

Paper Number:

DOE/MC/31089-97/C0723

Title:

Sorbent Development for Low-Temperature Moving-Bed Desulfurization

Authors:

R.E. Ayala

V.S. Venkataramani

T.L. Chuck

R.P. Gupta

Contractor:

GE Corporate Research and Development

P.O. Box 8

Schenectady, NY 12301

Contract Number:

DE-AC21-94MC31089

Conference:

Advanced Coal-Fired Power Systems '96 Review Meeting

Conference Location:

Morgantown, West Virginia

Conference Dates:

July 16-18, 1996

Conference Sponsor:

U.S. DOE, Morgantown Energy Technology Center

Disclaimer

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

Sorbent Development for Low-Temperature Moving-Bed Desulfurization

Raúl E. Ayala (ayala@crd.ge.com; 518-387-5850)

Venkat S. Venkataramani (venkata@crd.ge.com; 518-387-5322)

Timothy L. Chuck (chucktl@crd.ge.com; 518-387-6523)

GE Corporate Research and Development

One Research Circle, Bldg. K-1

Niskayuna, NY 12309

Raghubir P. Gupta (gupta@rti.org; 919-541-8023)

Research Triangle Institute

P.O. Box 12194

Research Triangle Park, NC 27709

Introduction

Coal gas desulfurization at elevated temperatures is now recognized as crucial for efficient and economic coal utilization in Integrated Gasification Combined-Cycle (IGCC) systems. Recent system studies of IGCC technology have suggested the temperature range of 350 °C to 550 °C (662 °F and 1022 °F), instead of temperatures above 1200 °F (648 °C), as a desirable range to remove coal gas contaminants, particularly sulfur species [Droog et al., 1993; Schreurs, 1994]. In general, the benefit to be gained at these “lower” temperatures (e.g., lower plant costs, hardware reliability, and engineering feasibility) outweighs the slight loss in desulfurization efficiency and still result in a lower overall cost of electricity. The U.S. Department of Energy/Morgantown Energy Technology Center (DOE/METC) has sponsored development of various configurations of high-temperature desulfurization systems using mixed metal oxide sorbents over the last decade [McDaniel et al., 1995], and a need exists for the development of more efficient sorbents for the lower end of the high temperature range of operation, i.e., the so-called “low” temperature sorbents.

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 [Bevan et al., 1995; Bevan et al., 1994]. Zinc titanate and other zinc-based oxides are being considered as sorbents for use in the Clean Coal Technology Demonstration Program at Tampa Electric Co.’s (TECO) Polk Power Station I. A key to success in the development of high-temperature desulfurization systems is the matching of sorbent properties, namely sustainable desulfurization kinetics, sulfur capacity, and mechanical durability over multiple cycles, to operate at the selected plant process operating conditions. Integrating desulfurization with gasifier and turbine components in the IGCC system results in a more efficient overall system [Rath et al., 1994; Buchanan, 1994; Corman, 1986].

Research sponsored by the U.S. Department of Energy’s Morgantown Energy Technology Center, under contract DE-AC21-94MC31089 with GE Corporate Research and Development, P.O. Box 8, Schenectady, NY 12301; telefax: 518-387-7258

Several other reasons related to sorbent operability favor desulfurization below 650 °C. Although the reaction rates for hot gas desulfurization using metal oxides increase with increasing temperatures and making it desirable to operate above 500 °C, the lower thermal stresses and propensity to sintering experienced by the sorbent at lower temperatures can lead to better sorbent reactivity and mechanical durability over a large number of cycles. The net effect is a reduction in the sorbent replacement cost. In turn, the benefit to be gained by lower temperature operation results in lower overall cost of electricity. However, no extensive study has been done on the development of advanced sorbents for the lower temperature application.

Objectives

In this program, the effort is geared towards developing advanced mixed-metal oxide sorbents for desulfurization in moving-bed systems in the temperature range 343-538 °C (650-1000 °F), where technical viability and process efficiency result in lower overall process costs. In addition, a cost assessment and a market plan for large-scale fabrication of sorbents will be developed. As an optional task, a long-term bench-scale testing of the best moving-bed sorbent formulation will be conducted.

The sorbents must have chemical characteristics that permit cyclic desulfurization and regeneration over many cycles without a drastic loss of activity. The sorbents must be capable of reducing the hydrogen sulfide level in the fuel gas to less than 20 ppmv in the specified temperature range and pressures in the range of 1 to 20 atmospheres. In addition, they must also have physical characteristics that are compatible with the selected reactor, e.g., pellet size/shape for sorbent flowability in moving beds, and maintain these properties over repetitive cycles. This paper will discuss in more detail recent developments in the fabrication and use of molybdenum-doped zinc titanate sorbents for moving-bed configurations at temperatures below 538 °C (1000 °F).

Project Description

This project is being pursued as part of DOE/METC Program “Advanced Sorbent Development” which includes development of sorbents for both moving-bed and fluidized-bed applications. GE Corporate Research and Development (GE-CRD) is acting as the main contractor to DOE and is also in charge of the development of moving-bed sorbents described in this paper. The Institute of Gas Technology (IGT) is acting as a subcontractor to GE-CRD in the development of sorbents for fluidized-bed applications. IGT’s work is presented under a separate paper at this conference.

The near-term thrust of moving-bed sorbent development is to support the commercialization of the GE hot gas cleanup demonstration system at Tampa Electric Co.’s Polk Station I, where desulfurization will take place near 430-500 °C (~800-930 °F). The long-term thrust is to develop moving-bed sorbents for use in future IGCC systems optimized to operate at temperatures as low as 343 °C (650 °F).

Three classes of sorbent materials are being considered for moving-beds: zinc-based materials (including zinc titanates), advanced (non-zinc) metal oxide materials, and proprietary materials

developed by independent vendors. Work on zinc titanate sorbent materials has been published under various DOE contracts [Ayala et al., 1995a; Gangwal and Gupta, 1993; Ayala 1993]. A study of non-zinc metal oxides suitable for desulfurization in the 343-538 °C range was performed last year and reported in the literature [Ayala et al., 1995b].

The implementation of hot coal gas desulfurization heavily relies on the development of regenerable sorbent materials that have high sulfur capacity and can efficiently remove H₂S (from several thousand ppmv levels down to a few ppmv) over many cycles of sulfidation/regeneration. Structural stability and good mechanical strength are also desirable features in a sorbent. Not surprisingly, only a few metal oxides can meet these stringent requirements.

Results

The effort in this project has concentrated in two aspects during the past year:

1. Screening of (non-zinc) metal oxides for applicability in the lower end of high temperature desulfurization (i.e., towards 343 °C, or 650 °F), and
2. Optimization of performance of molybdenum-doped zinc titanates for use in pilot- and demonstration-scale systems at temperatures near 430-500 °C (~800-930 °F)

Screening of metal oxides

The selection of metal oxides was presented last year [Ayala et al., 1995b] and it described the following metals as being potentially useful for our study: Zn, Cu, Co, Fe, Ce, Mo, Sn, W, and Ni. Many of these metals have weaknesses when considered as pure metal oxides for desulfurization, but become useful when considered in combination with others (e.g., Zn-Fe, Cu-Cr, Zn-Mo). In addition, inert binders and pore formers may be required for stable desulfurization and physical integrity of the formed (pelletized or agglomerated) particles.

The main criteria for selection was based on:

1. High desulfurization capability: thermodynamic equilibria and reasonable oxidation kinetics in the temperature range of 343-538 °C (650-1000 °F).
2. Minimization of undesired reactions under reducing gas conditions (e.g., interactions with HCl, CO, and H₂, and catalysis of gas phase reactions).
3. Ease of regeneration capability: thermodynamic stability and fast reaction kinetics compatible with the desulfurization temperature range.
4. Minimization of undesired reactions under oxidizing gas conditions (e.g., sulfate formation, hydrothermal stability).

It is important to emphasize that the selection of useful metals was made keeping in mind both i) short term goals (such as providing for support in the selection of the TECO sorbents within the next year), and ii) long-term goals (such as providing for laboratory evaluation of the next generation sorbents for use in future large-scale systems).

The cost of purchasing raw materials was also considered (Table 1). These costs will be kept in mind when developing formulations, but it was considered that it is too early to make decisions whether or not to use an oxide just because of its price, since the relative amounts of secondary components may be too small (e.g., <1%) to have a significant impact on the cost of the sorbent and yet have a tremendous impact on the durability of the material. As seen in Table 1, most cost fall in three ranges: low cost (\$0.5-1/lb), medium cost (\$2-5/lb), and high cost (\$8-10/lb). These costs have been estimated assuming purchases in large quantities (i.e., tons) and relatively good purity materials. Testing of mixed-metal oxides sorbents continues in the laboratory and results will be presented in the future. In this paper, the work on the Zn-Mo system (i.e., Mo-doped zinc titanates) will be presented, emphasizing the characterization and testing sequence from small laboratory samples to pilot-plant scale quantities.

Table 1.- Relative Cost of Sorbent Metal Oxide Raw Materials

Oxide	Cost, \$/lb
TiO ₂	0.5-1
ZnO	0.5-1
CuO	2-5
MnO ₂	2-5
ZrO ₂	2-8
NiO	3-5
CoO	7-10
CeO ₂	8-10
Cr ₂ O ₃	8-10
MoO ₃	8-10

Screening tests of Mo-containing zinc titanate

Zinc titanate has been under study for several years, and there is a significant amount of information on its performance characteristics in reducing (coal) and oxidizing (regeneration) gases. With respect to desulfurization ability, its performance has been excellent, and there is little doubt on its suitability for desulfurization at temperatures below 600 °C. However, as with any other sorbent, there is always a desire to improve its mechanical durability in order to reduce the sorbent replacement cost to minimize overall operating costs. The purpose of the screening tests at GE-CRD was to improve the mechanical durability of zinc titanate sorbent formulations by adjusting the additives concentration (e.g., molybdenum) and calcination conditions (i.e., endurance at various time/temperatures) that would result in improved performance in pilot plant tests. The improved formulation was targetted for testing at the GE-CRD pilot plant during Run 8 in September 1995.

Several formulations of zinc titanate sorbents were extruded, rounded, and calcined by United Catalysts Inc., (UCI). From attrition tests, the four most promising formulations were selected for bench-scale screening for twenty cycles at GE-CRD. The screening of four molybdenum-doped zinc titanate formulations was performed using a 7-cm (2.75 in.) ID fixed-bed bench reactor at

GE-CRD. Details of the bench reactor system and its operation have been given before [Ayala et al., 1994]. The cross sectional area of the reactor was divided into four quadrants, and each quadrant was filled with a different zinc titanate formulation.

The four formulations tested ranged in molybdenum content from zero percent (Formulation A) to 1.5% (Formulation B) to 2.0% (Formulations C and D). Formulations C and D differed in the calcination history (i.e., calcination temperature and/or time). For screening purposes, both absorption and regeneration were performed at 5 atm each, since GE-CRD's reactor does not have the capability to operate at 20 atm in its present configuration. Absorption was performed at 482 °C using a simplified coal gas composition similar to that of an oxygen-blown gasifier with high H₂S (39% CO, 10% CO₂, 30% H₂, 20% H₂O, 1% H₂S). Regeneration was performed between 482 °C and 760 °C using 1-4% O₂ in nitrogen. At the end of the twenty cycles, the sorbent bed was unloaded for chemical and reactivity analyses of the pellets. Figure 1 shows the outlet H₂S concentration (i.e., the H₂S breakthrough curve) of the composite four-formulation test. Figure 2 shows the comparison of envelope of breakthrough curves (at the 200 ppm outlet H₂S) taking the highest breakthrough time (~ 2 hr.) as 100% of initial sorbent performance. These resulting breakthrough measurements are the composite of the four formulations being tested in parallel in the same reactor (to make exposure conditions comparable). All absorptions had H₂S levels below 25 ppm prior to breakthrough. The results were very promising, with about 80% capacity maintained from cycles ten to twenty. In addition, the convergence of the envelope of breakthrough curves from 10 to 20 cycles suggests that the level of regeneration improved as we learned from each of the previous cycle results. The four sorbents were unloaded, and pellet quality (absence of hairline cracks) was better when molybdenum was present.

Figure 3 Figure 5 show the properties of the fresh and cycled samples. Some of the conclusions that can be drawn from those figures are:

- All formulations A, B, C, and D met the ASTM attrition criterion for fresh pellets (i.e., <4% ASTM attrition loss), but formulations B and D did not meet the ASTM attrition criterion for long-term operation (i.e., <5% ASTM attrition) (Figure 3). Formulation C had the lowest ASTM attrition for both the fresh (0.7%) and after 20 cycles (2.2%).
- The distribution of broken pellets and whole pellets after the ASTM attrition tests in the 20th regeneration samples is shown in Figure 4. Formulation C again fares better than the other three formulations tested.
- Sulfur capacity of the pellets was compared as fresh and after 20 cycles (Figure 5). Formulation C comfortably exceeded the minimum sulfur capacity required for TECO (i.e., 6 to 7 lb Sulfur/ft³, or approximately 3.2% wt. gain on TGA sulfidation for a bulk density of 100 lb/ft³). Weight gain for formulation C was more than twice the minimum.

Overall, formulation C (containing 2% equivalent molybdenum oxide) exhibited the best combination of desired properties for long-term operation and was recommended for subsequent preparation and testing for long-term (50 cycles) at RTI's bench-scale reactor system.

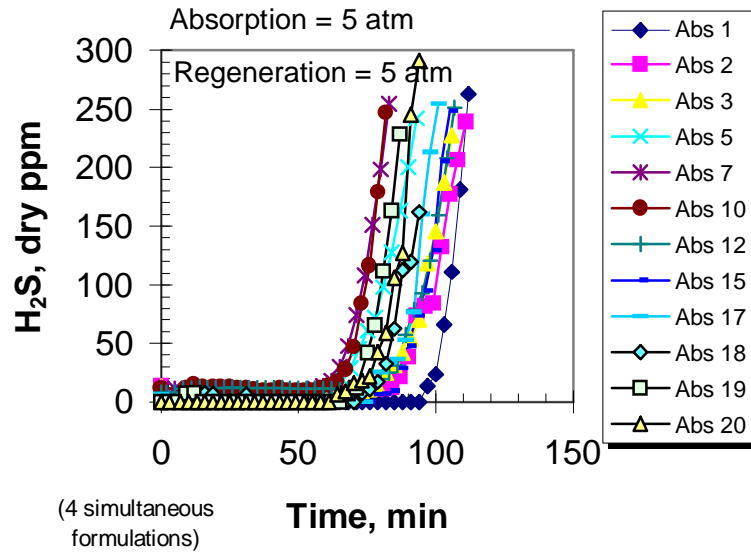


Figure 1.- H₂S breakthrough curve for the simultaneous bench reactor testing of four formulations at GE-CRD

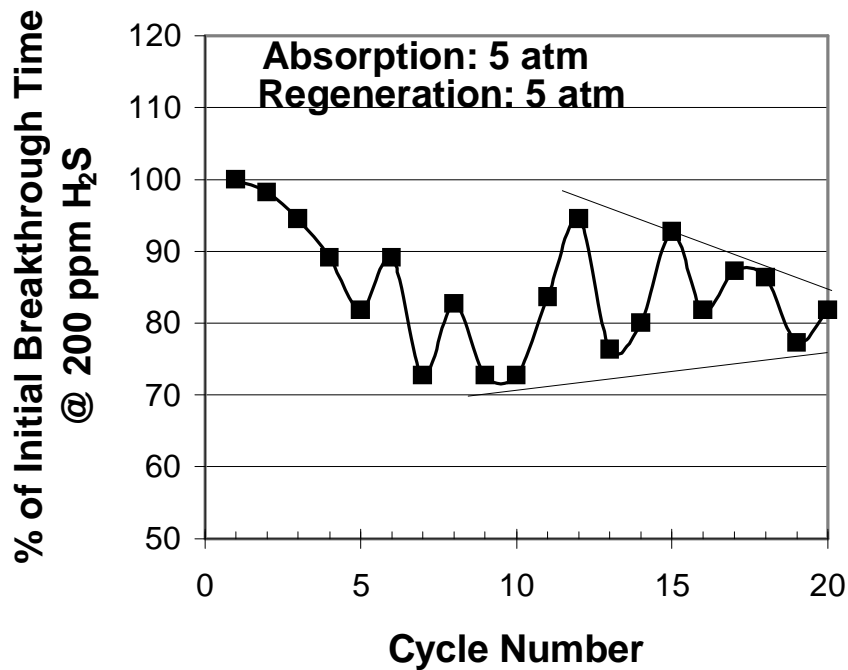


Figure 2.- Envelope of breakthrough curves for zinc titanate screening at GE-CRD

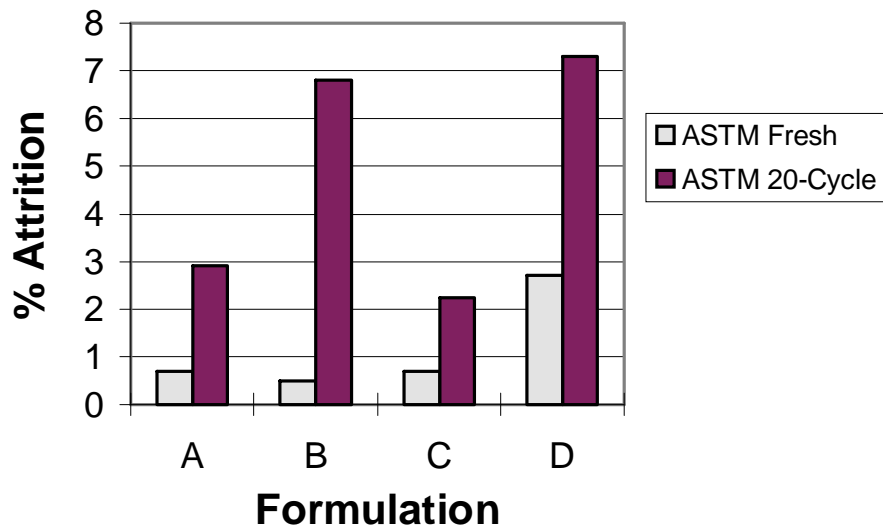


Figure 3.- ASTM attrition results on sorbents after the 20th regeneration in bench screening at GE-CRD

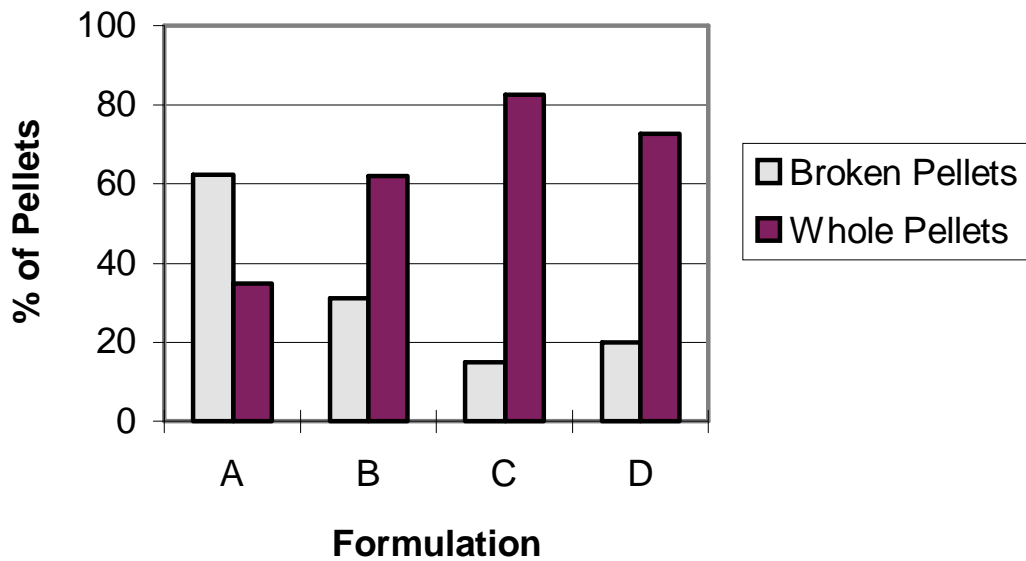


Figure 4.- Pellet Distribution after ASTM Attrition Test (20th. regeneration)

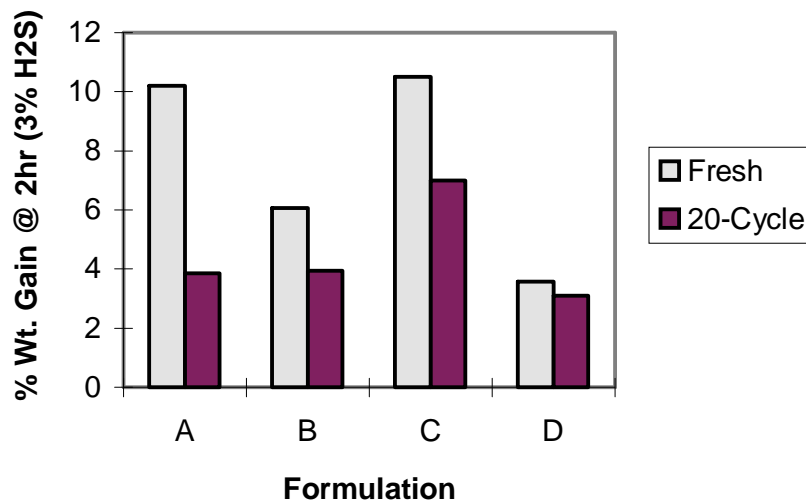


Figure 5.- TGA capacity of sorbents after 20-cycles at GE-CRD

50-cycle of Bench Test at Research Triangle Institute

In support of the effort for the selection of sorbent for the Tampa Electric Co's Polk Station, a subcontract was issued by GE-CRD to Research Triangle Institute to conduct an independent 50-cycle bench-scale test on one selected zinc titanate formulation. The test would provide information on the long-term chemical reactivity and mechanical durability of the pelletized sorbent for moving-bed applications. The selected sorbent for 50-cycle testing was Formulation C, previously shown in Figure 3 to Figure 5, which exhibited low ASTM attrition and high sulfur loading in the GE-CRD screening tests. The sorbent was fabricated again by UCI under similar calcinations conditions and designated as formulation PP3121. The testing at RTI proceeded according to the test protocol written at GE-CRD to provide uniformity in test procedures for the development of moving-bed sorbents. Conditions for the testing are shown in Table 2 and Table 3.

Table 2.- Gas compositions for 50-cycle test

	<i>Absorption</i>	<i>Regeneration</i>
CO	Balance	
CO ₂	10	
H ₂	20	
H ₂ O	20	
N ₂	16.3	Balance
H ₂ S	2.0	
O ₂		0-4

Table 3.- Target test conditions during absorption

<i>Parameter</i>	<i>Operating Condition</i>
Desired Sorbent Sulfur Loading	6-7 lb S/ft ³ of bed (96.2 g S/liter of bed) at the gas inlet location
H ₂ S Breakthrough point	200 ppm
Gas space velocity	≥2000 hr ⁻¹ (STP)*
Pressure	20 atm
Temperature	900 °F

* STP (standard temperature and pressure is defined at 20 °C and 1 atm).

The bed volume was adjusted to obtain the desired gas space velocity, meet the requirement of sulfur loading at the gas inlet location, meet the 200 ppmv breakthrough in a reasonable time (<5 hr.), and meet the test schedule for completion of the 50 cycles. Test conditions during absorption (Table 2) follow the TECO conditions, except for the reduced pressure (20 atm vs. 30 atm) and definition of breakthrough (200 ppmv vs. less than 50 ppmv). The reduced pressure is a result of limitations in the existing hardware; the definition of breakthrough was selected for ease of measurement and for historical comparisons. Regeneration was conducted at 7 atm and between 482 °C and 760 °C.

Figure 6 shows the raw data of the breakthrough curves for PP3121 zinc titanate. Pre-breakthrough H₂S concentrations were below the detection limit (<5 ppm H₂S) suggesting good desulfurization kinetics and thermodynamics. Target desulfurization is less than 50 ppmv for the Polk Station hot gas cleanup system.

Figure 7 shows the corresponding envelope of the breakthrough curves at the 200 ppm level. The bed performance stabilizes to a constant level as the number of cycles increases. This result suggests that steady state operation can be achieved, and loss in bed capacity is not a linear process with number of cycles. Hence, extrapolation of bed performance to longer number of cycles is possible.

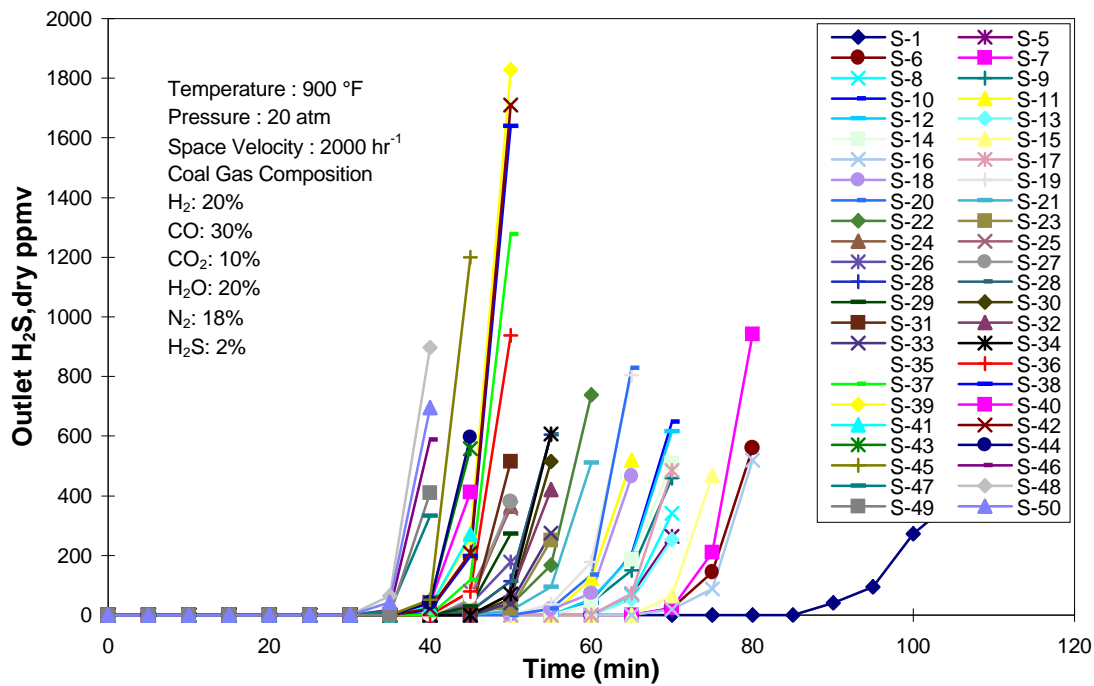


Figure 6.- H₂S Breakthrough Curves for 50-Cycle Test of Zinc Titanate at RTI

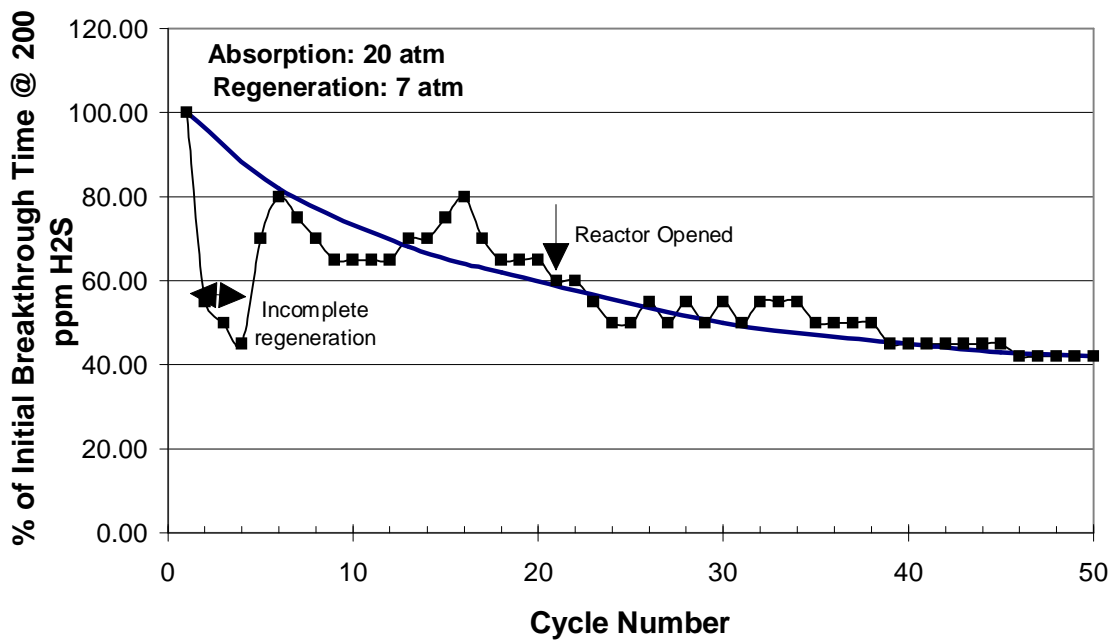


Figure 7.- Envelope of breakthrough curves for zinc titanate testing at RTI

Table 4 shows the comparison of sulfur loading for the fresh and cycled sorbents. The target sulfur loading depends on current bulk density as the sorbent densifies upon cycling. Sulfur loadings were measured by a thermogravimetric analyzer (TGA) as regenerable sulfide on gas inlet location samples. Sulfur analysis by the induction furnace (LECO) method were performed for reference and agreed with the TGA measurements.

Table 4 .- Sulfur Loading of Zinc Titanate Sorbent

<i>Sulfur Loading</i>	<i>Sulfur Loading as % Sulfur in sulfided pellet</i>
Target: 7 lb sulfur/ft ³ of bed	6.0-7.0 % (depending on bed bulk density)
Sulfur loading @ 21 cycle (60-min sulfidation)	5.5%
Sulfur loading @ 50th cycle (90-minute sulfidation)	6.1%

Given that the 60-minute absorption at cycle 21 resulted in below target sulfur loading, the absorption time was increased to keep loading within target range. Overall, the target sulfur loading at the gas inlet location was maintained over the 50 cycle test.

In addition to the current sulfur loadings on the pelletized sorbent at the end of selected sulfidations, the measurement of total sulfur capacity available in the powder was also made by TGA and shown in Table 5 and in Figure 8. Samples were in powder form to determine the intrinsic reactivity of the oxide while minimizing pore diffusion mass transfer resistances across the pellets. A sorbent is considered acceptable for long-term operation if its sulfur capacity is retained at 50% or higher of its initial (i.e., theoretical) capacity. In other words, if the sorbent decreases its capacity by no more than a factor of two at the end of fifty cycles.

Table 5.- Sorbent Sulfur Capacity

<i>Bed Capacity</i>	<i>% Sulfur Capacity by GE TGA Test (At 2-hr exposure)</i>
Target: as % of theoretical after 50 cycles	50%
Fresh	95%
After 21 cycles	60%
After 50 cycles	55%
After 50 cycles (at 3-hr exposure)	62%

The rate of sulfur loading on the sorbents as a function of time is given by the TGA curves presented in Figure 8. Standard GE TGA test was performed at 1 atm/538 °C/3% H₂S for 2 hours.

After the standard 2-hr TGA test, the 50-cycle powder sample was allowed to sulfide for 1 additional hour to determine if sorbent was saturated at that point. The measured the sulfur capacity was higher (62%) after one additional hour of sulfidation, confirming that the target sulfur loading requirement was exceeded comfortably and that further capacity was still available

in the sorbent. All samples exceeded the acceptance requirement for sulfur capacity, as shown in Table 5.

In addition to measuring the chemical reactivity of the cycled sorbent, the mechanical durability was also measured by ASTM D4058-81 attrition tests (Table 6).

Table 6.- Attrition Results of Zinc Titanate Bench Tests at RTI

<i>Sample Source</i>	<i>ASTM (D4058-81) Attrition Loss, %</i>
Target: Fresh sorbent	<4
Fresh	0.7
After 50 cycles: Target	<5
After 50 cycles: gas inlet location	8.0
After 50 cycles: gas outlet location	6.9
After 50 cycles: average	7.4

The attrition loss for the fresh sorbent were well below the initial target of 4% by the ASTM method. The target for the fresh sorbent is as defined in the performance specifications for pilot plant sorbent procurement. The attrition loss for the 50-cycle sorbent was above the target value. Given the fact that the chemical reactivity was satisfactory and exceeded the minimum requirements but the attrition was above target, the performance suggests that the calcination process should be differed to further increase pellet strength at the expense of lower reactivity. As we have stated in the past, calcination conditions determine a balance of reactivity and strength: generally speaking, the higher the reactivity (because of higher pellet porosity) the lower the pellet strength and the higher the ASTM attrition.

Overall, the PP3121 zinc titanate sorbent formulation exceeded minimum specifications of reactivity, sulfur capacity, H₂S equilibrium removal levels, and initial attrition losses. An improvement in the attrition resistance at the 50th cycle (i.e., 50th regeneration) is still desirable. In order to correlate any laboratory data with actual plant operation during evaluation of future sorbent formulations, a batch of this same zinc titanate composition was recommended for fabrication and testing at the GE-CRD pilot plant.

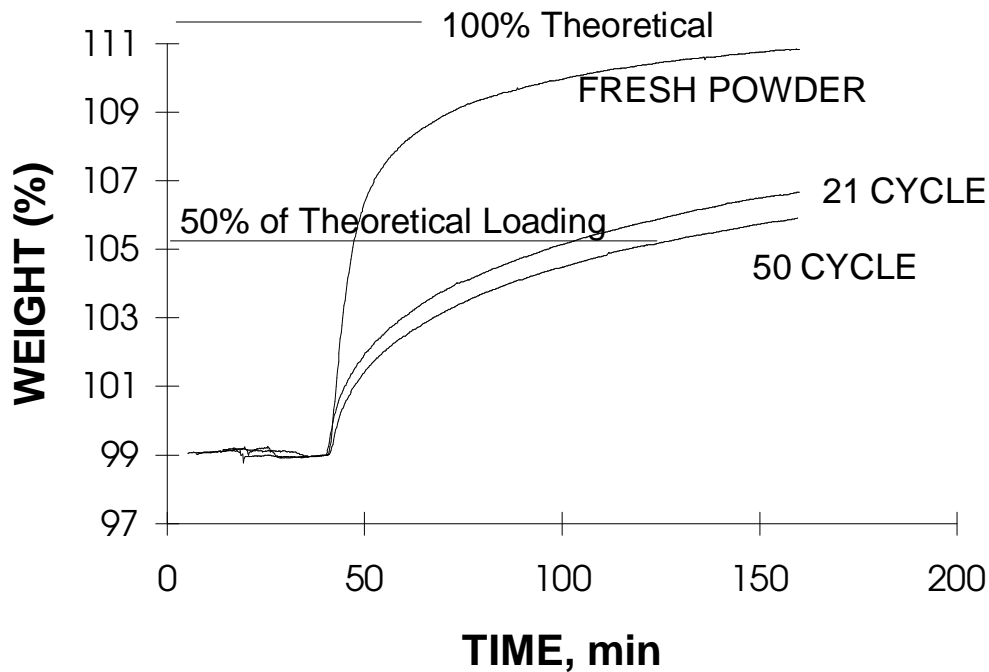


Figure 8.- TGA sulfur capacity of powdered samples after 50 cycles of testing at RTI

Pilot Plant Test Results

Formulation PP3121, and tested at RTI for fifty cycles, was again fabricated by UCI as a 6,400 Kg batch (~14,000 lb) (designation T-2594M) for testing in the GE-CRD pilot plant during Run 8 in September 1995. From the point of view of sorbent development, the purpose of the pilot plant testing was to collect data on the scaling factors of chemical reactivity and sorbent mechanical durability between laboratory tests and larger-scale systems. A second objective was to measure the manufacturability of large sorbent batches given laboratory target specifications.

Figure 9 shows the absorber outlet H₂S during operation of the GE-CRD pilot plant (Test 8) using the zinc titanate sorbent developed in the current sorbent program. Complete results of the pilot plant Test 8 are presented in a separate GE paper in this conference [Furman et al., 1996]. Absorption is carried out at 20 atm and close to 480 °C (~900 °F). After some initial excursions in the desulfurization performance during the first 100 hours, the sorbent and hardware were made to operate in integrated fashion, with close to 99% H₂S removal (from 3500 ppmv dry to 30-40 ppmv dry), achieving desired sorbent reactivity, while simultaneously accomplishing target SO₂ production in the regeneration loop (results not shown here). The attrition loss in the pilot plant test was measured at 1.7% under one set of conditions (i.e., a V-Wire screen in the regenerator fines separator) and 0.3% loss under another set of conditions after the test (i.e., a 1 mm x 1 mm square mesh screen at the same location). These measured pilot plant attrition losses compare favorably with the ASTM attrition losses of approximately 7% ASTM attrition loss measured in the laboratory, indicating that the large scale operation is less severe and cost of sorbent

replenishment is less than predicted from ASTM tests. No corresponding scaling factors are available for the TECO Demonstration plant, and these will be obtained when the demonstration system is placed in operation for the first time in the Fall of 1996.

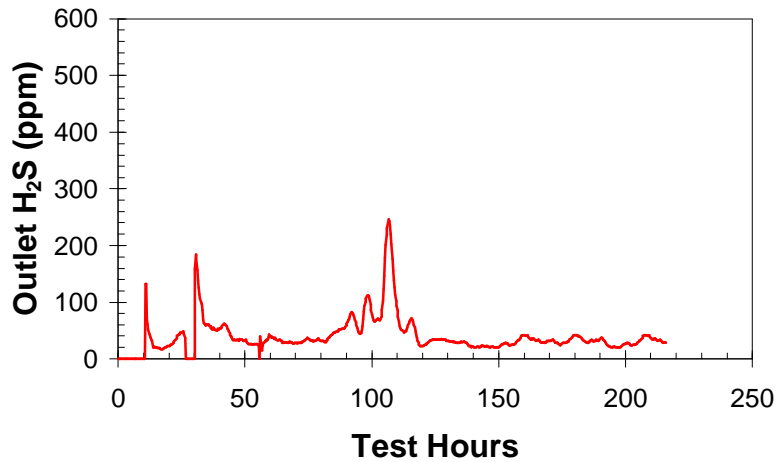


Figure 9.- Absorber outlet H₂S during pilot plant test 8

In conclusion, three levels of testing were performed on molybdenum-doped zinc titanate: laboratory screening at GE-CRD, long-term (50-cycle) bench-scale testing at RTI, and pilot plant testing (200-hr, Test 8) at the GE-CRD pilot plant. The results indicate that the flow of information and technology transfer from laboratory to pilot plant is consistent and prediction of large scale system operation is possible from laboratory and bench test results. Prediction of sorbent replenishment costs due to attrition at the Tampa Electric demonstration-scale plant cannot be made yet, but will be available after plant startup.

Benefits

Coal gas desulfurization to sufficiently low levels at elevated temperatures is now recognized as crucial to efficient and economic coal utilization in Integrated Gasification-Combined Cycle (IGCC) systems. As mentioned before, sensitivity studies of IGCC systems in The Netherlands [Schreurs, 1994; Droog et al., 1993] outlined the economic advantages of desulfurization at 350 °C or above over commercial low-temperature cleanup systems below 100 °C, while in the U.S. [Buchanan et al., 1994] an independent study compared different configurations of gasifiers, hot gas desulfurization (including moving-bed systems), particulate cleanup, and process integration to compare the performance of several system configurations. In both cases, the assumptions for successful implementation of hot coal gas desulfurization relied on the successful development of regenerable sorbent materials.

These sorbents must meet a minimum set of chemical reactivity and mechanical durability criteria to reduce operating costs in large systems. The present sorbent development program is aimed at

minimizing the risks (technical and cost) associated with scaling up of the moving-bed hot gas desulfurization process.

The early thermodynamic analysis by Westmoreland and Harrison in 1976 [Westmoreland and Harrison, 1976] set the stage for desulfurization candidates in the range 400 to 1200 °C (752-2182 °F). With the new requirements of lower temperatures (343-538 °C), an update of the thermodynamic analysis was needed to redefine the temperature regime of interest and the suitable metal oxide candidates for hot gas desulfurization. This resulting information, which we obtained and published last year [Ayala et al., 1995b], defines potential candidates worth pursuing for the next generation of suitable hot gas cleanup sorbents.

Over the past year, testing of zinc titanate sorbent in laboratory screening, long-term bench scale testing, and pilot plant scale operation, has proven that zinc titanate is a suitable sorbent for desulfurization in the target temperature range of 343-538 °C, and consistent with relatively easy regeneration requirements and minimal undesired side reactions. In this sense, the advanced sorbent development program is providing support to the development of more efficient and economically viable large-scale IGCC systems for power generation.

Future Activities

Previous laboratory data have indicated that desulfurization reactivity and mechanical strength of sorbent pellets are inversely proportional. Having demonstrated at the pilot plant that integrated operation of hot gas desulfurization using zinc titanate sorbent achieved 99% desulfurization simultaneously with good sorbent regeneration, the next step is to further increase the mechanical durability of the sorbent for lowering further plant operating costs. Additives/promoters for stabilization of pellet internal morphology will impart strength to the pellets. An alternate approach is to decrease the ratio of inert to active species for desulfurization. Several sorbent manufacturers and research laboratories are being contacted for implementation of these fabrication enhancements to the family of zinc-based sorbents.

Work will continue in the laboratory on the screening of (non-zinc) mixed-metal oxides. Formulations that exhibit good desulfurization/regeneration characteristics will be pelletized and calcined under suitable conditions for further testing in the laboratory and, eventually, under pilot plant operation.

Acknowledgments

The authors gratefully acknowledge the technical assistance of Daniel Cicero, P.E., the METC Contracting Officer's Representative. United Catalysts, Inc.'s cooperation is also appreciated for providing free of charge several sorbent formulations for testing. The contract period of performance is from September 30, 1994 to February 29, 1997.

References

- Ayala, T. Chuck, E. Gal, and R.P. Gupta. 1994. Development of High Temperature Desulfurization Sorbents for Moving-Bed Systems. In *Proceedings of the Coal-Fired Power Systems 94 – Advances in IGCC and PFBC Review Meeting*, p. 637. DOE/METC-94/1008. NTIS/DE94012252. Springfield, Va.: National Technical Information Service.
- Ayala, R.E. T.L. Chuck, and R.P. Gupta. 1995a. . Moving-Bed Sorbents. In *Proceedings of the Advanced Coal-Fired Power Systems '95 Review Meeting*, Vol II , pp 591-600. DOE/METC-95/1018 Vol 2. NTIS/DE95009733. Springfield, Va.: National Technical Information Service.
- Ayala, R.E., V.S. Venkataramani, J. Abbasian, and A.H. Hill. 1995b. Advanced Low-Temperature Sorbents. In *Proceedings of the Advanced Coal-Fired Power Systems '95 Review Meeting*, Vol I , pp 407-416. DOE/METC-95/1018 Vol. 1. NTIS/DE95009732. Springfield, Va.: National Technical Information Service.
- Bevan, D.J. Najewicz, R.E. Ayala, A. Feitelberg, and A. Furman. 1995. Integrated Operation of a Pressurized Gasifier, Hot Gas Desulfurization System and Turbine Simulator. In *Proceedings of the Advanced Coal-Fired Power Systems '95 Review Meeting*, Vol I , pp. 187-201. DOE/METC-95/1018. NTIS/DE95009732. Springfield, Va.: National Technical Information Service.
- Bevan, S., D.J. Najewicz, E. Gal, A.H. Furman, R. Ayala, and A. Feitelberg. 1994. Integrated Operation of a Pressurized Gasifier, Hot Gas Desulfurization System and Turbine Simulator. In *Proceedings of the Coal-Fired Power Systems 94 – Advances in IGCC and PFBC Review Meeting*, p. 222. DOE/METC-94/1008. NTIS/DE94012252. Springfield, Va.: National Technical Information Service.
- Buchanan, T.L., H.T. Chen, M.G. Klett, M.D. Rutkowski, and R. Zaharchuk. Optimization of Stream Cleanup in Three IGCC Systems. Final Report to U.S. DOE/Fossil Energy by Gilbert/Commonwealth, Inc., Reading, PA, USA under Contract DE-AC01-88FE61660.
- Corman, J.C. 1986. *System Analysis of Simplified IGCC Plants*, Topical Report. U.S. Dept of Energy, DOE/ET/14928-2233.
- Droog, H.A., A. Delwel, and R. Assink. 1993. Comparison of High-Temperature Gas Treatment Options with Low-Temperature Gas Treatment in IGCC's following Entrained Flow Gasification. In *Proceedings 12th EPRI Conference on Gasification Power Plants*. San Francisco, CA, Oct 27-29, 1993
- Furman, A.H., R. Ayala, A. Feitelberg, D. Najewicz. 1996. Integrated Operation of a Pressurized Fixed Bed Gasifier, Hot Gas Desulfurization System and Turbine Simulator. Paper 3.1. *Advanced Coal-Fired Power Systems '96 Review Meeting*. Morgantown, WV, July 16-18, 1996.

- Gangwal, S.K., and R.P. Gupta, 1993. Enhanced Durability of Desulfurization Sorbents for Fluidized-Bed Applications. In *Proceedings of the Coal-Fired Power Systems 93 – Advances in IGCC and PFBC Review Meeting*, p. 146-157. DOE/METC-93/6131. NTIS/DE93000289. Springfield, Va.: National Technical Information Service.
- McDaniel, M.H., D.J. Molloy, and V.K. Venkataraman. 1995. Editors. *Proceedings of the Advanced Coal-Fired Power Systems '95 Review Meeting, Vol I and II*, . DOE/METC-95/1018. NTIS/DE95009732. Springfield, Va.: National Technical Information Service.
- Rath, L.K., G.T. Lee, and P.H. Le. 1994. IGCC System Studies. In *Proceedings of the Coal-Fired Power Systems 94 – Advances in IGCC and PFBC Review Meeting*, p. 66. DOE/METC-94/1008. NTIS/DE94012252. Springfield, Va.: National Technical Information Service.
- Schreurs, H. 1994. Hot Clean Up of coal Gas. An Overview of Applicability. Netherlands Agency for Energy and the Environment Novem. August 31, 1994. Report No. 94/E0705/229100.
- Westmoreland, P.W., and D. P. Harrison. 1976. Evaluation of Candidate Solids for High-Temperature Desulfurization of Low-Btu Gases. *Env. Sci. Tech.*, 10, 659 (1976).