DOE/PC/94212--T3

Kinetics of Mn-Based Sorbents for Hot Coal Gas Desulfurization

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

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

By

M. T. Hepworth, Principal Investigator, Department of Civil Engineering,
University of Minnesota, Minneapolis, MN-55455.

July 15, 1995

Work Performed Under Grant: DE-FG-22-94PC94212

For:

U.S. Department of Energy
Pittsburgh Energy Technology Center
Pittsburgh, PA 15236-0940

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.

RECEIVED
USDOE/PETC
95 JUL 31 AM 10:07
ACQUISITION & ASSISTANCE DIV.

MASTER

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

1. INTRODUCTION

Hot gas desulfurization may be accomplished by using solid sorbents such as oxides of those metals that form stable sulfides. The effectiveness of a desulfurizing agent in treating such gases is related to the predicted equilibrium partial pressure of hydrogen sulfide which will be present in a phase combination of the reduced form of sulfide and oxide phases. The focus of much current work being performed by the Department of Energy on sorbent development is in the use of zinc ferrite, zinc titanate, and Z-Sorb. The latter sorbent is a commercial product consisting of ZnO, a promoter, and a proprietary supporting matrix designed to provide stability and prolong sorbent life. Although these Zn-based sorbents have been the subject of extensive pilot-scale and process development work, all sorbents produced to date still experience structural and reactive degradation over multi-cycle use at relatively moderate temperatures.

An effective alternative to zinc-based sorbents could be manganese sorbents which withstand high temperature operation and also maintain structural and reactive integrity over many cycles, as investigations by Ben-Slimane and Hepworth have indicated. Thermodynamic limits may prevent MnO from achieving the low sulfur specifications of the product gas for use in a molten carbonate fuel cell, but under the correct conditions the guideline for IGCC systems can easily be achieved. Furthermore, manganese sorbents could possibly be used in conjunction with a polishing sorbent (such as zinc oxide) possessing more favorable thermodynamic properties to reach levels acceptable for fuel cell applications (< 10 ppmv). Such an arrangement may not require that the zinc sulfide be regenerated since the sulfur concentration of the cleaned gas is low enough that the zinc oxide may be discarded when exhausted.

High-temperature desulfurization of coal-derived fuel gases is an essential process in emerging technologies, such as the integrated gasification combined cycle (IGCC), aiming to improve both the efficiency and environmental performance of electrical energy extraction from coal. Desulfurization of these gases at the gasifier exit temperature is preferable from an energy conversion efficiency viewpoint; however, there is currently very limited incentive for desulfurization at temperatures much above 900°C due mainly to the

difficulty of maintaining low alkali content in the fuel gas fed to the gas turbine. At higher temperatures a significant portion of the alkali is in the vapor phase and not easily removed from the gas; whereas at lower temperatures most of the alkali will have condensed on entrained particulate thus, particulate removal significantly lowers the alkali content. In addition, current gas turbine fuel flow control valve technology is well below 900 °C and extending it above 800 °C is regarded as a major challenge by the industry. Fortunately, properly designed heat recovery systems allow certain temperature adjustments without appreciable efficiency losses. For these reasons, the development of effective Mn-based regenerable sorbents in the temperature range 600 to 800 °C is considered essential in order to be competitive. It is likely that such sorbents will allow the best operating conditions in terms of temperature and efficiency, and most importantly the best economic incentive.

A commercial process for H₂S removal from fuel gases is likely to use fluidized beds, rather than fixed- or moving-beds, since they offer high pressure operation and excellent temperature control. In addition to enhancing reaction kinetics, high temperature operation minimizes or eliminates sulfate formation. Fluidized bed systems operate at 750 to 785 °C. Pellets suitable for fluidized bed applications must be on the order of 100 to 300 mm, depending on the design of the fluidized bed reactor. Therefore, this information is to be incorporated into design constraints for further Mn-based sorbent development.

2. THERMODYNAMICS

Thermodynamic calculations can show that operating conditions exist to achieve lower than 50 ppm H₂S content in the cleaned fuel gas. This amount of hydrogen sulfide is well within what current practice achieves. There is no thermodynamic reason why temperatures cannot be reduced below values of 800 °C for loading. In fact, the lower the temperature, the greater the extent of desulfurization as measured by terminal hydrogen sulfide levels in the cleaned gas. The reaction rate, however, decreases because the kinetic mechanisms for loading experience an Arrhenius-type decrease with decreasing temperature, i.e., the log of the rate constant decreases directly with increase in reciprocal temperature.

This decrease can in some measure be compensated for by an increase in the pore surface area of the pellet by increasing the number of inter-connected pores and decreasing the pore diameter. This is done by incorporating into the green pellet sufficient fine-sized volatile constituents such as hydrocarbon particles or molybdic oxide particles which upon heating to induration temperatures oxidize and/or evaporate. The aspect ratio of the introduced volatile constituent should be high to maximize the surface-to-volume ratio of the cavity formed when the particle evaporates or burns as is the case with carbon. Also in the case of MoO_3 , evaporation of this phase must occur prior to the formation of stable manganese molybdates since the chemical activity of manganese is significantly lowered in such compounds, and hence the desulfurizing power is reduced. The generic reaction equation may be expressed as:

For a fuel gas containing 5 vol.% H_2O and 1 vol.% H_2S (such as U-Gas), it can be shown that the concentration of hydrogen sulfide in this gas after equilibration with a mixed oxide is given by:

$$[\text{H}_2\text{S}] (ppmv) = 6 * 10^4 / (1 + K)$$

where K is the equilibrium constant for the above reaction. Table 1. Lists the reactions of several $\text{MnO.Me}_x\text{O}_y$ mixed oxides with H_2S and their equilibrium constants. As figure 1. shows, alundum provides the highest H_2S vapor pressure yet silica fuses with Mn upon induration, reducing reactive sites. Currently, TiO_2 has not been combined with Mn-oxides which requires further thermodynamic analysis. A plot of the H_2S concentrations equilibrated with MnO as a function of the sum of the fuel gas H_2O and H_2S inlet content is given for various desulfurization temperatures in figure 2.

3. EXPERIMENTAL RESULTS

The main purpose of this report is to present preliminary kinetic tests for several formulations at 760 °C. Table 2. Identifies the constituents of the three Mn formulations to be presented. Note that upon induration, all volatiles will be driven away and the indurated pellet composition of the three formulations should be equivalent. Tables 3, and 4, present assays for MnCO_3 and alundum as provided by the manufacturers.

Table 1. Equilibrium Constants for Several Desulfurization Reactions Involving $\text{MnO} \cdot \text{Me}_x\text{O}_y$

Reaction	Log(K)
A: $\langle \text{MnO} \rangle + (\text{H}_2\text{S}) = \langle \text{MnS} \rangle + (\text{H}_2\text{O})$	$\frac{3318}{T} - 0.297$
B: $\langle \text{MnO} \cdot \text{Al}_2\text{O}_3 \rangle + (\text{H}_2\text{S}) = \langle \text{MnS} \rangle + \langle \text{Al}_2\text{O}_3 \rangle + (\text{H}_2\text{O})$	$\frac{804}{T} + 0.085$
C: $\frac{1}{2} \langle 2\text{MnO} \cdot \text{SiO}_2 \rangle + (\text{H}_2\text{S}) = \langle \text{MnS} \rangle + \frac{1}{2} \langle \text{SiO}_2 \rangle + (\text{H}_2\text{O})$	$\frac{1919}{T} + 0.349$
D: $\langle \text{MnO} \cdot \text{SiO}_2 \rangle + (\text{H}_2\text{S}) = \langle \text{MnS} \rangle + \langle \text{SiO}_2 \rangle + (\text{H}_2\text{O})$	$\frac{1854}{T} - 0.153$
E: $\frac{1}{2} \langle 2\text{MnO} \cdot \text{TiO}_2 \rangle + (\text{H}_2\text{S}) = \langle \text{MnS} \rangle + \frac{1}{2} \langle \text{TiO}_2 \rangle + (\text{H}_2\text{O})$	$\frac{2334}{T} - 0.341$
F: $\langle \text{MnO} \cdot \text{TiO}_2 \rangle + (\text{H}_2\text{S}) = \langle \text{MnS} \rangle + \langle \text{TiO}_2 \rangle + (\text{H}_2\text{O})$	$\frac{2028}{T} - 0.232$
G: $\langle \text{MnO} \cdot \text{WO}_3 \rangle + (\text{H}_2\text{S}) = \langle \text{MnS} \rangle + \langle \text{WO}_3 \rangle + (\text{H}_2\text{O})$	$\frac{-704}{T} - 0.254$

Table 2. Composition of the various green (prior to calcination and induration) pellet formulations.

formulation designation	Raw material content in initial make-up, wt. %				
	MnCO ₃	Alundum	Bentonite	Dextrin	Activated Carbon
FORM4-A	81.31	16.73	1.96	-	-
FORM4-A-AC5	77.51	15.95	1.87	-	4.67
FORM4-A-DX10	74.05	15.23	1.79	8.93	-

Table 3. Chemical composition of MnCO₃.

Component	Chemicals MnCO ₃ wt. %
MnCO ₃	93.73
MnO ₂	0.25
CaO	0.124
Na ₂ O	0.056
H ₂ O	2.1
Fe	-

Table 4. Chemical composition of Alundum.

Component	Fepa F Alundum wt %
Al_2O_3	96.6
TiO_2	2.6

Preliminary thermogravimetric analyser (TGA) testing of the calcination and induration of formulations Form4-A-AC5 and Form4-A-DX10 are given in figure 3. Both formulations were tested in an air atmosphere, being lowered into the TGA hot zone at 350 °C. This temperature was maintained for 3.5 hours upon which 1.17 hours were required to raise the temperature to 1250 °C which was held for 2 hours. The dashed lines represent theoretical weight loss calculated from tables 2, 3, and 4, assuming all Mn is in the form of MnO, and that all porosity enhancers are volatilized (i.e. activated carbon and dextrin). Chemical analysis of indurated pellets will follow in the next report. Attempts at BET surface measurements with nitrogen for Form4-A were below detection limits. No attempt was made at BET analysis of Form4-A-AC5 or Form4-A-DX10. In the future, helium pynometry will be used for porosity characterization for all formulations, before and after calcination, and induration.

Reduction and sulfidation of the three formulations were conducted in TGA experiments while varying formulation induration temperatures. Table 5 lists the conditions for all TGA tests conducted on the various formulations.

Table 5. Conditions of TGA experiments for all formulations.

Gas flowrate and composition	1 L/min H ₂
H ₂ S concentration	30,000 ppmv
Sample Mass	600-800 mg
Reduction duration	30 minutes
Sulfidation duration	120 minutes
Pellet diameter average	6.0-6.5 mm
Reduction and sulfidation temperature	760 °C

Figures 4, 5 and 6 illustrate percent conversion data for all formulations indurated at 1200 °C, 1225 °C and 1250 °C respectively. All reduction/sulfidation tests were conducted on freshly indurated pellets with no multicyclic testing reported within. Interestingly, activated carbon pellets appear to have slightly improved sulfidation kinetics, while dextrin may not enhance sulfidation appreciably.

4. SUMMARY

Previously, manganese based sorbents have been described which show good high temperature fuel gas desulfurization properties. However, the current focus lies in creating Mn-based sorbents which desulfurize fuel gases in the range of 700-800 °C. Additives were included to pellet formulations increase surface area and reduce diffusional distances for sulfidation. Two formulations of Mn-based sorbents (Form4-A-AC5, and Form4-A-DX10) were tested in a TGA for calcination and induration characterization. Figure 3 shows that the dextrin formulation retains more weight than the activated carbon resulting from nonvolatiles within the dextrin. Sulfidation kinetic testing was conducted on three formulations of Mn-based sorbents indurated at 1200 °C, 1225 °C, and 1250 °C. Initially, pellets with activated carbon seem to show a slight improvement in sulfidation kinetics which yields larger percent utilizations after 2 hours. The formulations tested have surface

areas below the detection limit for BET surface area measurements using nitrogen. Strength and porosity measurements are to follow in the next quarterly report. Finally, additional effort will be made to research additives to promote increases in internal pellet surface area.

5. REFERENCES

1. *Clean Coal Technology, The New Coal Era*, DOE/FE-0217P, Nov. 1989, U.S. Department of Energy, Washington, DC 20585.
2. U.S. Bureau of the Census, *Statistical Abstract of the United States: 1993*, (113th edition), Washington, DC, 1993, pp. 571-585.
3. Unsworth, J.F., et. Al., *Coal Quality and Combustion Performance: An International Perspective*. Elsevier, Amsterdam, 1991.
4. Schmidt, D.K., "The System and Development Targets for IGCC", *Proceedings of the Coal Fired Power Systems 93 -- Advances in IGCC and PFBC Review Meeting*, DOE/METC-93/6131 (DE93000289), 1993, pp. 131-133.
5. Notestein, J.E., *Commercial Gasifier for IGCC Applications Study Report*, DOE/METC-91/6118 (DE91002051), Washington, DC, June 1990.
6. Hepworth, M.T.; Ben-Slimane, R.; and Zhong, S., "Thermodynamic Comparison of Several Sorbent Systems for Hot Coal-Derived Fuel-Gas Desulfurization". *Energy and Fuels*, 7, 1993, pp. 602-609.
7. Turkdogan, E.T., *Physical Chemistry of High Temperature Technology*, Academic Press, New York, 1980.
8. Woods, M.C. and Gangwal, S.K., "Reaction between H_2S and Zinc Oxide-Titanium Oxide Sorbents. 1. Single Pellet Kinetic Studies", *Ind. Eng. Chem. Res.*, Vol. 29, 1990, pp. 1160-1167.
9. Lew, S.; Jothimurugesan, K.; Flytzani-Stephanopoulos, M., "High-Temperature H_2S Removal from Fuel Gases by Regenerable Zinc Oxide-Titanium Dioxide Sorbents", *Ind. Eng. Chem. Res.*, Vol. 28, pp.535-541.
10. Mojtahedi, W.; Salo, K.; and Abbasian, J., "Desulfurization of Hot Coal Gas in Fluidized Bed with Regenerable Zinc Titanate Sorbents", *Fuel Processing Technology*, Vol. 37, 1994, pp.53-65.

11. Turkdogen, E.T. and Olsson, R.G., "Desulfurization of Hot Reducing Gases with Manganese Oxide Pellets", *Proceedings of the Third International Iron and Steel Congress*, Chicago IL., Apr. 16-20, 1978, pp. 488-491.
12. Ben-Slimane, R., and Hepworth, M.T., "Desulfurization of Hot Coal-Derived Fuel Gases with Manganese-Based Regenerable Sorbents. 1. Loading (Sulfidation) Tests", *Energy and Fuels*, Vol. 8, 1994, pp. 1175-1183.
13. Ben-Slimane, R., and Hepworth, M.T., "Desulfurization of Hot Coal-Derived Fuel Gases with Manganese-Based Regenerable Sorbents. 2. Regeneration and Multicyclic Tests", *Energy and Fuels*, Vol. 8, 1994, pp. 1184-1191.
14. Ben-Slimane, R., and Hepworth, M.T., "Desulfurization of Hot Coal-Derived Fuel Gases with Manganese-Based Regenerable Sorbents. 3. Fixed-Bed Testing", Accepted for publication in *Energy and Fuels*, March/April Issue, 1995.

Figure 1. H_2S equilibrium concentrations for various $MnO \cdot Me_xO_y$ sorbents.

Figure 2. 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 3. Calcination and induration of Form4-A-AC5, and Form4-A-DX10.
Calcination for 3.5 hours at 350 C.
Induration for 2 hours at 1250 C.
Pellet diameter average of 6.0 mm.

Figure 4. Percent conversion of Mn for formulations indurated at 1200 C.
Reduction and sulfidation were at 760 C.

Figure 5. Percent conversion of Mn for formulations indurated at 1225 C.
Reduction and sulfidation at 760 C.

Figure 6. Percent conversion of Mn for formulations indurated at 1250 C.
Reduction and sulfidation at 760 C.