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

**Annual Report
September 1992 - September 1993**

M. T. Hepworth

December 1993

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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DOE

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**For
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P.O. Box 880
Morgantown, West Virginia 26507-0880**

**By
University of Minnesota
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December 1993

MASTER

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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 ferrite and zinc titanate sorbents; however, prior studies at the U. S. Steel Fundamental Research Laboratories in Monroeville, PA, by E. T. Turkdogan¹ 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 Annual Topical Report documents progress in pelletizing and testing via thermo-gravimetric analysis of individual pellet formulations of manganese ore/ alumina combinations and also manganese carbonate/ alumina with two binders, dextrin and bentonite. It includes the prior Quarterly Technical Reports which indicate that the manganese carbonate material, being of higher purity than the manganese ore, has a higher degree of sulfur capacity² and more rapid absorption kinetics.

A 2-inch fixed-bed reactor has been fabricated and is now ready for subjecting pellets to cyclic loading and regeneration.

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.

²Capacity is defined as grams of sulfur absorbed per 100 grams of indurated pellets.

**HOT COAL GAS DESULFURIZATION
WITH MANGANESE-BASED SORBENTS**

Progress Report for the Period July 1, 1993 to September 30, 1993

**By
M. T. Hepworth, Department of Civil and Mineral Engineering
University of Minnesota, Minneapolis, MN**

October 15, 1993.

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

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

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 studies at the U. S. Steel Fundamental Research Laboratories in Monroeville, PA, by E. T. Turkdogan¹ 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 report documents progress in pelletizing and testing via thermogravimetric analysis of individual pellet formulations of manganese ore/alumina combinations and also manganese carbonate/ alumina with two binders, dextrin and bentonite. Preliminary results indicate that the manganese carbonate material, being of higher purity than the manganese ore, has a higher degree of sulfur capacity² and more rapid absorption kinetics.

A 2-inch fixed-bed reactor has been fabricated and is now ready for subjecting pellets to cyclic loading and regeneration.

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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.^{3,4} 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

³Woods, 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.

⁴Hepworth, 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.⁵

In this current program the following studies are being addressed:

- preparation and characterization 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 12 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

⁵Hepworth, 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

Since the prior studies by Turkdogan and Olsson were conducted on a manganese ore (Moanda ore), the starting point for the present investigation is using similar materials for comparison. Then manganese oxide derived from pure carbonate, similar to that which would be recovered from in-situ mining is studied. Accordingly, the following materials are being utilized: (Chemical analyses were reported in the Second Technical Report [12/1/1992 to 2/28/93])

- MnO_2 Moanda ore (Africa);
- Ultrafine MnCO_3 (93-95%) (Chemetals, Inc.);
- Manganese carbonate recovered from *in situ* leach liquors produced by the Salt Lake City Research Center of the U. S. Bureau of Mines
- Alundum (96.6% Al_2O_3) (Norton Materials, Inc.);
- Bentonite, inorganic binder (Aldrich Chemical Co.); and
- Dextrin, an organic binder.

Pelletization:

The procedures followed for pelletization were reported in the prior quarterly report.

Following the above procedure, six formulations were prepared using combinations of Moanda ore, manganese carbonate from Chemetals and manganese carbonate from the USBM, alundum, bentonite, and dextrin. The composition of the initial make up of samples is reported in Table 1.

Table 1

Formulation No.	Raw Material Content in initial make-up, wt.%					
	Moanda Ore	Alundum	MnCO ₃ (Chemetals) ⁶	MnCO ₃ (USBM) ⁶	Bentonite	Dextrin
1	68.18	22.73	-	-	-	9.09
2	73.53	24.51	-	-	1.96	-
3	-	15.51	75.4	-	-	9.09
4	-	16.73	81.81	-	1.96	-
5	-	15.51	-	75.4	-	9.09
6	-	16.73	-	81.31	1.96	-

Induration:

Twenty-four induration campaigns were conducted. As established by previous tests, Moanda-ore base pellets required a temperature of 1200°C and manganese-carbonate-based pellets required an induration temperature of 1250°C, to produce required strength minima (>5 lbs per mm of pellet diameter). In addition two time periods for induration were explored, namely, 1 hour and 2 hours.

⁶Calcination of manganese carbonate effectively reduces its mass upon loss of carbon dioxide. Precalcination mass was chosen to produce 75% by wt. MnO.

Two induration procedures were followed:

In both procedures, the pellets were dried to a constant weight at 110°C prior to induration.

- In the first procedure which was applied to the first 12 tests summarized in Table 2 below, the samples were pre-weighed and slowly introduced into a furnace already at the required temperature. After residence at temperature for the required time, they were slowly extracted and allowed to air-cool and then re-weighed. These weights are reported as W_0 and W_{f2} in the Table. Unfortunately this procedure produced thermal stresses resulting in cracking of the pellets.
- In the second procedure, the pellets were introduced into the furnace at 500°C and then furnace-heated to the desired induration temperature over a heating cycle of 150 minutes. (The manganese carbonate-based pellets, however, were allowed to dissociate to the oxide in a prior step at 350°C. For these pellets the weight of the decomposed pellets for some of the tests is reported as W_{f1} in Table 2 to serve as a check to determine whether the decomposition was complete.)

In interpreting Table 2, the recorded weight loss for the ore-based pellets is associated with the loss of structurally-bound water and also the loss of oxygen as MnO_2 is transformed to Mn_3O_4 , the stable form of manganese under induration conditions.

Table 2: Induration Conditions

Test I.D.	Formulation No.	Temp.,(°C)	Duration (hrs)	W ₀	W _{f1}	W _{f2}
IN93G29A.R33	1	1200	2	25.69	-	21.01
IN93G29B.R33	2	1200	2	27.04	-	23.77
IN93G29C.R33	1	1200	1	21.16	-	17.31
IN93G29D.R33	2	1200	1	26.21	-	23.08
IN93G29E.R34	3	1250	2	43.59	-	28.01
IN93G29F.R34	4	1250	2	41.40	-	29.31
IN93G29G.R34	3	1250	1	33.80	-	21.72
IN93G29H.R34	4	1250	1	32.76	-	23.20
IN93G29I.R35	5	1250	2	14.10	-	9.01
IN93G29J.R35	6	1250	2	16.17	-	11.41
IN93G29K.R35	5	1250	1	15.46	-	9.85
IN93G29L.R35	6	1250	1	12.90	-	9.15
IN93G30A.R36	1	1200	2	13.58	-	11.10
IN93G30B.R36	2	1200	2	16.83	-	14.72
IN93G30C.R36	1	1200	1	12.68	-	10.37
IN93G30D.R36	2	1200	1	20.37	-	17.88
IN93G30E.R37	3	1250	2	21.55	14.94	13.81
IN93G30F.R37	4	1250	2	24.17	19.20	16.90
IN93G30G.R37	3	1250	1	26.85	18.75	17.22
IN93G30H.R37	4	1250	1	26.19	20.93	18.55
IN93G30I.R38	5	1250	2	10.66	7.79	6.03
IN93G30J.R38	6	1250	2	4.00	3.32	2.84
IN93G30K.R38	5	1250	1	10.50	8.25	6.26
IN93G30L.R38	6	1250	1	2.09	1.79	1.50

Figure 1 displays the strength of representative pellets from the prior twenty-four induration tests each assigned an identification letter (I.D.) ranging from A₁ through L₁ for the first half of Table 2 and A₂ through L₂ for the second half of the table. The pellets were subjected to a crush test using an anvil and hydraulically loaded plate equipped with a pressure sensor. Tests were made on pellets which were approximately 4 mm in diameter. The loads are expressed in pounds per mm of diameter. Since the equipment is only capable of sensing loads of less than 9 pounds per mm of pellet diameter, identifications: B₁, D₁, B₂, and D₂, are shown as off-scale and represent values significantly higher than indicated.

From this table the strongest formulations are bentonite-bonded as expected. At the conclusion of these tests, four samples were selected for TGA analysis. They were given the following designations: FORM1-A, FORM2-A, FORM2-B, and FORM4-A. Letter "A" corresponds to induration for 2 hours at 1200°C for the ore-based pellets, and 1250°C for carbonate-based pellets; whereas, letter "B" corresponds to an induration time of 1 hour.

Chemical Analyses:

Table 3 summarizes the manganese assays and strengths of the formulations which were subjected to TGA analysis.

Table 3

Sample Designation	Weight %Mn	Strength, lbs/mm
FORM1-A	41.14	5.8
FORM2-A	37.48	14.7
FORM2-B	39.83	11.9
FORM4-A	44.22	5.4

Pellet Porosity and Surface Area:

BET surface area tests on indurated pellets have shown them to have a surface area less than 0.2 m²/gm, which is below the sensitivity of our equipment and therefore required krypton as a carrier gas. We are attempting to increase pellet surface area; however, TGA testing at this time does show them to be about as reactive as the zinc titanate pellets which have been studied by other investigators. Typical specific surface area values are as follows:

FORM2-A: 0.055 m²/gm
 FORM1-A: 0.127 m²/gm

Porosity tests made by combination of aqueous pycnometry on crushed pellets from formulation 2 in combination with mercury pycnometry showed the pellets to have a porosity of about 36%. In addition, several characterization measurements are being made with the help of outside laboratories, namely, the Twin Cities Research Center of the U. s. Bureau of Mines and also through METC.

Tests via TGA on Pellet Reactivity:

The TGA testing is divided into two campaigns the first being only comparative loading for one cycle, and the second for regeneration studies after repeated cyclic loading and regeneration. The second campaign activity is described in the section entitled Future Plans and will be executed in the next quarter.

During the first campaign, emphasis was placed upon studying the kinetics of sulfidation using the above four sorbents. The reaction variables included temperature (700° to 1000°C), H_2S content (0.5%, 1%, 2%, and 3% in $\text{H}_2/\text{H}_2\text{S}$ gas mixtures), and pellet diameter of approximately 3, 5, and 8 mm. As was established in prior reports, the reduction power of the reducing gas is not sufficient in the sulfiding atmospheres chosen to allow reduction of MnO to Mn° . For these same reasons, it was not considered important in these scoping tests to consider the kinetics of reduction since there are no losses to be expected by evaporation as would be the situation with zinc-based sorbents.

Figure 2 is a schematic diagram of the experimental equipment employed for TGA testing. The lower right-hand portion of the diagram shows the pan assembly which suspends up to twelve pellets in a platinum basket hung via nichrome extension wire from a Cahn 1000-Series microbalance. The sample and hangdown assembly are contained in an alumina reaction tube, which is positioned in a high-temperature molybdenum-wound furnace. The gas delivery systems and data acquisition systems are as depicted. Vent gases are scrubbed in a sodium hypochlorite solutions prior to flaring and venting.

The results of these TGA tests are shown in Figures 3 through 8, studies on loading of pellets described below:

Figure 3 shows results of TGA analysis on the four selected sorbents which were described above. In this plot and each of the plots (Figs 4-8) which follow, the weight of the pellets divided by the initial weight is expressed on the ordinate as a weight ratio: W/W_0 . Initially, this ratio for all pellets is unity; however, there is a decline in this value (reduction of Mn_2O_4 to

MnO) when the pellets undergo reduction with hydrogen during the initial 20 minutes. The actual reduction data are not shown on this plot but rather a minimum asymptotic value is reached within about ten minutes and is seen in these plots as a horizontal line. After the passage of 45 minutes of prior reduction, all pellets remained constant in weight for at least 20 minutes.

At this time, hydrogen sulfide is added at 3% by volume to the gas which is flowing at a rate of 500 cc per minute. In the lower right-hand corner of the diagram are the theoretical maximum weight ratios which the pellets could exhibit based upon total conversion of the manganese in the pellet, as determined by chemical analysis, to the stoichiometry: MnS .

Upon examining these calculated values, one should note that the formulation which resulted from manganese originating from purified carbonate (i. e., FORM4-A) has a greater capacity for sulfur than the formulations which originate from the ore. Furthermore, dextrin-based formulations also yield higher sulfur capacities based upon the fact that dextrin volatilizes upon induration of the pellet; whereas, bentonite is a non-volatile impurity which effectively lowers the manganese content of the pellet.

The asymptote for time periods exceeding 90 minutes for formulation 4-A actually exceeds the calculated value for sulfur capacity, which may indicate that the original sulfur assay is slightly on the low-side. The asymptotic value for formulation 1-A is very close to the calculated value; whereas, the asymptote for 2-A (Moanda ore plus bentonite) falls below the calculated value indicating that some of the manganese may be chemically combined with silicate compounds in the ore and therefore not available to react with hydrogen sulfide.

In continuing the examination of Figure 3, one should note the rapid kinetics upon switching to the loading gas, which is most pronounced in formulation 4-A, i. e. manganese carbonate plus bentonite. Formulation 1-A (ore plus dextrin) has somewhat slower kinetics followed by formulation 2-A (ore plus bentonite).

Figure 4 shows similar results for tests conducted at 900°C. In this Figure, formulation 2-B (ore plus bentonite indurated for 1 hour at 1200°C) has been included in the analysis. Again formulation 4-A shows the highest sulfur capacity and the most rapid kinetics of the four pellet groups.

From Figure 5 it is seen that tests conducted at 800°C show somewhat slower kinetics again with the pellet groups showing similar trends in

kinetics. Pellet groups 1-A, 2-B and 2-A do not reach their asymptotic values for complete loading within the time frame shown (i. e. three hours).

In Figure 6 for loading studies at 700°C the kinetics are significantly slower so that only a fraction of the pellet capacity is utilized for all four formulations within the time-frame of the three-hour test regime.

Figure 7 is a composite of the data for formulation 4-A, the best of all the formulations studied, for the temperatures 700, 800, 900, 950, and 1000°C. The theoretical capacity for this formulation is shown as a dashed line on the plot with reactivity rates for all temperatures (except 700°C) being rapid. It should be noted that earlier pellet strength tests on manganese pellets originating from the carbonate and indurated at 1200°C were even superior in reactivity to similar pellets indurated at 1250°C; however, the strengths of these pellets indurated at the lower temperature were not sufficient to maintain the strength requirements which were imposed.

Figure 8 is a similar plot to Figure 7 except that it is for formulation 1-A.

Regeneration tests:

Regeneration tests were limited to gas atmospheres containing air plus nitrogen. They were not conducted in the TGA system shown in Figure 2 but rather they were conducted on twenty pellets contained in a ceramic "boat" placed within a horizontal tube furnace subjected to loading in hydrogen plus hydrogen sulfide (3% H₂S) for exposure times of four hours at 800°C. In Figure 9 the time requirement to reach 90% regeneration is plotted against the number of cycles (expressed as "Run #") on the abscissa. For this plot formulation 1 was used. The regeneration was conducted at a temperature of 1000°C. The sulfur emerging from the system was determined by titration of the exit gas after it was sparged through an alkaline solution of peroxide and the amount of titer measured to calculate the quantity of sulfur emitted. The percent regenerated is actually determined as a function of the asymptotic value associated with no further demand for titer in the sparged solution. Typically, regeneration was complete in about 20 minutes; however, the regeneration was allowed to proceed for one hour to assure no further reaction.

In this figure (Figure 9), the time to reach 90% regeneration is seen to be initially high for fresh pellets and decline as the number of cycles increased. This increased rate of regeneration may be a result of cracking of pellets, which was observed under an optical microscope. This

improvement in reaction kinetics with repeated cycling is consistent with earlier observations by Turkdogan. Figure 9 shows that the per cent of the theoretical sulfur released is relatively constant at 85% over the ten cycles studied.

Finally in Figure 10, the kinetics of the regeneration tests are exhibited by examining the rate of titration of the acid gas released. It is seen that there is actually an increase in rate of regeneration with increasing cycles of loading with cycle 10 exhibiting significantly more rapid regeneration kinetics than cycle 2. Again this effect may be a result of micro-cracks in the pellet. Further study on the kinetics of cyclic loading and regeneration via TGA analysis is required along with microscopic examination of the pellets in both loaded and regenerated condition is required before final conclusions can be reached regarding the mechanism of this enhanced effect.

BENCH-SCALE TEST UNIT

A reactor system, pictured in Figure 11 has been constructed and tested. This Figure, which is a schematic of the reactor detail, shows the two-inch (I.D.) closed-end alumina reactor furnace tube equipped with an alumina perforated-disc plate suspended over alumina chips. A simulated coal 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, ranging from 800 to 1100°C then 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 (labeled in Figure 11 as GC).

The overall Schematic Diagram of the Experimental Arrangement for the Fixed-Bed Tests is shown in Figure 12. 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 flow-meters 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 mentioned above.

Initial testing will, however, be conducted using only hydrogen in

combination with hydrogen sulfide in a manner similar to that conducted by E. T. Turkdogan in his studies as discussed previously. After corroboration of his test results, then the gas mixture referred to above will be used as a loading gas.

Loading will continue at a rate of 2.5 liters per minute until break-through is observed. Breakthrough is defined as a sudden rise in the sulfur content of the gas as determined by gas chromatography. The bed will then be flushed with nitrogen in order to expel remaining hydrogen and a regeneration gas consisting of air plus nitrogen will be initiated with the sulfur content of the gas being continuously analyzed for sulfur dioxide. The regeneration step will be discontinued when the bed is 95% regenerated as determined by an approximate mass balance of the system based upon the calculated sulfur content of the off gas. The loading and regeneration cycles will then be repeated until at least ten cycles have been completed.

SUMMARY AND CONCLUSIONS TO DATE

Four sorbent formulations have been prepared using Moanda ore and manganese carbonate as starting materials in combination with alumina. Both dextrin and bentonite have been employed as bonding materials for pellet formation; however, dextrin, which appears to produce favorable porosity and is volatilized upon induration is a preferred binder. All pellets made met strength requirements. The carbonate required an induration temperature of 1250°C; whereas, the oxide (ore) requires an induration temperature of 1200°C.

Single loading tests via TGA analysis at temperatures ranging from 700°C to 1000°C show that the manganese carbonate source material bonded with bentonite exhibits the best combination of loading capacity and kinetics. Higher temperatures for loading (i. e. 800° to 1000°C) show much more favorable kinetics than at 700°C; however, the thermodynamics of sulfur removal in terms of the terminal sulfur levels achievable become less favorable (as described in the prior Quarterly Report).

A limited series of regeneration tests show that the kinetics of regeneration appear to improve with cyclic loading possibly as a result of micro-crack formation as seen by optical microscopy. These radial microcracks appear not to significantly impair pellet strength.

FUTURE WORK PLANS

Future work will continue characterization 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.

- 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).
- 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, and manganese ore-based bonded with dextrin and indurated at 1200°C for 2-hours.

Figure 1. Strength of Pellets from Several Induration Campaigns

FIGURE 2. SCHEMATIC DIAGRAM OF ASTRO-TGA APPARATUS

Figure 3. Normalized Weight vs. Time for Sulfidation of Three Formulations at 1000° C in a 3% H₂S-H₂ Gas Mixture.

Figure 4. Normalized Weight vs. Time for Sulfidation of Three Formulations at 900°C in a 3% H_2S - H_2 Gas Mixture.

Figure 5. Normalized Weight vs. Time for Sulfidation of Three Formulations at 800°C in a 3% H_2S - H_2 Gas Mixture.

Figure 6. Normalized Weight vs. Time for Sulfidation of Three Formulations at 700°C in a 3% H_2S - H_2 Gas Mixture.

Figure 7. Effect of Temperature on Sulfidation Kinetics of Sorbent FORM4-A

Figure 8. Effect of Temperature on Sulfidation Kinetics of Sorbent FORM1-A

Figure 9. Time Required to Reach 90% Regeneration for Several Sulfidation and Regeneration Cycles

Figure 10. Comparison of Regeneration Kinetics of Recycled Pellets

Figure 11. Schematic of Fixed-Bed Reactor Details

Figure 12 Schematic of Overall Experimental Arrangement for Fixed-Bed Tests

**HOT COAL GAS DESULFURIZATION
WITH MANGANESE-BASED SORBENTS**

Progress Report for the Period April 1, 1993 to June 30, 1993

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**For:
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Morgantown Energy Technology Center
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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 ferrite and zinc titanate sorbents; however, prior studies at the U. S. Steel Fundamental Research Laboratories in Monroeville, PA, by E. T. Turkdogan¹ 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 higher temperatures than zinc ferrite or zinc titanate.

This report gives the thermodynamic background for consideration of manganese-based sorbents as an alternative to zinc ferrite. To date the work which has been in progress for nine months is limited at this stage to thermogravimetric testing of four formulations of manganese-alumina sorbents to determine the optimum conditions of pelletization and induration to produce reactive pellets.

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.

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), and which appear to be capable of improved loading with

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.

each cycle and also load sulfur to a higher weight of pellet. 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% Comilog 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 pure manganese as a carbonate in a reactive form.⁴

In this current program the following studies are being addressed:

- preparation and characterization of manganese-based sorbents,
- the thermodynamics and kinetics of sulfur removal from hot fuel gases by this sorbent, and
- the cyclic loading and regeneration of the sorbent by oxidation and recovery of the sulfur.

This study will update 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

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.

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.

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 15 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

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 thermo-gravimetric analysis (TGA). Preliminary TGA tests are showing that sorbents prepared with the organic binder, dextrin, on Comilog ore appear to offer the best combination of strength, reactivity, and capacity
- 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

This section considers the reaction equilibria in the sulfidation and regeneration cycles. There are four oxides of manganese: MnO, Mn₃O₄, Mn₂O₃, and MnO₂. Figure 1 gives the oxygen potential as a function of temperature for converting oxides with superimposed equilibrium CO₂/CO ratios in the gas phase. As indicated by the dotted lines, MnO cannot be reduced to metallic manganese by CO or H₂ because of the unavoidable presence of trace amounts of CO₂ and H₂O in the reducing gas. In addition, the higher oxides of manganese are readily reduced to MnO even in very slightly reducing atmospheres.

The reducing gas is desulfurized by MnO according to the following reaction:

The equilibrium ratio of H₂O/H₂S for this reaction, as determined by Turkdogan and Olsson¹, is given by:

$$\text{Log}\left[\frac{p\text{H}_2\text{O}}{p\text{H}_2\text{S}}\right] = \frac{3330}{T} - 0.310 \quad (2)$$

In the desulfurization of hot reducing gases by MnO-based pellets, the extent of desulfurization achieved depends on the temperature and gas composition. The residual H₂S concentration in the desulfurized gas, calculated, using SOLGASMIX⁵, for the conditions of gas-solid equilibrium in the reactor, is shown in Figure 2 as a function of temperature for various typical oxygen-blown and air-blown gasifier gases⁵ the compositions of which are reported in Appendix A. It is seen from this figure that the lower the operating temperature and the lower the H₂O/H₂S ratio, the lower is the residual sulfur in the cleaned gas.

Most sulfur sorbents can be regenerated after sulfidation by reacting the sulfide with a CO₂-H₂O mixture. The decomposition of MnCO₃ to MnO occurs at 343°C with CO₂ evolving at one atmosphere. Because of this undesirable equilibrium condition, MnO cannot be regenerated by using a CO₂-H₂O mixture.

⁵SolgasMix Computer Program version by Morris, A. E., Flynn, H., and Carter, D: "Using the UMR Stepsol Package," Version 4.0 Released Feb., 1, 1990, Generic Mineral Technology Center for Pyrometallurgy, University of Missouri, at Rolla.

If the regeneration gas consisted of pure H_2O or CO_2 , the regeneration can be represented by the following reactions:

However, these two routes are not practically feasible because of the low SO_2 concentration in the product gases.

According to the above analysis, the regeneration of MnO must be oxidative, i.e., involving air, pure oxygen, oxygen-enriched air, oxygen-deficient air, or $\text{SO}_2\text{-O}_2$ mixture. It follows that we should consider the phase equilibria in the Mn-S-O system in the temperature range of interest to regeneration. Figure 3 is a stability equilibrium diagram for the Mn-S-O system at 800, 1000, and 1200°C. The logarithms of the equilibrium SO_2 and O_2 partial pressures represent the ordinate and abscissa, respectively.

As can be seen from Figure 3, the stoichiometric regeneration of the oxide by reacting the sulfide with an O_2 -containing regeneration gas at atmospheric pressure, the partial pressure of SO_2 in the product gas can never be high enough to form MnSO_4 at temperatures above 900°C. Consequently, under these conditions the overall reaction is:

The above reaction is thermodynamically favorable and proceeds essentially to completion in the temperature range 900 to 1200°C. Thus, the oxygen in the reactant gas is virtually converted to SO_2 . For example, if an $\text{O}_2\text{-SO}_2$ gas mixture is used, the product gas would be pure SO_2 for complete conversion. The regenerated manganese oxide would be in the form of Mn_3O_4 which should be subsequently reduced to MnO prior to recycle to the sulfidation stage. The maximum temperature of both sulfidation and regeneration can be as high as 1232°C, the eutectic temperature of the pseudo-binary system MnO-MnS .

It should be noted, however, that the oxidative regeneration of the oxide with the fore-mentioned gas is highly exothermic. Practical problems may be encountered in the control of the reactor temperature. This may be overcome by using a $\text{CO}_2\text{-H}_2\text{O-O}_2$ gas mixture where, in addition to the exothermic oxidation of MnS by O_2 , additional endothermic reactions may occur:

MnO is converted to Mn_3O_4 because of the availability of O_2 in the gas.

EXPERIMENTAL PROCEDURES AND RESULTS

Since the prior studies by Turkdogan and Olsson were conducted on a manganese ore (Comilog ore), the starting point for the present investigation is using similar materials for comparison. Then manganese oxide derived from pure carbonate, similar to that which would be recovered from in-situ mining is studied. Accordingly, the following materials are being utilized: (Chemical analyses are reported in Appendix B)

- MnO_2 Comilog ore (Africa);
- Ultrafine MnCO_3 (93-95%) (Chemetals, Inc.);
- Alundum (96.6% Al_2O_3) (Norton Materials, Inc.);
- Bentonite, inorganic binder (Aldrich Chemical Co.); and
- Dextrin, an organic binder.

Pelletization:

Blends consist of a manganese-containing compound, an alumina-based matrix, and a binder, based on desired compositions determined on a dry weight-percent basis. The amount of binder used should be as low as possible, not only to save on the cost, but also to provide a greater amount of chemically active sorbent in a given volume of packed bed. After each blend is mixed, an appropriate amount of water is added prior to pelletizing.

Pelletization is accomplished using a balling tire at a 40-60° inclination and a rotational speed of 40-50 rpm. Feed is prepared by adding binder to the dry mix, and mulling while adding water slowly to form a cohesive state. Moisture is added in controlled quantities via hand spray to the mix which is then passed through a 10-mesh sieve.

Seeds are prepared by moistening the tire interior, wiping it clean, and then slowly sprinkling about 7 wt.% of the prepared, moist feed mixture

into the tire rotating at 50 rpm. When seeds begin to form, they are removed and sieved through a 6-mesh screen. Fines are returned to the tire. This procedure is continued until all the feed has been agglomerated. Ideally, the seeds range between 2 to 3 mm in diameter.

In the subsequent balling operation, the seeds are returned to the rotating tire and sprayed to the glistening point (a visual observation of surface appearance). Spray is applied as needed to reach the incipient glistening point during the balling operation. When all the loose feed has been assimilated, the product is removed and screened to retain the 7 to 10-mm fraction. The moist pellets are stored in sealed containers pending evaluations.

The above two-step pelletizing procedure, in which seeds are first prepared, largely eliminates further seed formation during the balling step and the presence of undersized balls in the final gross product. The required moisture content for the feed depends on its average density. Balling is known to be optimal at 30 to 35% moisture on a volume basis, i.e., the approximate void fraction in dried pellets. For 33% moisture on a volume basis, it can be shown that the required amount of water to be added is given by the following equation:

$$Wt.\%H_2O = \frac{100}{[1 + \frac{67}{33} * (\rho_{Av})]} \quad (13)$$

where ρ_{Av} is the average density of the feed.

The average ball size in the gross product is dependent upon the number of seeds and the amount of new feed added to them. If too few seeds are used, not all the feed can be added; if too many, the feed may run out before the desired ball size is reached.

Following the above procedure, four formulations have been prepared:

- 1) 75 g comilog ore; 25 g alundum; 10 g dextrin
- 2) 75 g comilog ore; 25 g alundum; 2 g bentonite
- 3) 121 g manganese carbonate; 25 g alundum; 10 g dextrin
- 4) 121 g manganese carbonate; 25 g alundum; 2 g dextrin.

(Note that calcination of manganese carbonate reduces its mass from 121 g to 75 g manganese oxide).

Induration:

The pellets were dried to a constant weight at 110°C and then indurated. Induration is being conducted for a 12-hour cycle in air: heating from 25°C

to 300°C over a period of 1 hr; heating from 300°C to 400°C over a period of 4 hours (343°C is the decomposition temperature of manganese carbonate); heating from 400°C to 1200°C over a period of 5 hrs; and then holding at 1200°C for two hours for the ore samples and 1250°C for the carbonate samples; furnace cool overnight to room temperature. The room-temperature crush strength of the pellets has been found to be as high as 82 pounds dead weight (on a pellet of 5-8 mm in diameter).

The following are some preliminary data obtained using the above combinations of raw materials:

Formulation 1

- Moisture content of pellets: 12%
- Room Temperature green crush strength : 5.5 lbs
- Induration at T= 1200°C: weight loss was 13%
- Room temperature crush strength of indurated pellets: 72 lbs.

Formulation 2

- Moisture content of pellets :10.5 %
- Room Temperature green crush strength : 6.5 lbs
- Induration at T= 1200°C: weight loss was 11%
- Room temperature crush strength of indurated pellets: 85 lbs

Formulation 3

- Moisture content of pellets : 12.5%
- Room Temperature green crush strength : 3 lbs
- Induration at T 1250°C: weight loss was 40%
- Room temperature crush strength of indurated pellets: 35 lbs.

Formulation 4

- Moisture content of pellets :11 %
- Room Temperature green crush strength : 3.5 lbs
- Induration at T= 1250°C: weight loss was 38%
- Room temperature crush strength of indurated pellets: 42 lbs

Pellet Porosity and Surface Area

BET surface area tests on indurated pellets have shown them to have a surface area less than 0.2 m²/gm, which is below the sensitivity of our equipment. We are attempting to increase pellet surface area; however, TGA testing at this time does show them to be about as reactive as the zirconium titanate pellets which have been studied by other investigators.

Porosity tests made by combination of aqueous picnometry on crushed pellets from formulation 2 in combination with mercury picnometry showed the pellets to have a porosity of about 36%

Scoping Tests via TGA on Pellet Reactivity:

The reduction, sulfidation, and regeneration behavior of the above four formulations of manganese-based sorbents are being studied via TGA in alternate loading and regeneration cycles in scoping tests on individual pellets. The selection criteria for a "good" sorbent will be based upon strength (a minimum of 15 pounds dead weight on a 5-mm diameter pellet), surface area ($>2\text{m}^2/\text{g}$), sulfur capacity ($>70\%$ conversion of MnO to MnS), resistance to breakdown upon cycling, rate of loading (90% loaded in a 3 vol% H_2S atmosphere within 120 minutes), and rate of regeneration (90% regeneration in air within 10 minutes).

To date, all four formulations appear to satisfy these criteria; however, multiple cyclic loading has not yet been completed beyond three cycles per pellet.

The temperature ranges for loading which are being studied are between 600°C to 1000°C ; and for regeneration between 1050° to 1200°C . An optimum induration temperature for the dried pellets appears to be 1200°C for the comilog ore to 1250°C for the MnCO_3 .

Gas atmospheres in the preliminary loading tests on individual pellets are confined to pure hydrogen gas spiked with 3 vol% hydrogen sulfide.

Regeneration tests are limited to gas atmospheres containing air plus nitrogen. The provisional gas atmosphere for the fixed-bed loading tests is a gas composition simulating the Tampella U gas composition: 24.33% CO , 5.16% CO_2 , 13.19% H_2 , 5.35% H_2O , 0.118% H_2S , 5.35% H_2O , balance nitrogen, with the exception that the hydrogen sulfide level will be varied between 1 and 3% to achieve earlier break-through.

The Stanton-Redcroft unit which we have currently been using enables us to conduct only single-pellet tests; however, a Cahn micro-balance system has been made available to this study at the U.S. Bureau of Mines, Twin Cities Research Laboratories. This unit which is equipped with on-stream gas analysis can handle up to five pellets for each test. The use of this unit should accelerate testing.

Results of Scoping Tests (TGA):

Some representative scoping loading tests conducted on ca. 150 mg pellets using pure hydrogen followed by hydrogen containing 3 vol % H_2S are

summarized in Figures 4-7, which show the reduction and sulfidation kinetics of several of the formulations. All tests were for gas flow rates of 150 ml per minute, which represents an average superficial gas velocity of 35 cm per second corrected for a temperature of 800°C. Under these conditions, the maximum rate of delivery of sulfur to the pellet during the sulfidation portion of the test is at least 5 mg/minute, which is sufficiently high so as to assure that the kinetics are not controlled by the rate of input of sulfur to the system but rather are a result of either surface reaction kinetics or diffusion within the pellet.

In these figures, the weight of the pellet divided by its initial weight (W/W_0) is plotted against time in minutes for individual pellets tested at several temperatures. Figure 4 is for formulation 2 (i.e., Comilog ore plus alundum bonded with bentonite). The horizontal dashed lines on this figure drawn to represent the following calculated conditions: The line passing through 1.000 on the ordinate is for the initial mass ratio of the indurated pellet prior to reduction with the manganese represented by the formula Mn_3O_4 (sesqui-oxide). The lowest line represents the mass fraction for this formulation at which all the sesqui-oxide is converted to the monoxide (MnO). The top line represents the mass fraction which would occur upon complete reaction of the monoxide to the monosulfide (MnS). For the test "TGA Run 2-10-1" conducted at 700°C, (represented by open triangles) the first thirty minutes of the test are for exposure of the pellet to pure hydrogen (no H_2S). The start of the test was established by switching the gas atmosphere from nitrogen, which was used as an inert gas blanket during heat up of the pellet to hydrogen. The incubation period of 2 minutes did not appear for higher temperatures. The sharp loss of weight following this period represents the rapid reduction of the sesqui-oxide to the monoxide. The drop in mass ratio below the calculated composition of the monoxide may be a result of sub-oxide formation. After 30 minutes, when no further significant weight loss occurred the gas mixture was switched to hydrogen containing 3 vol % H_2S . The initial rapid weight gain followed by a more gradual rise after the first ten minutes occurred over the next hour.

The second plot for Run 1-15-1 conducted for another pellet of the same formulation at 900°C (solid squares) showed no initial incubation period and a similar reduction to the composition MnO occurring over a 40 minute period, after which the gas atmosphere was switched to the sulfidizing gas. For this higher temperature test, a more rapid rate of rise in weight is noted and a more rapid asymptotic approach to the composition MnS occurred over the subsequent 60-minute period for sulfidation.

Figure 5 includes the prior two tests on a time axis extended to 150 minutes. Also included in this figure is loading data for Run 4-12-1 for formulation 1 (Comilog ore plus alumina and dextrin) conducted at 800°C (half-filled circles). The time to achieve reduction of the sesqui-oxide to the monoxide is only 15 minutes. At this time the gas mixture was changed to sulfidizing and rose rapidly to become congruent with the Run 1-15-1 for formulation 2 conducted at 900°C. This test was continued for 130 minutes. The test results show an asymptotic approach to the MnS line. The gas mixture was then shifted to nitrogen plus air for a first regeneration starting at 120 minutes. The rapid drop in mass, associated with the conversion of the sulfide to the monoxide occurred over the next hour with an asymptotic approach to the initial mass associated with the sesquioxide composition.

Figure 6 compares the four formulations at tests conducted at 800°C. The comparison is made after a prior reduction step. The curves represent in descending vertical order formulations 1,2,3,and 4. In comparing these four formulations, the dextrin binder is somewhat superior to the bentonite binder with respect to kinetics and ultimate loading capacity. This effect may be a result of the increase in porosity of the pellet bound with an organic binder (dextrin) compared with the inorganic binder (bentonite). As the pellet is indurated, the dextrin would be expected to volatilize leaving a greater interconnected porosity.

As of this writing (6/14/93), only one formulation (# 1) has been subjected to limited cyclic testing in which loading is followed by regeneration in an air atmosphere at 1050°C. Figure 7 for loading and regeneration gives the results of cyclic testing for three cycles. The reduction in rate and capacity over three cycles is barely perceptible within the precision of the equipment.

SUMMARY AND CONCLUSIONS TO DATE

Four sorbent formulations have been prepared using comilog ore and manganese carbonate as starting materials in combination with alumina. Both dextrin and bentonite have been employed as bonding materials for pellet formation; however, dextrin, which appears to produce favorable porosity and is volatilized upon induration is a preferred binder. All pellets made met strength requirements. The carbonate required an induration temperature of 1250°C; whereas, the oxide (ore) requires an induration temperature of 1200°C.

Limited cyclic testing on individual pellets showed very little decline in kinetics and sorbent capacity over three cycles of loading and regeneration.

FUTURE WORK PLANS

Future work will continue characterization 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.

- **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).**
- **Perform bench-scale tests on the optimum sorbent pellets in a two-inch diameter reactor.**

Figure 1. Stability Diagram of Mn-O System as a Function of Oxygen Potential (P_{CO_2}/P_{CO}) and Temperature

Figure 2. Equilibrium H_2S Concentration in Desulfurized Gas as a Function of Temperature for Typical Air-Blown and Oxygen-Blown Gasifiers

Figure 3. Stability Diagram for the Mn-S-O System at 800°, 1000°, and 1200°C

Figure 4. Kinetics of Loading on Formulation 2 via TGA at 700° and 900°C

Figure 5. Kinetics of Loading at two Temperatures for Formulation 2 Compared with Loading and Regeneration Using Formulation 1

Figure 6. Comparative Loading Kinetics for Four Formulations at 800°C

Figure 7. Tests on Cyclic Loading (800°C) and Regeneration (1050°C) for Formulation 1

Appendix A. Typical Gasifier Exit Gas Compositions (Vol.%): (Typical Air-Blown Gasifier: GE Fixed-Bed (A & G), KRW Fluid-Bed (B & F), Texaco Entrained-Bed (C & H), and Lurgi Fixed-Bed (D), Tampella U-Gas (I); and Typical Oxygen-Blown Gasifiers: Texaco Entrained-Bed (J) and Shell (K).

(Vol.%)	A	B	C	D	E	F	G	H	I	J	K
CO	8.00	10.55	16.13	11.90	40.00	15.0	8.0	15.25	24.33	39.10	64.0
CO ₂	11.0	4.64	7.55	10.00	12.50	5.0	11.0	8.28	5.16	12.25	0.8
H ₂	16.0	8.26	10.70	17.40	27.84	10.0	15.0	10.79	13.19	30.13	31.6
H ₂ O	30.0	27.52	10.94	28.10	18.50	15.0	30.0	10.76	5.35	17.52	1.5
H ₂ S	3.00	0.28	0.42	1.00	1.08	0.5	0.5	0.5	0.118	1.00	1.4
COS	---	---	0.03	---	0.08	---	---	---	---	---	---
N ₂	29.0	48.73	54.22	28.70	---	53.7	32.2	53.92	49.90	---	0.7
CH ₄	3.00	0.24	---	3.00	---	0.5	3.0	---	1.84	---	---
NH ₃	0.50	0.02	0.1600	0.500	0.200	0.3	0.3	---	0.111	--	---
CO/CO ₂	0.73	2.27	2.14	1.19	3.20	3.00	0.73	1.84	4.72	3.19	80.0
H ₂ /H ₂ O	0.53	0.30	0.98	0.62	1.50	0.67	0.50	1.00	2.47	1.72	21.0

Note: Gas compositions A through E were provided by METC and those of F through K were supplied by R. Gupta from Research Triangle Institute.

APPENDIX B
Assays of Raw Materials

1) "Moanda" Comilog Ore (African Manganese Dioxide Ore): Received from: The Prince Manufacturing Company.

Typical Chemical Analysis of Comilog Ore

Species	Wt.%	Species	Wt.%	Species	Wt.%
Mn	51.2	P	0.109	S	0.019
MnO ₂	77.0	Co	0.099	V	0.012
MnO	3.36	CaO	0.08	As	0.007
Al ₂ O ₃	6.01	Zn	0.064	Cr	0.006
Fe	2.81	MgO	0.06	Mo	0.006
SiO ₂	2.56	Ni	0.058	Pb	0.004
K ₂ O	0.71	Cu	0.05	H ₂ O (bound)	5.16
BaO	0.22	CO ₂	0.04		
TiO ₂	0.22	Na ₂ O	0.04		

2) Alundum Fepa F, Size 600, Code 7102
Received from: Norton Industrial Ceramics Corporation
Typical Chemical Analysis

Species	Al ₂ O ₃	TiO ₂	SiO ₂	Fe ₂ O ₃	CaO	MgO	S	K ₂ O
Wt.%	96.60	2.60	0.60	0.20	0.10	0.40	0.02	0.02

3) Manganese Carbonate: Received from Chemetals, Inc.
This product contains approximately 93-95% MnCO₃; no typical analysis is available at the present time.

upon Comilog ore containing 51.2% Mn by weight. In this table, the following reactions were employed to determine the theoretical capacity of sulfur per 100 grams of sorbent:

Table I.
Theoretical Sorbent Capacities

Sorbent	Theoretical Capacity, g S/100 g of sorbent
Zinc Ferrite	39.8
Zinc Titanate	23.8
Mn Ore-based	24.0

Clearly, the Manganese ore-based sorbent pellet compares favorably with the optimized formulation of zinc titanate which was used extensively in pilot-scale and process development work.

- The ultimate degree of desulfurization, based upon measured and thermodynamic analysis of manganese-based pellets as compared with zinc-based material is less favorable as shown in Figure 1 (Figures follow p 13).
- Likewise in Figure 2, the rate of loading of manganese-based pellets compares favorably with zinc-based pellets especially upon multiple cycling". Since the loading behavior of Mn-based pellets is essentially independent of temperature between 700 and 1300°C⁶ and that of zinc titanate pellets is independent of temperature between 650 and 760°C¹⁷, a comparison between Mn-based pellets at 800°C and zinc titanate at 760°C is quite reasonable and valid. The regeneration data, however, cannot be compared for the same temperature because the zinc

^{**}This figure will be improved in the final proposal to include data on multiple cycling of Zn- and Mn-based sorbents.

Table II. Typical Gasifier Exit Gas Compositions (Vol.%): (Typical Air-Blown Gasifier: GE Fixed-Bed (A & G), KRW Fluid-Bed (B & F), Texaco Entrained-Bed (C & H), and Lurgi Fixed-Bed (D), Tampella U-Gas (I); and Typical Oxygen-Blown Gasifiers: Texaco Entrained-Bed (J) and Shell (K)).

(Vol.%)	A	B	C	D	E	F	G	H	I	J	K
CO	8.00	10.55	16.1	11.9	40.0	15.0	8.0	15.2	24.33	39.1	64.0
CO ₂	11.0	4.64	7.55	10.0	12.5	5.0	11.0	8.28	5.16	12.2	0.8
H ₂	16.0	8.26	10.7	17.4	27.8	10.0	15.0	10.7	13.19	30.1	31.6
H ₂ O	30.0	27.52	10.9	28.1	18.5	15.0	30.0	10.7	5.35	17.5	1.5
H ₂ S	3.00	0.28	0.42	1.00	1.08	0.5	0.5	0.5	0.118	1.00	1.4
COS	---	---	0.03	---	0.08	---	---	---	---	---	---
N ₂	29.0	48.73	54.2	28.7	---	53.7	32.2	53.9	49.90	---	0.7
CH ₄	3.00	0.24	---	3.00	---	0.5	3.0	---	1.84	---	---
NH ₃	0.50	0.02	0.16	0.50	0.20	0.3	0.3	---	0.111	---	---
CO/CO ₂	0.73	2.27	2.14	1.19	3.20	3.00	0.73	1.84	4.72	3.19	80.0
H ₂ /H ₂ O	0.53	0.30	0.93	0.62	1.50	0.67	0.50	1.00	2.47	1.72	21.0

The capability of regenerating Mn-based sorbents has been previously discussed^{2,6} and it was established that this regeneration must be oxidative, i.e., involving air, pure oxygen, oxygen-enriched air, oxygen-deficient air, or SO₂-O₂ mixture. It follows that we should consider the phase equilibria in the Mn-S-O system in the temperature range of interest to regeneration. Figure 5 is a stability equilibrium diagram for the Mn-S-O system at 800, 1000, and 1200°C. The logarithms of the equilibrium SO₂ and O₂ partial

Figure 1. Comparison of Equilibrium Concentration of H_2S in Desulfurized Gas as a function of Temperature for Manganese-Based and Zinc-Based Sorbents.

Figure 2. Comparison of Loading Kinetics via TGA of Mn-Based and Zn-Based Sorbents.

Figure 3. Oxygen Potential Diagram for the Mn-O System Showing Lines of Constant CO_2/CO Pressure Ratios

Figure 4. Equilibrium H_2S Concentration in Desulfurized Gas as a Function of Temperature for Typical Air-Blown and Oxygen-Blown Gasifiers.

Figure 5. Stability Diagram for the Mn-S-O System at 800, 1000, and 1200°C.

Figure 6. SO_2 Content of Regeneration Product Gas (on Wet & Dry Basis) as a Function of Feed Gas Composition. Feed Gas is at 800°C and Regeneration at 1100°C.

Figure 7. Representation of a Reacting Mn-Based Sorbent Pellet when Rate Controlling Steps are: a) Diffusion through the Gas Film, b) Diffusion through the Product Layer, and c) Surface Reactions

Table III. Time-Conversion performance equations for sulfidation and regeneration reactions using the shrinking-core model

Rate-Limiting	Sulfidation Reaction	Regeneration Reaction
Gas-Film	$F_{MnO} = \frac{3k_s(P^{\circ}_{H_2S} - P^e_{H_2S})}{RT\rho_{MnO}R_p} t$	Highly unlikely
Product Layer	$3-2F_{MnO}-3(1-F_{MnO})^{2/3} = \frac{6D_e(P^{\circ}_{H_2S}-P^e_{H_2S})}{RT\rho_{MnO}R_p^2} t$	$3-2F_{MnS}-3(1-F_{MnS})^{2/3} = \frac{9D_eP}{RT\rho_{MnS}R_p^2} \ln\left[\frac{5P-2P^e\alpha_1}{5P-2P^{\circ}\alpha_1}\right] t$
Surface Reaction	$1-(1-F_{MnO})^{1/3} = \frac{k_s(P^{\circ}_{H_2S}-P^e_{H_2S})}{RT\rho_{MnO}R_p} t$	Highly unlikely

**HOT COAL GAS DESULFURIZATION
WITH MANGANESE-BASED SORBENTS**

**Second Technical Report for the Period December 1, 1992 to March 1,
1993**

**By
M. T. Hepworth**

March 1, 1993.

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

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

**By:
Malcolm T. Hepworth, Department of Civil and Mineral Engineering
University of Minnesota, Minneapolis, MN**

INTRODUCTION

At present, the focus of work being performed on Hot Coal Gas Desulfurization is primarily in the use of zinc ferrite and zinc titanite sorbents; however studies at the U. S. Steel Fundamental Research Laboratories in Monroeville, PA, by E. T. Turkdogan¹ indicate that an alternate sorbent, manganese dioxide-containing ore in mixture with alumina (75 wt% ore + 25 wt% Al_2O_3) may be a preferable alternative to zinc-based sorbents.

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 pure manganese as a carbonate in a reactive form.

In the current program the following studies will be addressed:

- Preparation of manganese sorbent pellets and characterization tests on pellets for strength and surface area;
- Analysis of the thermodynamics and kinetics of sulfur removal from hot fuel gases by individual sorbent pellets (loading tests) by thermogravimetric testing;
- Regeneration tests via TGA on individual sorbent pellets by oxidation;
- Bench-scale testing on sorbent beds in a two-inch diameter reactor.

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

Gas atmospheres in the preliminary loading tests on individual pellets will be confined to hydrogen/water vapor mixtures spiked with 3 vol% hydrogen sulfide. Regeneration tests will be limited to gas atmospheres containing air plus nitrogen; the provisional gas atmosphere for the fixed-

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.

bed loading tests was decided upon at METC with the sponsor to be a gas composition simulating the Tampella U gas composition²: 24.33%CO, 5.16%CO₂, 13.19%H₂, 5.35% H₂O, 0.118% H₂S, 5.35% H₂O, balance nitrogen, with the exception that the hydrogen sulfide level will be varied between 1 and 3% to achieve earlier break-through.

PROGRESS TO DATE ON PROGRAM

Overall Observations:

A review of the experimental test plan from the November 16 meeting with the sponsor in Morgantown was presented in Appendix A of the prior Quarterly Report (Issued 12/1/93) and will not be repeated here.

More recently at a meeting held at METC on January 28, 1993, the following observations were made:

- Dr. E. T. Turkdogan in discussing his prior successful tests at the U. S. Steel Research Center compared the relative merit of lime, zinc oxide, and manganese oxide as desulfurizers as expressed in terms of the ratio of water vapor pressure to hydrogen sulfide pressure as a function of temperature. Although zinc-based compounds can attain a higher degree of desulfurization than manganese-based sorbents for a given total hydrogen content of the hot fuel gas, he indicated that over twenty cycles of loading and regeneration he saw no loss of reactivity of manganese-based sorbents when loaded and regenerated at elevated temperatures (700-900°C). Over this range of testing he observed manganese/alumina sorbents increased in reactivity with each cycle of loading, precluding the likelihood of sintering.

Dr. Turkdogan also has re-evaluated the thermodynamic data for the Manganese-Oxygen-Sulfur system, comparing his observations with other investigators. This comparison is presented in Appendix A to this report.

²Tampella U gas also contains 0.111% NH₃ and 1.84% CH₄, which will be disregarded in this study.

- The second observation was made that our prior plan to load our manganese-based sorbents at high temperatures, e. g., 900°C (1652°F) exceeds the temperatures required for combined-cycle operation. Presently the upper limit of turbine operation is 1100°F (593°C). Although Turkdogan did not operate his pellets in loading conditions this low in temperature, we should, in our initial tests, determine whether the reaction kinetics after several loading and regeneration cycles are as good for the manganese-based pellets as those reported with zinc ferrite. If the kinetics are poorer for manganese-based pellets, then the loading temperature can be raised but with some reduction in ultimate level of sulfur which can be removed as compared with zinc-based sorbents.
- As a third observation, upon regeneration, sulfation can be avoided by regenerating at temperatures above 1100°C (2012°F) (See Figure 1). These elevated temperatures can be achieved in practice by allowing the bed to rise in temperature by the exothermic reactions associated with the oxidation of sulfur. Initial regeneration studies will be made at this temperature and the results will be discussed in the next quarterly report.

Current Status of Test Work:

Starting materials:

Chemetals, Inc. is the source of manganese carbonate. Comilog ore (predominantly MnO₂ from Prince Mfg. Corp.) The purpose of using this material is to determine if the prior studies at U.S. Steel by E. T. Turkdogan in the late 1970's can be reproduced. Reagent grade manganese carbonate from the Chemetals source will be used as the standard against which material to be received from the U. S. Bureau of Mines as a product from their in situ mining project will be compared.

Pelletization:

Additives including Dextrin (5%) and Bentonite (2%), are being employed in a previously documented procedure (Appendix A of the prior Quarterly Report). Induration is being conducted for a 12-hour cycle in air: heating from 25°C to 300°C over a period of 1 hr; heating from 300°C to 400°C over a period of 4 hours (343°C is the decomposition temperature of manganese carbonate); heating from 400°C to 1200°C over a period of 5 hrs; and then holding at 1200°C for two hours; furnace cool overnight to room temperature. The room-temperature crush strength of the pellets has been found to be as high as 42.5 pounds dead weight (on a pellet of 5-8 mm in diameter). BET surface area measurements are pending.

Thermodynamics: The thermodynamics of the Mn-S-O system is being updated via help of our consultant, Dr. E. T. Turkdogan. Preliminary indications are that the theoretical calculations exhibit higher sulfur overpressures than were determined by experiment. (See Appendix A to this report).

Available raw materials:

- A small sample of MnCO_3 : Brought by Mr. R. Ben Slimane from the USBM - Salt Lake Laboratories.
- Manganese Ore obtained from the USBM Twin Cities Laboratories
- Manganous-oxide (MnO) ore obtained from Chemetals in Baltimore (55-83% MnO).
- Ultrafine MnCO_3 (93-95%) obtained from Chemetals.
- MnO_2 Comilog ore (Africa).
- MnO_2 ore (Australia)

(See Tabular data attached for assays on several of the feed stocks).

- Alundum (96.6% Al_2O_3) obtained from Norton Materials.
- Bentonite obtained from Aldrich Chemical Co.
- Dextrin, an organic binder.

Preliminary Results of Pelletization Procedures:

The following are some preliminary data obtained using the Australian ore:

Batch 1-4-1:

- Water content of pellets : 9.95%
- Room Temperature green crush strength : 6.4 lbs
- Induration at T 1240°C of 40 pellets : weight loss was 11.30%
- Room temperature crush strength of indurated pellets: 105.5 lbs!

Batch 1-4-2:

- Moisture content of pellets : 6.12%
- Room Temperature green crush strength : 6.0 lbs
- Induration at T=1200°C of 27 pellets : weight loss was 11.20%
- Room temperature crush strength of indurated pellets: 55 lbs

These pellets appear to have excessively high crush strengths. If BET measurements are low and also reactivities are low, then lower induration temperatures may be indicated in the preparation of future pellets.

Surface area measurements:

The B. E. T. method is used for the determination of the total area of solids on pellets. The pellets are crushed and an appropriate amount is taken from the size fraction plus 35 minus 20 mesh, in accordance with B. E. T. procedures.

Use of Gas chromatography to measure gas compositions:

The gas chromatograph which is being employed is a Hewlett Packard Model 5890 Series II. It can be used with the provided teflon column and a glass column each packed with Chromosil 310. It has five detector systems: flame ionization, nitrogen/phosphorous, electron capture, thermal conductivity, and flame photometric. The latter system should be able to detect H_2S levels in the off-gases in the range of between 1 and 200 ppm.

Assays of Feedstocks

1) "Moanda" Comilog Ore (African Manganese Dioxide Ore) and "GE" Manganese Dioxide Ore (Australian): Received from: The Prince Manufacturing Company. See subsequent pages for a typical analysis of these two ores.

Typical Chemical Analysis of Ore Feeds

Comilog (African) Ore		Australian Ore	
Species	Wt.%	Species	Wt.%
Mn	51.2	Mn	52.8
MnO ₂	77.0	MnO ₂	83.6
MnO	3.36	Al ₂ O ₃	3.4
Al ₂ O ₃	6.01	Fe	2.2
Fe	2.81	SiO ₂	2.8
SiO ₂	2.56	BaO	1.86
K ₂ O	0.71	K ₂ O	1.25
BaO	0.22	Na ₂ O	0.21
TiO ₂	0.22	MgO	0.2
P	0.109	SrO	0.16
Co	0.099	TiO ₂	0.13
CaO	0.08	P	0.06
Zn	0.064	CaO	0.05
MgO	0.06	V	0.03
Ni	0.058	Zn	0.019
Cu	0.05	Co	0.015
CO ₂	0.04	Ni	0.013
Na ₂ O	0.04	Cu	0.008
S	0.019	Pb	0.005
V	0.012	As	0.005
As	0.007	F	0.006
Cr	0.006	Cl	0.005
Mo	0.006	S	0.005
Pb	0.004	Cr	0.003
H ₂ O (bound)	5.16	Mo	0.004
		Sb	0.001
		B	0.001
		Li	0.001
		W	0.001
		Cd	0.0005
		H ₂ O (bound)	3.4

2) Alundum Fepa F, Size 600, Code 7102
Received from: Norton Industrial Ceramics Corporation

Typical Chemical Analysis:

Species	Al ₂ O ₃	TiO ₂	SiO ₂	Fe ₂ O ₃	CaO	MgO	S	K ₂ O
Wt. %	96.60	2.60	0.60	0.20	0.10	0.40	0.02	0.02

3) Manganese Carbonate: Received from Chemetals, Inc.

This product contains approximately 93-95% MnCO₃; no typical analysis is available at the present time.

4) Manganous Oxide (MnO) Ore, Industrial Grades: Received from Chemetals, Inc.

This product contains approximately 60% manganese.

Ingredient	Approximate %
Manganese Oxide	55 - 83
Manganese Tetroxide	75 - 85
Iron as Iron Oxide	4, max.
Silica as Silicon Oxide	5, max.
Aluminum Dioxide	8, max.
Barium as Barium Compounds	4, max.

Preliminary TGA Testing for Reactivity:

Preliminary experimental results using gases containing only H_2 for the reduction gas and H_2 containing 3% by volume H_2S are encouraging. Starting with Australian Ore (See previous table for assay,) pellets were made and subjected to induration in air atmosphere which converts the MnO_2 to Mn_3O_4 . Two tests on indurated pellets are reported here, the first a pellet weighing 122.1 mg (Run 2-10-1) is a loading test at $700^\circ C$ and the second on a pellet weighing 162.5 mg is a loading test at $900^\circ C$.

Figure 1 shows the ratio of weight at any time to starting weight W/W_0 in the TGA unit plotted as a function of time in minutes. The decline in weight over the first 30 minutes for Run 2-10-1 and for 40 minutes for run 1-15-1 is during the reduction stage (H_2 without H_2S). Hydrogen sulfide was added after these periods which were arbitrarily taken as the time subsequent to which very little measured change in weight was observed.

Shown on this figure is a dashed line corresponding to complete reduction of the starting Mn_3O_4 to MnO (Note that although the starting state of manganese is the compound MnO_2 , upon induration in air, at $1200^\circ C$ MnO_2 is reduced to Mn_3O_4 . See Figure 1A.) Also shown is a higher dashed line corresponding to the weight ratio which would pertain to complete conversion of the manganese oxide to the sulfide. After the addition of sulfur to the hydrogen, a sharp upward slope is shown corresponding to the sorption of sulfur and desorption of oxygen (the former having twice the atomic weight of the latter). The tests were arbitrarily discontinued at 100 minutes at which time the relative sorption of the pellet can be determined. For the lower temperature test ($700^\circ C$) sorption is approximately 49% complete; whereas, for the higher temperature test ($900^\circ C$), sorption is 81% complete.

Figure 1 Stability Diagram for the System Mn-S-O

Figure 2: Thermogravimetric Analysis of Pellets made from Australian Ore in Hydrogen followed by Hydrogen plus 3% Hydrogen Sulfide Atmospheres at 700°C and at 900°C

Figure 3: Stability Diagram of Mn-O System as a Function of Oxygen Potential (P_{CO_2}/P_{CO}) and Temperature.

APPENDIX A

Revision of Thermodynamic Data Mn-O-S System

by

E. T. Turkdogan

REPORT 1 TO UNIVERSITY OF MINNESOTA
PROJECT DOE/DE-AC21-92 MC 2946

November 24, 1992

RE-ASSESSMENT OF FREE ENERGY
DATA FOR MnO, MnS AND MnSO₄

Introduction

I have been aware for some time now that there are differences in the thermochemical tables from one set of compilation to another. Apparently it is not unusual to find differences of 5 to 15 kJ/mol in the standard free energies of formation of metal oxides, sulfides and other compounds. Because of such variations in the compiled free energy data, the estimated equilibrium constants of reactions will be uncertain by factors of two or three. Such level of uncertainty is not acceptable in the assessment of the equilibrium states of reactions in an industrial process.

In relation to the DOE sponsored project on the hot coal gas desulfurization using manganese base sorbents, the available thermochemical and reaction equilibrium data are re-assessed. The results are given in this report.

The following symbols and notations are used in the text and equations.

ΔG_{MX}° = The standard free energy of formation of compound MX from its elements in their standard states.

ΔG_r = The free energy change accompanying the reaction.

< > = Solid reactants.

() = Gaseous reactants.

MnO/MnS Equilibrium

Of particular importance to the desulfurization of hot reducing gases with MnO and its regeneration from MnS (spent sorbent), we should first re-assess the equilibrium sulfur and oxygen potentials for the reaction

Three independent studies have been made.

- (a) Using the emf method, Larson and Elliott¹ measured the state of equilibrium for the reaction at temperatures of 1021 to 1379 K.

$$\Delta G_r = 465,420 - 78.20T \quad \text{J/mol} \quad (3)$$

- (b) Turkdogan et al.² measured the equilibrium gas compositions for the formation of MnS from MnO by reacting the oxide with H_2 - H_2S - H_2O mixtures at temperatures of 973 to 1473 K.

$$\Delta G_r = -63,760 + 5.94T \quad \text{J/mol} \quad (5)$$

- (c) Using the emf method, Huang and Rosén³ recently measured the states of various reaction equilibria in the system

Mn-S-O. For the MnO/MnS reaction at temperatures of 914 to 1300 K.

$$\Delta G_r = 336,732 + 762.32T - 236.83T \log T \quad (7)$$

Combining these values of ΔG_r with the ΔG° values for SO_2 , H_2O and H_2S , we obtain the ΔG_r values for reaction (1). These are plotted in Fig. 1. For almost all reactions, the ΔG_r is practically a linear function of temperature. The results of Huang and Rosen (curve c) are not consistent with the expected ΔG_r -T relation.

The lines d and e are derived from the following compilation of the free energy data:

(d) From the thermochemical tables compiled by Barin et al.^{4,5} for MnO and MnS.

(e) Using the $\Delta G_{\text{MnO}}^\circ$ data compiled by Coughlin⁶ together with $\Delta G_{\text{MnS}}^\circ$ from the compilations by Cooper and Scarpiello⁷ and by Pankratz and King⁸.

The average of the lines d and e is taken for ΔG_r at temperatures of 900-1500 K.

$$\Delta G_r = 110,730 - 9.08T \text{ J/mol} \quad (8)$$

Combining this with $\Delta G_{\text{MnO}}^\circ$ compiled by Coughlin

$$\Delta G_{\text{MnO}}^{\circ} = -384,840 + 73.14T \text{ J/mol} \quad (10)$$

we obtain the following recommended value for $\Delta G_{\text{MnS}}^{\circ}$:

$$\Delta G_{\text{MnS}}^{\circ} = -274,110 + 64.06T \text{ J/mol} \quad (12)$$

Mn₃O₄/MnSO₄ Equilibrium

Several studies have been made of the Mn₃O₄/MnSO₄ equilibrium by determining the equilibrium dissociation partial pressures of SO₂ and O₂ in the reaction

As is seen from the plot in Fig. 2, the results of different investigations are in general accord with one another. As noted by Skeaff and Espelund⁴, MnSO₄ has two crystalline forms:

α -phase below 849°C and β -phase above 849°C.

The average of all the data may be represented by the following equations for temperatures of 900 to 1300 K.

$$\log p_{\text{SO}_2} (p_{\text{O}_2})^{1/2} = - \frac{15,625}{T} + 11.388 \quad (14)$$

$$\Delta G_r = 299,160 - 227.61T \text{ J/mol} \quad (15)$$

Mn₃O₄/MnO Equilibrium

The equilibrium measurements made by Hahn and Muan¹¹ and by Schwerdtfeger and Muan¹² are summarized by the following equation for temperatures of 1200 to 1813 K (mp Mn₃O₄).

$$\langle \text{Mn}_3\text{O}_4 \rangle = 3\langle \text{MnO} \rangle + \frac{1}{2}(\text{O}_2) \quad (16)$$

$$\Delta G_r = 232,210 - 116.98T \text{ J/mol} \quad (17)$$

Equilibrium H₂S/H₂O Ratio

in Desulfurized Hot Coal Gas

Combining ΔG_r in equation (8) with $\Delta G^\circ_{\text{H}_2\text{S}}$ and $\Delta G^\circ_{\text{H}_2\text{O}}$ values gives

$$\langle \text{MnS} \rangle + (\text{H}_2\text{O}) = \langle \text{MnO} \rangle + (\text{H}_2\text{S}) \quad (18)$$

$$\Delta G_r = 45,120 + 4.06T \quad (19)$$

$$\log \frac{p_{\text{H}_2\text{S}}}{p_{\text{H}_2\text{O}}} = - \frac{2357}{T} - 0.212 \quad (20)$$

Using this recommended equilibrium relation, the following estimates are made of the equilibrium H₂S contents of the desulfurized gas, depending on temperature and H₂O content of the hot coal gas.

<u>Temperature, K</u>	<u>%H₂O</u>	<u>ppm (vol.) H₂S</u>
1000	2	54
"	10	270
1300	2	188
"	10	940

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Fig. 1 Experimental and calculated free energy data for the reaction
 $\text{MnO} + \frac{1}{2}(\text{S}_2) = \text{MnS} + \frac{1}{2}(\text{O}_2)$

Average of lines d and e is recommended

$$\Delta G_r = 110,730 - 9.08 T \text{ J/mol}$$

Fig. 2 Experimental data for equilibrium constant

of reaction $\langle \text{MnSO}_4 \rangle = \frac{1}{2} \langle \text{Mn}_3\text{O}_4 \rangle + (\text{SO}_2) + \frac{1}{3}(\text{O}_2)$

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January 6, 1993

Dear Malcolm,

Thank you for your letter of December 29 enclosing a letter from your graduate student Rachid Ben Slimane. His calculations are correct and his comments are well taken. In fact, I was planning to write to you for a few minor corrections in my Report 1 and to discuss the point that was raised by Slimane.

First, let me take care of the corrections. Slight corrections have been made on the positions of the lines d and e in Fig. 1. Equations 8 and 12 should be as follows.

$$\Delta G_r = 111,130 - 9.06T \quad (8)$$

$$\Delta G_{\text{MnS}}^\circ = - 273,670 + 64.08T \quad (12)$$

The line d is from references 6, 7 and 8; the line e from 4 and 5.

It should be noted that $\Delta G_{\text{MnO}}^\circ$ from the thermochemical compilation of Barin and Knacke⁴ is the same as originally assessed by Joughlin⁶. The difference in the positions of the lines d and e in Fig. 1 is due to a difference of about 8.5 kJ between the $\Delta G_{\text{MnS}}^\circ$ values given in references 5 and 7(8). It should be noted that the thermochemical data on MnS given in the compilation by Barin et al⁵

is in fact based on the previous compilation made by K.C. Mills*.

In the re-assessment of experimental results of different investigators, coupled with the thermochemical calculations, one has to be impartial and unbiased. For that reason, my initial thought was to take the average of the lines d and e in Fig. 1 as given in my Report 1. However, upon further reflection, I felt that perhaps we should give more credence to the line e which is in the middle range of the experimental results from two independent investigations. The equation for line e is

$$\Delta G_r = 106,420 - 8.64T \text{ J/mol}$$

which is of course the sum of $\Delta G_{\text{MnO}}^\circ$ and $\Delta G_{\text{MnS}}^\circ$

$$\Delta G_{\text{MnO}}^\circ = - 384,840 + 73.14T \text{ J/mol (Coughlin)}$$

$$\Delta G_{\text{MnS}}^\circ = - 278,420 + 64.50T \text{ J/mol (Mills).}$$

Now, combining the equation for line e with equations for $\Delta G_{\text{H}_2\text{O}}^\circ$ and $\Delta G_{\text{H}_2\text{S}}^\circ$ gives

* K.C. Mills, "Thermodynamic Data on Inorganic Sulphides, Selenides and Tellurides", Butterworth Pub., 1974.

$$\Delta G_T = - 49,430 - 3.36T \quad \text{J/mol}$$

$$\log \left(\frac{P_{\text{H}_2\text{O}}}{P_{\text{H}_2\text{S}}} \right) = \frac{2582}{T} + 0.175 \quad (1)$$

which differs somewhat from the results of the earlier measurements made by Olsson and Vinters², thus

$$\log \left(\frac{P_{\text{H}_2\text{O}}}{P_{\text{H}_2\text{S}}} \right) = \frac{2330}{T} - 0.310 \quad (2)$$

The results obtained from the packed bed experiments of Olsson in Fig. 13 of our paper* are compared in the enclosed diagram with the dotted line for Equ.1. I am inclined to accept Equ. 1 in preference to Equ. 2.

However, in view of the importance of the equilibrium ratio $\text{Fe}_2\text{O}/\text{Fe}_2\text{S}$ in hot coal gas desulfurization with $\text{MnO}(\text{Al}_2\text{O}_3)$, I suggest that a few equilibrium measurements be made using the experimental technique employed by Rosenqvist** in determining the reaction equilibrium

I would be interested to know the outcome of Slimane's experimental work with the $\text{MnO}(\text{Al}_2\text{O}_3)$ pellets.

* E.T. Turkdogan and R.J. Olsson, Proc. 3rd Inter. Iron and Steel Congress, ASM, 1979, pp. 277-288.

** T. Rosenqvist, Trans. AIME, 1952, 191, 535-540.

Fig.1 Experimental and calculated free energy data for the reaction
 $\text{MnO} + \frac{1}{2}(\text{S}_2) = \text{MnS} + \frac{1}{2}(\text{O}_2)$

AIM

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Fig. 13--Comparison of H_2O/H_2S ratios from packed bed experiments with the equilibrium lines for Reaction $MnO + (H_2S) = (MnS) + (H_2O)$

----- Equ. 1

————— Equ. 2

temperature range 1800 to 2000 K.

$$\Delta G_{\text{MnO}}^{\circ} = - 360,170 + 65.62T \quad \text{J/mol} \quad (32)$$

REACTION EQUILIBRIA IN THE
SOLID Mn-S-O SYSTEM

An interest has been shown in some of the R & D laboratories on the possible use of the MnO based absorbents to desulphurise hot coal gases, as an extension of the earlier work that was done by Turkdogan and Olsson¹⁹. In the context of the present study, an assessment will be made of the previous experimental data on reactions involving solid MnO, MnS and MnSO_4 in relation to those calculated from the thermochemical tables.

Four independent studies have been made of reactions involving gases, MnO and MnS.

- (a) Using the emf method, Larson and Elliott²⁰ measured, over the temperature range 1021-1379 K, the state of equilibrium for the following reaction.

$$\Delta G_r = 465,420 - 78.20T \quad \text{J/mol} \quad (34)$$

- (b) Using the emf method, Huang and Rosen²¹ have recently measured the states of various reaction equilibria in

the Mn-S-O system. For reaction in Equ. 33, the following ΔG_r values were obtained over the temperature range 914 to 1300 K.

$$\Delta G_r = 336,732 + 762.32T - 236.83T \log T \quad \text{J/mol} \quad (35)$$

- (c) Using 10 mm dia. MnO pellets stacked in a packed-bed reactor (40 mm dia. and 190 mm deep), Turkdogan and Olsson¹⁹ studied the sulphidation of MnO with the H₂S-H₂ mixtures (with 1.1 to 3.3% H₂S) flowing through the bed at the rate of 3 l/min. The residual concentration of H₂S in the exhaust gas was measured periodically. After the initial 40 minutes of reaction time, the H₂S content of the exhaust gas reached a steady state, indicating the establishment of MnO/MnS equilibrium in the packed bed. Noting that the amount of water vapor in the exhaust gas is equal to the quantity of H₂S reacted, the partial pressure ratio $p_{\text{H}_2\text{O}}/p_{\text{H}_2\text{S}}$ in the exhaust gas is readily derived from %H₂S in the exhaust gas for the steady state condition and the composition of the ingoing H₂S-H₂ mixture. In a different type of experiment, using 50 mg MnO samples, Turkdogan et al.²² measured the equilibrium gas compositions for the formation of MnS from MnO by reacting the oxide with H₂-H₂S-H₂O mixtures of known composition at temperatures of 973 to 1473 K.

(d) In an earlier work done by Dewing and Richardson²³ on the MnO/MnS equilibrium, the method used was to circulate $H_2 + H_2S$ through a water vapour saturator and over a heated mixture of MnO and MnS. The H_2S content of the circulating gas was measured continuously by incorporating radio active-sulphur³⁵ in the gas mixture and introducing GM counter in the gas circuit.

The equilibrium constants p_{H_2O}/p_{H_2S} , obtained from the above mentioned studies, for the reaction

are plotted in Fig. 7. These two sets of equilibrium data may be represented by the following equations:

Dewing and Richardson data²³:

$$\log \left(\frac{p_{H_2O}}{p_{H_2S}} \right) = \frac{2016}{T} + 0.218 \quad (37)$$

Turkdogan et al. data^{19,22}:

$$\log \left(\frac{p_{H_2O}}{p_{H_2S}} \right) = \frac{3266}{T} - 0.288 \quad (38)$$

The line for Equ. 44 in Fig. 7 is discussed later.

By combining the experimental data on ΔG_r for MnO/MnS reactions in the foregoing studies (a to d), with the ΔG_{MX}° values for SO_2 , H_2O

and H_2S , we obtain the G_r values for the reaction

These ΔG_r values from four independent studies are plotted in Fig. 8. The lines e and f are derived using the $\Delta G_{\text{MnO}}^\circ$ data assessed by Coughlin¹⁷

$$\Delta G_{\text{MnO}}^\circ = - 384,840 + 73.14T \quad \text{J/mol} \quad (40)$$

and two different assessments of the $\Delta G_{\text{MnS}}^\circ$ values:

- (e) $\Delta G_{\text{MnS}}^\circ$ values assessed by Cooper and Scarpiello²⁴ and by Pankratz and King²⁵.
- (f) $\Delta G_{\text{MnS}}^\circ$ values derived from the thermodynamic data on inorganic sulphides, selenides and tellurides compiled by Mills²⁶.

There is a considerable spread in the experimental and calculated values of ΔG_r for the reaction in Equ. 39. The experimental results of Dewing and Richardson give the highest ΔG_r values. The curve b from the experimental work of Huang and Rosén is unrealistic, because within the temperature range considered, ΔG_r is expected to be a linear function of temperature.

In my assessment of the situation, I am inclined to give more credence to the line f which is in the middle range of the experimental results from two independent investigations using entirely different experimental techniques. The equation for line f is

$$\Delta G_r = 106,900 - 9.18T \quad \text{J/mol} \quad (41)$$

which is of course the sum of $\Delta G_{\text{MnO}}^{\circ}$ (Equ. 40) and $\Delta G_{\text{MnS}}^{\circ}$ from the compilation of Mills, for the range 298 to 1517 K.

$$\Delta G_{\text{MnS}}^{\circ} = - 277,940 + 63.96T \quad \text{J/mol} \quad (43)$$

Combining Equ. 41 with equations for $\Delta G_{\text{H}_2\text{S}}^{\circ}$ and $\Delta G_{\text{H}_2\text{O}}^{\circ}$ gives the following equilibrium relation for reaction in Equ. 36.

$$\log \left(\frac{P_{\text{H}_2\text{O}}}{P_{\text{H}_2\text{S}}} \right) = \frac{2557}{T} + 0.204 \quad (44)$$

This equation is used for the line drawn in Fig. 7.

There is another evidence from the results of an entirely different experiment which supports the reliability of Equ. 43 for the standard free energy of formation of MnS. In the early 1950's, Turkdogan et al.²⁷ studied the solubility of sulphur in solid iron and iron-manganese alloys. The equilibrium partial pressure ratios $P_{\text{H}_2\text{S}}/P_{\text{H}_2}$ obtained for the reaction

are reproduced in the second column of Table 2. The ΔG_r values obtained from these experimental data are given in the third column. Combining these ΔG_r values for reaction in Equ. 45 with $\Delta G_{\text{H}_2\text{S}}^{\circ}$ and $\Delta G_{\text{Mn}} = - 38.16T \quad \text{J/mol}$ for the ideal solution of Mn in solid iron at 1% Mn gives the $\Delta G_{\text{MnS}}^{\circ}$. It is seen that $\Delta G_{\text{MnS}}^{\circ}$ thus derived from the experimental data on the MnS solubility in solid iron agree well enough with those of Equ. 43.

4. $\{Mn\} + \frac{1}{2}(O_2) = \{MnO\}$ (super cooled liquid below m.p. 2053 K)

$$\Delta G_{MnO}^{\circ} = - 360,170 + 65.62T \text{ J/mol (1800 to 2000 K)}$$

5. $\langle MnO \rangle + \frac{1}{2}(S_2) = \langle MnS \rangle + \frac{1}{2}(O_2)$

$$\Delta G_r = 106,900 - 9.18T \text{ J/mol (900 to 1500 K)}$$

6. $\langle MnO \rangle + (H_2S) = \langle MnS \rangle + (H_2O)$

$$\Delta G_r = - 48,950 - 3.90T \text{ J/mol (900 to 1500 K)}$$

7. $\langle Mn \rangle + \frac{1}{2}(O_2) = \langle MnO \rangle$

$$\Delta G_{MnO}^{\circ} = - 384,840 + 73.14T \text{ J/mol (298 to 1517 K)}$$

This is from the compilation by Coughlin¹⁷.

8. $\langle Mn \rangle + \frac{1}{2}(S_2) = \langle MnS \rangle$

$$\Delta G_{MnS}^{\circ} = - 277,940 + 63.96T \text{ J/mol (298 to 1517 K)}$$

This is from the compilation by Mills²⁶.

9. $\langle MnSO_4 \rangle = \frac{1}{3}\langle Mn_3O_4 \rangle + (SO_2) + \frac{1}{3}(O_2)$

$$\Delta G_r = 299,160 - 227.61T \text{ J/mol (900 to 1300 K)}$$

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Table 2. The standard free energy of formation of MnS
 derived from data on MnS solubility in solid
 iron is compared with the thermochemical data

%Mn	$(p_{H_2S}/p_{H_2}) \times 10^4$	ΔG_r	$\Delta G_{MnS}^\circ, \text{kJ/mol}$	
		kJ/mol	From G_r	From Equ.43
1200°C				
0.37	4.40	- 106.85	- 180.18	- 183.73
1.07	1.52			
1.30	1.25			
1335°C				
0.37	10.85	- 104.61	- 176.72	- 175.09
0.70	5.70			
1.30	3.10

Fig. 7 Comparison of experimental data on reaction equilibrium $\text{MnO} + (\text{H}_2\text{S}) = \text{MnS} + (\text{H}_2\text{O})$ with that calculated from the compiled thermochemical tables, Equ. 44.

Fig. 8 Experimental and calculated free energy data for the reaction
 $\langle \text{MnO} \rangle + \frac{1}{2}(\text{S}_2) = \langle \text{MnS} \rangle + \frac{1}{2}(\text{O}_2)$

**HOT COAL GAS DESULFURIZATION
WITH MANGANESE-BASED SORBENTS**

Progress Report for the Period September 16 to Nov 30, 1992

**By
M. T. Hepworth**

December 1, 1992

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

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

**By:
Malcolm T. Hepworth, Department of Civil and Mineral
Engineering
University of Minnesota, Minneapolis, MN**

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INTRODUCTION

In earlier studies, zinc ferrite has been developed as a regenerable sorbent capable of removing hydrogen sulfide from hot coal gases. Manganese carbonate, precipitated from aqueous solutions and combined with alumina to form indurated pellets holds promise of being a highly-effective, inexpensive, regenerable sorbent for hot fuel gases. The thermodynamics for sulfur removal by manganese predicts sulfur removal to terminal levels in terms of the over-pressure of hydrogen sulfide to be somewhat higher than can be accomplished with zinc sulfide and iron sulfide; however, zinc can be reduced under coal gasification conditions and tends to volatilize, limiting the temperatures for which desulfurization can be effectively accomplished for recycling of sorbent to values less than 900°C. Also the capabilities for regeneration of manganese pellets (bonded to alumina in the approximate formula $(\text{MnO})_4 \cdot \text{Al}_2\text{O}_3$) under oxidizing conditions may be superior to that of zinc ferrite in that it can be loaded from a reducing gas and regenerated under at higher temperatures (regeneration up to 1300°C) provided the correct conditions to avoid sulfation are maintained. 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.

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 pure manganese in a reactive form.

In this current program the following studies will be addressed: preparation of a manganese sorbent, the thermodynamics and kinetics of sulfur removal from hot fuel gases by this sorbent, and the cyclic regeneration of the sorbent by oxidation and recovery of the sulfur.

This study will update earlier studies made at the laboratories of U. S. Steel undertaken by Dr. E. T. Turkdogan¹. Those studies, which utilized a manganese ore blend 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 are the manganese formulations the same as are planned; however, the initial success of the work of Turkdogan indicates that significant progress can be

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.

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.

In order to accomplish the program goals the following tasks will be undertaken:

- 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

PROGRESS TO DATE ON PROGRAM

1) Information Required for the National Environmental Policy Act was submitted on October 22, and the response of METC is pending at this time.

2) Sorbent preparation which does not require NEPA approval is in progress as outlined in the presentation made by the author at Morgantown on November 18 which is included as Appendix A of this report.

In that meeting a discussion ensued regarding the moisture content of the gas which might adversely impact the terminal levels of sulfur which may be achievable. In a letter from Hepworth to Venkataraman dated November 23, in a summary of the discussions regarding the recommended gas composition it was decided that we employ the Tampella U gas composition: 24.33%CO, 5.16%CO₂, 13.19%H₂, 5.35% H₂O, 1.0%H₂S, 5.35% H₂O, balance nitrogen.

An exception was made regarding the H_2S level to be 3% rather than 1% to achieve earlier breakthrough. Initial bed experiments would be made at 900°C with a 200 ppm break-through criteria.

In the same meeting, Dr. Turkdogan indicated that there were some discrepancies in the equilibria between MnS/MnO and gas atmospheres containing H_2O and H_2S , which he planned to address in a report to be issued shortly.

APPENDIX A

Review of Experimental Test Plan presented at Morgantown by M. T. Hepworth on November 16, 1992

EXPERIMENTAL TEST PLAN

INTRODUCTION:

In-situ leach solutions from bench-scale tests of core samples from the Emily District of Minnesota are currently being produced by the Twin Cities Laboratories of the U.S. Bureau of Mines. These solutions are produced by leaching the manganese contained in the cores with acidic solutions saturated with sulfur dioxide. Studies on the recovery of the contained manganese have been undertaken by oxidation and selective precipitation of iron from the manganese solution followed by carbonate precipitation of manganese in a test program conducted by the Salt Lake City Research Center of the U.S. Bureau of Mines. The manganese carbonate resulting from this procedure will very likely be a highly suitable feed material for sorbent pellet production since such pellet will, upon calcination and loss of the volatile carbon dioxide, have potential for a high degree of porosity and resulting high surface area.

OBJECTIVES:

The primary objective of this research is to develop high-temperature coal-gas desulfurization manganese-based sorbents at 700-1200 °C.

A number of sorbent pellet formulations will be prepared and screened for testing in bench-scale fixed-bed reactor at atmospheric pressure and high temperatures using simulated coal-derived fuel-gases. Sorbent screening criteria will include measurements of sorbent (fresh, used, and regenerated) crush strength, chemical reactivity by thermogravimetric analysis (TGA), heat effects by differential thermal analysis (DTA), surface area, pore volume, etc.

Each formulation will be tested for 10 cycles of adsorption and regeneration. One of the superior formulations will be tested for long-term (at least 50 cycles) durability and chemical reactivity in the bench-scale unit.

RESEARCH APPROACH:

- Conduct pelletization testing on product filter cake obtained from the U.S. Bureau of Mines Salt Lake City Research Center and determine the effect of pelletizing conditions on pellet properties such as porosity, strength, and surface area. Determine the effect of binder (type and amount) on green pellet strength and indurated pellet strength. Determine the effect of time and temperature of induration on surface area and crush strength.
- Examine the precipitation of leach solutions on alumina spherical substrates to produce a sounder pellet which may be more amenable as a desulfurization catalyst.
- Concurrent with these pelletization studies, set up a gas train in conjunction with existing thermogravimetric analysis (TGA) apparatus. Employ this apparatus to determine equilibrium loading and calcining levels for sulfur adsorption. Preliminary kinetic data on suspended particles may also be obtained using TGA plots.
- Prepare pellets from natural or synthetic manganese-containing material and study the role of pelletization conditions on pellet performance:
 - Additives employed
 - Green pellet strength
 - Induration time and temperature
 - Indurated pellet strength
 - Indurated pellet porosity
 - Indurated pellet surface area
 - Indurated pellet reactivity
- Determine the role of precipitant (especially soda ash and ammonium carbonate) on pellet porosity (e.g. occluded carbonate may lead to bloating of the pellet and a resulting greater porosity and associated surface area).

SORBENT CHEMICAL COMPOSITION:

The choice of pellet composition is based upon prior studies by Turkdogan and Olsson³, who used combinations of manganese ore (Comilog ore) and alumina and made the following observations:

- The pellets made with a powder mixture of Comilog ore and alumina were more reactive during sulfidation than those made with ore alone and also responded better to the regeneration treatment.

- The reactivity of the pellets increased further when more ore was replaced by alumina in the blend. However, since a decrease in the ore content of the pellet decreased its sulfur-loading capacity, an optimum pellet composition appeared to be about 75% ore and 25% alumina by weight.
- Because of lack of porosity, the sulfidation of Comilog ore granules was sluggish.
- Pellets made from blends of finely ground Comilog ore and alumina powder performed well both in the sulfidation and regeneration steps, even after many cycles.
- The reaction of the pellets with the H_2S was sufficiently rapid that the exhaust gas was essentially at equilibrium with the solids MnS/MnO .
- In addition, the pellets containing alumina had a greater resistance to deterioration at high temperatures than the 100% ore pellets. At temperatures of practical interest ($< 1400\text{ }^{\circ}C$) the alumina does not react with manganese sulfide and oxide in the sulfidation and regeneration cycles. The alumina provided a support matrix, thus preventing sintering and maintaining open porosity in the pellet for easy gas diffusion. With alumina present in the pellets, even the MnS - MnO eutectic at $1232\text{ }^{\circ}C$ did not impede the reactivity of the pellets at $1300\text{ }^{\circ}C$.

RAW MATERIALS:

The following is a list of the raw materials which will be used in making up the pellets:

- $MnCO_3$, reagent grade
- $MnCO_3$, in-situ project filter cake product
- MnO_2
- Al_2O_3
- Alundum
- Dextrin
- Wheat starch
- Corn starch
- Bentonite

PELLETIZING ACTIVITIES:

The objective of the pelletizing tests is to predict the type and amount of binders necessary to achieve pellets that will be suitable for use in a cyclic fixed-bed gas cleaning reactor. Different binder amounts for selected formulations will be studied in an attempt to develop an optimized process.

Blends will consist of a manganese-containing compound, an alumina-based matrix, and a binder, based on desired compositions determined on a dry weight-percent basis. The amount of binder to be used should be as low as possible, not only to save on the cost, but also to provide a greater amount of chemically active sorbent in a given volume of packed bed. After each blend is mixed, an appropriate amount of water is added prior to pelletizing.

Pelletization is to be accomplished using a balling tire at a 40-60° inclination and a rotational speed of 40-50 rpm. Feed will be prepared by adding binder to the dry mix, and mulling while adding water slowly to form a cohesive state. Moisture will be added in controlled quantities via hand spray to the mix which will then be rubbed through a 10-mesh sieve.

Seeds will be prepared by moistening the tire interior, wiping it clean, and then slowly sprinkling about 7 wt.% of the prepared, moist feed mixture into the tire rotating at 50 rpm. When seeds begin to form, they will be removed and sieved through a 6-mesh screen. Fines will be returned to the tire. This procedure will be continued until all the feed has been agglomerated. Ideally, the seeds will range from 2 to 3 mm in diameter.

In the subsequent balling operation, the seeds will be returned to the rotating tire and sprayed to the glistening point (a visual observation of surface appearance). Feeding will occur at about the 7:00 o'clock position on the tire as it rotates clockwise. Spray will be applied as needed to reach the incipient glistening point during the balling operation. When all the loose feed has been assimilated, the product will be removed and screened to retain the 7 to 10 mm fraction. The moist pellets will be stored in sealed containers pending evaluations.

The above two-step pelletizing procedure, in which seeds are first prepared, largely eliminates further seed formation during the balling step and the presence of undersized balls in the final gross product. The required moisture content for the feed depends on its average density. Balling is known to be optimal at 30 to 35% moisture on a volume basis, i.e., the approximate void fraction in dried pellets. For 33% moisture on a volume basis, it can be shown that the required amount of water to be added is given by the following equation:

$$Wt. \% H_2O = \frac{100}{[1 + \frac{67}{33} * (\rho_{Av})]}$$

where ρ_{Av} is the average density of the feed.

The average ball size in the gross product is dependent upon the number of seeds and the amount of new feed added to them. If too few seeds are used, not all the feed can be added; if too many, the feed may run out before the desired ball size is reached.

Representative pellets from each run will be subjected to the following screening physical and chemical tests:

SORBENT CHARACTERIZATION METHODS:

Fresh and spent (partially or completely converted) sorbents will undergo characterizations of various desired physical and chemical properties:

- Moisture content: Dry the pellets to a constant weight at about 110°C and determine moisture content by difference (initial wt. - final wt.)
- Room-temperature green ball compressive strength
- Room-temperature dried ball compressive strength²
- High-temperature exposure test of dried pellets in an inert atmosphere for MnCO₃-based pellets, and in a reducing atmosphere (such as H₂) for MnO₂-based pellets. It is desirable that the induration temperature be maintained below approximately 1200°C to preclude sintering, which will adversely affect the porosity and surface area of the sorbent pellet.
- Room-temperature compressive strength of pellets after high-temperature exposure
- Physical pellet properties, such as dimension (diameter) and

²The strength of the green pellet will be taken as the load in pounds (or Newtons) required to crush the pellet in a compression tester. The average load required to break each of 20 pellets selected at random will be taken as the pellet compression strength.

weight will be routinely measured.

- Surface area measurements will be based on the standard BET method using physical sorption of nitrogen at liquid nitrogen temperatures.
- Pore volume will be measured using two methods, the density method and mercury porosimetry. The density method is simpler to use and will be routinely applied. True density, ρ_t , of the solid pellet will be estimated on the basis of its chemical composition. Actual pellet density, ρ_a , will be obtained from actual weight and volume measurements.

The pore volume is obtained by subtracting the true pellet volume from its actual volume. It can be shown that the pore volume is given by:

$$m \left[\frac{1}{\rho_a} - \frac{1}{\rho_t} \right]$$

where m is the mass of the pellet. The porosity of the pellet will be obtained by dividing the pore volume by the actual volume of the pellet, and is given by:

$$\rho_a * \left[\frac{1}{\rho_a} - \frac{1}{\rho_t} \right] * 100$$

on a percent basis. Pore volume will also be measured, along with pore size distribution, using mercury porosimetry of selected samples. Mercury porosimetry is based upon the resistance of a non-wetting liquid, mercury, entering the pores of the pellet. The relationship between pore radius, r (angstroms) and applied penetration pressure, P (psi) is given by the equation:

$$r = \frac{8.57 * 10^5}{P}, \text{ \AA}$$

Radial crush strength of the fresh and spent pellets will be measured using

a crush strength tester based on ASTM Method D4179-82 (see appendix for description). A minimum crush strength of 15 pounds DWL (dead weight load) per pellet is sought because the sorbent pellets will be used in tall packed columns in a commercial situation. The crush tester will be configured to allow collection of the crushed pellet for pulverization followed by X-ray diffraction (XRD) measurement. XRD crystalline phases will be identified using standard powder diffraction techniques and pattern library and the mean crystallite size of the phases will be obtained. Semiquantitative values of the amount of the phases as a percent of total crystallinity will also be estimated.

SEM-EDX will be applied to partially converted pellets. The energy dispersive x-ray analysis accessory (EDX) to the scanning electron microscope (SEM) allows a semiquantitative elemental (sulfur and metals) analysis as a function of position within the pellet. By sectioning the pellet in the middle, along its diameter, one may be able to validate (or invalidate) the assumption of a shrinking core model.

It must be noted that since only a single pellet will be run in each TGA experiment, it is not possible to perform all the characterization tests for each experimental condition. The number and type of characterizations will be adjusted as TGA results become available. The number of possible characterizations would be severely limited with only a single pellet. It may be necessary to modify the electrobalance to incorporate four pellets at a time while measuring the weight and temperature changes of a single pellet. This should be done in order that additional sorbent pellets can be exposed to the reactive gas stream. This modification will allow more characterizations to be performed on pellets that have the same history as has been successfully done by Woods et al.

DATE

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8/18/94

END