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Kinetics of Mn-Based Sorbents for Hot Coal Gas Desulfurization

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

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ABSTRACT

In earlier studies^{1,2}, zinc ferrite and zinc titanate were developed as regenerable sorbents capable of removing hydrogen sulfide from hot fuel gases originating from coal gasification. Manganese ore as well as manganese carbonate, precipitated from aqueous solutions, combined with alumina to form indurated pellets hold promise of being a highly-effective, inexpensive, regenerable sorbent for hot fuel gases.³ Although the thermodynamics for sulfur removal by manganese predicts somewhat higher hydrogen sulfide over-pressures (i.e. poorer degree of desulfurization) than can be accomplished with zinc-based sorbents, zinc tends to be reduced to the metallic state under coal gasification conditions resulting in loss of capacity and reactivity by volatilization of reactive surfaces. This volatilization phenomenon limits the temperatures for which desulfurization can be effectively accomplished to less than 550 °C for zinc ferrite and 700 °C for zinc titanate⁴; whereas, manganese-based sorbents can be utilized at temperatures well in temperatures exceeding 700 °C.

Also the regeneration of manganese-based pellets under oxidizing conditions may be superior to that of zinc titanate since they can be loaded from a simulated reducing coal-derived gas and then be regenerated at higher temperatures (up to 1300 °C). Upon regeneration of the loaded sorbent, sulfur can be obtained from the off-gases by the combination of the products of the regeneration or, alternatively, sulfuric acid may be made from the sulfur dioxide since the regeneration process results in a much smaller volume of gaseous reaction product and, hence, forming a SO₂-strength which is suitable for autogenous sulfur acid production.

The topics that will be addressed by this study include:

- Preparation of an effective manganese-based sorbent,
- Thermodynamics and kinetics of sulfur removal from hot fuel gases by this sorbent,
- Analysis of kinetics and mechanisms by which sulfur is absorbed by the sorbent (i.e., whether by gaseous diffusion, surface-controlled reaction, or pore diffusion), and

¹ Grindley, T. and Steinfeld, G., "Development and Testing of Regenerable Hot Coal-Gas Desulfurization Sorbent", DOE/METC/16545-1125, 1981.

² Woods, M.C., et. al., "Reaction between H₂S and Zinc-Oxide Sorbents. 1. Single-Pellet Kinetic Studies", I&EC RESEARCH, 1990, pp. 1160-1167.

³ Hepworth, M.T. and Ben-Slimane, R., 1993, Quarterly report #3, "Hot Coal Gas Desulfurization with Manganese-Based Sorbents", DE-AC21-92MC29246.

⁴ Gupta, R.P., "Enhanced Durability of Desulfurization Sorbents for Fluidized-Bed Applications", *Coal-Fired Power Systems 93 - Advances in IGCC and PFBC Review Meeting*, June 28-30, 1993.

- Cyclic sulfidation and regeneration of the sorbent and recovery of the sulfur.

Emphasis is upon supporting the application of this sorbent for commercial use via fundamental studies on reaction mechanisms during loading and regeneration.

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INTRODUCTION

High-temperature desulfurization of coal-derived fuel gases can be accomplished by using solid sorbents such as oxides of those metals that form stable sulfides. The effectiveness of a desulfurizing agent in treating coal gasifier gases is related to the predicted equilibrium partial pressure of sulfur which will be present in a phase combination of the reduced form of sulfide and oxide phases. A thorough review of sorbent systems, up to 1990, has been given by Swisher and Schwerdtfeger.^[22] An updated literature review was presented in the previous Quarterly Report^[23]. The focus of much current work being performed by the Morgantown Energy Technology Center (METC) of the Department of Energy on hot coal-derived fuel gas desulfurization is in the use of zinc-based sorbents. Extensive research, however, casts doubt that these sorbents can be utilized even for the mild conditions associated with fixed-bed operation. Accordingly, METC has shown interest in formulating and testing manganese-based pellets as alternative effective sulfur sorbents in the 700 to 1200 °C temperature range.

In addition to reduction of zinc oxide and the subsequent volatilization of elemental zinc, zinc-based sorbents experience structural and reactive degradation over multi-cycle use at relatively moderate temperatures. In the previous Quarterly Report it was concluded that an effective alternative to zinc-based sorbents could be manganese sorbents, which the work of Ben-Slimane and Hepworth have shown them to withstand high temperature operation and also maintain structural and reactive integrity over many cycles. Although manganese sorbents are not as effective in removing H_2S to ultra low levels, as is the case with zinc, under the correct conditions the guideline for IGCC systems can easily be achieved. Furthermore, manganese sorbents could possibly be used with a polishing sorbent to reach levels acceptable for fuel cell applications (< 10 ppmv). The following is a brief summary of the investigations conducted to date by Ben-Slimane and Hepworth.

To substantiate the potential superiority of Mn-based pellets, a systematic approach toward the evaluation of the desulfurizing power of single-metal sorbents was developed based on thermodynamic considerations.^[3] This novel procedure considered several metal-based sorbents and singled out manganese oxide as a prime candidate sorbent capable of being utilized under a wide temperature range, irrespective of the reducing power (determined by CO_2/CO ratio) of the fuel gas. Then, the thermodynamic feasibility of using Mn-based pellets for the removal of H_2S from hot-coal derived fuel gases, and the subsequent oxidative regeneration of loaded (sulfided) pellets was established. It was concluded that MnO is the stable form of manganese for virtually all commercially available coal-derived fuel gases. In addition, the objective of reducing the H_2S concentration below 150 ppmv to satisfy the integrated gasification combined cycle system requirement was shown to be thermodynamically feasible.

A novel process is developed for the manufacture of Mn-based spherical pellets which have the desired physical and chemical characteristics required during the long-term cyclic sulfidation and regeneration in a high-temperature desulfurization operation.^[8] Screening sulfidation tests on a number of formulations, consisting of a Mn-containing

compound (ore or MnCO_3), alundum (Al_2O_3), and organic or inorganic binders, were carried out using $\text{H}_2\text{S-H}_2$ gas mixtures in a thermogravimetric (TGA) apparatus at temperatures ranging from 700 to 1000 °C. A formulation, designated FORM4-A, was found to possess the best combination of sulfur capacity, reactivity, and strength.^[4] Regeneration tests determined that for $T \geq 900$ °C, loaded pellets can be fully regenerated with air in 10 to 15 minutes, without sulfate formation, in strict accordance with thermodynamic guidelines. Repeated cycling of the leading sorbent formulation (FORM4-A) was then conducted in the TGA apparatus, up to 5 consecutive cycles. One important finding was that the capacity of the pellets for sulfur pickup from fuel gas and the kinetics of reduction, sulfidation, and regeneration reactions improved with recycling without compromising the strength.^[10]

Testing of the leading Mn-based sorbent pellets was carried out in a 2-inch fixed-bed reactor to evaluate the long-term durability and regenerability of the sorbent using a Tampella-U fuel gas for sulfidation and air for regeneration. Consistent with TGA results on individual pellets, the fixed-bed tests showed small improvement in capacity and kinetics with the sulfur capacity being about 22% by weight of the original pellet, which corresponds to approximately 90% bed utilization. In addition, a re-assessment of the equilibrium states of reactions in the Mn-S-O system was presented based on the results obtained by Turkdogan.^[5]

The shrinking unreacted-core model was found to approximate the kinetic behavior of Mn-based pellets during both the sulfidation and regeneration stages. Kinetic analysis of TGA experimental data determined that beyond approximately 35% reaction completion, sulfidation and regeneration reaction rates were controlled primarily by gaseous counter-diffusion through the porous product layer.^[24,25]

Currently, however, there is very limited incentive for desulfurization at temperatures much above 900 °C due mainly to the difficulty of maintaining low alkali content in the fuel gas fed to the gas turbine. At higher temperatures a significant portion of the alkali is in the vapor phase and not easily removed from the gas; whereas at lower temperatures most of the alkali will have condensed on entrained particulate and thus, removing the dust also significantly lowers the alkali content. In addition current gas turbine fuel flow control valve technology is well below 900 °C and extending it above 800 °C is regarded as a major challenge by the industry. For these reasons, the development of effective manganese-based regenerable sorbents in the temperature range 600 to 800 °C is considered essential as a primary goal in this investigation.

In this Quarterly Report, the favorable characteristics of manganese-based sorbents are discussed based on thermodynamic considerations. Thermodynamic guidelines are outlined to show the superiority of manganese as an effective sulfur sorbent. A broad-based exploratory effort is fully justified in order to identify potentially more effective alternative sulfur sorbents in the temperature range 600 to 800 °C. Exploratory experimental efforts have been attempted to improve FORM4-A sorbent reactivity and overcome its limitations below 900 °C. Kaolin ($\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$), bauxite ($\text{Al}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$), MoO_3 , alundum, and activated carbon were added in different proportions to manganese carbonate and bentonite

(inorganic binder) as structure modifiers. The overall goal is to increase pellet macroporosity, thereby improving its reactivity at lower temperatures. The fabricated sorbents were tested for their strength and reactivity with H_2S -containing loading gases. Reactivity evolution (conversion vs time) experiments were carried out in a thermogravimetric analysis apparatus using H_2S concentration of 15 ml/min.

THERMODYNAMIC ANALYSIS

Figure 1 is a stability diagram for the manganese-oxygen (Mn-O) system as a function of temperature and oxygen potential, as expressed in terms of the CO_2 to CO ratio. A fortuitous feature of this system is the wide range of stability of manganese in the form of MnO. It is also seen that even under slightly reducing conditions, higher oxides of manganese are readily reduced to MnO. But most importantly, the reduction of MnO to elemental manganese is not feasible even under severely reducing conditions. As it will be shown subsequently, MnO is the stable form of manganese for virtually all commercial fuel gases currently being produced.

In order to illustrate the thermodynamic method used in this analysis, a typical high-sulfur Illinois No. 6 coal has been used as the coal producing a gaseous product. The ultimate analysis of this coal is given in Table I. This coal was factored into the calculations as 100 grams of coal on a dry basis plus 9.3 grams of moisture. The gaseous species considered include N_2 , CO, CO_2 , H_2O , H_2 , H_2S , S_2 , COS, SO_2 , SO_3 , O_2 , S, S_4 , SO, CS, CS_2 , NO, NO_2 , CH_4 , and NH_3 . Calculations are based on a single coal composition; however, the results reported in this study are applicable to a broad range of coal-derived gas compositions. For a system in which coal gases are equilibrated with a combination of two solid phases (MnO and MnS, for example), the Gibbs phase rule predicts the number of degrees of freedom as $F = C + 2 - P$, where C is the number of components and P is the number of phases (three in this analysis, gas plus two solids). The components are metal, oxygen, and sulfur. Most of the discussion below is for a three-phase, three-component system. For such a system, the number of degrees of freedom (F) is two, and therefore at a fixed total pressure of 1 atm, at a given temperature the system is uniquely defined by two independent parameters.

These calculations are carried out using a thermodynamic software package known as STEPSOL and developed at the University of Missouri-Rolla based on the well-known program SOLGASMIX. STEPSOL simulates semibatch metallurgical reactors on an IBM-PC or compatible, is capable of handling systems up to 14 elements, 84 species, and 19 phases through up to 24 steps, and is thus valuable in the calculation of chemical equilibria in complex systems.

Figure 2, however, shows the oxygen partial pressure or equivalent CO_2 to CO ratio which results from establishing a given equivalence ratio for the single-phase gas composition (absence of any solid phase) resulting from gasification of the referenced coal (at a series of fixed temperatures and 1 atm pressure). Gasification is carried out by

Table IA Major Types of Coal Found in the U.S.

Proximate Analysis, Weight Percent					
Type of Coal	Fixed Carbon	Volatile Matter	Moisture	Ash	Range of Heating Value (Btu/lb)*
Anthracite	82	5	4	9	13,000 - 16,000
Bituminous:					
Low-volatile	66	20	2	12	11,000 -
Medium-Volatile	64	23	3	10	15,000
High-Volatile	46	44	6	4	
Subbituminous	40	32	19	9	8,000 - 12,000
Lignite	30	28	37	5	5,500-8,000

Table IB Ultimate Analysis of a Typical Bituminous Coal (Illinois No. 6)

Constituent	Percent by Weight
Carbon	67.87
Hydrogen	5.0
Nitrogen	1.2
Total Sulfur	3.87
Oxygen	10.56 (not included in ash)
Ash	11.5
Total	100.0 (dry basis)
Moisture	9.3
Gross Heating Value	28415 kJ/kg

* to convert Btu/lb to the S.I. unit of kJ/kg, multiply by 2.326

reacting the coal with air at a temperature ranging from 800 to 1100 °C (practical range). The amount of air supplied is a fraction of the amount stoichiometrically required for the complete combustion of coal components. The reciprocal of this fraction is known as the equivalence ratio and represents the ordinate in Figure 2. The atmosphere of the fuel gas produced is characterized by the partial pressure of oxygen (abscissa), or more practically, by the logarithm of the CO₂ to CO ratio. It is seen from this figure that this latter parameter ranges from -1.6 to 2, depending on temperature and equivalence ratio. Reference to Figure 1 shows that for all these combinations of gasifier operating conditions MnO is the stable form of manganese.

Figure 3 shows the resulting equilibrium partial pressures of predominant sulfur-bearing species (H₂S, COS, and SO₂) and the total amount of sulfur in the gas during the gasification of an Illinois No. 6 coal at 800 °C. Again the equivalence ratio is varied from 1 to 2.5. The solid line in Figure 3 represents the total sulfur species, as calculated according to the following equation:

$$P_t = \sum(iP_{S_i}) = P_{H_2S} + P_{COS} + P_{SO_2} + 2P_{S_2} + \dots \quad (1)$$

It is seen that as the conditions get more reducing, the value of the H₂S partial pressure asymptotically approaches that of the total pressure. For equivalence ratios associated with gasification (i.e. > 1), oxidized sulfur in the species SO₂ becomes negligible with respect to lower-valent sulfur in COS and H₂S, the latter being the majority sulfur species as shown. As the equivalence ratio approaches unity, the conditions get more and more oxidizing and sulfur exists predominantly as SO₂. Figure 3 also shows that COS, the second most important sulfur species, has a concentration approximately an order of magnitude lower than that of H₂S. It follows that desulfurization of coal-derived fuel gases at high temperature consists essentially of H₂S removal. As H₂S is removed, other sulfur-bearing species equilibrate in the gas phase and are proportionately reduced. Figure 3 also shows the MnO/Mn₃O₄ equilibrium line where the wide range of MnO stability is clearly displayed. It is evident from Figure 3 that H₂S is the dominant gaseous sulfur species at equilibrium for essentially all reducing conditions explored in this work. Desulfurization with sorbents, then, is essentially a process of removal of the species H₂S from the gas phase. Of course, as H₂S is removed, the other minority species equilibrate in the gas phase and also are proportionately reduced.

Concentration of H₂S (ppmv) resulting from the gasification of an Illinois No. 6 coal as a function of temperature and equilibrium ratio is shown in figure 4. At 900 °C and at a equilibrium ratio of 2.1 H₂S concentration in the fuel gas is about 5500 ppmv. Figure 5 shows the H₂S concentration in ppmv in the cleaned gas as a function of equivalence ratio and temperature for Illinois No. 6 coal. Figure 6 also shows the percent of sulfur removal from fuel gas as a function of equivalence ratio and temperature. At a equivalence ratio of 2.4 almost 99% of sulfur is being removed from the fuel gas at 900 °C. Figure 7 compares the equilibrium (theoretical) SO₂ emission on gasification of an Illinois No. 6 coal after desulfurization with MnO at various temperatures.

KINETIC CONSIDERATIONS

Figure 9 shows the grain model, a theoretical model for a gas - porous solid reaction. This model is based on a spherical pellet consisting of solid non-porous spherical grains. These solid grains each behave according to the shrinking core model, a theoretical model for a gas - non-porous solid reactions. There are four possible rate controlling mechanisms with the grain model: gas film diffusion, pore diffusion, product layer diffusion, and chemical reaction. Table II gives the mathematical expressions, $t(x)_j$, for the individual rate controlling steps. Therefore, the time required to achieve a certain fractional conversion for the overall reaction, $t(x)$, is simply the sum of the times required to achieve a certain fractional conversion of all of the individual steps.

$$t(x) = \sum t(x)_j$$

This states that the slowest rate controlling step is the dominating mechanism in the reaction.

All of the rate controlling steps are dependant on the molar density of manganese in the solid (ρ_{Mn}), the stoichiometric coefficient (b), (for the case of MnO reacting with H_2S $b=1$), and the concentration gradient between the bulk H_2S concentration and the equilibrium H_2S concentration (C_{Ao}). In addition, the radius of the grains (r_g), radius of the pellet (r_p), the porosity (ϵ), the reaction rate constant (k), the effective diffusivity through the pores (D_e), the effective diffusivity through the product layer (D_p), and the mass transfer coefficient (h_D) affect one or more of the rate controlling mechanisms. An analysis of the important rate controlling steps and the variables which they depend on can identify possible ways to improve the kinetics of the reaction. The kinetics of individual pellets affect the quality of the breakthrough curve in a fixed-bed or fluidized bed system.

Gas film diffusion is a measure of the gas delivery to the system, and therefore is unimportant to the breakthrough kinetics. In the temperature range of interest for desulfurization it is assumed possibly that product layer diffusion is the controlling step with the chemical reaction having a minimal effect. Therefore, this analysis will concentrate on improving the kinetics of product layer diffusion and the chemical reaction, with an emphasis on how increasing the internal surface area of the pellet will affect the kinetics. The first task is to identify the variables that are dependent and independent of surface area. The molar density (ρ_{Mn}), the stoichiometric coefficient (b), the concentration gradient (C_{Ao}), the reaction rate constant (k), the effective diffusivity (D_p) and the fraction converted (x) are all independent of the surface area. Therefore, the radius of the grain (r_g) is the only dependent variable in the two rate controlling steps.

The relationship between the radius of the grain and the surface area can be calculated by examining a unit volume pellet with a surface area of unity ($1 \text{ m}^2/\text{g}$), unit volume pellet with an order of magnitude increase in surface area ($10 \text{ m}^2/\text{g}$), and a unit

Table II. Rate controlling steps of the grain model.

Rate controlling mechanism	Mathematical expression, $t(x)_i$
gas film diffusion	$\frac{\rho_{Mn} r_p}{3bh_d C_{Ao}} (x)$
pore diffusion	$\frac{(1-\epsilon)\rho_{Mn} r_p^2}{6bD_e C_{Ao}} (2(1-x) - 3(1-x)^{\frac{2}{3}} + 1)$
product layer diffusion	$\frac{\rho_{Mn} r_g^2}{6bD_p C_{Ao}} (2(1-x) - 3(1-x)^{\frac{2}{3}} + 1)$
chemical reaction	$\frac{\rho_{Mn} r_g}{bkC_{Ao}} (1 - (1-x)^{\frac{1}{3}})$

volume pellet with a two order of magnitude increase in surface area ($100 \text{ m}^2/\text{g}$). The one assumption that will be made is that the porosity of the three pellets are the same. The following relationships are for the surface area and the volume of the pellets.

$$SA_p = 4\pi r_g^2 n \quad \text{and} \quad V_p = \frac{4/3\pi r_g^3 n}{1-\epsilon}$$

For both of these equations the radius of the grain (r_g) and the number of grains (n) are variable. Carrying out this analysis produces the following ratio of the grain radii.

$$\frac{r_g (SA=10\text{m}^2/\text{g})}{r_g (SA=1\text{m}^2/\text{g})} = 0.1 \quad \text{and} \quad \frac{r_g (SA=100\text{m}^2/\text{g})}{r_g (SA=10\text{m}^2/\text{g})} = 0.1$$

Therefore, there is an inverse linear relationship between the grain size and the internal surface area.

This leads to the relationship between the internal surface area and the kinetics of the reaction, or the time to reach a certain fractional conversion. The analysis must be split into diffusion controlled and chemical reaction controlled processes. In a diffusion controlled mechanism the kinetics are inversely proportional to the square of the radius of the grain, therefore the reaction kinetics are directly proportional to the square of the internal surface area. In a chemical reaction controlled mechanism, there is an inverse linear relationship between the radius of the grain and the kinetics, therefore the reaction kinetics are linearly proportional to the internal surface area.

This analysis concludes that the reaction between H_2S and MnO in the temperature range of interest, where product layer diffusion dominates, is highly dependent on surface area ($t(x) \propto SA^2$) and to a lesser extent, where chemical reaction dominates, moderately dependant on surface area ($t(x) \propto SA$). Both the shrinking core model and the grain model along with further mathematical analysis will appear in the MS thesis of Rick Stuart at the University of Minnesota entitled *Kinetic Testing of an In-Situ Mined Manganese Based Fuel Gas Sorbent*, projected completion in April 1995.

As the reaction temperature rises, the intrinsic reactivity of the solid, the diffusivity in the pores space, and the diffusivity in the product layer increase; and hence one expects higher reaction rates at higher temperature. However, the temperature effect is not as strong for large particles sulfided under the same conditions as the smaller particles. For instance, Efthimiadis *et al* [6] explained the differences in the temperature effect for the two particle sizes. It can be realized that the reaction rate constant and the diffusivity in the product layer, which vary exponentially with the temperature control the reaction rate for smaller particles (53-62mm) and that the intraparticle diffusion, which is affected rather weakly by

the temperature, is the controlling step for the sulfidation of larger particles (297-350mm). The weak effect of the reaction temperature on the sulfidation rates of porous sorbents of large sizes is also noticed by Focht *et al*^[7]

EXPERIMENTAL INVESTIGATIONS AND RESULTS

The Prior studies by Turkdogan and Olsson^[5] were conducted on an African rich pyrolusite (MnO_2) ore which assayed 63% Mn (primarily as Mn_3O_4) upon calcination in air at 1000 °C. The comparative experimental investigations by Ben-Slimane and Hepworth *et al*^[4] concluded that a MnCO_3 -based sorbent pellet offers the best combination of reaction kinetics and sulfur loading capacity. For these reasons, the present investigation employed similar materials: manganese carbonate and bentonite along with a third compound (alundum/kaolin/bauxite/ MoO_3 /activated carbon) to increase the macroporosity.

Assays of Feedstocks:

MnCO_3 (Source: CHEMETALS, Inc., Baltimore, MD).

Crude clays (source : Harbison-Walker Refractories, Eufaula, AL).

Alundum Fepa F, size 600, code 7102: Obtained from Industrial Ceramics Corporation (Norton Materials) in Worcester, MA.

Molybdenum (VI) Oxide (MoO_3): Aldrich Chemical Company, Inc., Milwaukee.

Activated Carbon: Darco KB < 100 mesh wet powder, Water < 30%, Surface Area 1600 m^2/gm (dry basis), Pore Volume ~ 2 cm^3/gm (dry basis).

After receiving the clay samples, they were dried at a constant temperature(110 °C) for 24 hrs to remove free moisture. Then the samples were ground to < 150 mesh in ball mill. The particle size of each of the material is shown in Table III.

Table III. Average particle size of the raw materials

Material	Particle diameter (mm)	Material	Particle diameter (mm)	Material	Particle diameter (mm)
MnCO_3	< 74	Kaolin-45	< 100	MoO_3	10-20
Alundum	< 37	Kaolin-60	< 100	Act. Carbon	< 125
Bentonite	< 37	Bauxite-70	< 100		

Sorbent Pellet Preparation:

Five pellet formulations were prepared using combinations of a manganese-containing compound, an alumina-based matrix, a binder and MoO_3 or activated carbon based on desired compositions determined on a dry weight-percent basis. The composition of initial make up of the formulations prepared using this procedure is reported in Table IV.

Table IV. Initial Make up of Formulations

Formulation No.	MnCO_3	Alundum	Bentonite	MoO_3^{**}	Activated Carbon	K-45	K-60	B-70
1	79.17		1.91			18.92		
2	78.48		1.89				19.63	
3	78.02		1.88					20.10
1D	79.75	16.41	1.92	1.92				
2D	79.75	16.41	1.92		1.92			

Pellet Characterization:

Table V summarizes strengths of the formulations which have to be subjected to TGA analysis and BET surface area test. Typical specific surface area of $> 0.2 \text{ m}^2/\text{gm}$ is expected by BET analysis. Porosity tests will be carried out after analysing the BET data. As the formulations containing clays (K-45; K-60; B-70) fused during induration, they were not considered for further analysis. Preparation of new formulations and induration at lower temperature are under progress now.

Table V. Strengths of Formulations Studied

Sample Designation	Strength, lbs/mm
FORM1-D	5.5
FORM2-D	6.0
FORM4-A	5.4

Tests via TGA on Pellet Reactivity:

Figure 10 is a schematic diagram of the experimental equipment employed for TGA testing. Figure 11 and 12 show the results of TGA analysis at 900°C on the two selected sorbents (FORM1-D and FORM2-D) which were described above. The kinetics of

sulfidation for both FORM1-D and FORM2-D are almost equal. FORM1-D used MoO_3 and FORM2-D used activated carbon as a surface modifier to enhance macroporosity.

SUMMARY AND CONCLUSIONS

Desulfurization at the gasifier exit temperature is preferable. However, properly designed heat recovery systems will allow certain temperature adjustments without appreciable efficiency losses.

Repeated cycling of the leading sorbent formulation (FORM4-A) was conducted in the fixed-bed reactor up to 50 consecutive cycles. The results are reported in Figure 13 which shows the effect of cycling on the sulfur capacity of FORM4-A pellets at 900°C upon repeated loading and regeneration. Improvements in capacity and reaction kinetics after five cycles is attributed to the formation of radial cracks which reduced the diffusion distance required to transport the sulfur into the pellet and oxygen out of the pellet. Normally, and especially in the case of Zn-based sorbents, the onset of small cracks leads to sorbent spalling and reduced usable life due to increased "dust" loadings in an exit gas stream²¹.

The breakthrough curve for sulfidation at 900°C on the 48th cycle is shown in Figure 14. The concentration of H_2S in the exhaust gas (on wet basis) appears to reach a steady state value of approximately 225 ppmv for at least the first 5 hrs of the loading test. Breakthrough occurred after a total reaction time of 6 hrs which corresponds to 15.5% loading.

New sorbent formulations have been prepared using manganese-carbonate as starting material in combination with alumina and other oxides. Both dextrin and bentonite have been employed as bonding materials for pellet formation. All pellets made so far met strength requirements.

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Figure 1. Stability Diagram for the Mn-O System as a Function of Oxygen Potential and Reciprocal Temperature.

Figure 2. Equivalence Ratio vs Oxygen Partial Pressure (also CO_2 to CO ratio) at Several Temperatures for an Illinois No.6 Coal.

Figure 3. Equilibrium Partial Pressure of Predominant Sulfur-Bearing Species During the Gasification of an Illinois No. 6 Coal at 800°C .

Figure 4. Concentration of H₂S (ppmv) Resulting from the Gasification of an Illinois No. 6 Coal, as a function of Temperature and Equilibrium Ratio.

Figure 5. Concentration of H₂S(ppmv) in the Cleaned Gas as a Function of Equivalence Ratio and Temperature. Gasification and Desulfurization (with MnO) are Carried at the Same Temperature (Illinois No. 6).

Figure 6. Percentage of Sulfur Removal from Fuel Gas as a Function of Equivalence Ratio and Temperatures. Illinois No. 6 Coal

Figure 7. Equilibrium (Theoretical) SO₂ Emissions on Gasification of an Illinois No. 6 Coal After Desulfurization With MnO at Various Temperature.

Figure 8. Lines of Constant H₂S Concentration in Cleaned Gas as a Function of Desulfurization Temperature and H₂S and H₂O Content of the Fuel gas. Vertical Dashed Lines are for Some Commercial Gases as Indicate (Gas K:Shell; Gas I:Tampella-U-Gas; Gas C: Texaco Entrained-Bed; Gas J: Texaco Entrained-Bed (oxygen blown); Gas A: GE Fixed-Bed)

Figure 9a. Grain Model of a Gas-Solid Reaction.

Figure 9b. Shrinking Core Model of a Gas-Solid Reaction.

Figure 10. Schematic of the ASTRO thermogravimetric (TGA) Apparatus.

Figure 11. Normalized Weight vs Time for Reduction and Sulfidation of FORM1-D at 900°C in a 3% H_2S - H_2 Gas Mixture.

Figure 12. Normalized Weight vs Time for Reduction and Sulfidation of FORM2-D at 900 °C in a 3% H_2S - H_2 Gas Mixture.

Figure 13. Effect of Cyclic Loading and Regeneration on Sulfur Capacity of FORM4-A pellets at 900 °C.

Figure 14. Breakthrough Curve for 48th-Cycle Sulfidation at 900 °C of FORM4-A Pellets.