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Kinetics of Mn-Based Sorbents for Hot Coal Gas Desulfurization

Quarterly Progress Report for the period of July 15 to September 15, 1995.

Task 2: Exploratory Experimental Studies: Single Pellet Tests; Rate Mechanism Analysis

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1. INTRODUCTION

The Morgantown Energy Technology Center (METC) of the U.S. Department of Energy (DOE) is actively pursuing the development of reliable and cost-effective processes to clean coal gasifier gases for application to integrated gasification combined cycle (IGCC) and molten carbonate fuel cell (MCFC) power plants. A large portion of gas cleanup research has been directed towards hot gas desulfurization using Zn-based sorbents. However, zinc titanate sorbents undergo reduction to the metal at temperatures approaching 700 °C^{1,2}. In addition, sulfate formation during regeneration leads to spalling of reactive surfaces^{2,3}.

Due to zinc-based sorbent performance, METC has shown interest in formulating and testing manganese-based sorbents. Westmoreland and Harrison evaluated numerous candidate sulfur sorbents and identified Mn as a good candidate⁴. Later, Turkdogan and Olsson tested manganese-based sorbents which demonstrated superior desulfurization capacity under high temperatures, and reducing conditions⁵. Recently, Ben-Slimane and Hepworth conducted several studies on formulating Mn-sorbents and desulfurizing a simulated fuel gas⁶. Although thermodynamics predicts higher over-pressures with Mn verses Zn, under certain operating conditions Mn-based sorbents may obtain < 20 ppmv, illustrated by Figure 1. In addition, the manganese-sulfur-oxygen (Mn-S-O) system does not reduce to the metal under even highly reducing gases at high temperatures (550-900 °C)^{4,6}.

Currently, many proposed IGCC processes include a water quench prior to desulfurization. This is for two reasons; limitations in the process hardware (1000 °C), and excessive Zn-based sorbent loss (about 700 °C). With manganese the water quench is obviated due to sorbent loss, as Mn-based sorbents have been shown to retain reactivity under cycling testing at 900 °C^{7,8}. This reduces system hardware, and increases thermal efficiency while decreasing the equilibrium H₂S over-pressure obtainable with a manganese sorbent.

2. METHODS AND MATERIALS

In this report, formulation variables considered in preparing manganese-based sorbents included:

- MnO to substrate stoichiometric ratio (2:1 to 6:1).
- Manganese grade; a reagent MnCO₃ and an ore MnO₂.
- Substrate; alundum and titanate.
- Binder; weight percent bentonite (0-5%).
- Induration temperature (> 1100 °C).

Feedstocks are listed below for materials not previously reported: Mn ore and titanate (rutile). The compositions of manganese carbonate, alundum, bentonite, dextrin, and activated carbon are in the previous two quarterly reports. Assays for the manganese ore and titanate are given below.

Table 1. Chemical analysis of an African (Comilog) ore.

Species	Wt %	Species	Wt %
Mn	51.2	Zn	0.064
MnO ₂	77.0	MgO	0.06
MnO	3.36	Ni	0.058
Al ₂ O ₃	6.01	Cu	0.05
Fe	2.81	CO ₂	0.04
SiO ₂	2.56	Na ₂ O	0.04
K ₂ O	0.17	S	0.019
BaO	0.22	V	0.012
TiO ₂	0.22	As	0.007
P	0.109	Mo	0.006
Co	0.099	Pb	0.004
CaO	0.08	H ₂ O (bound)	5.16

Table 2. Titanate Impurity assay from the manufacturer; Fisher Scientific, Fair Lawn, New Jersey (Balance TiO_2).

Species	Wt %
Fe	0.003
Pb	0.006
Water Soluble Salts	0.03
Zn	0.002

Eight formulations were prepared in addition to the Form-4A's yielding eleven total. As a result, of the increasing cumbersome designations, Form-4A is redesignated; C4-2. Also, the previous formulas (Form-4A with volatile porosity enhancers) were also renamed as follows; Form-4A-AC5 is C4-2A, and Form-4A-DX10 is C4-2D. The formula designations and their theoretical sulfur capacity are given in Table 3. The first letter represents the manganese source, i.e., Ax-x, corresponds to the Mn-ore based formulations while the Cx-x designation represents the manganese carbonate mixtures. The first number designates the type and molar ratio of substrate to Mn. In addition, the last digit represents amount of binder. As all formulations to date have been indurated for 2 hours, the temperature alone can be added to the formulation designation fully describing the pellet mixture and manufacture.

Table 3. Formula designations and theoretical sulfur capacity.

Formula	Sulfur Capacity Sg / 100g sorbent	Formula	Sulfur Capacity Sg / 100g sorbent
A1-0	28.8	C4-5	28.2
A1-2	28.1	C5-2	31.4
A2-2	29.8	C5-5	30.1
C4-2	29.3	C6-2	25.5
C4-2A	29.3	C7-2	23.0
C4-2D	29.3		

All new formulations were pelletized as described elsewhere¹⁰ and were subjected to the following criteria:

- Induration temperature > 1100 °C
- Diameter 3.5-4.0mm
- Crush Strength > 3.0 lb / mm
- Reactivity > C4-2 (our baseline designation)
- Regeneration of Mn component > C4-2

Previous pellets were 5.5 mm in diameter and were required to have a 5.0 lb/mm crush

strength; however, new formulations are 4 mm. Assuming the strength varies with the square of the pellet diameter, the strength was prorated by normalizing the crush load to the pellet cross-sectional area to yield approximately 1 lb/mm² thus the decrease in the strength requirement with decreasing diameter. An average diameter for each pellet was taken by measuring across each axis (3 measurements). Five pellets from each formulation were crushed per induration temperature. The induration temperature minimum criteria is included to limit the extent of sintering during multi-cycling.

Once a formula was pelletized, it was indurated at various temperatures to obtain the lowest temperature providing 3 lb/mm crush strength. Formulations with greater than 3 lb/mm crush strength are to be sulfided as outlined in the previous quarters report with one exception. The formulations containing the African ore will be regenerated in air at 900 °C and sulfided for a second time. Due to calcium and sodium impurities forming stable sulfates to very high temperatures, a second sulfidation is required to establish the regenerable fraction.

With the current availability of Hg porosimetry, formulations passing the sulfidation test will have pore characterization of freshly indurated and regenerated pellets. If the conversion is equal to or greater than C4-2 for a given sulfidation temperature further physical characterization will follow (i. e., sulfur analysis at various fractional conversions, crush strength, and Hg porosimetry).

3. RESULTS

The first screening for the freshly indurated mixtures is crush testing. Below are the

crush strength data for; the 4 mm ore mixtures (Figure 2.), and the 4 mm carbonate mixtures (Figure 3.). From the graphs of crush strength, the following (Table 4.) summarizes the lowest induration temperature tested which produced pellets with strength > 3 lb/mm.

Table 4. Induration temperature to produce 3 lb/mm crush strength per formulation.

Formulation	Crush Strength (lb/mm)	Induration Temperature °C
A1-0	3.21	1125
A1-2	3.55	1125
A2-2	5.74	1175
C4-2	3.67	1250
C4-5	3.80	1150
C5-2	3.81	1250
C5-5	3.19	1150
C6-2	5.37	1100
C7-2	3.90	1150

Due to the limited number of larger pellets; C4-2, C4-2A, and C4-2D (all diameters approximately 5.5 mm), crush strength testing was not conducted. The sulfidation of; C4-2, C4-2A, and C4-2D, indurated at 1200 °C with sulfidation at 600 °C are shown in Figure 4. The results of sulfidation at 760 °C for; C4-2, C4-2A, and C4-2D (indurated at 1200 °C) are with sulfidation results at 600 °C for comparison in Figure 5.

4. CONCLUSIONS

Presently, eleven formulations are being tested for; crush strength, and reactivity. The sorbent capacities given in Table 3. range from 23.0- 31.4gS / 100g of freshly indurated sorbent. These values are theoretical yet they are relatively large compared to zinc titanate-based sorbents currently available.

In comparing the strengths of the ore-based (Ax-x designations, Figure 2.) to the carbonates (Cx-x designations, Figure 3.), it is evident that the ores require significantly lower induration temperatures to obtain the required strength. The ore impurities (primarily Alumina and Silicate) allow for higher molar ratios of Mn to substrate for a given induration temperature and crush strength. The degree of pellet sintering during manufacture is related to the duration and temperature of induration, increasing with both. Here, the temperature is minimized in order for maximum retention of pore integrity.

The sulfidation kinetics for; C4-2, C4-2A, and C4-2D, are seen to be nearly identical at 600 °C. This is in contrast to the same formulations sulfided at 760 °C. Further testing and reproducibility indices will aid kinetic interpretation. Furthermore,

the application of Hg porosimetry will yield a direct measure into the internal pellet structure for analysis of surface area enhancement through volatile mixture additions. The purpose is to develop a Mn-based formulation which has appreciable reactivity below 900 °C. Currently, two cubic feet of formulation C4-2 (indurated at 1250 °C) are being tested at the Morgantown Energy and Technology Center (METC). Early results at METC show formulation C4-2-1250 to hold a steady state concentration of < 15 ppmv at 537 °C (1000 °F) in a fixed-bed reactor using a simulated Shell (oxygen-blown) gas.

5. REFERENCES

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Figure 1. H_2S equilibrium concentrations for various fuel gas desulfurization temperatures as a function of the sum of inlet fuel gas H_2O and H_2S concentrations.

Figure 2. Crush strength data for various manganese ore-based formulations as a function of induration temperature.

Figure 3. Crush strength data for the manganese carbonate-based formulations as a function of induration temperature.

Figure 4. Sulfidation kinetics at 600 °C for 6.25-6.5 mm pellet diameter, indurated at 1200 °C.

Figure 5. Effect of temperature on sulfidation kinetics for 6.25-6.5 mm pellet diameter, indurated at 1200 °C.