Testing and Analysis of METC10 Sorbent

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ABSTRACT:

A novel regenerable sorbent has been developed by the in-house research staff at the U.S. Department of Energy's Federal Energy Technology Center. The sorbent, identified as METC-10, has demonstrated very high attrition resistance as well as very high and stable reactivity conducted under numerous testing regimes under both simulated and actual fuel gas conditions. The sorbent, the only one to do so, has exceeded all test conditions required for for use in the Tampa Electric Company (TECO) Clean Coal Technology (CCT) demonstration project, including a required sulfur loading of 6.7 lb/ft^3, attrition of <5 wt%, as well as regeneration under the very drastic conditions of 10% SO_2 at 510 ^oC under 5-7 atmospheres. In addition, the sorbent was also tested at 370 ^0C (700 ^0F) under conditions similar to those expected to be encountered at TECO. At this low temperature, it was possible to achieve a sulfur loading 17 wt%, indicating that the sorbent is suitable for applications over a wide range of temperatures.

INTRODUCTION

The U.S. Department of Energy's Federal Energy Technology Center (Formally METC) during the last 20 to 25 years has funded research, development, and demonstration (RD&D) projects in the field of advanced power generation. Of this work, the Integrated Gasification Combined Cycle (IGCC) system is one of the more promising advanced power systems. It has been predicted that IGCC systems, with hot gas cleanup, will be able to offer significant improvements in environmental performance and overall plant efficiency compared to conventional pulverized coal-fired plants, which have efficiencies of 33 to 35 percent. It is expected that IGCC with hot gas cleanup will achieve efficiencies in excess of 52 percent and will be capable of producing power at a 20 percent lower cost of electricity then that of conventional coal based systems. Furthermore, it is predicted that this increase in efficiency will be able to reduce CO_2 emissions by 35 percent.

Development of a suitable regenerable sorbent is one of the major barrier issues in the Hot gas Cleanup program for Integrated Gasification Combined Cycle (IGCC) systems. The development of a regenerable sorbent has posed a challenging problem for the last 20 years (Lew et al.,1989), a challenge which until recently, that has gone unmet. Various formulations of zinc ferrite and zinc titanate in the form of extrudates and spherical pellets have been studied at FETC and out side facilities for removal of sulfurous gases from coal gasification streams (Siriwardane et al., 1990, 1993, 1994). Problems of decrepitation, spalling, and loss of reactivity have occurred after sulfidation and regeneration of these sorbents.

A series of novel sorbents containing zinc oxide have been developed at FETC to address these problems (Siriwardane et al.,1994,1996). These FETC developed sorbents showed superior performance during both 20-cycle high pressure fixed-bed tests with steam regeneration and a 50-cycle high pressure fixed-bed test with dry regeneration, during tests conducted at FETC. In addition, one of the FETC developed sorbents (METC10) was tested in the moving bed reactor at the General Electric (GE) pilot plant. Despite several operational problems at the facility, very promising results were obtained during the testing. However, regeneration conditions at the GE pilot plant did not completely simulate the very drastic regeneration conditions (10% SO_2 , 482 - 510 ^{0}C at 5-7 atmospheres/ high pressure) encountered at TECO and subsequently, the test results were not conclusive.

The drastic regeneration conditions at TECO may contribute to the formation of sulfate and deterioration of the sorbent. The METC10 sorbent was modified to obtain the necessary characteristics to withstand the drastic regeneration conditions encountered at TECO, with the modified sorbent subsequently being identified as METC10-M. The modified sorbent was then tested in a fixed bed for 25 sulfidation/regeneration cycles at Research Triangle Institute(RTI) with regeneration conditions which totally simulated those encountered at the TECO/CCT project (Turk and Gupta, 1997). The excellent results obtained from this study will be discussed in this paper.

In addition, METC10 sorbent suitable for the fluidized/transport reactor beds was also tested in a bench scale reactor. Superior attrition and sulfur capacity values were obtained for these sorbents as well.. Promising results obtained from these studies will also be discussed in this paper.

OBJECTIVES

One of the objectives of this work was to determine optimum operating conditions for achieving target performance of the METC10-M sorbent and to assess its compatibility for use in the Tampa Electric Company's (TECO's) Hot Gas Cleanup Unit.

The minimum criteria for consideration as sorbent candidates for TECO's evaluation include:

a. The H_2S leakage (pre-breakthrough level) prior to target sulfur loading of 6.7 lb/ft^3 (at gas inlet) must be below 100 parts per million by volume (ppmv).

b. The sorbent must maintain a minimum of 50 percent of theoretical capacity throughout 25 cycles of testing, but never less than 6.7 lbs/ft^3 of sulfur loading.

c. The sorbent attrition determined by American Society for Testing Materials (ASTM) Standard D4058-81 must be $\leq$4 percent for the fresh material and $\leq$5 percent for the 24-cycle regenerated material.

d. The sorbent must be regenerable at 900 to 950 °F in the presence of 8 to 10 vol% of SO_2 in the regenerator feed gas.

In addition to the TECO CCT project, another objective of this work is to prepare fluid/transport bed reactor sorbents suitable for the Pinon Pine/clean coal project(CCT) and the FETC process design unit (PDU). The sorbent should have an attrition value (measured using the ASTM three hole attrition method) of less than 5 wt% and sulfur absorption capacity greater than 6 wt%. Sorbent should be able to retain its sulfur capacity during multicycle testing.

EXPERIMENTAL

Fixed Bed Testing of METC10-M Sorbent at RTI

The METC10-M sorbent was developed by FETC in-house researchers. The parent version of this sorbent (METC10) was tested in General Electric's (GE's) pilot plant facility in March 1996. The current version, designated as METC10-M, was an improved version of the parent material. United Catalysts Inc. (UCI) prepared the current formulation under guidance from FETC using equipment large enough to produce a sorbent batch with the physical and chemical characteristics that would be obtained for a commercially prepared sorbent batch. This sorbent was supplied as 3-mm ellipsoidal pellets.

The 25-cycle test was performed in a bench-scale sorbent test facility at RTI, which can be operated at high temperature and high pressure. This facility consists of a specially designed reactor system in which the sorbent is held in a quartz cage and exposed to simulated coal gas or regeneration gases. The quartz reactor provides an inert surface that does not adsorb H_2S or catalyze reactions between coal gas components or regeneration gases. During sulfidation, a reactor effluent slipstream, from which the steam has been condensed, is analyzed by a Varian 3300 gas chromatograph (GC) for H_2S, COS, and SO_2 every 5 to 7 min. From this information, H_2S concentration as a function of time is monitored. During regeneration, reactor effluent slipstreams are fed to on-line O_2 and SO_2 analyzers. Concentration of the SO_2 in the reactor feed is continuously monitored by another on-line SO_2 analyzer. The regeneration feed gas containing 3.5% O_2 and 8% SO_2 in N_2 was generated by pumping controlled quantities of liquid SO_2, vaporizing liquid SO_2, and mixing the vaporized SO_2 into an air-nitrogen mixture generated by blending metered quantities of air and nitrogen.

METC10-M was subjected to a 25 cycle test at RTI using the approved test protocol provided by the U.S Department of Energy's Federal Energy Technology Center. These test conditions completely simulated those encountered at TECO/CCT project. Sulfidation was performed at 482 ^{0}C (900 ^{0}F) and 2,026.5 kPa (20 atm) utilizing simulated TECO coal gas (1.2% H_2S, 35.8% CO, 12.2% CO_2, 26.8% H_2, 18.1% H_2O, and 5.95% N_2). Regeneration was performed at 510 ^{0}C (950 ^{0}F) and 5 atm with 3.5 % O_2 in the presence of 8% SO_2. Space velocity during both sulfidation and regeneration was 2000 hr^{-1}.

The sorbent was loaded only up to 6.7 lb/ft3 of sulfur during all sulfidation cycles except at the 25 th sulfidation. The run was stopped after the 24 th regeneration and the sorbent was examined. Out of the sorbent removed from the reactor, 110 g of the sorbent were kept for characterization. The remaining sorbent was loaded into the reactor and the 25 th sulfidation cycle was performed. This last sulfidation cycle was carried out until breakthrough. To account for the reduced sorbent charge in the reactor, the total gas flow was reduced to maintain the same space velocity. At the end of this sulfidation, the reactor was opened and the sorbent was removed for analysis.

Fluid Bed Testing of METC10 Sorbent

METC10 sorbent suitable for the fluid/transport reactor bed testing was prepared at Contract Materials Processing (CMP) utilizing spray drying technique. These sorbents were tested in a bench scale low pressure fluid bed reactor for 3&1/2 cycles. Sulfidations were performed at 538 ^{0}C (1000 ^{0}F) and 260 kPa (1 atm), utilizing simulated KRW coal gas (47% nitrogen, 8% steam, 5% CO_2, 24% CO, and 14% H_2) with 2% H_2S. The superficial velocity for all sulfidations was 0.16 ft/sec. The outlet H_2S was monitored using on line gas chromatography. All dry regenerations in the low pressure reactor were done at 260 kPa (1 atm) with 6% oxygen diluted with nitrogen at 538 ^{0}C. The sorbent was loaded up to 6.7 wt% during sulfidations but the last sulfidation cycle was conducted up to breakthrough.

RESULTS

a. Fixed Bed Testing of METC10-M Sorbent at RTI

Scoping Tests and Base Line Tests of METC10-M at RTI

Initial scoping tests to identify optimum operating conditions for the 25-cycle test indicated that the METC10-M sorbent could be regenerated readily at 950 $^\circ$F, 3.5 vol% O_2 and a space velocity of 2,000 h^{-1}. Exposure to increasing levels of SO_2 (up to 10 vol%) during regeneration did not have any adverse effect on the ability of this sorbent to remove the desired amount of sulfur from simulated coal gas streams or to be regenerated at 900 $^\circ$F. Baseline tests with this sorbent conducted in accordance with the test protocol, in which SO_2 was not added to reactor feed gas during regeneration, confirmed that the desired sulfur loading of 6.7 lb/ft^3 was easily attainable with no H_2S breakthrough. Pre-breakthrough H_2S levels in the reactor effluent were <20 ppmv as shown in Figure 1. Regeneration was easily initiated at 900 to 950 °F with 3.5 vol% O_2 and a space velocity of 2,000 h^{-1}. No change was observed in either the sulfidation or the regeneration from cycle to cycle during this 10-cycle baseline test. Following these scoping and baseline tests, the METC10-M sorbent was subjected to the 25-cycle test.

<u>Sulfidation Results of the Twenty Five Cycle at RTI</u>

Hydrogen sulfide concentration in the reactor effluent is shown as a function of time in Figure 2. As can be seen, H_2S concentration in the reactor effluent remains < 20 ppmv during the 125 min sulfidation for the first 24 cycles. No change in this pre-breakthrough H_2S level was observed over 24 cycles.

The breakthrough behavior of the sorbent was also confirmed by the estimated sulfur loading calculated based on the mass balance for sulfur around the reactor system as shown in Figure 3. A horizontal line at 20.7 g of sulfur loaded indicates that the desired sulfur loading (6.7 lb/ft^3 at gas inlet) was achieved prior to H_2S breakthrough. The breakthrough curve generated during the 25th sulfidation shows a calculated sulfur loading capacity of approximately 17 wt% after 25 cycles of testing and being exposed to high SO_2 concentrations during regeneration. The breakthrough time at the 25th cycle as shown in Figure 2, was very similar to that at the 10th cycle as shown in Figure 1, indicating that the sorbent had a very stable sulfur capacity and was not affected by the presence of the 8% SO_2 in the regenerated gas stream.

<u>Regeneration Results from the Twenty Five Cycle Test at RTI</u>

A typical temperature profile during regeneration is shown in Figure 4. These results clearly indicate that the sorbent initiates nicely at 950 °F with 3.5% O_2 at a space velocity of 2,000 h^{-1}, both with and without the presence of SO_2 in the regeneration feed gas. The peak temperature of the sorbent bed due to the exothermic reaction during the regeneration was between 1,150 and 1,200 °F with the temperature wave moving from the bottom of the bed to the top section. Furnace settings were maintained at 950 °F during the entire regeneration. Typical plots of concentrations of SO_2 and O_2 during regeneration are shown in Figure 5 . The oxygen was fully consumed during the reaction and total outlet SO_2 concentration was about 10 to 11 %. The regeneration performance of the sorbent was very consistent during all the regeneration cycles. After 24 cycles, the sorbent had essentially the same performance during regeneration as it had after four cycles.

Physical and Chemical Characterization of the Sorbent after Twenty Five Cycle Test at RTI

Various physical and chemical properties of fresh and reacted sorbent removed at various stages are shown in Table 1. As can be seen, the sulfur loading at breakthrough was 17 percent after the 10-cycle baseline as well as at the 25-cycle test with SO_2 regeneration, indicating that the presence of SO_2 had no effect on the sorbent performance. The capacity of the sorbent at the 25th cycle was twice the sulfur loading required for the TECO/CCT project. The ASTM attrition of the fresh material was 0.6 percent and it increased to 1.2 percent after 10 cycles of baseline testing and 1.8 percent after 25 cycles. The crush strength of the 25-cycle sulfided material was 18 lb/pellet compared to 6 lb/pellet for the fresh material. Scanning electron photomicrographs indicated that there were no micro cracks in samples after 25th sulfidation and 24th regeneration.
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Sulfidations Studies of METC10-M at 370 ^{0}C(700 F)

Sulfidations of METC10-M sorbent was also performed at RTI at 371 ^{0}C (700 ^{0}F) in order to determine whether it is suitable for low temperature applications. The sorbent was tested at 371 ^{0}C (700 ^{0}F) at RTI under conditions similar to those used in the 25 cycle test. Sorbent sulfur capacity was 17 wt% ,which is similar to that at 510 ^{0}C (950 ^{0}F). Thus, the sorbent can be utilized even at 371 ^{0}C (700 ^{0}F) for hydrogen sulfide removal.

Table 1. Physical and Chemical Properties of Fresh and Reacted METC10-M Sorbent

Property	Fresh	After 10th sulfidation (baseline test)	After 24th regeneration	After 25th sulfidation
Measured sulfur loading at gas inlet (wt%)	NA	17	NA	17
ASTM attrition (wt%)	0.6	1.2	1.8	1.8
Crush strength (lb/pellet)	6	22	13	18
Sulfate sulfur (wt%)	NA	0	0.8	0

NA = Not applicable

b. Fluidized Bed Testing of METC10 Sorbent at FETC

The first batch of the METC10 sorbent (ID # 313-2) prepared at CMP utilizing a spray drying method had an average particle size of 143 microns and a packing density value of 1.07 g/cc. Attrition loss, utilizing the ASTM air jet attrition method, was measured and are shown in Table 2, along with the sulfur loading values obtained after reaction. The first batch of sorbent (313-2) had a reasonable attrition resistance. Sulfur loading values after both Thermo-Gravimetric Analysis (TGA) testing and bench scale fluid bed testing indicated that the sulfur capacity of the sorbent was excellent, as shown in Table 2. The measured sulfur loading value of the sample that was exposed to dry regeneration during bench scale testing was similar to that of the sample exposed to steam regeneration, indicating that the steam regeneration had no effect on the sorbent performance.

This sorbent formulation (313-2) was modified to improve the attrition resistance and properties of the modified formulations (501-3 and 501-4) are listed in Table 2. Attrition values of these sorbents, after twenty hours, were 2.2 and 2.6 respectively, indicating that the attrition resistance values of both these sorbents were excellent. TGA sulfur capacities of both these sorbents after 9&1/2 cycles of testing also showed excellent results. Sulfur loading measured after bench scale testing further confirmed the high sulfur capacities of these sorbents, as shown in Table 2.

Table 2 - Physical and Chemical Properties of Fluidizable METC10 Sorbents

Property	METC10 313-2	METC10 501-3	METC10 501-4
ASTM attrition (wt%) - 5 hour loss - 20 hour loss	 5 10	 2.3 2.6	 2.1 2.2
Measured sulfur loading (LECO) after 9& 1/2 cycles of TGA testing (wt%)	23	20.9	21.9
Measured sulfur loading (LECO) after bench scale fluidized bed testing (wt%)	21	18.6	19

SUMMARY AND CONCLUSIONS

Based on scoping, baseline and 25-cycle fixed bed testing of the METC10-M sorbent (suitable for either fixed bed or moving bed applications) at RTI, the following conclusions can be made:

- The sorbent is capable of absorbing 6.7 lb/ft^3 of sulfur (at gas inlet) without H_2S breakthrough.
- The prebreakthrough H_2S concentration was below 20 ppmv over 25 cycles.
- No change in sulfur capacity was observed over 25 cycles of testing.
- This sorbent can be easily regenerated at 900 to 950 °F with 3.5% O_2 at a space velocity of 2,000 h^{-1}.
- Presence of up to 8 percent SO_2 in the regeneration feed gas did not have any adverse effect on the sorbent performance.
- Sorbent was able to maintain its mechanical strength over 25 cycles of testing. The crush strength of the pellets increased from 6 lb/pellet for the fresh to 18 lb/pellet for the 25-cycle sulfided material while the ASTM attrition increased from 0.6 to 1.8 percent.
- The METC10-M sorbent had a sulfur loading of 17 wt% and attrition of 1.8 wt% at the end of 25 cycles. The required sulfur loading and attrition for TECO operation (6.7 lb/ft^3 and $\leq$5 wt%) were both met and exceeded throughout the bench-scale testing.
- Sorbent had a sulfur capacity of 17 wt% and can be utilized for hydrogen sulfide removal even at 371 ^{0}C (700 ^{0}F).

Based on the fluidized bed testing of METC10 sorbent following conclusions can be made.

- Sorbents with attrition resistance >97 % can be prepared utilizing spray drying technique.
- Both TGA and bench scale studies indicated that the METC10 fluidized/transport bed sorbent had an excellent sulfur capacity (~20 wt%).

FUTURE WORK

Development of a fluidized bed/transport bed sorbents will be continued. Multi cycle testing will be conducted in the high pressure fluidized bed reactor. Fluidized bed testing will also conducted in the FETC modular gas clean up rig under actual coal gas conditions. Transport reactor testing will be conducted in both FETC and Kellogg transport reactors. Experiments supporting the TECO/CCT project will also be continued.

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