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**Hot Coal Gas Desulfurization With
Manganese-Based Sorbents**

**Quarterly Report
April - June 1994**

**M. T. Hepworth
R. Ben Slimane**

June 1994

Work Performed Under Contract No.: DE-AC21-92MC29246

**For
U.S. Department of Energy
Office of Fossil Energy
Morgantown Energy Technology Center
Morgantown, West Virginia**

**By
University of Minnesota
Minneapolis, Minnesota**

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P.O. Box 880
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ABSTRACT

The focus of work being performed on Hot Coal Gas Desulfurization at the Morgantown Energy Technology Center is primarily in the use of zinc titanate sorbents; however, prior studies¹ indicated that an alternate sorbent, manganese dioxide-containing ore in mixture with alumina (75 wt% ore + 25 wt% Al_2O_3) appears to be a strong contender to zinc-based sorbents. Manganese, for example, has a lower vapor pressure in the elemental state than zinc; hence, it is not as likely to undergo zinc-depletion from the sorbent surface upon loading and regeneration cycles. Also manganese oxide is less readily reduced to the elemental state than iron; hence, the range of reduction potentials for oxygen is somewhat greater than for zinc ferrite. In addition, thermodynamic analysis of the manganese-oxygen-sulfur system shows it to be less amenable to sulfation than zinc ferrite. Also manganese chlorides are much less stable and volatile than zinc chlorides. Potential also exists for utilization of manganese at higher temperatures than zinc ferrite or zinc titanate.

This Seventh Quarterly Report documents progress in bench-scale testing of a leading manganese-based sorbent pellets (FORM4-A). This formulation is a high-purity manganese carbonate-based material. This formulation was subjected to 20 consecutive cycles of sulfidation and regeneration at 900°C in a 2-inch fixed bed reactor. The sulfidation gas was a simulated Tampella U-gas with an increased hydrogen sulfide content of 3% by volume to accelerate the rate of breakthrough, arbitrarily taken as 500 ppmv. Consistent with thermo-gravimetric analysis (TGA) on individual pellets, the fixed bed tests show small improvement in capacity and kinetics with the sulfur-loading capacity being about 22% by weight of the original pellet, which corresponds to approximately 90% bed utilization!

Included with this report is an Appendix which describes this formulation and regeneration and multicycle tests carried out via thermogravimetric analysis (TGA) on individual FORM4-A pellets.

¹Turkdogan, E. T. and Olsson, R. G.: "Desulfurization of Hot Reducing Gases with Manganese Oxide Pellets", *Proceedings Third International Iron and Steel Congress* ASM Metals Park, Ohio, 1979, pp.277-288.

INTRODUCTION

Zinc ferrite and zinc titanate are being developed as regenerable sorbents capable of removing hydrogen sulfide from hot coal gases. Utilization is only about 10% sulfur loading at best; in addition, it drops significantly with recycling. Also zinc ferrite tends to spall and be limited in temperature to effective utilization below about 600°C.

Manganese-based sorbents combined with alumina to form indurated pellets hold promise of being highly-effective, inexpensive, regenerable sorbents for hot fuel gases. These sorbents are effective in making very strong (> 50 pounds crush strength for a 4-mm pellet), which can be loaded and regenerated at higher temperatures than zinc ferrite (which is limited to about 1100 to 1200°F or 593° to 649°C), and which appear to be capable of improved loading with each cycle and also load sulfur to a higher capacity. The thermodynamics for sulfur removal by manganese predicts sulfur removal to terminal levels (in terms of the over-pressure of hydrogen sulfide) somewhat less favorable than can be accomplished with zinc oxide; however, zinc can be reduced under coal gasification conditions and tends to volatilize, limiting the temperatures for which desulfurization can be effectively accomplished to values less than 700°C.^{2,3} Also the capabilities for regeneration of manganese pellets (with an alumina filler @ 75 wt% Moanda ore, 25 wt% Al₂O₃) under oxidizing conditions may be superior to those of zinc ferrite in that they can be loaded from a reducing gas and regenerated at higher temperatures (regeneration up to 1300°C). Upon regeneration of the loaded sorbent, sulfur can be obtained from the off-gases by combination of the products of the regeneration: hydrogen sulfide and sulfur dioxide or alternatively, a high strength sulfur dioxide gas mixture suitable for sulfuric acid manufacture can be produced.

A significant domestic source of manganese in Minnesota is being explored for an *in situ* leach process which has potential for producing large tonnages of solutions which may be ideal for precipitation and recovery of

²Woods, M. C., Gangwal, S. K., Jothimurugesan, K., and Harrison, D. P.: "Reaction between H₂S and Zinc Oxide-Titanium Oxide Sorbents. 1 Single-Pellet Kinetic Studies", *I & EC Research*, 1990, 29, p. 1160-1167.

³Hepworth, M.T. and Jha, M.C., "Enhanced Durability and Reactivity for Zinc Ferrite Desulfurization Sorbent," *Proceedings of the Eighth Annual Gasification and Gas Stream Cleanup Systems Contractors Review Meeting*, Vol. 1, DOE/METC-88/6092.

pure manganese as a carbonate in a reactive form.⁴

In this current program the following studies are being addressed:

- preparation and thermogravimetric analysis (TGA) of manganese-based sorbents;
- thermodynamics and kinetics of sulfur removal from hot fuel gases by this sorbent;
- cyclic loading and regeneration of the sorbent by oxidation and recovery of the sulfur.

Current Status of Test Work:

The following tasks have been completed (★), are being undertaken (◆), or will be undertaken (■) during the last three months of the contract:

- 1) (★)Providing Information Required for the National Environmental Policy Act;
 - 2) (◆)Sorbent Preparation and Characterization Tests on Individual Pellets*
 - 3) (★)Provision for Bench-Scale Test Unit
 - 4) (◆)Bench-Scale Testing
 - 5) (■,◆)Data Analysis
- * Characterization testing is continuing simultaneously with the Bench-Scale, fixed-bed tests.

⁴Hepworth, M. T.: *Selective Mining Methods for Minnesota, MN Initiative Project: Manganese Recovery from In-Situ Leach Liquors*, Final Report to U. S. Bureau of Mines from the Mineral Resources Research Center 1992.

The program consists of the following studies:

- Establish the thermodynamic feasibility for the use of manganese-based sorbents for the removal of sulfur in comparison with other oxide systems.
- Prepare and characterize manganese sorbent pellets. Initial characterization is based upon strength and surface area.
- Determine the comparative kinetics of loading and regeneration of individual sorbent pellets via thermogravimetric analysis (TGA). Preliminary TGA tests are showing that sorbents prepared with the organic binder, dextrin, on Moanda ore appear to offer the best combination of strength, reactivity, and capacity. Sorbents prepared with bentonite on manganese carbonate appear to offer the best combination of capacity and reactivity. Further testing will utilize these two leading sorbents.
- Build a two-inch reactor fixed-bed test unit. This unit is currently built and being tested.
- Perform bench-scale tests on the optimum sorbent pellets in a two-inch diameter reactor.

EXPERIMENTAL PROCEDURES AND RESULTS

The test work reported in this quarterly report is directed to formulation FORM4-A which is described more fully in the Quarterly Technical Progress Report of October 15, 1993 and in the Appendix to the present (7th) Quarterly Report. This formulation has been shown to possess the most favorable loading and regeneration characteristics of all the formulations tested. It is made up of 81.31% by weight manganese carbonate (from Chemetals), 16.73% by weight Alundum (containing 96.6% Al_2O_3 from Norton Materials, Inc.), and 1.96% bentonite as a binder. Upon forming pellets, they were first dried at 110°C, then heated to 350°C to allow for weight losses as a result of dissociation of the carbonate. They were then heated to 1250°C and indurated for two hours in an air atmosphere before removal from the furnace. The average size of the pellets was 4 mm and they had an average strength of 5.4 pounds per mm of diameter. The final manganese assay of the indurated pellets was 44.22% by weight, which corresponds to a theoretical sulfur capacity of 25.8% sulfur, (i.e. 25.8 gS/100g sorbent).

Details of the loading (sulfidation) tests were reported in the Appendix to the previous report. It was concluded that sorbent pellets composed of high purity manganese carbonate, alundum, and bentonite as a binder were potentially highly effective for the removal of sulfur from simulated fuel gases at high temperature (800 to 1000°C).

The results from regeneration and multicycle tests, as reported in the appendix in this report, show that these sorbent pellets are also capable of being regenerated after sulfidation by reacting the sulfide with air or oxygen-deficient air. Pellets which underwent loading and regeneration over five consecutive cycles showed a slight improvement in capacity and reaction kinetics.

BENCH-SCALE TESTING

The overall schematic diagram of the experimental arrangement for fixed-bed tests is shown in Figure 1. The split or two-zone furnace is positioned with respect to the bed to accomplish gas preheating and careful control of the bed temperature. Gas combinations for flows can be produced via control of bottled gases through the valves and flowmeters shown in the diagram. The water content of the system is controlled by a metering pump acting on liquid water which is discharged into a heated stainless tube to vaporize the water and provide the gas composition required by the Tampella-U Gas composition, as reported earlier.⁴

The details of the reactor system are depicted in Figure 2. This figure shows the two-inch (I.D.) closed-end alumina reactor tube equipped with an alumina perforated-disc plate suspended over alumina chips. The coal-derived fuel gas simulating the Tampella-U Gas is passed through a small central tube (without contacting the reaction zone of manganese pellets) through the perforated disc and into a preheat zone of alumina chips which supports the disc. The gas is then discharged from the small central tube into the larger tube and moves upward, after reaching temperature, into gas preheat zone of a two-zone furnace. The gas, now at temperature, contacts the sorbent bed consisting of pellets ranging in size from 4 to 5 mm in diameter. The off-gas then is flared and discharged to a hood. A sample is taken via gas chromatograph (labelled in Figure 9 as GC).

A minor problem has arisen during the regeneration step in that sulfur tends to form and plug the exit tube during the early stages of regeneration (examination of the plug showed it to be elemental sulfur). This problem was overcome by reducing the air flow rate to limit the rate of heat release by the highly exothermic regeneration reaction and prevent the pellets from sintering. The addition of an after-burner on top of the

pellet bed resulted in more oxidizing conditions and hence less tendency for sulfide sulfur (S^{2-}) to oxidize to the intermediate elemental form (S^0) rather than to 4-valent (S^{+4}).

Loading proceeded at a rate of 3.5 liters per minute until breakthrough is observed. Breakthrough is defined as a sudden rise in the sulfur content of the gas as determined by gas chromatography. The bed is then flushed with nitrogen in order to expel remaining hydrogen and a regeneration gas consisting of air is initiated with the sulfur content of the gas being continuously analyzed for sulfur dioxide. The regeneration step is discontinued when the concentration of sulfur dioxide in the exit gas is measured below 500 ppmv. The loading and regeneration cycles are then repeated until twenty (20) cycles are completed.

Figure 3 shows the effect of cycling on the sulfur capacity of FORM4-A pellets at 900°C upon repeated loading and regeneration. The sulfur loading capacity (defined as grams sulfur per 100 grams of original pellet mass) shows a slight improvement with each cycle. The effect diminishes with each cycle since loadings approaching 23% S, (i. e., is ~90% of the maximum theoretical value) at 12 cycles. This sulfur capacity is calculated using mass balances, based upon gas analyses for H_2S entering and leaving the reactor. Before break-through the H_2S concentration in the cleaned gas approach more closely the equilibrium value, which is an indication of an improvement in pellet reaction kinetics with increasing cyclic loading. These results are consistent with the previous results from TGA tests on individual pellets.

FUTURE WORK

Under the present contract a program was undertaken to optimize pellet formulations and evaluate them by multiple cyclic tests in a fixed-bed reactor; however, now that the FORM4-A pellets have been shown to be highly effective through repeated cycling, effort should be redirected toward exploring several parameters of fixed bed operation which may be more consonant with actual test conditions. For example after ten cyclic loadings of the pellets, a long cycle of loading at a lower H_2S content, more nearly representing the actual fuel gas compositions, should be undertaken. Upon completing this long cycle to break-through, the bed should be examined in vertical layers to explore the degree of sulfidation which has occurred on single pellets.

Also single-particle regenerations on selected pellets from the above long test should be explored by DTA as well as TGA analysis to determine the thermal effects which occur upon oxidation of the sulfides. The results on single pellet tests could then be compared with the thermal effects (e. g., local temperature rises) which would occur in fixed bed environments. The effect of space velocity, i. e. gas flow rates in fixed bed tests could also be explored.

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APPENDIX A

Paper Accepted for Publication in Energy and Fuels

entitled

**"Desulfurization of Hot Coal-Derived Fuel Gases with Manganese-Based
Regenerable Sorbents. 2. Regeneration and Multicycle Tests"**

Figure 1. Schematic of Overall Experimental Arrangement for Fixed-Bed Tests.

Figure 2. Schematic Diagram of Reactor Details.

Figure 3. Effect of Cyclic Loading and Regeneration on Sulfur Capacity of FORM4-A Pellets at 900 °C.

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