Bench-Scale Testing of Attrition Resistant Moving Bed Sorbents

James H. Swisher (jims@siu.edu; 618 453-7324)
E&A Associates
126 Misty Lake Drive
Murphysboro, IL 62966

Raghubir P. Gupta (gupta@rti.org; 919 541-8023)
Research Triangle Institute
P.O. Box 12194
Research Triangle Park, NC 27709-2194

Introduction

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.[1] 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.[2] A similar plant based on the Shell gasification technology is operating in the Netherlands.

In two new plants now under construction, the Tampa Electric Plant in Florida and the Sierra Pacific Power Plant in Nevada, incorporating hot-gas cleanup technology is desirable. Unfortunately, some nagging problems remain with both sulfur sorbent and particle filter technology that may result in the use of cold-gas, 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. They include various zinc titanate formulations and proprietary materials developed by the U.S. Department of Energy/Morgantown Energy Technology Center (DOE/METC) staff and the Phillips Petroleum Company.

The investigators on this project are now completing their third year of effort on a superstrong zinc titanate sorbent. Prior to this year, various formulations were prepared and evaluated for their potential use in fixed- and fluidized-bed hot-gas desulfurization systems.[3,4] A unique feature, the reason for the high strength, is that the zinc titanate is contained in a matrix of titanium dioxide. The formulation with the best combination of properties has a starting composition of 33.5 wt% ZnO and 66.5 wt% TiO_2. It was prepared from 2 µm oxide powders and calcined at 1,000 °C (1,832 °F) . Its crush strength is compared to values obtained by prior

---

Research co-sponsored by the U.S. Department of Energy's Morgantown Energy Technology Center and the Illinois Dept. of Commerce and Community Affairs under Cooperative Agreement No. DE-FC22-92PC92521 (Year 4) with E&A Associates, 126 Misty Lake Drive, Murphysboro, IL 62966; telefax (618)-985-2919.

investigators listed in Table 1. It can be seen that a crush strength of more than six times that of prior investigators was achieved.

Table 1. Crush Strength Comparisons for Zinc Titanate Sorbents

Investigators/ References	Crush Strength (lb/in.)
Swisher, Yang, and Gupta[3]	1,279
Mei, Gasper-Galvin, Everett, and Katta[5]	97
Ayala, Gal, Gupta[6]	69-183
Grindley[7]	206

A scanning electron micrograph of the sorbent after a 10-cycle fluidized-bed test is shown in Figure 1. The relatively coarse oxide powders in the starting material produce an initial network of large pores in the sorbent. During repeated sulfidation-regeneration cycles, a network of finer pores develops. The consequence of this structural change is that the chemical reactivity of the sorbent increases with cycle number. This year, the R&D has focused on General Electric (GE) Company's moving bed application for the sorbent,[8] and the pellets have been made with commercial equipment in the pilot plant of United Catalysts, Inc. (UCI). Details of the chemical compositions and manufacturing procedures will not be discussed because a patent application is being prepared. It should be noted, however, that modifications had to be made to the sorbent to achieve the desired properties when pellet making was shifted from the laboratory to the pilot plant, and minor modifications are still in progress.

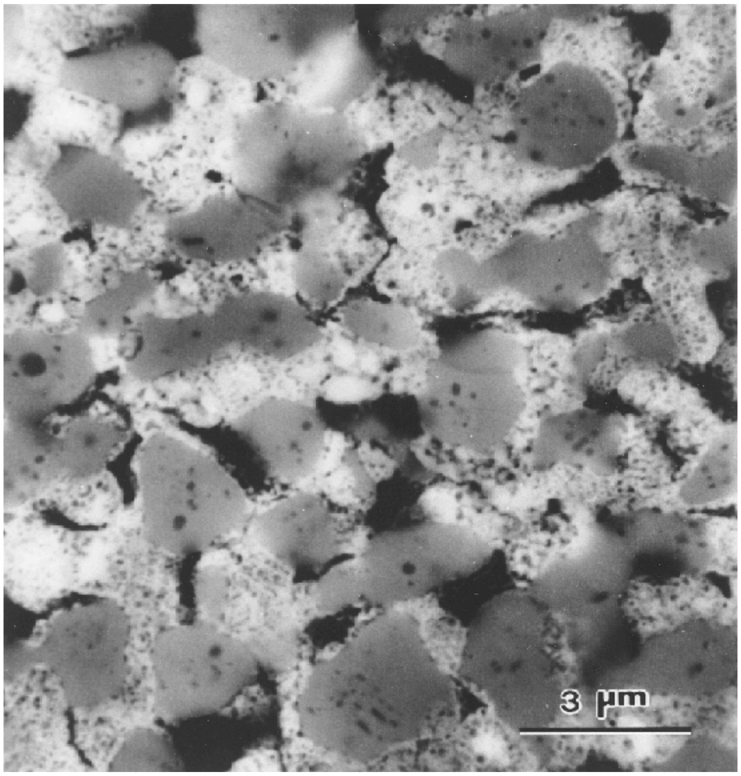

Figure 1. Scanning electron micrograph (backscatter image) of a specimen after a ten-cycle fluidized-bed test. The dark phase is TiO_2, and the light phase is Zn_2TiO_4.

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:

- Specify properties and procure 3- to 5-mm diameter pellets from a catalyst manufacturing company.
- 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.

Project Description

The prime contractor in the project this year is E&A Associates. Contractual arrangements were made for sorbent manufacturing with UCI, and for sorbent characterization and testing with the Research Triangle Institute (RTI). Several 5-lb batches of pellets were produced by a proprietary extrusion and rolling process. The starting materials, calcining temperature, and chemical composition of the sorbent were varied with the goal of matching or improving on the properties of hand-made pellets studied previously.[3] It is important to mention that the sorbent was originally developed for desulfurization temperatures in the range of 550 to 650 °C (1,022 to 1,202 °F). For the moving-bed application, desulfurizing the coal gas at 482 °C (900 °F), which could require a minor change in the formulation to impart needed reactivity at lower temperatures, is desirable.

In March, a formulation designated as ICCI-1 was selected for a multicycle test. The selection was made on the basis of physical property data and thermogravimetric analysis (TGA) measurements of chemical reactivity. A schematic drawing of the apparatus used by RTI for the fixed-bed tests is shown in Figure 2. This test rig has been used extensively for long-term tests on various sorbents including zinc ferrite, zinc titanate, and Z-Sorb. A simulated Texaco coal gas representing the GE moving-bed system for the TECO demonstration plant is generated by mixing and preheating metered quantities of individual gases. The composition of the mixture is listed in Table 2. The H_2S concentration was made artificially high at 2 vol% (20,000 ppmv) to

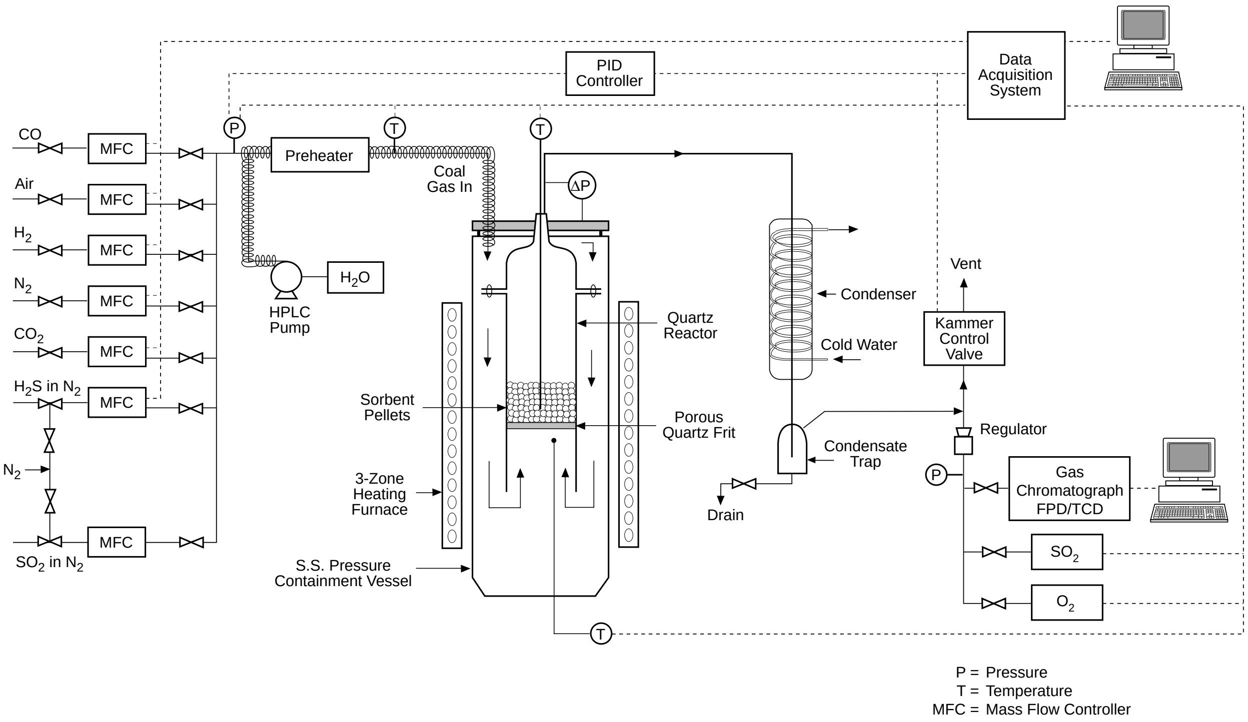

Figure 2. Apparatus used at RTI for multicycle qualification tests.

obtain breakthrough in a reasonable amount of time. Sulfidations were carried out at a total pressure of 20 atm (280 psig) and a space velocity of 2,000 h^{-1} (STP). Regenerations were carried out in a mixture of 3 vol% O_2 and 97 vol% N_2 at a pressure of 7 atm (88 psig).

Table 2. Gas Composition for Fixed-Bed Tests

Component	Concentration (vol%)
CO	30
CO_2	10
H_2	30
N_2	18
H_2O (steam)	20
H_2S	2

The test on formulation ICCI-1 consisted of 20 sulfidation-regeneration cycles. The results led to a development iteration to strengthen the material. In April, another multicycle test was started on the improved formulation, ICCI-2. After 20 cycles, the test was interrupted so that the reactor could be opened to inspect the pellets. An additional 30 cycles were carried out in June. This test duration of 50 cycles is preferred by GE in the qualification of sorbent materials for testing in its moving-bed pilot-plant system.

A considerable effort in the project is being made on technology transfer. Emphasis in this task is on networking with potential raw materials suppliers, manufacturers, and users of the sorbent being developed. Numerous organizations have been contacted so far as a part of this effort.

Results

Because the results for the two formulations subjected to multicycle fixed-bed tests should be discussed in detail, only brief mention will be made of the materials prepared initially. In the exploratory work, variations were made with raw materials, binder additions, and calcining temperatures to try to achieve the physical properties and TGA reactivity desired. One of the reasons that several attempts were needed was that a transition had to be made from the use of reagent-grade oxide powders to raw materials that could be purchased in large quantities at a reasonable price. The outcome of the exploratory work was the selection of a formulation called ICCI-1 for in-depth evaluation.

Properties of ICCI-1

Results are shown in Figure 3 for the TGA reactivities of ICCI-1, ICCI-2 (to be discussed later), and hand-made material evaluated previously.[3] The TGA tests were carried out at 538 °C (1,000 °F) at 1 atm pressure. The gas composition for sulfidation was essentially the same as that given in Table 2, the only difference being that the H_2S concentration was 1.2 vol% instead of 2 vol%. Note that ICCI-1 was more reactive than the hand-made material. While this result is good per se, it raises the question of whether or not mechanical properties were compromised too much in obtaining the high reactivity.

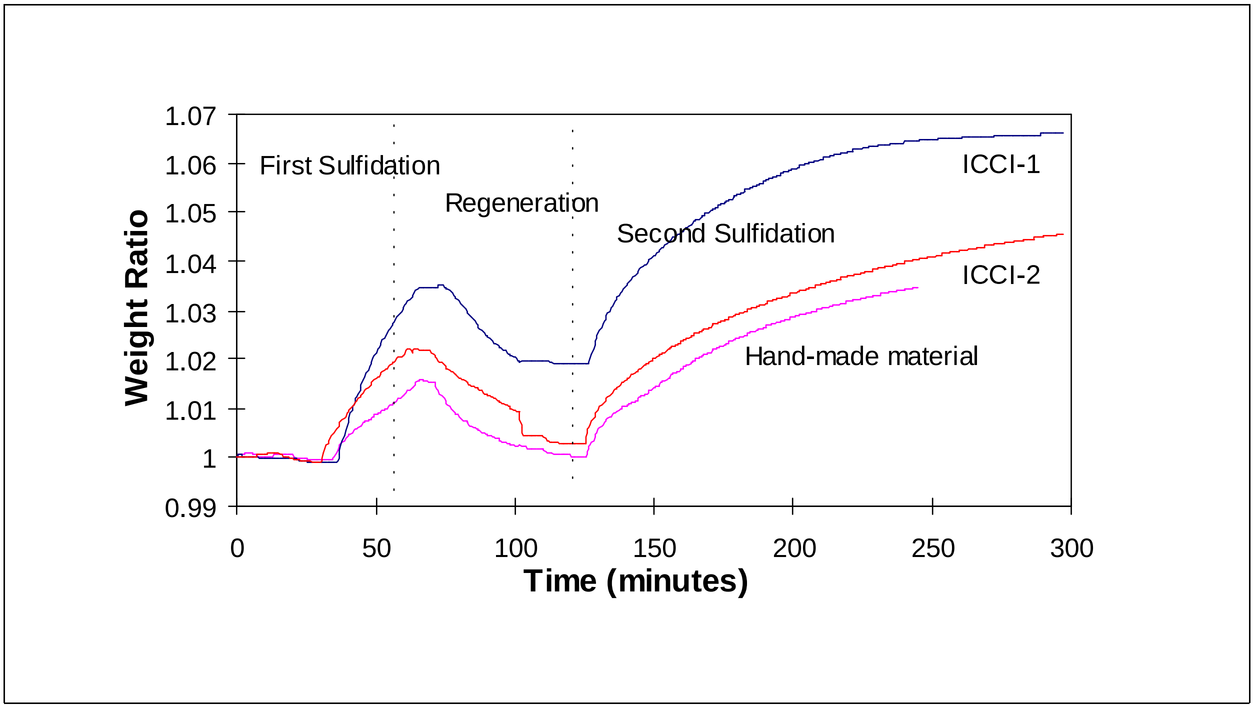

Figure 3. TGA reactivities of ICCI-1, ICCI-2, and hand-made material from prior investigation.[3]

H_2S breakthrough data for ICCI-1 are plotted in Figure 4. With breakthrough defined as 200 ppmv H_2S in the exit gas, the breakthrough times ranged from 105 to 144 min with no trend up or down as the number of cycles increased. It is not understood why breakthrough occurred sooner in Cycles 5, 6, and 7 than in the others. The average sulfur capacity of the sorbent calculated from the breakthrough data ranged from about 7 to 9 lb S/100 lb fresh sorbent. The important conclusion to be drawn from the results is that the sorbent did not degrade in reactivity. When the reactor was opened to inspect the pellets after 20 cycles of testing, some of the pellets near the inlet end of the reactor contained surface cracks. Pellets near the outlet end showed no signs of degradation. Because this was the first time cracking had ever been observed in 3 years of research, it was decided to prepare a stronger formulation and restart the 50-cycle test. Before doing that, however, extensive physical property measurements were made on pellets from both the inlet and outlet ends of the reactor. The results are summarized in Table 3, along with property data for the fresh material. The bulk density of the fresh material was 96.8 lb/ft^3.

A comparison of the physical property data shows that the fresh sorbent and the sample taken near the gas exit have nearly the same properties. The reason for this is that the material near the gas exit did not absorb much sulfur at breakthrough. The sample taken near the gas inlet had poorer crush strength and attrition resistance, which correlates with the surface cracking that was observed. The changes in pore characteristics are similar to those observed before,[3] except that the decreases in percent porosity and pore volume are larger than expected. Perhaps regeneration of the sample was incomplete, leaving the pores constricted by residual zinc sulfide.

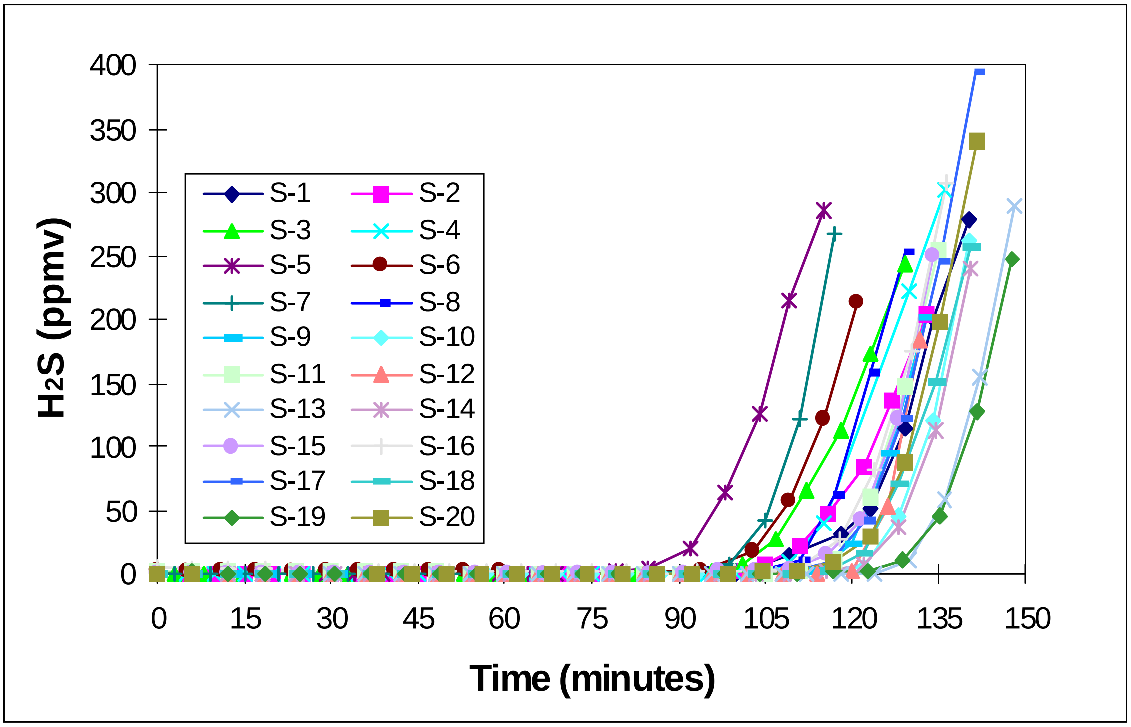

Figure 4. H_2S breakthrough results for ICCI-1 sorbent.

Table 3. Physical Property Data on ICCI-1 Sorbent Before and After Testing[a]

		20-cycle Regenerated	
Property	**Fresh**	**Near gas inlet**	**Near gas outlet**
Average pellet size (mm)	4.45	4.78	4.45
Crush strength (lb/pellet)	27.3	11.3	32.0
ASTM attrition (%)	1.25	6.7	3.1
BET surface area (m^2/g)	1.84	3.40	1.84
Mercury pore volume (cm^3/g)	0.174	0.112	0.172
Median pore diameter (Å)	4419	2983	4556
Porosity (%)	44.5	30.4	44.4

[a] Sorbent in oxidized state.

The physical property results on ICCI-1 highlight an important difference between the fixed-bed test simulation and actual conditions present in a moving-bed reactor. In the latter, sulfur uptake is more uniform in the sorbent material. Thus, in the fixed-bed simulation, the sorbent near the inlet to the bed is subjected to an overtest. To partially correct for this problem, it was decided, with GE staff approval, to adjust the procedure for future tests. With this change, sulfidation would be continued to breakthrough in some but not all of the cycles.

ICCI-2

Referring back to Figure 3, the TGA reactivity of ICCI-2 is lower than that of ICCI-1. This decrease was expected and is a consequence of the higher strength of ICCI-2. A fixed-bed test on ICCI-2 was started in April. Prior to starting the 20-cycle test, a 2-cycle oxidation-reduction pretreatment with hydrogen at 500 °C followed by oxidation in diluted air was used to modify the pore structure and improve initial reactivity.[3] The cycling procedure for sulfidation and regeneration was modified slighty, as mentioned above. Sulfidation to breakthrough was carried out for cycles 1 to 5, 10, 15, and 20. In other cycles, sulfidation was carried out for 75 min, which was about 20 min less than the time required for breakthrough. This procedure corrected, in part, for the oversulfiding of the pellets at the inlet end of the reactor during the testing of the ICCI-1 sorbent.

H_2S breakthrough data for the ICCI-2 sorbent are shown in Figure 5. The breakthrough time can be seen to improve during the first three cycles as the secondary pore structure developed

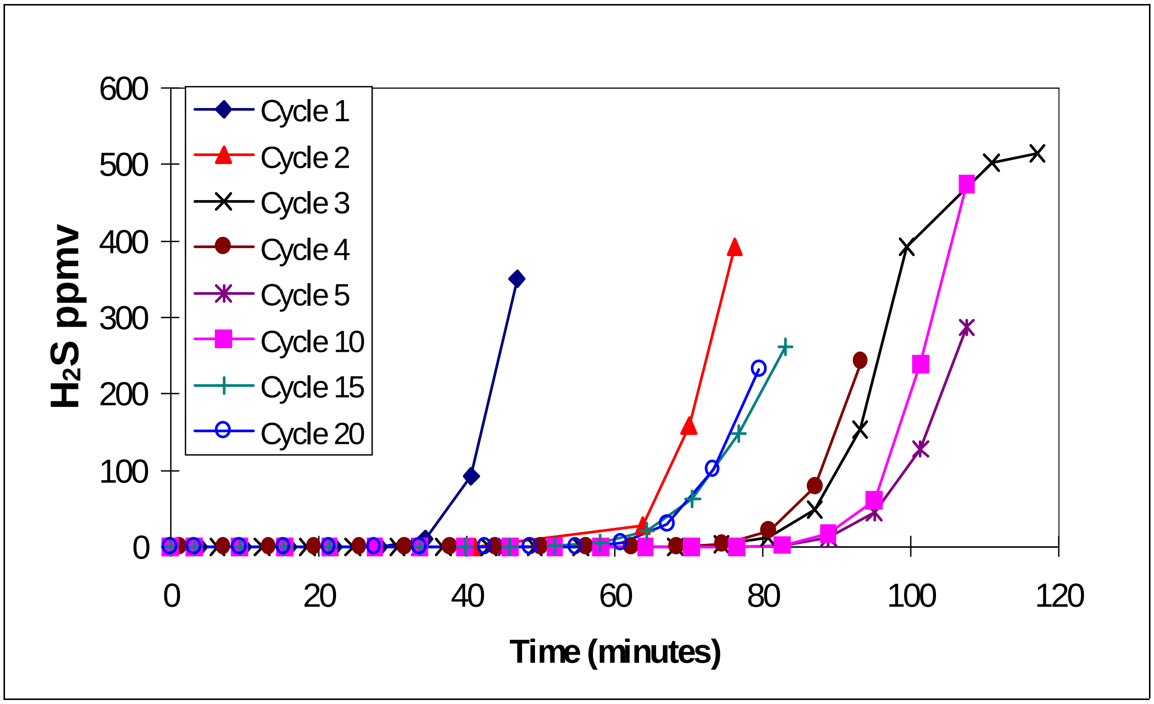

Figure 5. H_2S breakthrough results for ICCI-2 sorbent.

beyond that which occurred during the activation pretreatment. Some loss in breakthrough time occurred during cycles 10 to 15, an effect that is not presently understood. The same effects can be seen in Figure 6, where the calculated sulfur pickup at breakthrough is plotted versus cycle number. When the pellets were inspected after the twentieth sulfidation, the surface cracking of pellets near the inlet end of the reactor was barely noticeable and was much less than with the ICCI-1 sorbent. A summary of the sorbent's physical properties before and after the test is provided in Table 4. The fresh material is in the oxidized state and the tested material is in two different states of sulfidation, so direct comparisons should be made with caution. Probably the only important conclusion that can be drawn from Table 4 is that mechanical property degradation was much less with the ICCI-2 sorbent than with the ICCI-1 material. If one extrapolates the attrition loss data to 50 cycles, assuming a linear change through the bed and a linear change with cycle number, the result is an average attrition loss of 4.15% over 50 cycles. The goal set by GE is 5%, so the data appear promising. Thus, the effort to strengthen the pellets produced the desired result, and a better compromise was reached between mechanical properties and chemical reactivity. While this progress is encouraging, the investigators feel that further improvements are possible because the properties of the ICCI-2 sorbent are still not quite as good as those obtained with hand-made pellets. In view of promising performance of the ICCI-2 test during the 20-cycle test, authorization was given to continue the test for another 30 cycles. This effort is funded by a budget supplement provided by DOE/METC.

Because of the progress being made, a special task was included in this year's contract on technology transfer. A list of many of the organizations contacted is given in Table 5. Of the

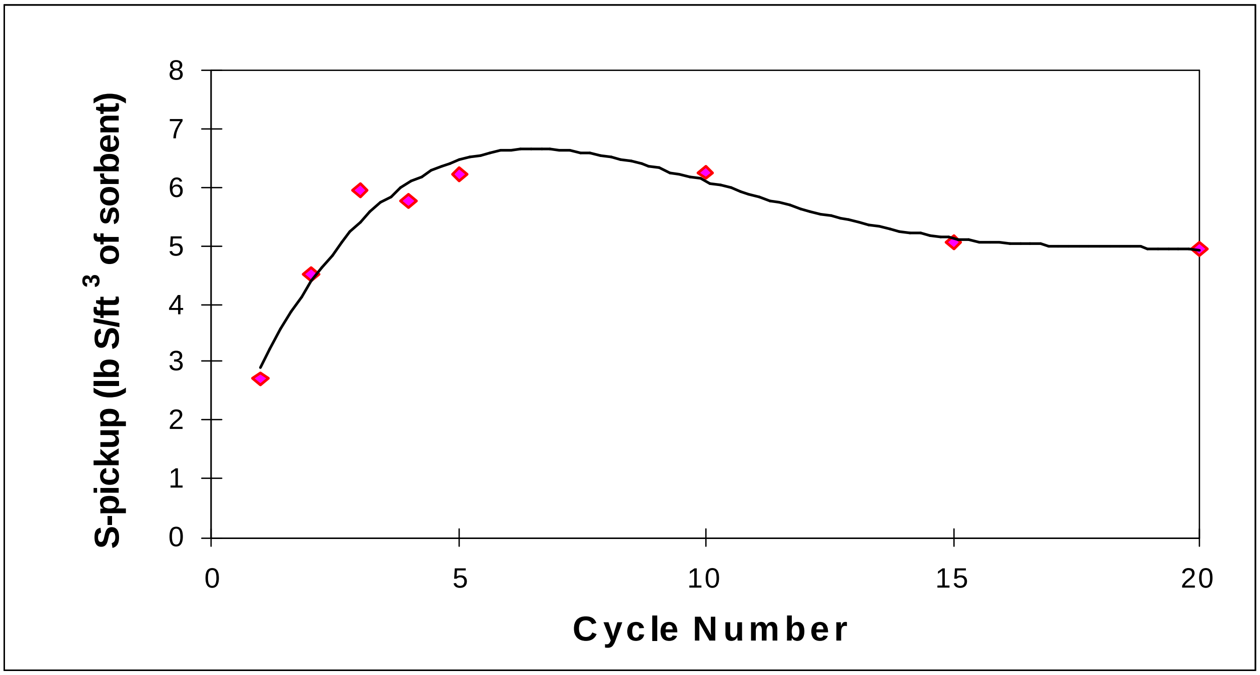

Figure 6. Calculated sulfur capacity of ICCI-2 sorbent.

Table 4. Physical Property Data on the ICCI-2 Sorbent Before and After Testing

		After 20th sulfidation	
Method	**Fresh**	**Near gas inlet**	**Near gas outlet**
Average pellet size (mm)	4.05	3.75	3.69
Bulk density (lb/ft^3)	93.2	102.0	98.1
Crush strength (lb/pellet)	30.4	22.1	18.5
ASTM attrition (%)	1.9	4.0	2.8
BET surface area (m^2/g)	1.11	2.52	1.63
Mercury pore volume (cm^3/g)	0.159	0.102	0.139
Median pore diameter (Å)	6458	4829	6116
Porosity (%)	42.0	29.0	38.0
Sulfur (wt%)[a]	0.0	8.5	3.8

[a] TGA measurement

potential sorbent manufacturers, only UCI showed an interest in making material for evaluation tests, presumably because there is no assured market for IGCC sorbents as yet. The response from potential users and other organizations was more enthusiastic. They realize that all the technology problems are not solved and that cold-gas cleanup may continue to be used. However, there appears to be a consensus that hot-gas cleanup has sufficient promise that additional R&D is justifed.

The part of the technology transfer task on materials suppliers proved to be critically important because the properties of the sorbent depend on the choice of raw materials. Therefore, the identity of any information obtained from these companies will not be published at

Table 5. Technology Transfer Contacts

Catalyst manufacturers	United Catalysts, Norton, Degussa
Potential user	General Electric, Kellogg, Destec, Public Service of Colorado
Raw materials suppliers	Total of 12 potential suppliers of ZnO, TiO_2, and binders
Others	EPRI, Parsons Power Group, TDA Research, Phillips Petroleum

this time. Samples from several companies were evaluated, and one of them prepared a new grade of powder for our possible use.

Benefits

The market potential for IGCC systems in the long term is enormous. In 1993, DOE projected that IGCC plants may produce as much as 130 GW of electricity in the year 2040.[9] This power estimate corresponds to 1.2 million tons/day of coal consumption, much of which would be high-sulfur bituminous coal. A clear description of expected benefits of IGCC systems was expressed by Feibus et al.[10] In their words,

> One of the most fundamental and important advantages exhibited by the IGCC power plant over direct combustion systems is the ability of the plant to control sulfur emissions to any extent necessary at a reasonable cost. The penalties imposed by the IGCC system, as a result of increasing the level of sulfur removal from 90 to 99.5, are a loss in efficiency of 1.3%, an increase in the capital cost of 3.5%, an increase in the heat rate of 1.5%, and an increase in the levelized cost of electricity of 2.6%.

These values were calculated for early plant designs with cold-gas rather than hot-gas desulfurization. The implication is that high-sulfur bituminous coal can be used in IGCC systems at an affordable cost.

With successful development of hot-gas desulfurization (HGD) technology, the efficiency of IGCC systems can be increased by 2% to 3%. There is an ongoing debate on the optimum temperature for desulfurization. The undesirable effects of desulfurizing at temperatures above 500 or 600 °C lie mainly in the affordability and technology readiness of valves, particle filters, and materials of construction. In a recent report by Buchanan et al., the effect of desulfurization temperature on the total cost of producing power from IGCC plants was analyzed.[11] While there did not seem to be a significant direct effect, there may be indirect benefits of using a high temperature related to lower emissions, less solid waste, etc.

There are three IGCC plants in the United States in operation or in the final stages of construction–the Wabash River, Tampa Electric, and Sierra Pacific Plants.[12] Now in operation, the Wabash River Plant, with cold-gas cleanup, repowers an old facility with an efficiency gain from about 31% to 38% and an increase in power output of 150%. When the Tampa Electric Plant goes online later this year, it will use 1,900 tons/day of bituminous coal. If the sorbent being developed here were to be used in the three plants mentioned above, approximately 150,000 tons/year of the sorbent would be needed.

Future Activities

Under a separate contract from the Illinois Clean Coal Institute, a 14,000 lb lot of sorbent will be produced. Small but important changes in preparation procedures are being made to further improve properties. It is hoped that the material will be tested in GE's moving-bed pilot plant later this year.

Acknowledgments

The authors wish to acknowledge the contibutions to the project of David Wolfe and his staff at UCI; Daniel Banerjee and Herman Feldman, ICCI; and Daniel Cicero and Thomas Dorchak, DOE/METC.

References

1. L. Lamarre, "Worldwide Activity in IGCC," *EPRI Journal*, Vol. 19, No. 5, 1994, pp. 6-15.

2. T. Moore, "Repowering as a Competitive Strategy," *EPRI Journal*, Vol 20, No.5, 1995, pp. 6-13.

3. J. H. Swisher, J. Yang, and R.P. Gupta, "Attrition-Resistant Zinc Titanate Sorbent for Sulfur," *Ind. & Eng. Chem. Research*, Vol. 34, 1995, pp. 4463-4471.

4. J. Yang, "Improving the Properties of Zinc Titanate-Based Sorbents for Sulfur Removal," Ph.D. Dissertation, Southern Illinois University, Carbondale, IL, 1995.

5. J. S. Mei, L. Gasper-Galvin, C.E. Everett, and S. Katta, "Fixed-Bed Testing of a Molybdenum-Promoted Zinc Titanate Sorbent for Hot Gas Desulfurization," in D.L Bonk, Ed., *Proceedings of Coal-Fired Power Systems 93–Advances in IGCC and PFBC Review Meeting*, Report No. DOE/METC-93/61131, U.S Department of Energy/Morgantown Energy Technology Center, Morgantown, WV, 1993, pp. 315-325.

6. R.E. Ayala, E. Gal, and R.P. Gupta, "Testing of Zinc Titanate Desulfurization Sorbents for Moving Bed Applications," in D.L Bonk, Ed., *Proceedings of Coal-Fired Power Systems 93–Advances in IGCC and PFBC Review Meeting*, Report No. DOE/METC-93/61131, U.S. Department of Energy/Morgantown Energy Technology Center, Morgantown, WV, 1993, pp. 136-145.

7. T. Grindley, "Effect of Chlorine on Hot Gas Desulfurization Sorbents," In V.P. Kothari and J.L. Beeson, Eds., *Proceedings of the Tenth Annual Gasification and Gas Stream Cleanup Systems Contractors' Review Meeting*, Vol. 1, Report No. DOE/METC 90/6115, U.S. Department of Energy/Morgantown Energy Technology Center, Morgantown, WV, 1990, pp. 215-226.

8. R.E. Ayala, A.H. Furman, and D.J. Najewicz, "Integrated Operation of a Pressurized Fixed Bed Gasifier, Hot Gas Desulfurization System and Turbine Simulator," in *Proceedings Advanced Coal-Fired Power Systems '95 Review Meeting*, U.S. Department of Energy/Morgantown Energy Technology Center, Morgantown, WV, 1995, pp. 187-201.

9. "IGCC Product Plan," U.S. Department of Energy, Washington, DC, April 1993.

10. H. Feibus, G. Voelker, and S. Spadone, "The Role of Advanced Coal Cleaning Technology in the Reduction of Sulfur Dioxide Emissions," In D.S. Gilleland and J.H. Swisher, Eds., *Acid Rain Control II. The Promise of New Technology*, Southern Illinois University Press, Carbondale, IL, 1986, pp. 51-84.

11. T.L. Buchanan, H.T. Chen, M.G. Klett, and M.D. Rutkowski, "Extended Parametric Sensitivity Studies on IGCC Systems," Final Report on Contract No. DE-ACO1-88 FE 61660, U.S. Department. of Energy, Washington, DC, March 1994.

12. "Clean Coal Technology Demonstration Program: Program Update 1995," Report No. DOE/FE-0346, U.S. Department of Energy, Washington DC, April 1996.