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Hot Coal Gas Desulfurization With Manganese-Based Sorbents

**Quarterly Report
October - December 1993**

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

January 1994

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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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Morgantown Energy Technology Center
P.O. Box 880
Morgantown, West Virginia 26507-0880**

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January 1994

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 ferrite and 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) may be a viable alternative 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 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. Potential also exists for utilization of manganese at higher temperatures than zinc ferrite or zinc titanate.

This Fifth Quarterly Report documents progress in pellet testing via thermogravimetric analysis of pellet formulation FORM4-A of a manganese ore/alumina combination. This formulation, described more fully in the Quarterly Technical Progress Report of October 15, 1993, consists of manganese carbonate combined with alundum.

A 2-inch fixed-bed reactor has been fabricated and is now ready for subjecting pellets to cyclic loading and regeneration; however, a minor problem has arisen during the regeneration cycle in that sulfur tends to form and plug the exit tube during the early stage of regeneration. This problem is about to be overcome by increasing the flow rate of air during the regeneration cycle resulting 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}).

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, however, and 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.

This study will extend earlier studies made at the laboratories of U. S. Steel undertaken by Dr. E. T. Turkdogan. Those studies, which utilized a manganese ore blended with alumina, were successful in achieving desulfurization from reducing gases. This earlier work was not undertaken with the gas mixtures which are proposed for this study, nor were the manganese formulations the same as are planned; however, the initial success of the work of Turkdogan indicates that significant progress can be made in moving forward toward developing a high-temperature regenerable sorbent.

The developed information will be of value to METC in determining whether or not a manganese-based regenerable sorbent holds real promise for sulfur cleanup of hot fuel gases. This information is necessary before pilot-scale testing leading to commercial development is undertaken.

Current Status of Test Work:

The following tasks have been completed (★), are being undertaken (◆), or will be undertaken (■) during the next 9 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
- * In this report, however, further characterization studies (TGA) are described pending solution to minor problems associated with the bench-scale equipment.

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.

THERMODYNAMIC CONSIDERATIONS

The prior quarterly report detailed thermodynamic considerations for the use of manganese as a sorbent and will not be repeated here.

EXPERIMENTAL PROCEDURES AND RESULTS

THERMOGRAVIMETRIS ANALYSIS

The test work reported in this quarterly report is directed to formulation FORMA-4 which is described more fully in the Quarterly Technical Progress Report of October 15, 1993. This formulation has been shown to possess the most favorable loading and regeneration characteristics of all the formulations tested. It is made up of 81.81% 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 for 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).

The equipment used in the TGA has been described previously. The thermogravimetric tests focused on studying the effects of regeneration parameters (Temperature, O_2 content, pellet diameter) and on repeated loading and regeneration of FORM4-A pellets which exhibited the best performance from a kinetic point of view. Since up to fifteen pellets can be used in each reduction/sulfidation test, various tests were needed to provide enough fully-loaded pellets for the various regeneration tests. This provided opportunity to determine reduction and loading reproducibility. The reduction and sulfidation were carried out under standard conditions of $900^\circ C$ and 3% H_2S/H_2 gas mixtures at 500 cc per minute delivery for a total of 1.75 grams of pellets. Reduction was carried out with pure hydrogen for the first 45 minutes and then the hydrogen sulfide was added. Fifteen indurated pellets of a uniform size and mass were used in each test. Figure 1 shows the reproducibility of loading tests for five separate tests at $900^\circ C$ with 3% by volume hydrogen sulfide in Hydrogen. The curves shown indicate the upper and lower limit of the data with a "best-agreement" curve shown between these limits. The tests shown are for fresh pellets (first loading cycle). In all subsequent figures, W_0 refers to the mass of the indurated pellet and W to the mass of the pellet as a function of time.

Note that for the reduction portion of the curve (the lower flat plateau) the reproducibility is particularly good, with reduction completed in fifteen minutes. The reproducibility of sulfidation is excellent for the first 45 minutes after the initial reduction period (total time lapse of 90 minutes); however, deviations in degree of loading occur thereafter.

Figure 2 is similar to Figure 1 except that it gives the error bars on the data to indicate the range of the results. The baseline curve shown is therefore a limitation on precision of future test results.

A total of five regeneration tests were then carried out using five pellets during each test. The regeneration gas was air flowing at 500 cc per minute and regeneration temperatures varied between 800 and $1000^\circ C$ in increments of $50^\circ C$. The purpose was to determine the temperature at which loaded pellets can be fully regenerated. The results from these tests are reported in Figure 3. The loading curve is taken as the mean from Figure 2; however, the right-hand portion of this curve shows the regeneration portion after a total time lapse of 165 minutes. These results appear to be in strict accordance with thermodynamic predictions that were outlined in a prior report, viz.: at $800^\circ C$ the loaded pellets first oxidize (and hence lose weight) for about 3 minutes at which time sulfation with an concurrent weight gain becomes predominant. When all the MnS is transformed to $MnSO_4$, sulfate decomposition starts and the pellet begins to show a weight loss. Continuing at higher temperatures, at $850^\circ C$, the

same trend is observed; however, the oxidation of the pellets appears to be faster than sulfation. This is reasonable since the driving force for the decomposition of sulfate is greater. The regeneration kinetics appear to be a weak function of temperature over the range 900 to 1000°C. In this range regeneration is essentially complete in 10 to 15 minutes and sulfation does not occur. Again this is in agreement with the prior analysis of the Mn-O-S system as described in the prior Quarterly Report.

Figure 4 shows the effect of oxygen content in N₂/air gas mixtures on regeneration kinetics for four oxygen levels: 5, 10, 15, and 21 (air)% by volume. Even for the lowest oxygen level, the flow rates and mass of samples were chosen so that the rate of delivery was not rate-limiting. These kinetics are presently under analysis. The plot shows an expected increase in rate in the three values 5, 10, and 15% oxygen; however, the decrease in rate for the sample exposed to air (21%) requires further study which may be clarified by surface morphology. A possibility for this reduced rate may be overheating of the pellet surface and possible glazing.

Figures 5, 6 and 7 show the effect of cycling upon reduction, loading, and regeneration kinetics, respectively. In Figure 5, The first cycle for reduction exhibits the slowest kinetics as compared with subsequent cycles. In Figure 6 which exhibits loading kinetics, although the loading kinetics improve with cycling, the loading capacity diminishes slightly for each cycle after the first cycle.

In Figure 7 the regeneration kinetics show the same trend, namely that multiple cycling improves the kinetics but reduces capacity. A speculation at this time is that some manganese sulfur interactions are more tightly bonded and remain less readily accessible to regeneration by oxygen. It is worth noting that these observations are in agreement with prior findings of Turkdogan and Olsson. As discussed in prior reports, repeated cycling of the pellets resulted in improved sulfidation and regeneration kinetics. This desirable phenomenon was attributed to coarsening of the pellet pores.

In Figure 8, all the cycles are combined in one composite diagram. Repeated cycling of these pellets is currently being continued for a total of 10 cycles.

BENCH-SCALE TESTING

The bench scale apparatus, which was described fully in the prior quarterly report, is temporarily out of service because of plugging problems which have been encountered upon regeneration of pellets. The plug in the exhaust tube occurs during the early stages of the regeneration cycle. Examination of the plug showed it to be elemental sulfur. Turkdogan found that elemental sulfur was evolved in the early stages of regeneration, but he did not encounter plugging. This problem is about to be overcome by increasing the flow rate of air during the regeneration cycle resulting in more oxidizing conditions and hence less tendency for sulfide sulfur (S_{-}) to oxidize to the intermediate elemental form (S_0) rather than to 4-valent (S_{+4}).

FUTURE WORK PLANS

Future work will continue TGA tests on individual pellets followed by bench scale testing in a two-inch reactor of the optimum pellet formulation as determined by on-going TGA testing.

- Determine the comparative kinetics of loading and regeneration of individual sorbent pellets via thermogravimetric analysis (TGA).
- The same work as described in Figure 8 is planned for pellets from FORM1-A, which exhibited the best combination of strength, capacity, and reactivity. In addition, tests are being conducted to determine the effect of pellet diameter on regeneration kinetics. These results from the above tests and a thorough analysis of all kinetic data will be included in the next quarterly report.
- Perform bench-scale tests on the optimum sorbent pellets in a two-inch diameter reactor. There now appear to be two formulations: manganese carbonate-based bonded with bentonite and indurated for 2 hours at 1250°C, (i. e., FORM4-A) and manganese ore-based bonded with dextrin and indurated at 1200°C for 2-hours, (i.e., FORM1-A).
- Solve plugging problem by use of heated exit tube and by increasing the rate of oxidant (air plus nitrogen) or alternately, increase furnace exit diameter and maintain exhaust tube above melting point of sulfur.
- Finally, two papers entitled "Desulfurization of Hot Coal-Derived Fuel Gases with Manganese-Based Regenerable Sorbents: 1. Loading (Sulfidation) Tests" and "2 Regeneration and Repeated Cycling Tests" are being completed and will be submitted to the sponsor prior to submission for publication in the journal *Energy and Fuels*.

Figure 1 Reproducibility of Loading Tests at 900°C with 3% by volume H₂S in Hydrogen.

Figure 2 Reproducibility of Loading Tests at 900°C with 3% by volume H₂S in Hydrogen showing Average Value and Error Bars

Figure 3 Reduction and Sulfidation Tests at 900°C with Regeneration at Temperatures Ranging from 800° to 1000°C

Figure 4 Effect of Oxygen Content Upon Regeneration Kinetics for Four Oxygen Levels

Figure 5 Effect of Cyclic Loading upon Reduction Kinetics for 6 Cycles

Figure 6 Effect of Cyclic Loading upon Loading Kinetics (Sulfidation) for 6 Cycles

Figure 7 Effect of Cyclical Loading upon Regeneration Kinetics for 6 Cycles

Figure 8 Composite Plot Showing Effect of Cyclical Loading over 6 Cycles upon Reduction, Sulfidation, and Regeneration Kinetics

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