involves international cooperation between the United States and Finland by an agreement signed in 1993. Initial testing of fluidized-bed desulfurization with two different zinc titanate formulations has shown promising results.

Research done by the principal investigator and his co-workers on zinc titanate sorbents is now in its fourth year. During the first two years, exploratory research was done on the benefits of adding excess titania to zinc titanate.<sup>13</sup> The best combination of properties was obtained when pellets were prepared from coarse (2  $\mu\text{m}$ ) ZnO and TiO<sub>2</sub> powders sintered for 3 hours at 1,000 °C. The starting composition was 33.5 wt.% ZnO and 66.5 wt.% TiO<sub>2</sub>, which corresponds to Zn<sub>2</sub>TiO<sub>4</sub> + 50 percent excess TiO<sub>2</sub>. Its crush strength was more than six times that of the strongest material prepared by prior investigators, and it performed quite well in fixed- and fluidized-bed tests carried out at RTI.

In last year's project, the effects of several dopants on the properties of zinc titanate sorbents were studied.<sup>14</sup> Chromium doping was found to have a beneficial effect on reducing vaporization losses of Zn at temperatures above 650 °C. Otherwise, there were no clear advantages to doping. The results of all 3 years of work are described in more detail elsewhere.<sup>15</sup>

In this year's project, E&A Associates is collaborating with the Research Triangle Institute (RTI) on a follow-on to the research done earlier on the super-strong zinc titanate formulation containing excess titania. The intent is to prepare the sorbent using a commercially available extrusion process and to obtain more comprehensive bench-scale test data. Successful completion should provide justification for scale-up tests next year.

### EXPERIMENTAL PROCEDURES

The starting materials for sorbent preparation are 2- $\mu\text{m}$  size ZnS and TiO<sub>2</sub> powders purchased from the Johnson Matthey Company. ZnS is purchased rather than ZnO because the latter is not readily available with the particle size desired. Roasting of ZnS to ZnO is carried out by heating in air for 20 hours at 850 °C. Blending of the oxide powders is done in a 3 percent solution of starch in water. The slurry is partially dried until it has a consistency similar to toothpaste. The starch serves as a binder to provide good green strength to the pellets and also to impart controlled porosity during sintering.

Fabrication of green pellets is accomplished by a proprietary extrusion process developed by United Catalysts, Inc. (UCI). The dimensions of the cylindrical pellets are 4-mm diameter and 5- to 7-mm long. The goals on pellet density and porosity are 2.8 to 3.0 g/cm<sup>3</sup> and 35 to 39 percent, respectively. Two 5-lb (2.3-kg) batches are being produced by UCI. They will be characterized by RTI and the best of the two will be used for a 50-cycle fixed-bed test. Characterization will consist of thermogravimetric analysis (TGA) chemical reactivity, crush strength, chemical composition, BET surface area, pore size distribution and x-ray diffraction phase (XRD) identification.

A schematic drawing of the apparatus being used at RTI for the 50-cycle test is shown in Figure 1. This test rig has been used extensively for long-term tests on various sorbents including zinc ferrite, zinc titanate, and Z-Sorb. A simulated coal gas representing the GE moving-bed system will be generated by mixing metered quantities of H<sub>2</sub>, CO, CO<sub>2</sub>, N<sub>2</sub>, H<sub>2</sub>S, and H<sub>2</sub>O. The gas will be preheated and fed to the reactor. The sulfidation temperature, pressure, and regeneration conditions will be determined in consultation with GE in order to obtain the maximum amount of useful information.

Prior to beginning the sulfidation-regeneration sequence, a two-cycle pretreatment will be carried out to activate the sorbent. In our previous ICCI study, we found that a zinc reduction-oxidation pretreatment improved the sorbent reactivity in subsequent cycles owing to a finer pore structure. This pretreatment will consist of two cycles of reduction

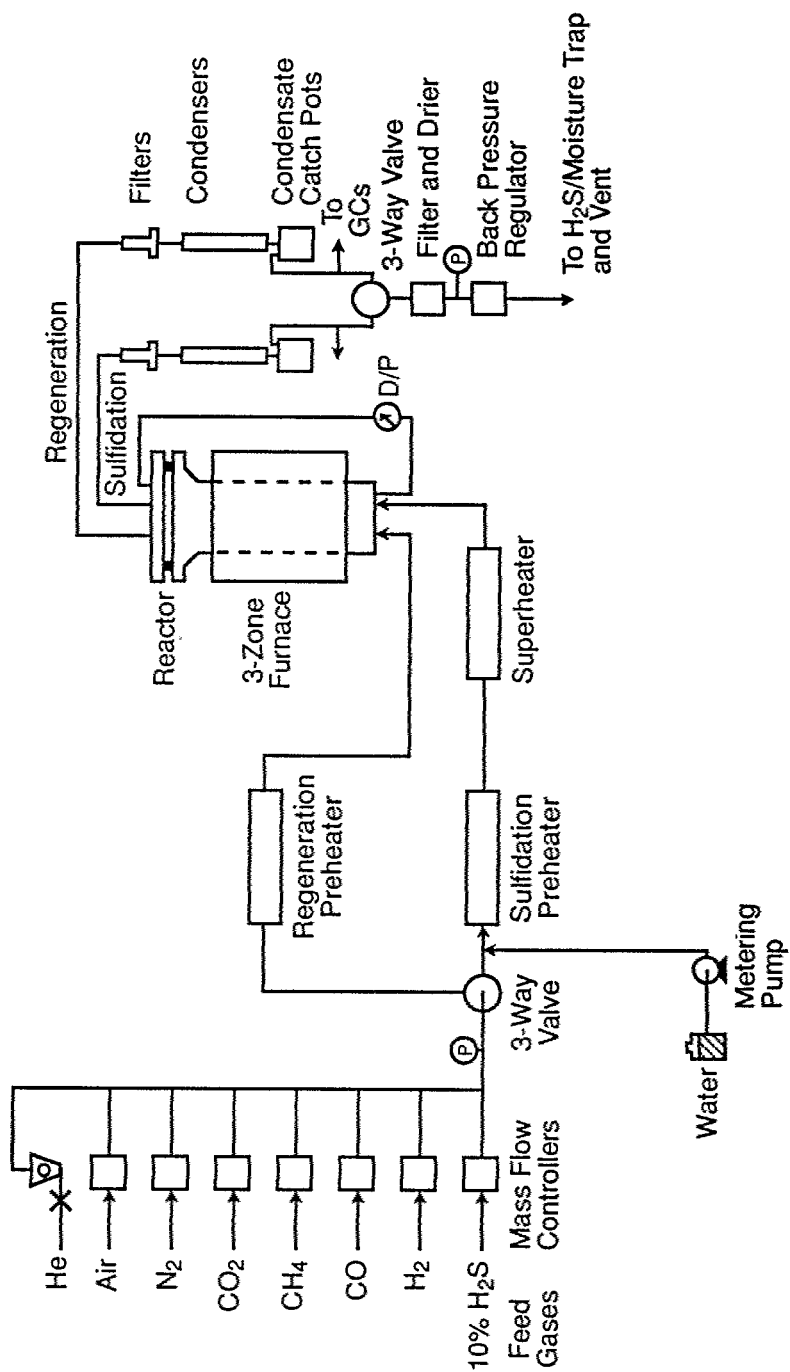


Figure 1. Bench-scale sorbent test facility at the Research Triangle Institute

in hydrogen or a hydrogen-carbon monoxide mixture at 500 °C, followed by oxidation in air or an N<sub>2</sub>-O<sub>2</sub> mixture.

To determine the changes in physical and chemical properties, the test will be briefly interrupted at the end of 25 cycles to extract a sorbent sample for physical and chemical characterization. At the end of 50 sulfidation-regeneration cycles, the sorbent will be fully characterized for its physical and chemical properties. A detailed data analysis will be performed to calculate the sulfur capacity, breakthrough behavior, and regeneration characteristics.

The technology transfer task emphasizes networking with potential manufacturers and users of the sorbent being developed. Potential manufacturers are UCI, Norton, and Degussa, whereas the potential users include GE, Kellogg, Destec, Tampa Electric, and Enviropower. Contact will also be made with the Electric Power Research Institute (EPRI), and plans will be made to participate in the 1996 DOE/METC Annual Contractors' Review Meeting. In this effort, the investigators will acquaint these organizations with the status of sorbent development and solicit feedback on manufacturability and systems needs.

## RESULTS AND DISCUSSION

The ICCI contract was not received until November 6, 1995, so work on the project proceeded at a reduced pace until that time. Nevertheless, a considerable amount of administrative work was done to facilitate the sorbent preparation and testing tasks to be emphasized during the second and third quarters. The accomplishments are summarized below.

### Sorbent Preparation

Enough TiO<sub>2</sub> and ZnS powder for the entire project, assuming no serious difficulty, was purchased from the Johnson Matthey Company. The ZnS was then converted to ZnO by the Principal Investigator for shipment to UCI. At UCI's request, a confidentiality agreement was prepared by E&A Associates and signed by both parties. A Request for Quote (RFQ) was sent to UCI for the preparation of two 5-lb (2.3-kg) batches of the sorbent. The specifications and procedures to be used were discussed at an informal meeting last summer. UCI has responded to the RFQ by telephone, and written confirmation is expected soon. Due to a backlog of work, UCI has indicated that our preparation probably cannot start until 4 weeks after receipt of the order. This delay may or may not cause difficulty with completing the project on time.

### Sorbent Characterization and Testing

RTI has the responsibility for this entire task. A subcontract is currently being negotiated with RTI. Characterization work on the extrudates prepared by UCI will begin as soon as RTI receives the sorbent, hopefully in the early part of January.

### Technology Transfer

Originally, this task was not scheduled to begin until December. However, time became available earlier because of the delay in obtaining official contract approval. In principle, the discussions held on sorbent preparation with UCI, Norton, and Degussa are a form of technology transfer. It was learned in these discussions that Norton and Degussa are not eager to get involved in sulfur sorbent development because the market potential is not well established.

Discussions were held with two staff members at EPRI about the use of hot-gas cleanup in IGCC systems. The feedback received is that hot-gas cleanup deserves a fair chance, but that they have concerns about more than the performance of sulfur sorbents and particle filters. The other concerns include trace impurities (ammonia, alkalis, HCN, etc.), sorbent cost, and sorbent elutriation. When the total cost of handling these problems is considered, cold-gas cleanup may turn out to be better. It was stated that EPRI has made major contributions to the Wilsonville Coal Gasification Project, which includes hot-gas desulfurization, so EPRI is a stakeholder. Copies of some of our ICCI reports were sent to one of their staff members.

A question that will arise if scale-up of this year's test occurs is the availability of large quantities of 2- $\mu\text{m}$  size ZnO and TiO<sub>2</sub> powders. A survey was made 2 years ago of ZnO availability. It was determined that one company has produced what it calls ceramic as opposed to pigment grades of ZnO. The Eagle Zinc Company in Illinois maintains no inventory of the size needed but can produce it in tonnage quantities. A sample of Eagle Zinc material was studied briefly at that time, and it appeared to be satisfactory.

A new survey has been started to determine commercial sources of 2- $\mu\text{m}$  size TiO<sub>2</sub> powder. Johnson Matthey, the supplier of powders for past and current lab-scale research, states that its supplier can provide large quantities if given sufficient lead time on orders. Johnson Matthey would not identify its supplier. A number of other potential suppliers are being contacted.

Dialogue has started with METC and GE staff on quantities, cost, and schedule for a possible large-scale test. It was mentioned that there may be an opening in the test schedule in 1996. Beyond 1996, there may not be any more DOE-sponsored tests of this type.



Finally, in what might well be the best form of technology transfer, former Ph.D. student, Dr. Jing Yang, has joined the staff of TDA Research, Inc. He worked for 3 years with the Principal Investigator on zinc titanate research, and he is now working on a zinc titanate project funded by DOE's small business innovative research (SBIR) program.

### CONCLUSIONS AND RECOMMENDATIONS

It is premature at this stage of the project to draw conclusions or make recommendations. The administrative work required to begin the experimental tasks is essentially complete. The sorbent preparation work will start a month later than planned, so technology transfer activities were started this quarter instead of in January.

### DISCLAIMER STATEMENTS

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