DOE/MC/25003-94/C0384

DEVELOPMENT OF SORBENTS FOR HIGH-TEMPERATURE DESULFURIZATION IN MOVING-BED SYSTEMS

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Conf-9406131--36

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Contract Number:

DE-AC21-88MC25003

Conference Title:

Coal-Fired Power Systems 94 -- Advances in IGCC and PFBC Review Meeting

Conference Location:

Morgantown, West Virginia

Conference Dates:

June 21-23, 1994

Conference Sponsor:

U.S. Department of Energy, Office of Fossil Energy, Morgantown Energy Technology Center

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9a.1 Development of Sorbents for High-Temperature Desulfurization in Moving-Bed Systems

CONTRACT INFORMATION

Contract Number	DE-AC21-88MC25003
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METC Project Manager	Daniel C. Cicero
Period of Performance	September 21, 1988 to January 31, 1995

Schedule and Milestones

FY94 Program Schedule

	S	O	N	D	J	F	M	A	M	J	J	A	S
Sorbent Preparation	—	—	—	—									
Bench-Scale Mods. and Testing	—	—	—	—	—	—	—	—	—	—	—	—	—
Bench-Scale Analysis			—	—	—	—	—	—	—	—			—
Topical Report*													

* Task Scheduled for FY95

OBJECTIVES

The objective of the option 3 program within this contract is to develop chemically reactive and mechanically durable mixed-metal oxide sorbent formulations that are suitable for moving-bed, high-temperature, desulfurization of coal gas. One optimum formulation will be evaluated in a pressurized 50-cycle bench-scale test.Work on zinc ferrite formulations was performed under the base program (Ayala, 1991). Work on zinc titanate formulations was initiated under the option 2 program (Ayala, 1993) and is continued under the present option 3 program along with testing of other mixed-metal oxides.

BACKGROUND INFORMATION

GE is developing a moving-bed, high-temperature desulfurization system for integrated gasification combined-cycle (IGCC) power systems in which zinc-based regenerable sorbents are currently being used as desulfurization

sorbents (Furman et al., 1992). In addition to zinc ferrite, zinc titanate and other novel mixed-metal oxides are being considered as sorbents, particularly for highly reducing coal gases where iron-containing sorbents can potentially undergo excessive sorbent physical degradation. A key to sucess in the development of high-temperature desulfurization systems is the development of a sorbent for the selected process operating conditions.

Mixed-metal oxide sorbents have been studied quite extensively in the past, including various types of zinc titanates (e.g., Zn_2TiO_4 and $Zn_2Ti_3O_8$) (Gangwal and Gupta, 1993) or as combinations of other metal oxides such as vanadium, copper, manganese, cobalt, tin, and others; see for instance (Lynch and Hepworth, 1993). During absorption from coal gases, H_2S reacts with zinc titanate according to the reaction

$$Zn_2TiO_4 + 2H_2S \Rightarrow 2ZnS + TiO_2 + 2H_2O \quad (1)$$

Similarly, during regeneration, zinc sulfide reacts with oxygen in the regenerant gas to revert back to the original oxide.

$$2ZnS + TiO_2 + 3O_2 \Rightarrow Zn_2TiO_4 + 2SO_2 \quad (2)$$

However, the regeneration zinc may lead to undesired side reactions, depending on process conditions, such as the formation of zinc sulfate according to

$$ZnO + SO_2 + \tfrac{1}{2}O_2 \Rightarrow ZnSO_4 \quad (3)$$

Zinc sulfate formation is undesired because (a) it results in significant density differences between the starting and ending solid phases that induces mechanical stresses within the pellet, and (b) the sulfate so formed during regeneration reacts with the H_2 and CO in the coal gas in subsequent desulfurization cycles, that results in the release of SO_2 according to

$$2ZnSO_4 + 5H_2 \Rightarrow ZnO + ZnS + SO_2 + 5H_2O \quad (4)$$

Although the feasibility of removing H_2S to very low levels (e.g., < 50 ppmv) from coal gases has been shown to be viable in most studies of mixed-metal oxides, one of the major limitations for large-scale use of mixed-metal oxides is the observed weakening and physical deterioration of the pellet and spalling during repetitive use in cycles of absorption and regeneration (Ayala el al., 1993). A need exists to determine best operating conditions that minimize sulfate formation and prevent mechanical degradation.

PROJECT DESCRIPTION

Program participants are: GE Corporate Research and Development (GE-CRD, prime contractor), GE Environmental Systems, Inc., (GEESI, subcontractor), and Research Triangle Institute (RTI, subcontractor). United Catalysts, Inc. (UCI) and Phillips Petroleum Company (PPC), acting as vendors, provided the sorbent samples for testing.

Sorbents developed for moving-bed systems must comply with a minimum of chemical and mechanical durability performance characteristics in order to be considered acceptable for long-term operation. Among the desired properties, a sorbent must have:

- High chemical reactivity, as measured by the rate of sulfur absorption and the total sulfur loading on the sorbent.
- High mechanical strength, as measured by the pellet crush strength and the attrition resistance.

- Suitable pellet morphology, as given by pellet size and shape to promote good bulk flowability and reasonable porosity to increase reactivity.

RESULTS

During the current year, several zinc-based sorbent formulations were tested in the laboratory, including UCI's zinc titanate sorbents and PPC's Z-Sorb sorbent, a family of proprietary sorbent formulations. Preparation methods for UCI's zinc titanate sorbents have been described previously (Ayala, 1993). Preparation methods for Z-Sorb formulations are considered proprietary to PPC, and only analyses that describe performance in hot gas desulfurization are presented here.

Table 1 shows the physical properties of the sorbents tested in the program. Both L-4103 B2 and T-2535M are zinc titanate formulations (Zn_2TiO_4) fabricated by UCI and contain 2.0-2.5% MoO_3 as pore modifier and 3% bentonite binder. L-4103 B2 was prepared as a laboratory formulation while T-2535M2 was produced as a larger batch (6,000 lb) for use in the GE moving-bed pilot plant in Schenectady, New York.

Formulations labeled Z-Sorb A and Z-Sorb B are standard formulations sold under the trade name Z-Sorb III. The other Z-Sorb formulations were developed for GE with a larger pellet size by PPC for GE's moving-bed system. Formulation Z-Sorb C was supplied as a one-gallon batch for laboratory evaluation, while Z-Sorb E was supplied as a 12,000 lb batch for use in the GE moving-bed pilot plant. One major difference between zinc titanate and Z-Sorb sorbents is their bulk density (Table 1), with Z-Sorb being a less dense material.

Testing of the sorbent formulations and assessment of their suitability for use in moving-bed desulfurization systems was carried out by measuring single-pellet chemical reactivity of fresh and cycled sorbents in a thermogravimetric analyzer (TGA), desulfurization performance in bench-scale reactor tests, and mechanical durability and sulfate formation in the cycled pellets. Details of experimental procedures have been published previously (Ayala, 1993; Ayala et al., 1993)

Table 1. Physical Properties of Sorbent Formulations

	L-4103 B2	T-2535M2*	Z-SORB: A, B	Z-SORB C	Z-SORB E*
Pellet Length, mm	5.0	6.1	3.6-3.9	6.5, 7.3	6.4
Pellet Diam., mm	4.0	4.9	2.6-2.9	6.4	4.3
Pellet Mass, mg	200	214	27-32	280	114
Crush Strength, lb/pellet	23.2	17.1	7.6-7.1	14.9	10.2
Attrition Resistance, %	95-96.6	96-98.5	99.6-99.1	98.3	98.4
Bulk Density, lb/ft^3	107	~100	~60	~60	~60

* Tested at the GE-CRD Pilot Plant also.

Table 2. Conditions for Bench-Scale Testing of Zinc Titanate and Z-Sorb

Cycle Number:	Gas Composition	Temperature
A1-A8 (6 hr)	39% CO, 10% CO_2, 30% H_2, 20% H_2O, 1% H2S	1000 °F
R1-R5	0.5-21% O_2, bal. N_2	1000-1300 °F
R6-R8	0.5-20% O_2, 5% SO_2, bal. N_2	1000-1300 °F
R8+1400 °F(2 hours)	20% O_2, 5% SO_2, bal. N_2	1400 °F

A- Absorption; R-Regeneration

Fresh Sorbent Chemical Reactivity

Figure 1 shows the comparison of single-pellet chemical reactivity measured by thermogravimetric analysis (TGA) for various zinc titanate and Z-Sorb formulations. Standard conditions for TGA are 1000 °F, 3% H_2S (Ayala, 1993). The weight gained by a single pellet as a function of time is directly proportional to the amount of H_2S absorbed by the pellet according to equation (1). A strong correlation is seen between the pellet size and the relative reactivity of the pellets: the smaller the pellet size (i.e., a higher ratio of pellet surface area to volume) the higher the weight gained as a function of time, as typical of pore-diffusion controlled reactions.

A desirable rate of H_2S absorption in moving-bed desulfurization systems is a TGA chemical reactivity of 50% of theoretical sulfur loading in less than 1 hr for fresh material, an a minimum of 50% in 2 hours for extended cyclic testing. Overall, pellets with an average diameter greater than 6 mm may not be sufficiently reactive for development of large-scale systems.

Bench-Scale Testing

In order to compare side by side the relative desulfurization performance of zinc titanate and Z-Sorb, an accelerated 8-cycle test in the bench-scale reactor system was performed. L-4103 B2 zinc titanate and Z-Sorb B were loaded in two reactors of the bench unit. The specific objective of the bench test was to determine the limits of operability for the two sorbents under identical conditions, particularly with respect to pellet spalling and mechanical deterioration due to zinc sulfate formation. Conditions for absorption and regeneration reactions are shown in Table 2. Pressure was held constant at 1 atm for both absorption and regeneration. The gas composition for absorption (cycles A1-A8) was chosen to simulate an oxygen-blown gasifier coal gas similar to that proposed for the Tampa Electric hot gas cleanup system program, except for the slightly higher H_2S and H_2O. The H_2S concentration was kept artificially high at 1% to accelerate the testing. Absorption time was held constant at 6 hours for each of the sorbents regardless of the level of H_2S leaving the reactors.

For regeneration, the test conditions were varied to examine their effect on zinc sulfate formation, reactivity and durability of the sorbents. Regenerations R1 to R5 in Table 2 were conducted without added SO_2 (while maintaining the regeneration maximum temperature below 1300 °F). Regenerations R6 through R8 were conducted adding 5% SO_2 to the regenerant gas to simulate the effect of recycled SO_2. In addition,

Table 3. Desulfurization Performance by Sorbents

	L-4103 B2 Zinc Titanate	Z-Sorb B
Max. Sulfur Capacity (lb S/100 lb fresh)	25	20
Pre-breakthrough outlet H_2S	<20 ppm H_2S	<10 ppm H_2S
% Total S (Abs. 5)	6.03 - 8.87	10.62 - 16.17
% of Max Sulfur Capacity	27 - 40	58-88
lb Sulfur/ft^3 of bed	7.3-10.7	7.0-10.7
% Carbon	0.14-0.18	0.14-0.20

after the R8 regeneration the bed temperature was raised to 1400 °F under 20% O_2 and 5% SO_2 to test the response of the sorbents to extremely harsh conditions of accelerated regeneration at high temperatures.

Desulfurization Performance

Table 3 shows the results of desulfurization by zinc titanate and Z-Sorb after the fifth absorption in the bench-scale reactor system. Both sorbents were exposed for six hours to simulated coal gas. Zinc titanate has a theoretical maximum sulfur capacity of 25 lb/100

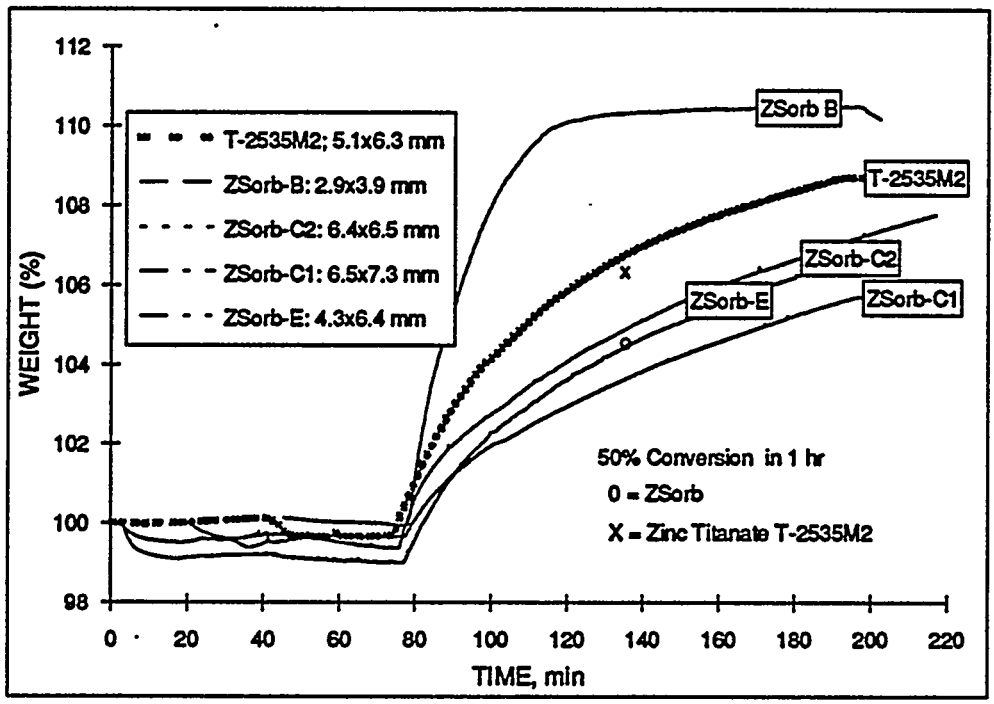

Figure 1. Comparison of fresh pellet TGA chemical reactivity

Table 4. Physical Appearance of Cycled Sorbents

	5th Reg.	8th Reg.	8th Reg. +1400F *
Zn Titanate:			
Pellet Color	white	gray	light gray /yellow
%Cracking	none	none	> 40%
Z-Sorb B:			
Pellet Color	off-white	off-white /yellow	off-white /green
%Cracking	none	none	almost none

* Held for 2 hrs

lb of fresh sorbent while Z-Sorb B has a capacity of 20 lb/100 lb of fresh sorbent. Both sorbents did an excellent job at desulfurization, with H_2S levels leaving the reactor prior to breakthrough of less than 10 ppmv for Z-Sorb B and less than 20 ppmv for zinc titanate. These levels correspond to more than 99% desulfurization (based on 1% H_2S in the inlet gas). Comparison of the total sulfur in the sorbents at the gas inlet and gas outlet locations shows that Z-Sorb B is a more reactive sorbent on a mass basis (comparing 10.6 to 16.2% sulfur in Z-Sorb versus 6 to 8.9% sulfur in zinc titanate). However, after adjusting for bulk densities of the sorbents, both sorbents had a comparable sulfur loading per unit volume of bed between 7 and 10.7 lb sulfur per ft^3 of bed. This result is very important for future reactor design because it suggests that a reactor vessel designed for zinc titanate can operate with Z-Sorb under similar process conditions.

Finally, Table 3 also compares the amount of carbon deposits found in both sorbents after the 6-hr absorption with the simulated coal gas containing 20% H_2O. There is no significant difference in the amount of carbon collected on the sorbents and it appears that cycled Z-Sorb does not catalyze the formation of carbon deposits from the Boudouard reaction ($2CO \leftrightarrow C + CO_2$).

Mechanical Durability of Sorbent Pellets

The level of pellet mechanical deterioration during cycling was assessed, first, semi-quantitatively by measuring the fraction of pellets showing signs of hairline cracking or spalling, and then by measuring crush strength and attrition resistance of the cycled sorbents. Table 4 presents the physical appearance of the sorbents at various stages of testing and shows that zinc titanate suffered severe degree of surface cracking after the 2-hr treatment to 1400 °F (i.e., 8th. Reg + 1400 °F). Z-Sorb B, on the other hand, did not suffer any significant degree of cracking, or very minimal at worst.

The mechanical durability of the pellets was assessed quantitatively by measuring the crush strength (Figure 2) and attrition resistance (based on ASTM D 4058-81 test) (Figure 3). Again, experimental procedures have been described previously (Ayala, 1993). The qualitative observation that zinc titanate deteriorated during the heat treatment to 1400 °F was corroborated by the measurement of crush strength and attrition resistance. Crush strength decreased in L-4103 B2 zinc titanate by almost a factor of two, from 23 to 13 lb/pellet and attrition resistance decreased from 96.6% to 88.0% in the same period. Note that crush strength of the 5-mm diameter zinc titanate is not directly comparable to the strength of the 3-mm Z-Sorb B because of the difference in pellet size and the fact that the pellets, being ellipsoids in shape (i.e., cylinders or spheres with rounded edges), do not have an easily measurable contact

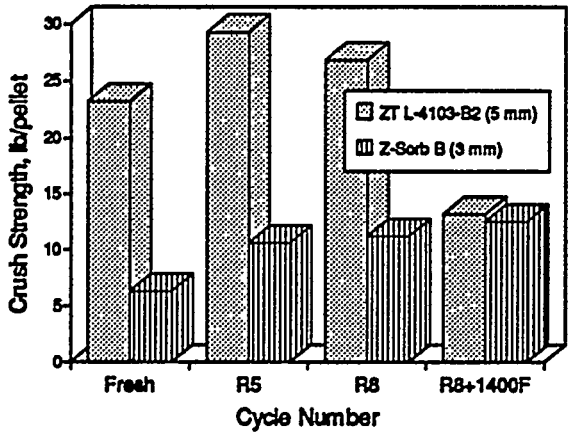

Figure 2. Comparison of Crush Strength During Bench-Scale Testing

line to scale the force per pellet to force per unit length.

Figure 4 shows the corresponding concentration of sulfate sulfur in the sorbents as a function of regeneration cycle for the two sorbents. Zinc titanate underwent mechanical deterioration when the sulfate sulfur level increased from approximately 2% after regeneration R8 to approximately 4% under the 1400 °F treatment. The sulfate sulfur level found in the sorbents correlated very well with the crush strength, attrition resistance, and physical appearance of the zinc titanate through the various

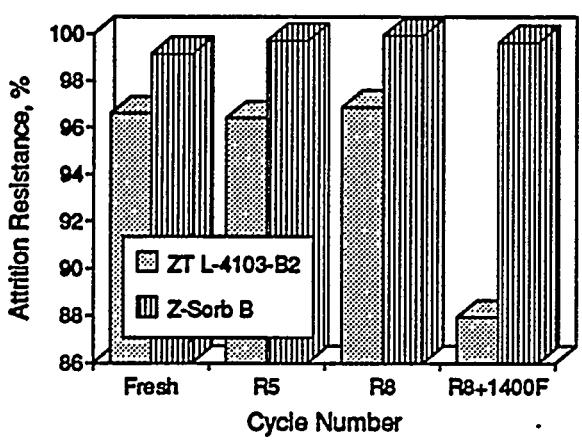

Figure 3. Comparison of Attrition Resistance During Bench-Scale Testing

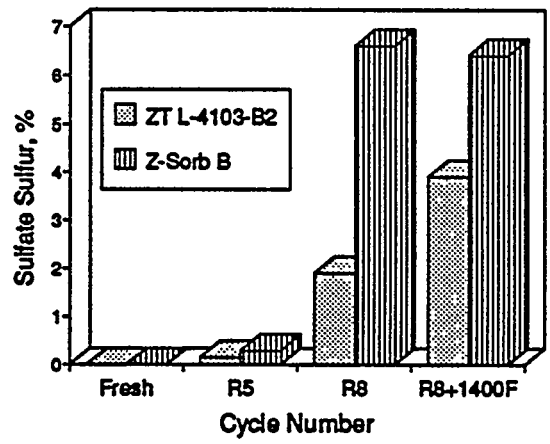

Figure 4. Comparison of Sulfate Formation During Bench-Scale Testing

cycles. On the other hand, Z-Sorb showed that despite forming larger amounts of sulfate sulfur, as high as 6%, did not develop a significant amount of measurable cracks and the sorbent did not lose mechanical strength. The superior mechanical durability of Z-Sorb B compared to L-4103 B2 zinc titanate was clear after the parallel accelerated bench testing of the two sorbents.

The following conclusions can be drawn from the atmospheric testing of L-4103 B2 zinc titanate and Z-Sorb B:

- Reactivity of Z-Sorb B towards H_2S removal from simulated coal gases is comparable to that of zinc titanate when pellets of similar size and shape are considered. The reactivity of the Z-Sorb pellets is a strong function of pellet size.

- Sulfur loading of Z-Sorb B after 6 hours of absorption is higher than that of zinc titanate on a mass basis, but very similar when presented on a bed volume basis. The difference being a result of the lower bulk density of Z-Sorb compared to zinc titanate

- Carbon formation due to the CO dissociation (Bouduard reaction) in cycled Z-Sorb was no different from that of zinc titanate.

- The mechanical durability of zinc titanate deteriorates dramatically under regeneration conditions of high SO_2/air at 1400 °F because of high rate of sulfate formation that produces internal stresses in the pellets resulting in the formation of hairline cracks and spalling.

- Both zinc titanate and Z-Sorb are suitable for operation in a moving-bed system under regeneration conditions below 1400 °F. The higher mechanical durability of Z-Sorb at 1400 °F gives a wider range of operability of the sorbent during pilot plant operation where optimum process conditions are being explored in support of the moving-bed desulfurization system for the TECO Clean Coal Technology Program.

FUTURE WORK

Having determined the conditions for proper regeneration of zinc-based materials, a long-term 50-cycle test of the best Z-Sorb formulation will be initiated in the modified bench-scale reactor system. The test will include:

- Pressurized sulfidation at 10 atm

- Pressurized regeneration up to 7 atm using recirculated gases for closer simulation of the pilot-plant regeneration recycle loop

The objective of the pressurized long-duration test would be to quantify sorbent performance over many cycles (long-term durability) at one set of selected conditions for absorption and regeneration.

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