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Testing and Analysis of METC10 Sorbent

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ABSTRACT:

Development of a suitable regenerable sorbent is a major barrier issue in the Hot Gas Cleanup program for Integrated Gasification Combined Cycle systems. This has been a challenging problem for the last 20 years. Many of the sorbents developed in prior work did not retain their reactivity and physical integrity during repeated sulfidation/regeneration cycles. This paper is a report on a promising sorbent (METC10) developed at the Morgantown Energy Technology Center (METC) which has demonstrated sustained reactivity and physical integrity during repeated sulfidation and regeneration cycles.

METC10 sorbent was tested in a low pressure (260 kPa/23 psig) fixed-bed reactor at 538^{0}C (1,000^{0}F) with simulated air blown Kellogg Rust Westinghouse (KRW) coal gas. The sorbent was subjected to 3.5 sulfidation/regeneration cycles using steam as the regeneration diluent. There were no appreciable changes in reactivity during the 3.5 cycles and spalling or other physical deterioration was not observed.

Sorbent pellets, which were prepared by a commercial vendor (United Catalysts, Inc.) to METC specifications, were exposed to fifty sulfidation/regeneration cycles using conditions typical of the Tampa Electric Company (TECO) Clean Coal Technology (CCT) demonstration project. After the fiftieth sulfidation cycle, both the sulfur loading value (more than 6 lb/ft^3) and the attrition (less than 5 wt%) satisfied the requirements necessary for the TECO/CCT project. These sorbent pellets were also tested with real coal gas for 240 hours in a moving bed reactor at General Electric (GE) company. Sulfur absorption was according to the sorbent movement rate and the attrition rate was very low during 240 hours of the pilot plant operation.

INTRODUCTION

The U.S. Department of Energy (DOE) has funded research, development, and demonstration (RD&D) projects for many years in the field of advanced power generation. The Integrated Gasification Combined Cycle (IGCC) system is one of the most promising advanced power systems. It has been predicted that IGCC systems with hot gas cleanup will 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 of 52 percent by the year 2010 and will be capable of producing power at a 20 percent lower cost of electricity when compared to conventional coal based systems. Furthermore, this increase in efficiency will reduce CO_2 emissions by 35 percent.

Development of a suitable regenerable sorbent is a major barrier issue in the hot gas cleanup program for IGCC systems. This has been a challenging problem during the last twenty years (Lew et al.,1989, Woods et al., 1989). Various formulations of zinc ferrite and zinc titanate in the form of extrudates and spherical pellets have been studied at METC for removal of sulfurous gases from coal gasification streams (Mei et al., 1993, Siriwardane et al., 1994). Problems of decrepitation and spalling have occurred after sulfidation and regeneration of these sorbents. A series of novel sorbents containing zinc oxide have been developed at METC to address these problems. These METC-developed sorbents showed superior performance during both twenty-cycle high pressure fixed-bed tests with steam regeneration and a fifty-cycle high pressure fixed-bed test with dry regeneration conducted at the METC. One of the METC developed sorbents (METC10) was tested in the moving bed reactor at the General Electric pilot plant. The results of the sorbent testing, in both the bench scale reactors and the GE moving bed reactor, and sorbent analysis data are discussed in this paper.

OBJECTIVES

The overall objective of this project was to develop regenerable sorbents for hot gas desulfurization in IGCC systems. The major criteria for the development of novel sorbents included reasonable chemical reactivity and physical durability during repeated sulfidation/regeneration cycles. The sorbent should be able to withstand reducing gas atmospheres at elevated temperatures and pressures during sulfidation. During regeneration, the sorbent should be able to withstand steam which is added to regeneration air to maintain temperature control.

A series of METC sorbents were prepared and tested. Sorbents METC2, METC9, and METC10 have been tested both in the low pressure and the high pressure reactors with steam regeneration (Siriwardane et al., 1994). Sorbent pellets of

METC10, prepared by a commercial vendor to METC specifications, were tested under conditions typical of UCI the TECO/CCT demonstration project.

Results of the both low pressure and high pressure fixed-bed reactor testing of METC10 will be discussed in this paper. Fifty cycles of sulfidation reactions were completed for commercially (UCI) prepared METC10 under conditions typical of the TECO/CCT demonstration project. METC10 was also tested in the moving bed reactor at the GE pilot plant.

EXPERIMENTAL

METC10 sorbent was prepared at METC by a solid state mixing method (physical mixing of sorbent constituents with water) utilizing a mixer pelletizer. The sorbents contained about 50 wt% of zinc oxide. The solid materials were thoroughly mixed in the mixer pelletizer and a sufficient amount of water was added to the mixture to form pellets. Sorbent pellets in the size ranges of both -5+8 mesh and -4+5 mesh were utilized for low pressure reactor testing.

All of the sulfidations in the low pressure reactor were performed at 538 °C (1000 °F) and 260 kPa (38 psia), utilizing a feed gas containing 2000 ppmv H_2S. The superficial velocity for all sulfidations in the low pressure reactor was maintained at 0.09 m/s (0.30 ft/s) and the space velocity was 2000 h^{-1}. The outlet H_2S concentration was monitored using detector tubes and gas chromatography. All regenerations in the low pressure reactor were done at 272 kPa (39.7 psia) and the gas velocity was maintained constant during each stage at 0.04 - 0.05 m/s (0.13 - 0.15 ft/s) . The steam regenerations were conducted in three stages. The temperatures of the stages were 538, 593, and 649 °C (1000, 1100, and 1200 °F). The steam concentration in all three stages was 50% wt, with a varying concentration of oxygen and nitrogen. The oxygen concentrations during the three stages were 1.0, 2.5, and 3.5 %, respectively.

METC10 (3 mm pellets) prepared by a commercial vendor, UCI, was also tested in the high pressure reactor which contained a 5.5 cm (2.2-inch) inside diameter reactor. The reactor was constructed of Incoloy 800HT alloy steel pipe. A gas distributor was fixed at the bottom of the cage to support the sorbent. The inside of the sorbent cage was Alon-processed to prevent corrosion of stainless steel by sulfurous gases in the presence of steam. The reactor was housed inside a three-zone furnace equipped with separate temperature controllers for each zone. The details of this system are reported by Mei et al., 1993. The reactor bed height was 15 cm (6 in), the pressure was 2,026.5 kPa (293.2 psia), and the temperature of the bed was 482^{0}C (900^{0}F). The gas composition utilized during the sulfidation was 20,000 ppmv H_2S, 18 percent nitrogen, 20 percent steam, 10 percent carbon dioxide, 30 percent carbon monoxide, and

20 percent hydrogen which simulated the TECO coal gas. Regeneration was performed with 2 percent oxygen and nitrogen at 594^0 to 705^0C ($1,100^0$ to $1,300^0$F). After the regeneration with air, 100 percent nitrogen was introduced at 732^0C ($1,350^0$F). The pressure during the regeneration was 793 kPa (102.8 psia). Both sulfidation and regeneration were performed in the upflow direction, and the space velocities during the sulfidation and regeneration were 2000 hr^{-1}.

METC10 was tested in the moving bed reactor at the GE pilot plant. Sorbent movement rate was between 400 - 600 lbs/hr. Typical coal gas composition in the GE gasifier was 10% nitrogen, 16% steam, 13.7% CO_2, 30.1% CO, 30% H_2, and 0.25-0.40 % H_2S. Absorber in the moving bed reactor was at a temperature of 482 ^{0}C (900^0F) and a pressure of 2,026.5 kPa (293.2 psia). Coal gas was introduced at the bottom of the absorber and the outlet H_2S was monitored at both the top of the reactor bed and a location one third below the top of the reactor bed in the absorber. Air, recycled SO_2, and H_2O were present in the regeneration gas stream.

RESULTS

Results of the METC10 Testing in the Low Pressure Unit

The sulfidation breakthrough curves of METC10 in the low pressure unit are shown in Figure 1. There was an increase in sulfur capacity from sulfidation 1 to 2, but the sulfur capacity decreased in the third sulfidation. The sulfidation breakthrough curves overlapped after the third sulfidation, indicating sorbent stabilization at that point. As shown in Figure 1, the outlet hydrogen sulfide concentration was zero for about twenty-eight hours indicating that the efficiency of the sorbent was excellent. It is clear that the sulfur capacity of METC10 is excellent, and regeneration can be performed utilizing steam.

Results of the Commercially Prepared METC10 Testing in the High Pressure Unit

Results of the two and half cycle test of METC10 is shown in Figure 2. During the first sulfidation cycle, the breakthrough time (200 ppmv outlet H2S) was 1 hour and 15 minutes and it increased to 4 hours at the third sulfidation as shown in Figure 2. The solid analysis of the sorbent indicated 18-19 weight percent sulfur per 100g of the fresh sorbent after the third sulfidation cycle. The packing density of the fresh sorbent was 106 lb/ft^3 (in the 2"x6" bed). The required sulfur loading is about 6 weight percent for the TECO/CCT demonstration project. Thus, the sulfur absorption capacity of METC10 far exceeds the required sulfur loading.

The results of the fifty-cycle testing of METC10 are shown in Table 1. The sulfur loading value measured by the LECO sulfur analyzer at the gas inlet location after the fiftieth sulfidation cycle was more than the required sulfur loading of 6 weight percent. The crush strength of the sorbent was higher than that of the fresh sample. Scanning electron photomicrographs of the sorbent, after the fifty-cycle testing, indicated that there was no cracking or spalling of the pellets. The attrition loss (ASTM D 4058-92) was less than the value of 5 percent required for the moving bed operation TECO/CCT demonstration project. The commercial METC10 showed a superior level of performance during the fifty-cycle testing and met all the criteria as a possible sorbent for the Tampa Electric CCT project.

TABLE 1

Characteristics of the Fresh and Sulfided METC10

Measurement	Fresh	Third Sulfidation	Twentieth Sulfidation	Fiftieth Sulfidation
1. Crush Strength	31 N	71 N	85 N	80 N
2. Sulfur loading at the gas inlet	----	18 wt%	18 wt%	14 wt%
3. Attrition	<1%	1.5%	3.5%	4.5%

Results of the Testing of METC10 in the Moving Bed Reactor at the GE Pilot Plant

The attrition loss of the sorbent after 240 hours of moving bed reactor operation at GE was 0.45%, and this indicated that the attrition resistance of the sorbent was excellent. During the moving bed testing at GE, the outlet H_2S (at the top of the absorber) was maintained at 100 ppm when proper oxygen concentrations and temperatures were utilized during the regeneration. The H_2S outlet concentration detected at a location one third below the top of the sorbent bed in the absorber was below 50 ppm. Thus, the 100 ppm H_2S detected at the top of the reactor bed in the absorber was mainly due to the decomposition of residual sulfate formed during the regeneration. Solid analysis of the sorbent from the absorber indicated that the sulfur absorption was in agreement with the sorbent movement rate. After 168 hours of operation the temperatures in the regenerator dropped below 538 C^0 (1000 F^0) due to mechanical problems and proper regeneration could not be achieved. The sorbent pellets collected at various times during the moving bed operation were analyzed for reactivity utilizing both the bench scale reactor and the thermogravimetric analyzer (TGA). Mercury pore volume analysis and atomic absorption analysis were also conducted to determine the changes in the pore structure and the elemental composition of these sorbent pellets. Both bench scale reactor studies and the TGA reactivity studies indicated that there was sufficient reactivity in the sorbent pellets collected after 240 hours of moving bed operation. Elemental analysis indicated that there was a minimal loss of some elements in the sorbent pellets. The concentration of the HCl released during the first 72 hours of moving bed operation was in the range of 50-250 ppm. The elemental loss in the sorbent pellets occurred during that time period. Analysis of pore volume and average pore diameter indicated that the pore structure of the sorbent pellets collected after 240 hours of moving bed operation was similar to that of the activated METC10 sorbent pellets.

CONCLUSIONS

METC10 sorbent showed a superior level of performance during 3.5 cycles of low pressure fixed bed testing. The METC10 sorbent also performed extremely well during the high pressure fifty-cycle fixed bed reactor test. This sorbent functioned well in the reducing gas environment at high temperatures which will be present in the coal gasification process. This sorbent was prepared with readily available materials utilizing solid state mixing which is very inexpensive.

Steam regeneration did not adversely affect the performance of METC10 during the 3.5 cycles of low pressure testing. Crush strengths of the sorbents after the fourth sulfidation cycle were greater than those of the original sorbents. This sorbent was spalling resistant and had excellent chemical and physical durability during the three and half cycle test. Overall performance of these sorbents were superior to other zinc-based sorbents tested previously at METC.

Commercially prepared METC10 sorbent performed well during the fifty-cycle high pressure testing under conditions suitable for the TECO/CCT demonstration project. During the fifty-cycle test, this sorbent retained sufficient reactivity, and physical durability (as measured by crush strength and attrition resistance) was also excellent.

METC10 sorbent performed well during the GE moving bed operation when proper temperatures and oxygen concentrations were utilized during the regeneration. Sufficient reactivity was retained in the sorbent pellets after 240 hours of operation of the moving bed reactor. Attrition loss, after 240 hours of moving bed operation, was 0.45% and this indicated that the attrition resistance of the sorbent was excellent.

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