KINETICS OF MN-BASED SORBENTS FOR HOT COAL GAS DESULFURIZATION

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ABSTRACT

Manganese-based sorbents have been investigated for the removal of hydrogen sulfide (the primary sulfur bearing compound) from hot coal gases prior to its use in combined cycle turbines. Four formulations of Mn-based sorbents were tested in an ambient-pressure fixed-bed reactor to determine steady state H_2S concentrations, breakthrough times and effectiveness of the sorbent when subjected to cyclic sulfidation and regeneration testing. In previous reports¹⁶⁻¹⁷, the sulfidation and regeneration results from cyclic testing done at 600°C were presented. Manganese-based sorbents with molar ratios > 1:1 Mn:Substrate were effective in reducing the H_2S concentration in simulated coal gases to less than 100 ppmv over five cycles. Actual breakthrough time for formulation C6-2-1100 was as high as 73% of breakthrough time based on wt% Mn in sorbent. Regeneration tests determined that loaded pellets can be fully regenerated in air/steam mixture at 750°C with minimal sulfate formation. In this report, the results from cyclic crush strength tests, sulfur profile tests and cyclic testing at 550°C and lower flowrate cyclic testing are presented. Crush strength testing done after 5 cycles showed decreases in strength from 12.6% to 57.9%. Cyclic testing at 550°C showed pre breakthrough concentrations as low as 10 ppmv. Cyclic testing done at 2 L/min and 3 L/min did not show any significant difference in pre breakthrough concentrations or capacity.

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INTRODUCTION

Currently, the Morgantown Energy Technology Center, Department of Energy (DOE/METC) is actively investigating alternative hot fuel gas desulfurization sorbents for application to the Integrated Gasification Combined Cycle (IGCC)¹. A sorbent must be highly active towards sulfur at high temperature and pressures, and under varying degrees of reducing atmospheres. Also, it must regenerate nearly ideally to maintain activity over numerous cycles. Furthermore, regeneration must yield a sulfur product which is economically recoverable either directly or indirectly.

Several metal oxides have been investigated²⁻⁴ as regenerable sorbents for the removal of hydrogen sulfide (the primary sulfur bearing compound) from hot fuel gases. MnO was shown to have an intrinsic reaction rate approximately one order of magnitude greater than the rate of reaction with either CaO or ZnO and two orders of magnitude greater than the reaction rate with V₂O₃³. Manganese also shows desulfurization potential in the temperature range of 600-700°C where metal oxides currently known to be reactive with H₂S are unsatisfactory².

In response to stability difficulties of single and binary metal oxide sorbents, increasing effort is being directed towards incorporation of an inert component into sorbent formulation as witnessed by the various Zn-titanates⁵⁻⁹. The inert component increases pore structure integrity, stabilizes the active metal oxide against reduction and increases the pellet durability. This report will address the testing of Mn-based sorbents in an ambient pressure fixed-bed reactor. In previous reports¹⁶⁻¹⁷, the sulfidation and regeneration results from cyclic testing done at 600°C were presented. This report will present the results from cyclic crush strength tests, sulfur profile tests and cyclic testing at 550°C and lower flowrate cyclic testing.

METHODS AND MATERIALS

Composition

Variables that were considered in formulating Mn-based sorbents included:

- substrate composition,
- Mn to substrate molar ratio,
- non-volatile binder wt %,

The only source of manganese used was from a commercially available MnCO₃. Alundum and titanate were both tested as substrate based on previous considerations¹⁵. Molar ratios of Mn to substrate were varied from 1:1 to 4.33:1.

Bentonite was used as a non-volatile binder at 0 and 2 % by weight. All chemical compositions, vendor information, and particle sizes have been reported previously¹⁰⁻¹⁴.

Preparation

Feed powders were hand mixed and pelletized in a balling wheel forming "green" pellets. Green pellets were air dried for one day and then dried to a constant weight at 105°C. Dry pellets were calcined for four hours at 350°C. Immediately after calcination, pellets were placed in a high-temperature furnace (pre-heated to 500°C), where the temperature was ramped up for 2 to 2.5 hours until final induration temperature was achieved. The pellets were indurated at this temperature for two hours. The indurated pellets were 1.2 to 2.6 mm in size.

Formulation Designations

Each pellet formulation can be fully described by the following designation, ex. C6-2-1100. The letter describes the manganese source (C for MnCO₃). The first number describes the substrate composition and molar ratio of Mn to substrate (4 for 4.33:1 Mn :alundum, 6 for 4.33:1 Mn:titania, 8 for 2:1 Mn:titania and 11 for 1:1 Mn:alundum). The second number is the weight percent bentonite binder. The last number is the temperature at which the pellets were indurated in degrees Centigrade. Table 1 summarizes the formulations tested in the fixed-bed reactor.

Formulation Designation	Molar Ratio Mn:Substrate	Substrate	Wt% Bentonite	Induration Temperature °C
C4-2-1175	4.33:1	Alundum	2	1175
C6-2-1100	4.33:1	Titania	2	1100
C8-0-1200	2:1	Titania	0	1200
C11-0-1160	1:1	Alundum	0	1160

Table 1. Formulations of Pellets Tested in the Fixed-bed Reactor and Their Designations.

CHARACTERIZATION

Indurated pellets were characterized both physically and chemically using crush strength testing, fixed-bed testing, x-ray diffraction (XRD) and sulfur analysis.

Crush strength testing, sulfur analysis and fixed-bed testing will be presented in this section.

Crush Strength

The first characterization done on freshly indurated and cycled pellets was crush strength. Crush strength tests were conducted on all freshly indurated pellets with the requirement of 4.45 N/pellet/mm² (1 lb/pellet/mm²) of diameter. Thus, a 1 mm pellet should have a crush strength of 1 lb/pellet and a 3 mm pellet should have a crush strength of 9 lb/pellet. This assumption was made previously¹⁵ and assumes the crush strength increases proportionally with the pellet cross-sectional area. Pellets were indurated at the minimum temperature required to achieve this strength. Crush strength tests were also conducted on pellets that had been sulfided and regenerated over several cycles to determine the strength retention of the pellets.

Fixed-Bed Testing

After crush testing on freshly indurated pellets proved satisfactory, they were tested in an ambient pressure fixed-bed reactor to determine steady state H₂S concentrations, breakthrough times and effectiveness of the sorbent when subjected to cyclic testing. The reactor consists of a 2.54 cm (1") ID quartz tube positioned vertically in the two-zone furnace. The preheat zone was maintained at 200°C. The reaction temperature was 600°C and was monitored using a type K thermocouple positioned directly above the sorbent bed. Sulfidation and regeneration gases entered the reactor in an upward direction. Exit gases were cooled in a cold trap where vapors such as water and sulfur were condensed and collected. The gases were then scrubbed in a hypochlorous acid solution (sulfidation) or a hydrogen peroxide and sodium hydroxide solution (regeneration) prior to flaring and venting. See a previous report¹⁶ for schematics of the reactor tube and fixed-bed experimental apparatus.

For each test, 8.9 to 9.5 cm (40 to 55 g) of sorbent was added to the reactor tube in the reaction zone. The reactor was heated in a nitrogen atmosphere to the desired operating temperature. Simulated coal gases spiked with 2.2 mol% H₂S were then introduced into the reactor at either 3L/min or 2L/min. Volumetric flow rates of the gases were calibrated with rotameters using a wet test meter. Elevated H₂S concentrations were employed to reduce the sulfidation breakthrough time. Exit gases were sampled after the cold trap and were analyzed using detector tubes for H₂S until breakthrough occurred. The test conditions for sulfidation are summarized in Table 2.

Sample mass	40-55 g
Sulfidation temperature	Varied see Table 3
Average pellet diameter	1.2-2.6 mm
Gas composition	Shell (oxygen blown)*
Gas flow rate	Varied see Table 3
H ₂ S concentration	2.2 mol %
Pressure	1 atm

Table 2. Conditions of Fixed-Bed Sulfidation Experiments for all Formulations.

*Refers to a simplified Shell-type fuel gas with the following composition: 64 mol% CO, 27% H₂, 2.2% H₂S, 2% H₂O, 2% CO₂ and 2.8% N₂

Test Designation	Temperature (°C)	Gas Flow Rate
1FB	600	3
2FB	600	3
3FB	600	3
4FB	600	3
5FB	600	3
6FB	600	3
7FB	600	3
FB1A	550	3
FB2A	550	2

Table 3. Sulfidation Gas Flow Rates and Temperatures.

The sorbent was regenerated in air, oxygen depleted air, or steam after each sulfidation test. Regeneration of the sorbent was conducted at 750°C and 900°C. Regeneration in air was conducted at 900°C. Regeneration in oxygen depleted air and air/steam mixtures was conducted at 750°C. Five cycles of sulfidation and regeneration were conducted for tests 1FB-7FB and four cycles for tests FB1A and FB2A to determine the sorbent's activity retention. The test conditions for regeneration are summarized in Table 4. The regeneration gas compositions and temperatures are listed in Table 5.

Sample mass	40-55 g
Regeneration temperature	750-900°C
Average pellet diameter	1.2-2.6 mm
Gas composition	Varied (see Table 4)
Gas flow rate	1 L/min
Pressure	1 atm

Table 4. Conditions of Fixed-Bed Regeneration Experiments for all Formulations

Test Designations	Formulation	Regeneration Gas Composition	Regeneration Temperature (°C)
1FB	C6-2-1100	1000 cc/min air	900
2FB	C6-2-1100	100 cc/min O ₂ 900 cc/min N ₂	750
3FB	C6-2-1100	50 cc/min O ₂ 950 cc/min N ₂	750
4FB	C6-2-1100	400 cc/min steam 600 cc/min air	750
5FB	C8-0-1200	400 cc/min steam 600 cc/min air	750
6FB	C8-0-1200	800 cc/min steam 200 cc/min N ₂	750
7FB	C4-2-1175	400 cc/min steam 600 cc/min air	750
FB1A	C6-2-1100	500 cc/min steam 500 cc/min air	750
FB2A	C6-2-1100	500 cc/min steam 500 cc/min air	750

Table 5. Regeneration Gas Compositions and Temperatures

RESULTS AND DISCUSSION

Results from the fixed-bed sulfidation and regeneration tests 1FB-7FB were presented in previous reports¹⁶⁻¹⁷. Results from cyclic crush strength, sulfur analysis, and fixed-bed (FB1A and FB2A) testing will be presented in this section.

Crush Strength

Results from previous reports¹⁶⁻¹⁷ showed that the crush strengths of freshly indurated pellets were highly sensitive to the temperature at which they were indurated. Thus in an attempt to minimize this sensitivity, the pellets were indurated for different lengths of induration. Figure 1 shows the results from the crush strength testing of freshly indurated sorbent with varying induration lengths. As can be seen in the figure, a large increase in the induration length has little impact in the crush strength. Thus very long induration lengths may be needed to minimize induration temperature effects.

Figure 2 shows the crush strengths of freshly indurated pellets and pellets after 5 sulfidation and regeneration cycles for formulations C4-2-1175 and C8-0-1200. Sorbent from test 5FB had the largest decrease in crush strength (57.9%) while sorbent from test 4FB had only a 17.9% decrease. The sulfidation and regeneration conditions were the same (sulfidation at 600°C using Shell gas and regeneration at 750°C, using a steam/air mixture), however, the sorbent formulations were different. C4-2-1175 contains 2% bentonite binder while C8-0-1200 does not contain any bentonite. Sorbent from test 6FB had the smallest decrease in crush strength. This test used C8-0-1200 formulation, however, the sorbent was regenerated with a steam/N₂ mixture. These regeneration conditions do not allow for the formation of sulfates as does the steam/air mixture and may be why it had the smallest decrease in crush strength after 5 cycles.

Figure 3 shows the crush strengths of freshly indurated pellets and pellets after 4 or 5 sulfidation and regeneration cycles (5 cycles for 1FB-7FB and 4 cycles for FB1A and FB2A) for formulation C6-2-1100. Sorbent from test 1FB had the largest decrease in crush strength. In this test, regeneration was carried out at 900°C using pure air. However, sorbent from tests 2FB, and 3FB using oxygen depleted air had less decrease in crush strength (21.8% and 14.6% respectively). Sorbent from test 7FB had used air/steam mixture for regeneration and had a 24.1% decrease in crush strength. Sorbent from test FB1A and FB2A had a decrease in crush strength after four cycles of 40.0% and 46.7%. The difference in these two tests is the sulfidation gas flow rate (3L/min and 2L/min). As seen in the above results, there isn't any significant difference in the crush strength of the two sorbents after 4 cycles.

Sulfur Analysis

Figure 4 shows the sulfur profiles for sorbent from tests 1FB-7FB after the 5th regeneration. Sorbent from these tests all had approximately the same weight percent of sulfur remaining in the sorbent. Sorbent from tests 3FB and 6FB did, however, have slightly less weight percent of sulfur remaining. Regeneration of

test 3FB was conducted using very oxygen depleted air (50 cc/min O₂ and 950 cc/min N₂) and thus probably did not form as much sulfate as tests with regeneration in higher oxygen concentration (e.g. test 1FB).

Fixed-bed Testing

Results from the sulfidation and regeneration fixed-bed testing for tests 1FB-7FB were presented in previous quarterly reports¹⁶⁻¹⁷. Figures 5 to 9 show the results from the fixed-bed sulfidation and regeneration testing for tests FB1A and FB2A. Four cycles of sulfidation and regeneration were conducted for each test. Results from each test are described separately. A summary of the lowest pre breakthrough concentration achieved in the exit gases, breakthrough times, highest SO₂ concentrations achieved in the exit gases and the time for regeneration is given in Table 6. The theoretical breakthrough time (T*) was calculated based on the wt % Mn in the sorbent, the H₂S concentration, the gas flow rate and equilibrium concentration as predicted by the HSC program. Actual breakthrough time was arbitrarily chosen as the time to achieve an H₂S concentration greater than 100 ppmv. Regeneration time is based on the time to achieve an exit SO₂ gas concentration of less than 10% of the highest concentration achieved. The regeneration times were then average over the last three cycles.

Test Designation	FB1A	FB2A
Amount of Sorbent (g)	47.86	47.88
Weight % Mn	55.8	55.8
Gas Flow Rate (L/min)	3	2
Lowest H ₂ S Pre breakthrough Concentration (ppmv)	10	10
Theoretical Breakthrough (T*, min)	165	207-302
Actual Breakthrough Time (T, min)	47-72	NA
T/T*	0.27 - 0.44	0.31 - 0.41
Highest SO ₂ Concentration Achieved in Exit Gases (mol%)	6.8	6.4
Average Regeneration Time (min)	132	135

Table 6. H₂S Pre breakthrough Concentrations, Breakthrough Times, Highest Concentration of SO₂ Achieved in Exit Gases and Average Regeneration Times.

Test FB1A

Figure 5 is the sulfidation breakthrough plot for test FB1A. This test was conducted using simulated Shell gas at 3 L/min for sulfidation. The lowest concentration of H_2S achieved in the exit gases was 10 ppmv, however, prior to breakthrough, the H_2S varied from 10 to 100 ppmv. The higher concentrations at the beginning of the sulfidation may be attributed to the reduction of sulfates from the previous regeneration to SO_2 . The initial higher concentration was not seen during the first sulfidation as it was during subsequent sulfidations. The increase in H_2S during the second sulfidation cycle at about 50 minutes may have been caused by channeling.

Figure 6 is the sulfidation breakthrough plot again for test FB1A but plotted as exit H_2S concentration versus dimensionless time (actual time/theoretical breakthrough time). This plot shows the capacity of the sorbent for each of the four sulfidation cycles. Time/T^* varied from 0.27 for the first cycle to 0.38 - 0.44 for subsequent cycles.

Figure 7 shows the regeneration curves for test FB1A. SO_2 concentrations varied from 5.5 to 6.8%. These concentrations are high enough so that the exit gas may be saleable for sulfuric acid production. The average regeneration time for regeneration cycles greater than 1 was 132 minutes.

Test FB2A

Figure 8 is the sulfidation breakthrough plots for test FB2A. This test was conducted using simulated Shell gas at 2 L/min for sulfidation. The lowest H_2S concentration achieved in the exit gases was again 10 ppmv. The ratio Time/T^* varied from 0.30 for the first sulfidation cycle to 0.36 - 0.41 for the subsequent sulfidation cycles.

Figure 9 shows the regeneration curves for test FB2A. Regeneration in 50% air and 50% steam regenerated the sorbent completely while minimizing sulfate formation and large increases in temperature. The highest SO_2 concentration achieved in the exit gases was 7.4 mol%. The average regeneration time for regeneration cycles greater than 1 was 135 minutes.

CONCLUSIONS

The crush strength of a manganese-based pellet was highly sensitive to the temperature at which it was indurated. A large increase in the induration length had little impact in the crush strength. Thus very long induration lengths may be needed to minimize induration temperature effects.

Crush strength testing done after 5 cycles showed decreases in strength from 12.6% to 57.9%. The lowest decrease in crush strength was for sorbent regenerated in a steam/N₂ mixture. However, as shown in previous reports¹⁶⁻¹⁷, a steam/N₂ mixture did not completely regenerate the sorbent. The largest decrease in crush strength was for a sorbent that did not contain any bentonite binder. Thus bentonite may be necessary component of the pellets.

Cyclic testing at 550°C showed pre breakthrough concentrations as low as 10 ppmv. Cyclic testing done at 2 L/min and 3 L/min did not show any significant difference in pre breakthrough concentrations or capacity.

Regeneration in 50% air and 50% steam regenerated the sorbent completely while minimizing sulfate formation and large increases in temperature. Regeneration in 50% air and 50% steam produced SO₂ concentration as high as 6.8% and may be used in sulfuric acid production.

Future work will focus on the durability of the manganese pellets over many sulfidation and regeneration cycles with regeneration in an air/steam mixture.

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Figure 1. Average Crush Strength for fresh C6-2 pellets, 1.30 - 2.30 mm in diameter

Figure 2. Average crush strength of fresh pellets and pellets after 5 cycles in fixed bed

Figure 3. Average Crush Strength for C6-2-1100 formulations fresh and after 5 cycles in fixed bed *A second batch of C6-2-1100 was prepared with slightly different fresh strength, 4 cycles

Sulfur Profiles

Figure 4. Sulfur Weight percent in sorbent after 5 cycles in fixed bed

Figure 5. FB1A sulfidation breakthrough curves for C6-2-1100, with regeneration in 50 mol% air and 50% H₂O, at 750°C. T* is the theoretical time to breakthrough.

FB1A Sulfidation Breakthrough at 550°C

Figure 6. FB1A sulfidation breakthrough curves for C6-2-1100, plotted as H₂S concentration versus dimensionless time. T* is the theoretical time to breakthrough.

Figure 7. FB1A regeneration curves for C6-2-1100. Regeneration in 50 mol% air and 50% H₂O, with a standard space velocity of 333/hr.

FB2A Sulfidation Breakthrough at 550°C

Figure 8. FB2A sulfidation breakthrough curves for C6-2-1100, with regeneration in 50 mol% air and 50% H₂O, at 750°C. T* is the theoretical time to breakthrough.

Figure 9. FB2A regeneration curves for C6-2-1100. Regeneration in 50 mol% air and 50% H₂O, with a standard space velocity of 333/hr, at 750°C.