CHAPTER IV: DESULFURIZATION OF HOT COAL-DERIVED FUEL GASES WITH MANGANESE-BASED REGENERABLE SORBENTS. 1. LOADING (SULFIDATION) TESTS

This paper is a slightly edited version of a paper accepted for publication in the November/December issue of the American Chemical Society Journal "Energy & Fuels."

Acknowledgement. We express our appreciation to the Department of Energy, Morgantown Energy Technology Center, under Contract DE-AC21-92MC29246 and also the U.S. Bureau of Mines, Twin Cities Research Center, Grant USDI-BM/C0299002-Mod.3 for providing support for this study. We are indebted to the Twin Cities Research Center for the use of their TGA apparatus which made this work possible.

Desulfurization of Hot Coal-Derived Fuel Gases with Manganese-Based Regenerable Sorbents. 1. Loading (Sulfidation) Tests

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In earlier studies, zinc ferrite and zinc titanate were developed as regenerable sorbents capable of removing hydrogen sulfide from hot coal-derived fuel gases. Manganese ore as well as manganese carbonate, precipitated from aqueous solutions, combined with alumina to form indurated pellets is shown to hold promise of being a highly-effective, inexpensive, regenerable sulfur sorbent for hot fuel gases. Although the thermodynamics for sulfur removal by manganese predicts somewhat higher hydrogen sulfide over-pressures 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 activity by volatilization of reactive surfaces. This volatilization phenomenon limits the temperatures to which desulfurization can be effectively accomplished to less than 550 °C for zinc ferrite and 700 °C for zinc titanate; whereas, manganese-based sorbents can be utilized at temperatures well in excess of 700 °C. This paper addresses the physical and chemical behavior of several sorbent formulations fabricated from manganese and alumina, establishes the thermodynamic feasibility of hydrogen sulfide removal from hot simulated coal gases using these sorbents, and presents an analysis of the sulfidation reaction kinetics based on thermogravimetric experimental results.

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4.1 Introduction

The Integrated Gasification Combined Cycle (IGCC) is one of the most promising proposed processes for advanced electric power generation that is likely to replace conventional coal combustion. This emerging technology not only will improve considerably the thermal efficiency but will also reduce or eliminate the environmentally adverse effects normally associated with coal combustion. The IGCC process gasifies coal under reducing conditions with essentially all the sulfur existing in the form of hydrogen sulfide (H_2S) in the product fuel gas. The need to remove H_2S from coal-derived fuel gases is a significant concern which stems from stringent government regulations and also, from a technical point of view, a need to protect turbines from corrosion. Westmoreland et al.[1] and Hepworth et al.[2] carried out comparative studies on several proposed sorbent systems which consisted almost entirely of metal oxides. Metal oxides have been proposed because they tend to be more reactive at high temperature where desulfurization is desirable to conserve the sensible heat in gasifier fuel gas. A sulfur concentration limitation of approximately 150 ppmv (parts per million by volume) for IGCC systems has been established; therefore, a sorbent system capable of reducing H_2S concentration from about 5000 to 150 ppmv is sought.[3]

Zinc ferrite and zinc titanate have received much attention over the past twelve years because, from a theoretical point of view, they have desirable properties: high sulfur capacity, ability to remove H_2S from coal-derived fuel gas to levels of a few ppmv, and the feasibility of regeneration with air. Because it is economically necessary to recycle sulfur sorbents for at least 100 cycles, research has focused almost entirely on making the zinc-based sorbents durable. Unfortunately, extensive research carried out by the Morgantown Energy Technology Center (METC) of the Department of Energy (DOE) casts doubt that zinc ferrite or zinc titanate can be utilized even for fixed-bed operation. The desirable properties of Zn-based sorbents as well as their practical limitations will be discussed in detail in a later section of this paper.

Given the limited success of the zinc-based sorbents, METC has shown interest in formulating and testing manganese-based sorbent pellets.[4] There are a number of studies that led to the consideration of Mn-based sorbents. Westmoreland *et al.*[1] screened the high-temperature desulfurization potential of 28 solids, primarily metal oxides, based upon thermodynamic considerations alone. This earlier work, which was subsequently followed by kinetic studies,[5] predicted manganese oxide stability and a high degree of desulfurization to temperatures in excess of 1000 °C. In addition, manganese showed desulfurization potential in the range of 600 to 700 °C where traditional metal oxides known to be reactive with H_2S proved unsatisfactory. These kinetic studies determined the initial rates for the reaction between H_2S and MnO, CaO, ZnO, and V_2O_3 over a temperature range of 300 to 800 °C. The relative magnitude of reaction rates decreased in the order: $MnO > CaO \approx ZnO > V_2O_3$. They concluded that MnO possessed favorable properties for a high temperature desulfurization process and highly recommended that further studies be carried out.

Turkdogan and Olsson[6] examined the feasibility of using manganese oxide pellets to desulfurize hot reducing gases. They found that a mixture of manganese ore and alumina formed into pellets in a 3:1 weight ratio readily accepted sulfur from hot (800 °C) H_2-H_2S gas mixtures and that the pellets could be regenerated with air, or other oxidizing gases. They explored the cyclic loading and regeneration of these pellets through 18 consecutive cycles. Their pellets exhibited high strength and rapid loading kinetics which did not show a decline in reactivity or capacity through the regimes which they explored. Interestingly, repeated cycling of the pellets resulted in improved sulfidation and regeneration kinetics, unlike the situation with Zn-based sorbents, as will be discussed later. This desirable phenomenon with manganese pellets was attributed to transport between pellet pores, possibly by development of cracks.

During their investigation of zinc ferrite Jha and Hepworth[7] substituted MnO for some of the zinc oxide as a means of enhancing the durability and reactivity of the zinc ferrite and reported favorable results. In a recent study Hepworth et al.[2] developed a systematic approach for the evaluation of the behavior of single and mixed-metal sorbents for removing sulfur from hot coal-derived fuel gases, based on thermodynamic considerations. A range of metal systems including iron, nickel, magnesium, calcium, manganese, copper, sodium, and zinc were examined. This study 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. This paper addresses the physical and chemical behavior of several sorbent formulations fabricated from manganese and alumina, establishes the thermodynamic feasibility of H_2S removal from hot simulated coal gases, and presents an analysis of the sulfidation kinetics based on thermogravimetric experimental results.

4.2 Thermodynamic Considerations

There are four stable oxides of manganese: MnO, Mn_3O_4, Mn_2O_3, and MnO_2. Figure 4.1 is a stability diagram for the Mn-O system as a function of oxygen potential and temperature with superimposed equilibrium CO_2/CO ratios in the gas phase. A very desirable feature of this system is its resistance to reduction to elemental manganese by CO or H_2 because of the unavoidable presence of trace amounts of CO_2 and H_2O in the reducing gas. In addition, the higher oxides of manganese are readily reduced to MnO even in very slightly reducing atmospheres. This implies that MnO is the stable form of manganese for virtually all commercially available coal-derived fuel gases.

The reducing coal-derived fuel gas is desulfurized by MnO according to reaction 1

$$MnO_{(s)} + H_2S_{(g)} = MnS_{(s)} + H_2O_{(g)} \tag{4.1}$$

The equilibrium ratio of H_2O/H_2S for this reaction has been determined by

Turkdogan and Olsson,[6] and is expressed by

$$Log\left[\frac{pH_2O}{pH_2S}\right] = \frac{3330}{T} - 0.310 \qquad (4.2)$$

In the desulfurization of hot reducing gases by Mn-based pellets, the extent of desulfurization achieved depends on temperature and gas composition. The residual H_2S concentration in the desulfurized gas, calculated using SOLGASMIX[2,8], for the conditions of gas-solid equilibrium in the reactor, is shown in Figure 4.2 as a function of temperature for various typical oxygen-blown and air-blown gasifier gases, the compositions of which are reported in Table 4.1.* It is seen from this figure that the lower the operating temperature and the lower the H_2O/H_2S ratio, the lower is the residual sulfur in the cleaned gas. Noting that the amount of water vapor produced in the exhaust gas is equal to the quantity of H_2S reacted, the concentration of H_2S in the exhaust gas can be expressed as a function of temperature and H_2O content of the clean gasifier fuel gas. This is given by equation 3, where T denotes absolute temperature in °K.

$$[H_2S]\ (ppmv) = \frac{(\%H_2O)_{fuel\ gas}}{10^{\frac{3330}{T} - 4.310}} \qquad (4.3)$$

This equation may be used to predict the concentration of H_2S in a fuel gas following equilibration with MnO. It is seen that the objective of reducing the concentration of H_2S below 150 ppmv to satisfy the IGCC system requirement is thermodynamically feasible. See inset in Figure 4.2 for the Tampella-U and Shell (oxygen-blown) gases.

4.3 Experimental Investigations and Results

4.3.1 Sorbent Pellet Preparation. The prior studies by Turkdogan and Olsson[6] were conducted on an African rich pyrolusite (MnO_2) ore which assayed 63%

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

Table 4.1 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	10.55	16.13	11.9	40	15	8	15.2	24.33	39.1	64
CO_2	11	4.64	7.55	10	12.5	5	11	8.28	5.16	12.25	.8
H_2	16	8.26	10.7	17.4	27.84	10	15	10.7	13.19	30.13	31.6
H_2O	30	27.52	10.94	28.1	18.5	15	30	10.7	5.35	17.52	1.5
H_2S	3	.06	.42	1	1.08	.5	.5	.5	.118	1	1.4
COS	-	-	.03	-	.08	-	-	-	-	-	-
N_2	29	48.73	54.22	28.7	-	53.7	32.2	53.9	49.9	-	.7
CH_4	3	.24	-	3	-	.5	3	-	1.84	-	-
NH_3	.5	.2	.16	.5	.2	.3	.3	-	.111	-	-
CO/CO_2	.73	2.27	2.14	1.19	3.2	3	.73	1.84	4.72	3.19	80
H_2/H_2O	.53	.3	.98	.62	1.5	.67	.5	1	2.47	1.72	21

Mn (primarily as Mn_3O_4) upon calcination in air at 1000 °C. A significant domestic source of manganese in Minnesota is being explored for an in-situ leach process[9] which has potential for producing large tonnages of solutions which may be ideal for precipitation and recovery of pure manganese as a carbonate[10] in a reactive form. For these reasons, the present investigation employed similar materials: Moanda manganese ore,[*] regular manganese carbonate,[#] alundum,[**] bentonite,[##] and dextrin.[***]

Four pellet formulations were prepared using combinations 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 was as low as possible, not only to save on the cost, but also to provide a greater amount of chemically active sorbent. After each blend is mixed, an appropriate amount of water is added prior to pelletizing. The composition of the initial make up of the formulations prepared using this procedure is reported in Table 4.2.

Twenty-four induration campaigns were conducted. Preliminary tests indicated that Moanda ore-based pellets required a temperature of 1200 °C and manganese carbonate-based pellets required an induration temperature of 1250 °C, to produce a required strength of greater than 22 N per mm of pellet diameter (5 lbs/mm). In addition, two time periods for induration were explored,

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[*] Moanda manganese ore (77% MnO_2, 3.36% MnO, 6% Al_2O_3, 2.81% Fe, 2.56% SiO_2, 5.16% H_2O (bound)) was obtained from the Prince Manufacturing Company in Quincy, IL.

[#] Regular manganese carbonate (approximately 93-95% pure) was obtained from Chemetals, Inc. in Baltimore, MD.

[**] Alundum (96.6% Al_2O_3, 2.6% TiO_2) was obtained from Industrial Ceramics Corporation (Norton Materials) in Worcester, MA.

[##] Bentonite, an inorganic binder, was obtained from the Aldrich Chemical Company, Inc. in Milwaukee, WI.

[***] Dextrin (type IV), an organic binder, was obtained from the Sigma Chemical Company in St. Louis, MO.

Table 4.2 Initial Make up of Formulations

Formulation No.	Raw Material Content in initial make-up, wt.%				
	Moanda Ore	Alundum	$MnCO_3$###	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	81.31	1.96	-

namely, 1 hour and 2 hours. The strongest formulations are bentonite-bonded as expected. At the conclusion of these tests, four formulations were selected for thermogravimetric analysis (TGA). 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.

Table 4.3 summarizes the manganese assays and strengths of the formulations which were subjected to TGA analysis. In addition, BET surface area tests on indurated pellets have shown them to have a surface area less than 0.2 m^2/g, which is below the sensitivity of our equipment and therefore required krypton as a carrier gas in an outside laboratory. Typical specific surface area values are 0.055 and 0.127 m^2/g for FORM2-A and FORM1-A, respectively. These low specific surface area values are caused by rapid sintering which occurs during induration at high temperature. Porosity tests made by combination of aqueous and mercury pycnometry on crushed pellets from formulation 2 showed the pellets to have a porosity of about 36%.

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

Table 4.3 Manganese Assays and Strengths of Formulations Studied.

Sample Designation	Weight %Mn	Strength, N/mm
FORM1-A	41.14	25.5
FORM2-A	37.48	64.7
FORM2-B	39.83	52.4
FORM4-A	44.22	23.8

4.3.2 Pellet Reactivity via Thermogravimetric Analysis (TGA). The TGA testing is divided into two campaigns the first being only comparative loading for one cycle, and the second for regeneration studies and repeated cyclic loading and regeneration. The second campaign activity will be described in a following paper.

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), fuel gas H_2S content (1%, 2%, and 3% in H_2/H_2S gas mixtures), and pellet diameter in the range 5-10 mm. As was established earlier, the reducing power of the fuel gas is not sufficient to cause the reduction of MnO to elemental Mn. Accordingly, it was not considered important in these loading tests to place any particular emphasis on the kinetics of reduction since there are no losses to be expected by evaporation as would be the situation with zinc-based sorbents.

Figure 4.3 is a schematic diagram of the experimental equipment employed for TGA testing. The upper right-hand portion of the diagram shows the Cahn 1000-Series automatic recording balance assembly which holds up to twelve pellets in a nichrome wire-mesh basket suspended with a nichrome chain from the left pan of the balance. The reactor consists of an alumina tube positioned in a high-temperature molybdenum-wound furnace. The reaction temperature was monitored by using a Pt/Rd thermocouple positioned directly below the sorbent pellets. The weighing unit was constantly blanketed with nitrogen during each test. The gas delivery and data acquisition systems are as depicted. Vent gases are scrubbed in a sodium hypochlorite solution prior to flaring and venting.

For each test, pellets were selected at random from a large batch of indurated pellets. The furnace pressure was 1 atm and the total flowrate was 500 cc/min. Before the heat was turned on, the reactor chamber was evacuated to 0.03 atm and then backfilled with nitrogen. The reactor was heated in a nitrogen atmosphere flowing at 1 L/min to the desired operating temperature before the balance platform was lowered to position the pellets in the center of the 10-cm-long hot zone. Five minutes after the sample was lowered into the hot zone, the nitrogen flow was shut off and the reactive gas mixture was started . Chemically pure (>99.9 %) hydrogen and hydrogen sulfide were metered into the TGA apparatus; flows were regulated by needle valves using calibrated rotameters.

Finally, the nitrogen flow was turned on and the pellets were raised into the cold zone. The results of these TGA tests are shown in Figures 4 through 9, which are studies on loading of pellets as described below.

Figure 4.4 shows the results of TGA analysis at 1000 °C on the four selected sorbents which were described above. In this plot and the plots which follow, the weight of the pellets divided by the initial weight is expressed on the ordinate as a weight ratio: W/W_o. Initially, this ratio for all pellets is unity; however, there is a decline in this value (reduction of Mn_3O_4 to MnO) when the pellets are exposed to hydrogen during the initial reduction period. Each reduction phase lasted 45 minutes although all pellets remained constant in weight for at least 20 minutes. Each of the sorbents appears to have lost the expected percentage of its original weight; FORM4-A pellets, which contain high manganese concentrations lost appreciably more weight than did the pellets containing lower proportions of manganese. Total percent loss at the conclusion of the reduction period ranged from 2% to 5% for FORM2-B and FORM4-A, repectively.

As indicated on the figures describing sorbent screening tests, 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 because of the higher manganese content of the calcined carbonate. (see Tables 4.2 and 4.3). 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 at 1000 °C 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 general, however, and at longer reaction times, each curve would approach its final weight corresponding to complete sulfidation.

In continuing the examination of Figure 4.4, 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 4.5 shows similar results for tests conducted at 900 °C. Again formulation 4-A shows the highest sulfur capacity and the most rapid kinetics of the four pellet groups. From Figure 4.6 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).

Results from similar loading tests at 700 °C indicated that 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 4.7 is a composite of the data for formulation 4-A, the best of all the formulations studied, for the temperatures 760, 800, 900, and 1000 °C. The theoretical capacity for this formulation is shown as a dashed line on the plot with reactivity rates for all temperatures 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 as pre-selection criteria.

Figure 4.8 shows the effect of fuel gas H_2S content, over the range 1 to 3% by volume and a constant temperature of 900 °C, on sulfidation kinetics of FORM1-A pellets. The results are as expected, with the sulfidation rate increasing with the H_2S content. At 1% H_2S, the reaction was about 88% complete when the run was terminated after the 2-hr period. However, the reaction was progressing normally, and it appears that complete sulfidation would be achieved if the reaction time had been extended.

Figure 4.9 shows the effect of pellet diameter on sulfidation kinetics at 900 °C for FORM1-A. As expected, the smaller pellets reacted faster, but differences are not too appreciable.

4.4 Kinetic Considerations

As established by the previous thermodynamic analysis, the sulfidation reaction is represented by equation (4.1). This reaction is heterogeneous in which a gas contacts a solid, reacts with it, and then transforms it into products. During sulfidation the pellets contain sufficient amounts of non-reactive impurities (alumina matrix and inorganic binder in some instances) which remain as non-flaking materials. Sulfidation reaction also forms firm product material of somewhat similar specific volume as the reactant : i.e., oxide (MnO) to sulfide (MnS). Accordingly, the sorbent pellets may be assumed to remain unchanged in size during sulfidation although they undergo structural changes. Such an assumption is made in the modeling of metallurgical processes such as the roasting of sulfide ores and the subsequent reduction of the resulting oxides to metals. In addition, the sulfidation reaction is controlled to a large extent by diffusion and may thus be considered irreversible. An additional assumption may be made about the reaction being elementary (i.e., first-order with respect to H_2S)

and the concentration gradients being linear to simplify the mathematical treatment of the problem.[11,12]

Evidence from a wide variety of situations indicates that the shrinking-core model approximates the behavior of real particles closely in most cases.[11] In this model the reaction proceeds at a narrow front which moves into the solid particle and the reactant is completely converted as the front progresses.

In the following analysis, rate equations (time-conversion) describing the progress of the sulfidation reaction with time have been derived, with reference to Figure 4.10, using the following steps which are conceptualized to occur in series:

Step 1: Diffusion of gaseous reactant H_2S through the gas film surrounding the pellet to the exterior surface of the pellet.

Step 2: Penetration and diffusion of H_2S through the newly-formed product layer, MnS, to the surface of the unreacted core.

Step 3: Reaction of H_2S with the reactive component of the pellet, MnO, at the reaction front to exchange sulfur with oxygen and release H_2O.

Step 4: Diffusion of the gaseous product, H_2O, through the product layer, MnS, to the exterior surface of the pellet.

Step 5: Diffusion of H_2O through the gas film to the bulk of the reducing fuel gas.

It must be noted that diffusion steps 2 and 4 could be considered as one step as a countercurrent diffusion in a binary gas mixture. The resistances of the different steps usually vary greatly from one another and the step with the highest resistance is taken as the rate-controlling step.

Time-Conversion performance equations for the sulfidation reaction obtained using the shrinking-core model are given by equations (4.4), (4.5), and (4.6) for diffusion through gas film control, diffusion through product layer control, and surface reaction control, respectively. The symbols used in these equations and their units are as follows: t:time (s); R_p: radius of reduced pellet (cm); k_g: mass transfer coefficient between reducing fuel gas and sorbent pellet (cm/s); k_s: first-order rate constant for the surface reaction (cm/s); superscript o: initial value of parameter; superscript e: equilibrium value of parameter; ρ_i: molar density of component i in pellet (mol/cm^3); F_i: fractional conversion of component i in *reduced* pellet (dimensionless); D_e: effective diffusivity (cm^2/s); R: universal gas constant (cm^3-atm/mol-°K); T: absolute temperature (°K); P: total pressure (atm); P_i: partial pressure of gaseous component i (atm), and C_1, C_2, and C_3: constants of integration.

$$F_{MnO} = \frac{3k_g(P^{o}_{H_2S} - P^{e}_{H_2S})}{RT\rho_{MnO}\,R_p}\,t + C_1 \tag{4.4}$$

$$3 - 2F_{MnO} - 3(1 - F_{MnO})^{2/3} = \frac{6D_e(P^{o}_{H_2S} - P^{e}_{H_2S})}{RT\rho_{MnO}\,R^2_p}\,t + C_2 \tag{4.5}$$

$$1 - (1 - F_{MnO})^{1/3} = \frac{k_s(P^{o}_{H_2S} - P^{e}_{H_2S})}{RT\rho_{MnO}\,R_p}\,t + C_3 \tag{4.6}$$

The sulfidation rate is likely to be controlled primarily by countercurrent diffusion through the porous layer of manganese sulfide (MnS) formed. Therefore, the rate data for the sulfidation reaction of FORM4-A pellets at 800, 900, and 1000 °C are plotted in Figure 4.11 in accordance with equation (4.5). It is seen that beyond about 35% reaction, when the product layer becomes sufficiently thick, the results follow closely the limiting rate equation. The effective gas diffusivity, D_e, is then calculated from the slopes of the regression lines the equations of which are indicated in the legend. Figure 4.12 displays D_e (on a log scale) as a function of reciprocal temperature. In the range 850 to 1000 °C the temperature dependence of the effective diffusivity is given by the following equation.

$$Log(D_e) = \frac{-1656}{T} + 2.2 \tag{4.7}$$

4.5 Mn-Based Sorbents vs Zn-Based Sorbents

The theoretical capacity of manganese-based pellets for sulfur compares favorably with zinc ferrite and zinc titanate as shown in Table 4.4. In generating this table, the overall reactions of the active components of manganese-based pellets, zinc ferrite, and zinc titanate with the major sulfur-bearing species in gasifier gases, H_2S, are as represented by equations (4.1), (4.8), and (4.9), respectively.

$$3ZnO_{(s)}+2Fe_3O_{4(s)}+9H_2S_{(g)}+2H_{2(g)} = 3ZnS_s+6FeS_{(s)}+11H_2O_{(g)} \quad (4.8)$$

$$Zn_2TiO_{4(s)} + 2H_2S_{(g)} = 2ZnS_{(s)} + TiO_{2(s)} + 2H_2O_{(g)} \quad (4.9)$$

It is also assumed that Fe_3O_4 is the stable form of Fe after reduction of $ZnFe_2O_4$, and that the optimized zinc titanate formulation is composed of 1.5 ZnO:1.0 TiO_2. Furthermore, the manganese ore-based formulation is based upon Moanda ore containing 51.2% Mn by weight.

Clearly, even the manganese ore-based sorbent pellet, which has a lower capacity than the Mn carbonate-based formulation, 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 of manganese-based pellets is less favorable than would be achieved with Zn-based sorbents. For example, for a fuel gas containing 5% H_2O and 1% H_2S, desulfurization at 1000 °K (727 °C) achieves 57 ppmv H_2S with MnO and 6 ppmv H_2S with ZnO, based on data compiled by Turkdogan.[13]

Table 4.4 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
Mn carbonate-based	25.8

To compare the rate of sulfidation of Mn-based pellets with that of Zn-based sorbents, the results from sulfidation tests on L-3140 sorbent[3] at 760 and 870 °C are superimposed on the results reported above in Figure 4.7, as shown in Figure 4.13. The goal of exposing the Zn-based sorbent to the H_2S-free reducing gas is to quantify the weight loss which is solely due to ZnO depletion. At 760 °C this physical loss of reactive component is negligible; however, at 870 °C this phenomenon becomes noticibly more severe leading to lower sorbent capacity for sulfur. More importantly, the rate of sulfur pick-up from hot coal-derived fuel gases using Mn-based pellets compares favorably with that which is obtained using Zn-based sorbents.

One major problem associated with zinc-based sorbents is sulfate formation which is found to occur whenever SO_2 is present in the regeneration gas. Sulfation leads to volume expansion and swelling of sorbent pellets eventually causing them to spall and crack. For example: a 5 to 6-mm diameter loaded pellet expands to 9 mm after regeneration when sulfate was formed.[14] Certainly, in a fixed-bed operation some of the pellets will be saturated with sulfur and the regeneration gas will contain some SO_2. Therefore, sulfate formation is unavoidable along with accompanying spalling and cracking.

The role of chlorides in the gas system should be considered in any study because of the potential volatility of metal chlorides. The presence of HCl in the coal gas causes extensive volatilization of zinc in the form of $ZnCl_2$. All fuel gases contain some hydrochloric acid, under reducing conditions. Zinc chloride ($ZnCl_2$) has a boiling point of 1005 °K (732 °C); whereas, manganese chloride ($MnCl_2$) has a boiling point of 1504 °K[15] (1231 °C). The higher boiling point of manganese makes it much less susceptible to volatilization and losses from the sorbent than zinc. Losses of zinc as high as 5-10% by weight from the exit of a fixed-bed reactor have been reported,[14] even after one cycle of loading and regeneration. It follows that any gas system which is used as an environment for comparing the cyclic loading and regeneration behavior between manganese oxide and zinc-based sorbents should take into account the presence of chlorides in the fuel gases.

A fortuitous feature of the manganese-oxygen-sulfur system is its resistance to reduction to elemental manganese under the range of most of the fuel gas compositions for which it would be utilized as a sorbent. Furthermore the sulfidation and regeneration can be carried out at the same temperature, for example (800 °C) without the formation of sulfates. Another favorable feature of the manganese-oxygen-sulfur system is its resistance to fusion as a result of temperature rises which may occur in the exothermic step of regeneration since the system is relatively refractory and non-volatile (i.e., lacks low melting-point phases) even in the presence of trace chloride impurities. For the case of zinc ferrite, it was found that temperature excursions as small as 50 °C could destroy the sorbent reactivity.[16] Exit gas temperatures from commercial gasifiers are likely to be in excess of 650 °C; in addition, operation of the desulfurization process at higher temperatures increases the overall IGCC plant efficiency. Manganese-based pellets appear to be capable of much higher temperatures of loading and regeneration than zinc without degradation; however, this question remains to be fully explored.

4.6 Summary and Conclusions

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) required an induration temperature of 1200 °C.

Single loading tests via TGA analysis at temperatures ranging from 700 to 1000 °C show that the manganese carbonate source material bonded with bentonite exhibits the best combination of loading capacity and kinetics. The manganese ore-based formulation (FORM1-A) exhibited the best combination of sulfidation capacity, kinetics, and strength. Both formulations, however, are deemed to be successful in reducing the H_2S concentration in the coal-derived fuel gas to less than 150 ppmv.

4.7 References

1. Westmoreland, P.R.; Harrison, D.P. Evaluation of Candidate Solids for High-Temperature Desulfurization for Low-Btu Gases. *Environ. Sci. Technol.* **1976**, 10, 659-661.
2. Hepworth, M.T.; Ben-Slimane, R.; Zhong, S. Thermodynamic Comparison of Several Sorbent Systems for Hot Coal-Derived Fuel-Gas Desulfurization. *Energy Fuels* **1993**, 7, 602-609.
3. Woods, M.C.; Gangwal, S.K.; Jothimurugesan, K.; Harrison, D.P. Reaction between H_2S and Zinc Oxide-Titanium Oxide Sorbents. 1. Single-Pellet Kinetic Studies. *Ind. Eng. Chem. Res.* **1990**, 29, 7, 1160-1167.
4. Hepworth, M.T.; Ben-Slimane, R. Hot Coal Gas Desulfurization with Manganese-Based Regenerable Sorbents. *Proceedings of the Coal-Fired Power Systems 93 -- Advances in IGCC and PFBC Review Meeting, 1993,* David L. Bonk editor, DOE/METC - 93/6131, NTIS, Springfield, VA, pp. 432-444.
5. Westmoreland, P.R.; Gibson, J.B.; Harrison, D.P. Comparative Kinetics of High-Temperature Reaction Between H_2S and Selected Metal Oxides. *Environ. Sci. Technol.* **1977**, 11, 488-491.
6. Turkdogan, E.T.; Olsson, R.G. Desulfurization of Hot Reducing Gases with Manganese Oxide Pellets. *Proceedings of the Third International Iron and Steel Congress ASM;* ASM International: Materials Park, OH, 1979, 277-288.
7. Jha, M.C.; Hepworth, M.T. Enhanced Sorbent Durability for Hot Gas Desulfurization; DOE Contract DE-AC21-84MC21168, Final Report, 1986.
8. Flynn, H.; Morris, A.E.; Carter, D. An Iterative Gas-Phase Removal Version of SOLGASMIX. *Proceedings of the 25th CIM Conference of Metallurgists, TMS-CIM,* Toronto, Ontario, 1986.
9. Marozas, D.C.; Paulson, S.E.; Petrie, L.M. Evaluation of the Potential for Selective in Situ Leach Mining of Manganese Ores, 1992, *SME Annual Transactions,* Vol. 292, pp. 1819-1828.
10. Petrie, L; Marozas, D.; Paulson, S; Redden, L. A Geochemical Approach to Lixiviant Development for Manganese in Situ Leach Mining; *Hydrometallurgy,* Vol. , pp. 1011-1027.

11. Levenspiel, O. *Chemical Reaction Engineering*, p. 368, 2nd Edition, John Wiley & Sons, Inc., 1972.
12. Szekely, J.; Evans, J.W.; Sohn, H.Y. 1976, *Gas-Solid Reactions*, p. 132, Academic Press, New York.
13. Turkdogan, E.T. Physical Chemistry of High Temperature Technology, Academic Press: New York, 1980.
14. Venkataraman, V. K. Private Communication: Information on Workshop "Status and Direction of Research and Development for High Temperature Sulfur Removal Sorbents," Morgantown Energy Technology Center, January 28, 1993.
15. Handbook of Chemistry and Physics, 67th Edition, 1986-1987, CRC Press, Inc., Boca Raton, FL.
16. G.D. Focht; P.V. Ranade; D.P. Harrison. High-Temperature Desulfurization Using Zinc Ferrite: Reduction and Sulfidation Kinetics. *Chemical Engineering Science*, Vol. 43, No. 11, pp. 3005-3013, 1988.

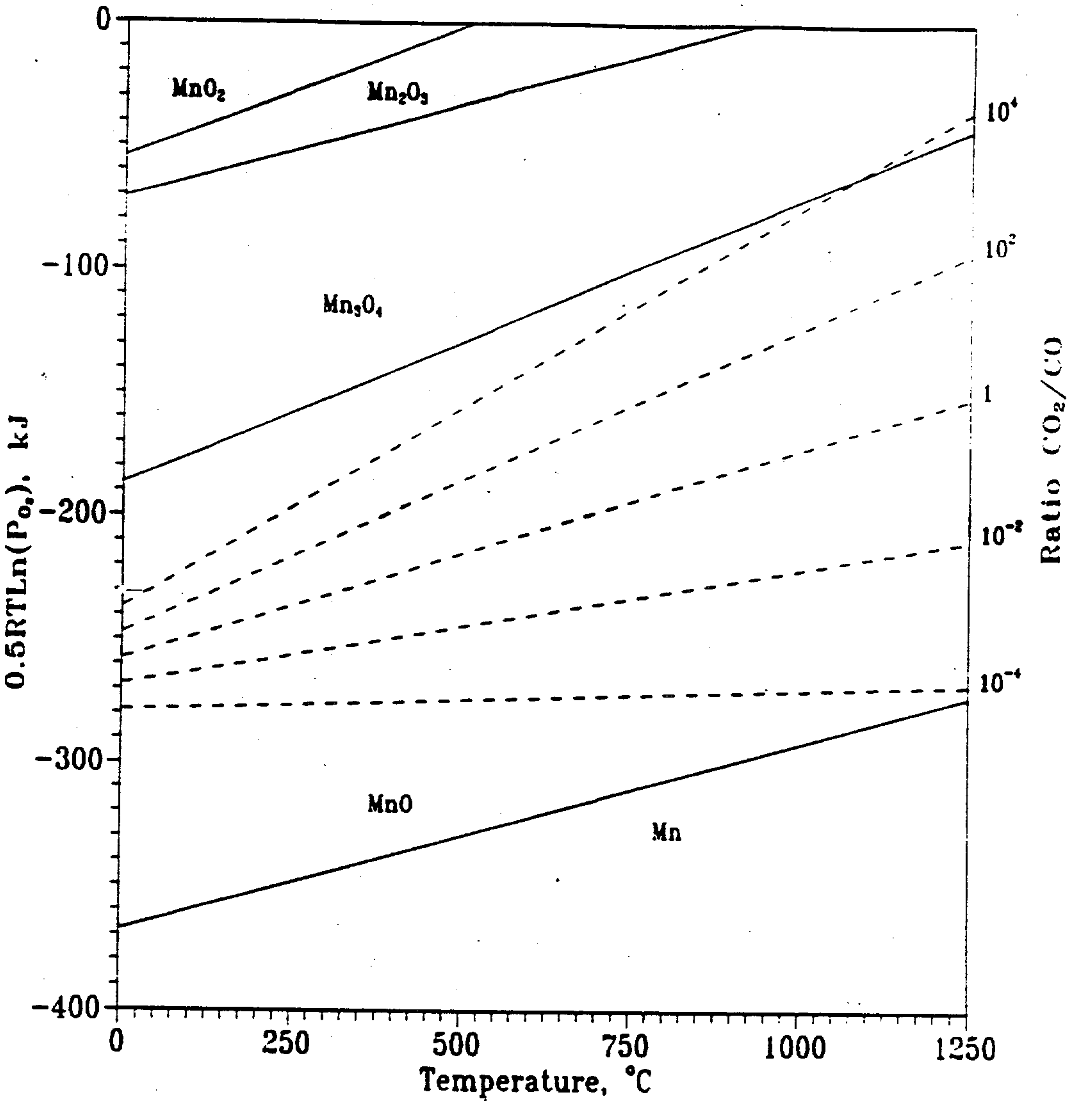

Figure 4.1 Oxygen potential diagram for the Mn-O system showing lines of constant CO_2/CO ratios.

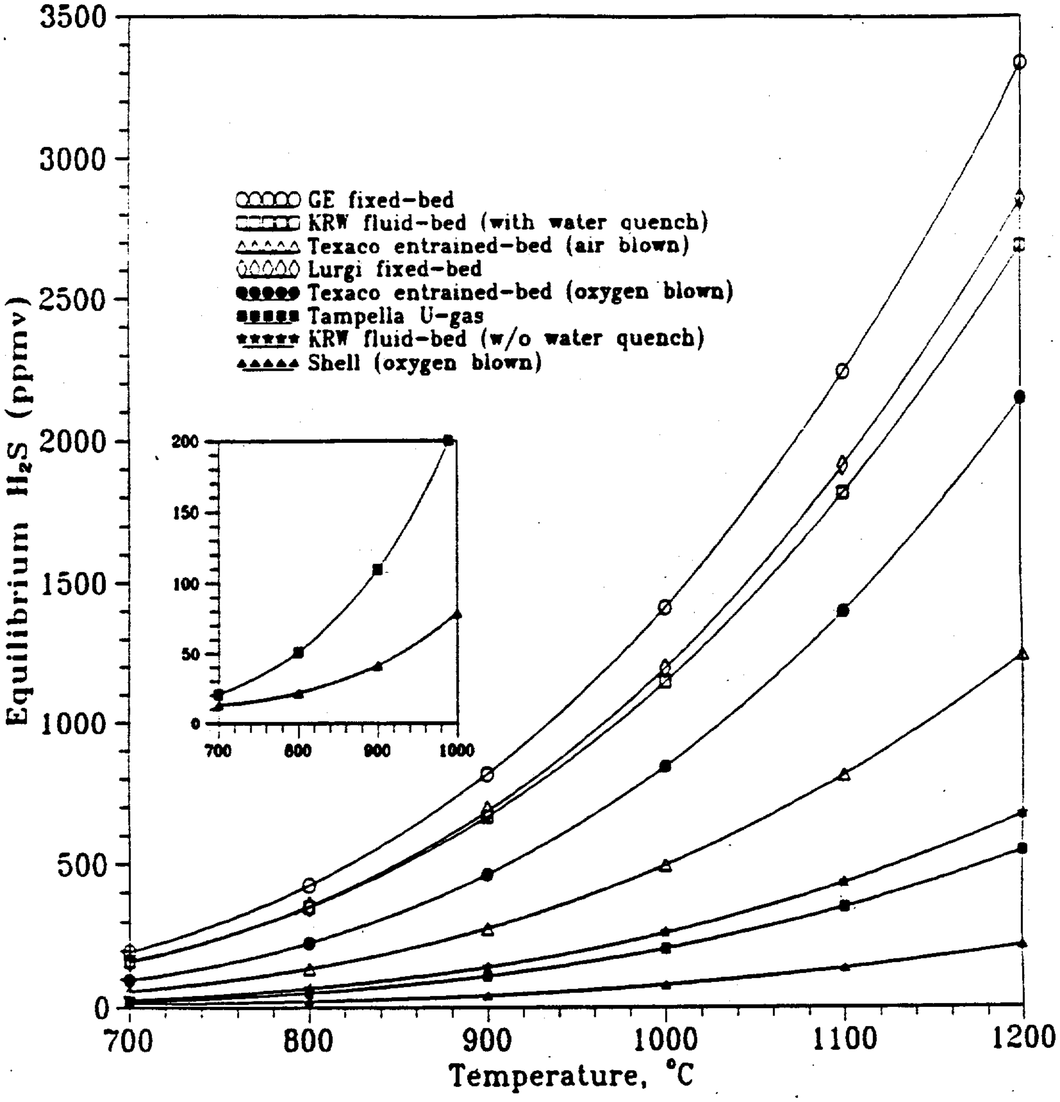

Figure 4.2 Equilibrium H_2S concentration in desulfurized gas as a function of temperature for typical air-blown and oxygen-blown gasifiers.

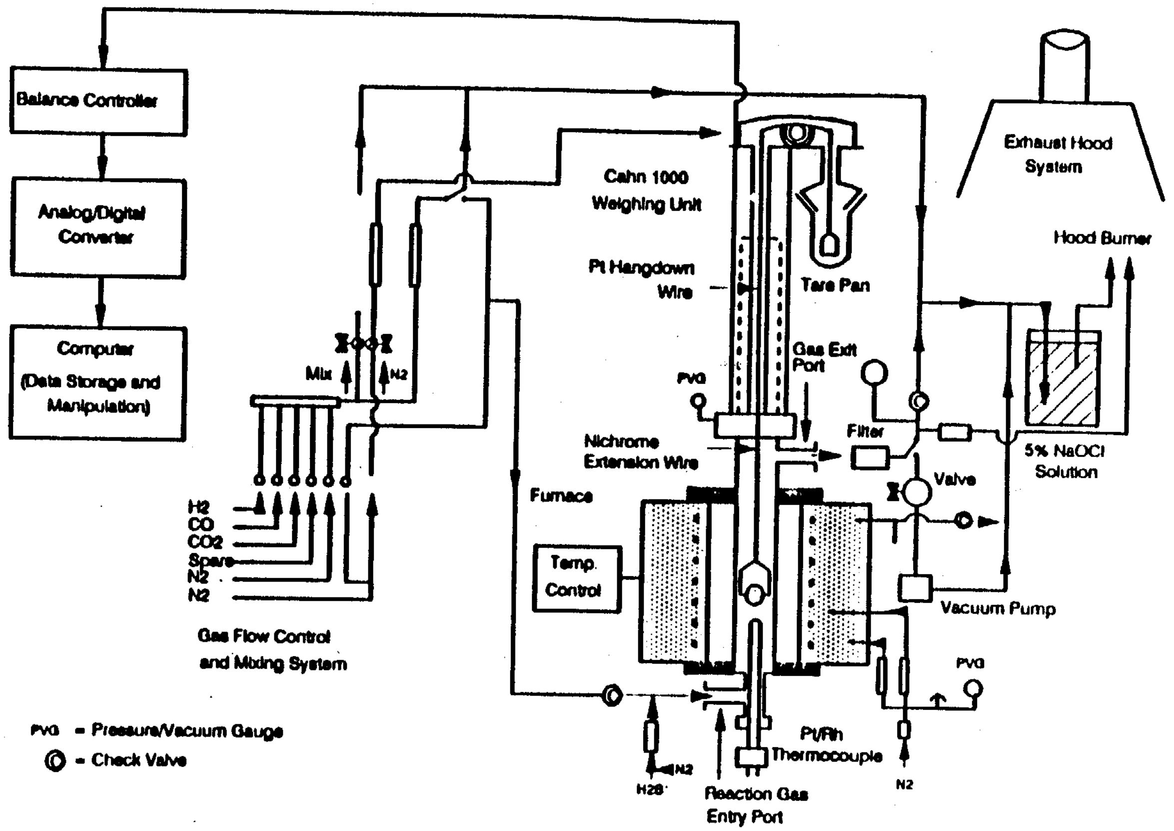

Figure 4.3 Schematic of the ASTRO thermogravimetric (TGA) apparatus.

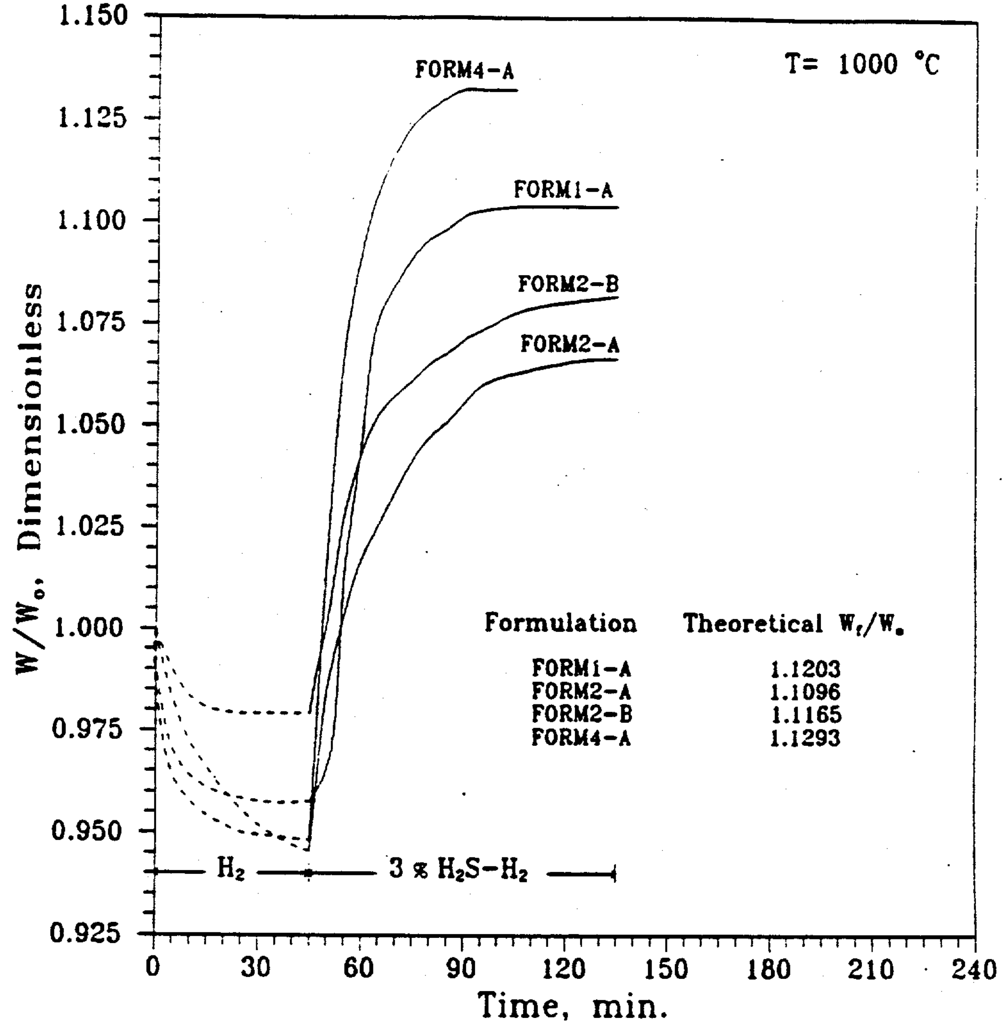

Figure 4.4 Normalized weight vs time for reduction and sulfidation of four manganese-based formulations at 1000 °C in a 3% H_2S-H_2 gas mixture.

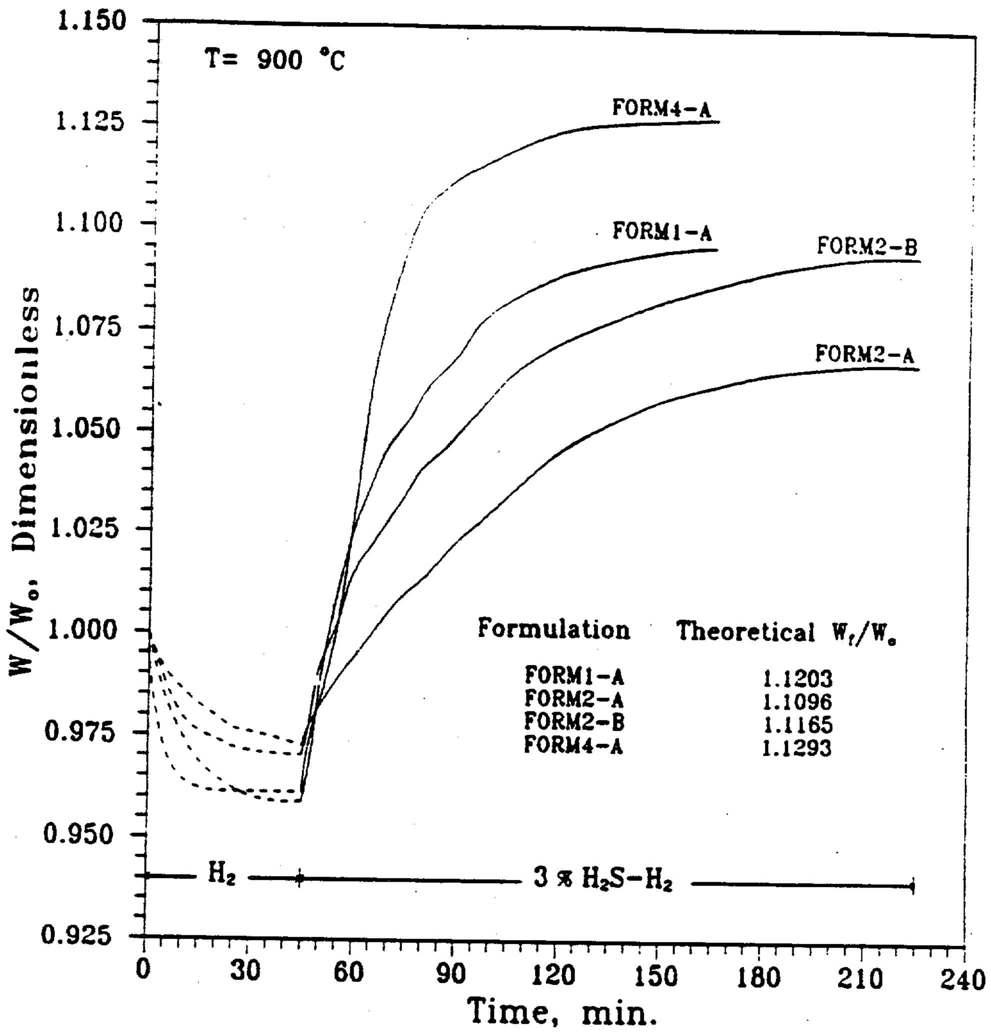

Figure 4.5 Normalized weight vs time for reduction and sulfidation of four manganese-based formulations at 900 °C in a 3% H_2S-H_2 gas mixture.

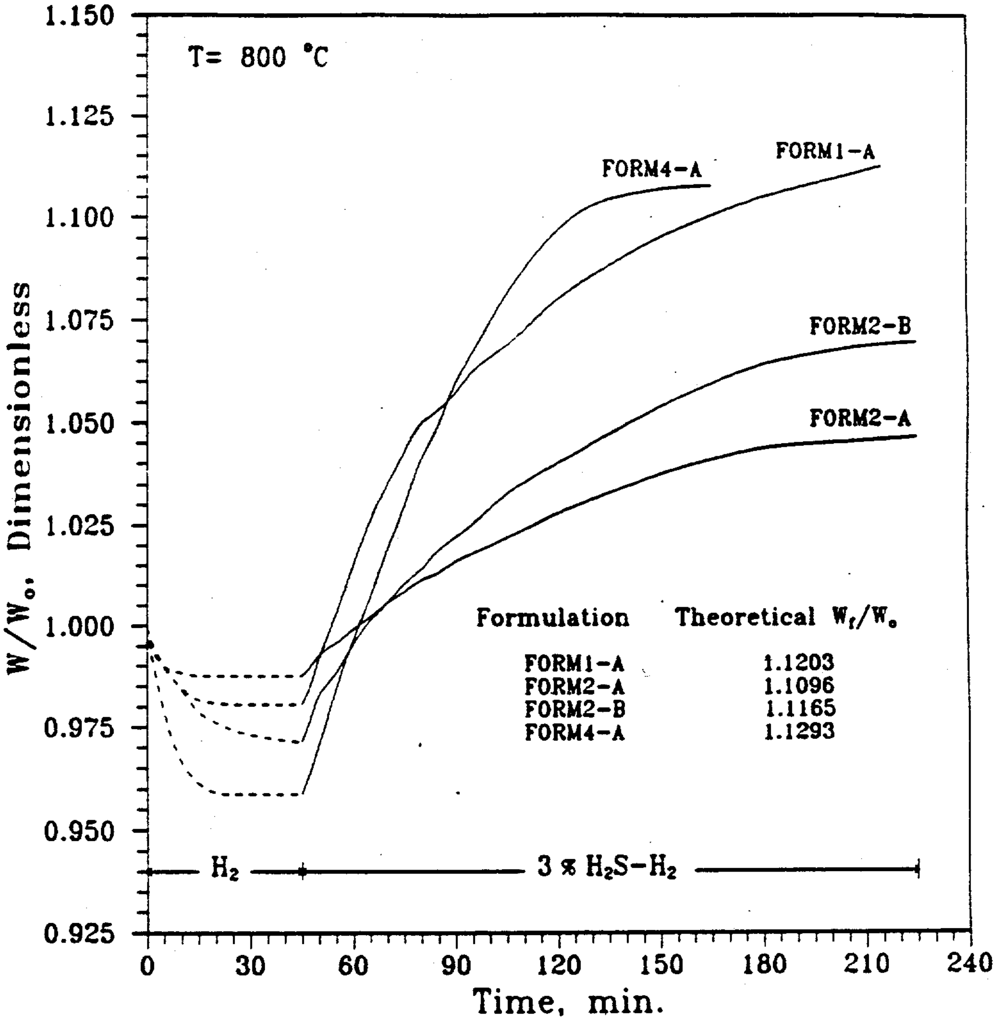

Figure 4.6 Normalized weight vs time for reduction and sulfidation of four manganese-based formulations at 800 °C in a 3% H_2S-H_2 gas mixture.

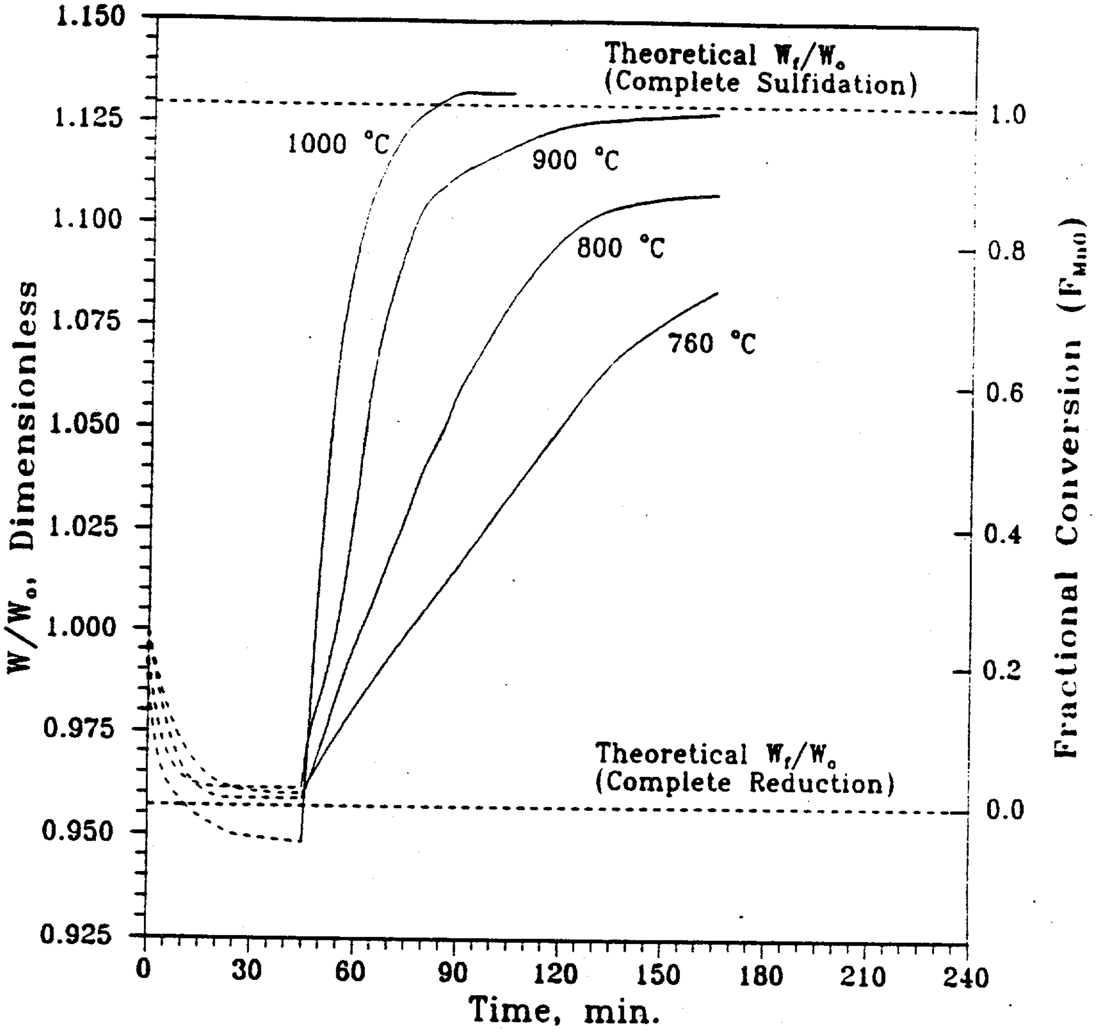

Figure 4.7 Effect of temperature on sulfidation kinetics of FORM4-A pellets.

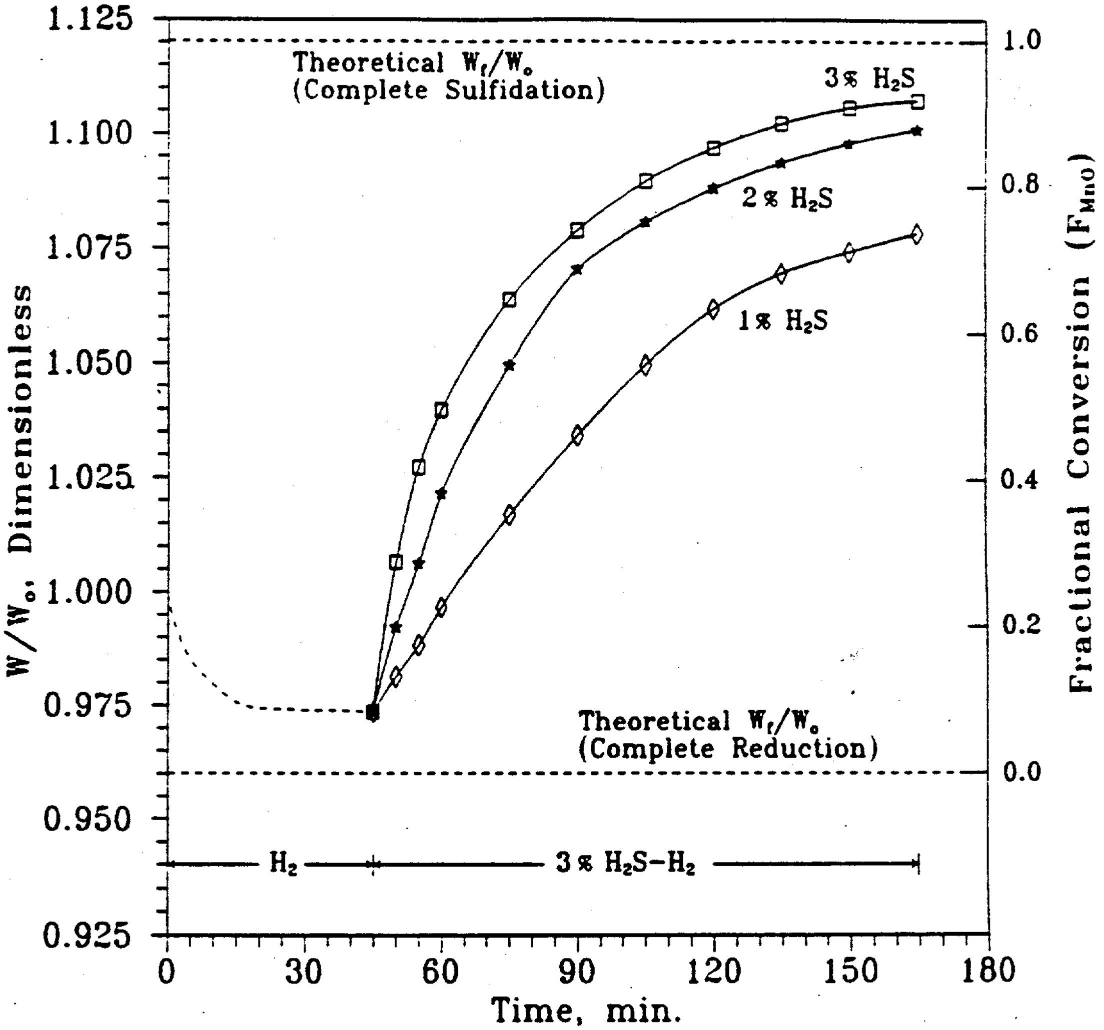

Figure 4.8 Effect of H_2S concentration on sulfidation kinetics of FORM4-A pellets at T= 900 °C.

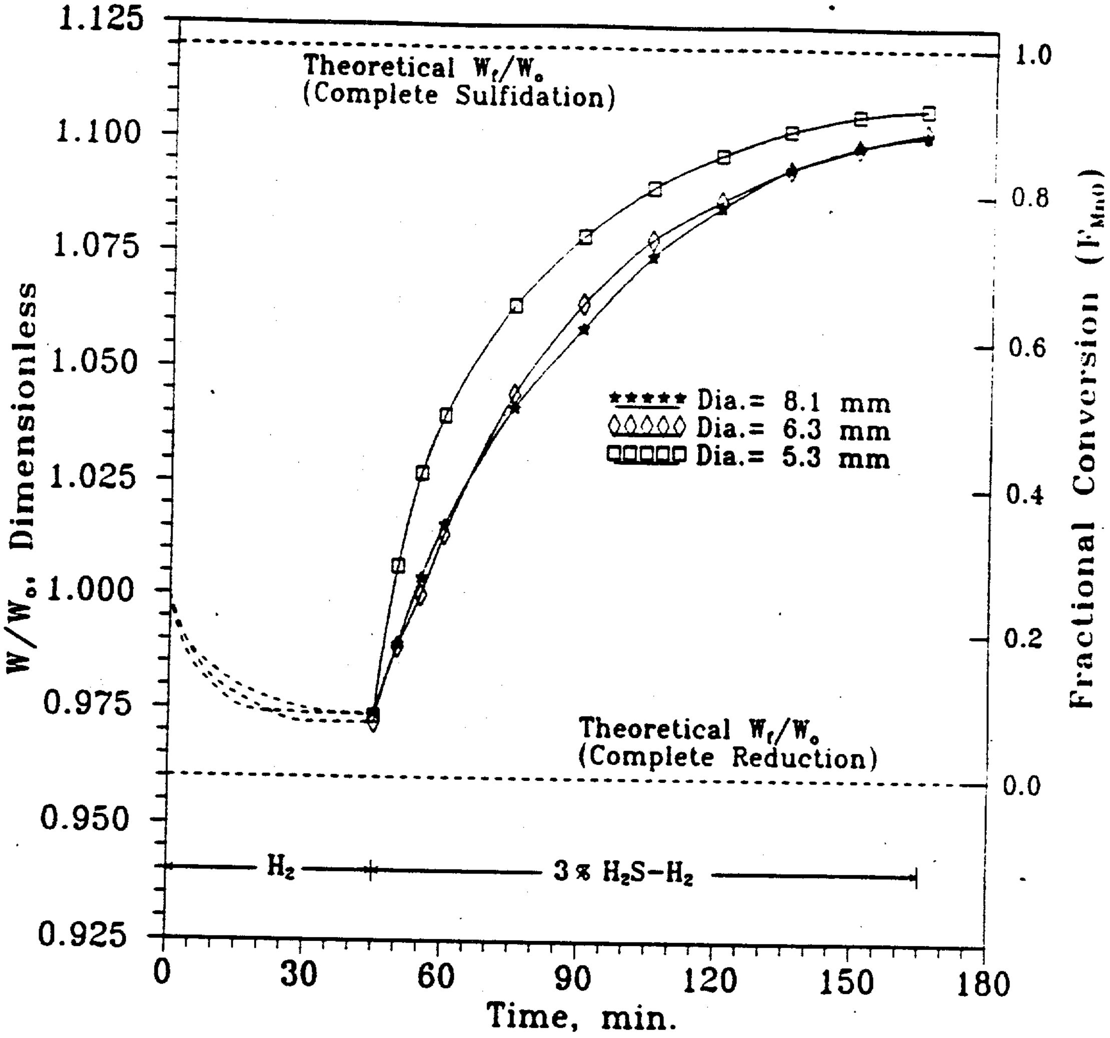

Figure 4.9 Effect of pellet diameter on sulfidation kinetics of FORM1-A sorbent at T= 900 °C.

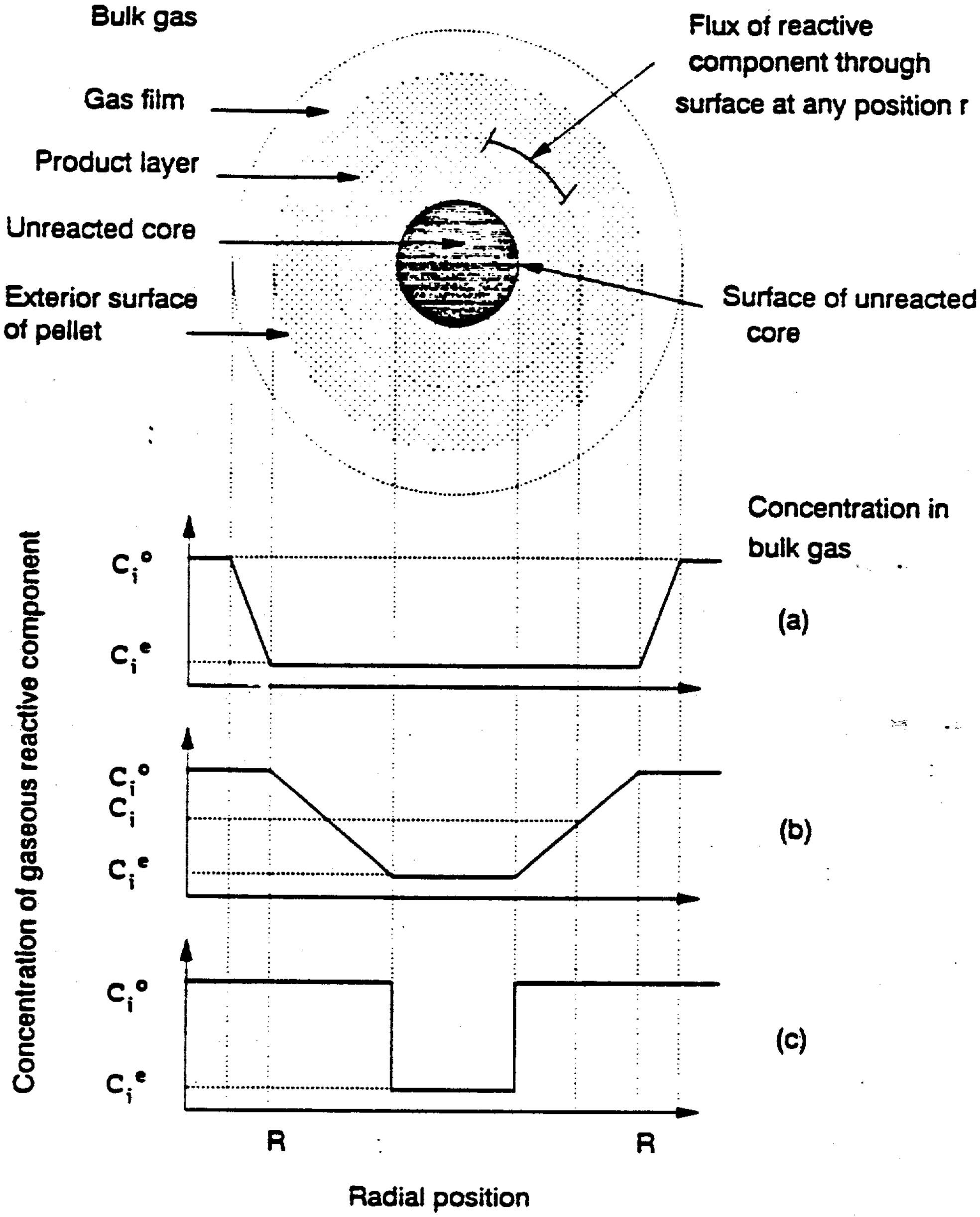

Figure 4.10 Representation of a reacting Mn-based sorbent pellet when rate controlling steps are: a) diffusion through the gas film, b) diffusion through the product layer, and c) surface reactions

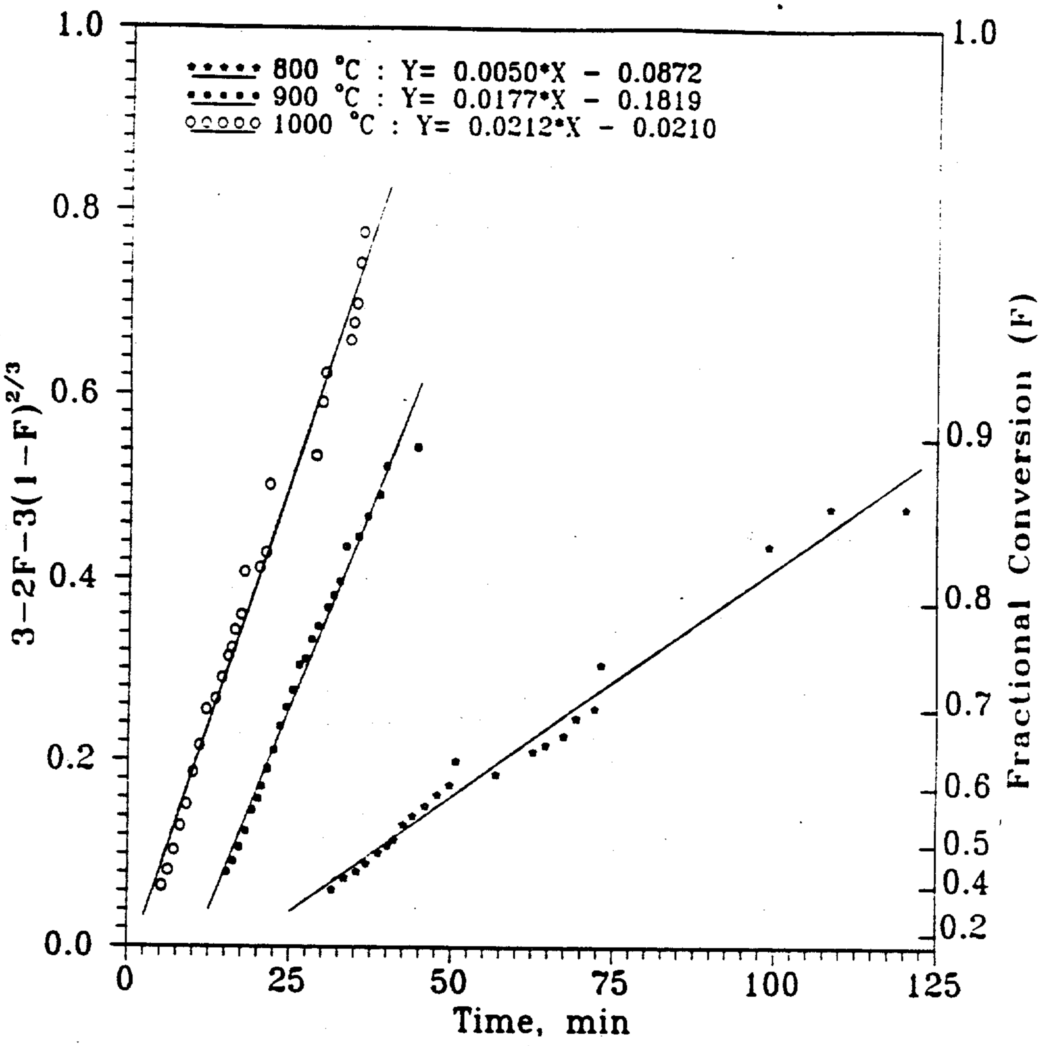

Figure 4.11 Reaction rate data for sulfidation of 4.8-mm diameter FORM4-A pellets at 800, 900, and 1000 °C, plotted according to equation (4.5) for diffusion through product layer control

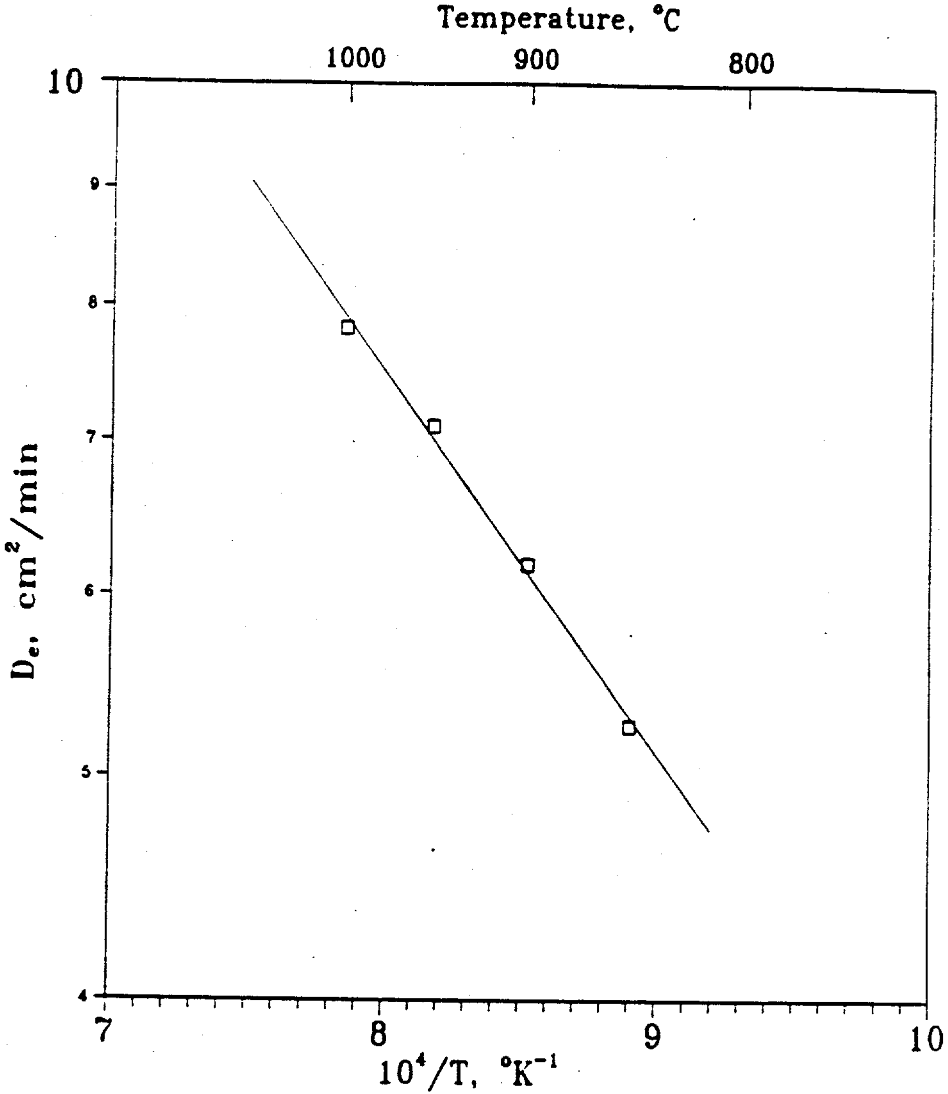

Figure 4.12 Effective diffusivity (D_e) dependence on temperature (i.e., Arrhenius plot.)

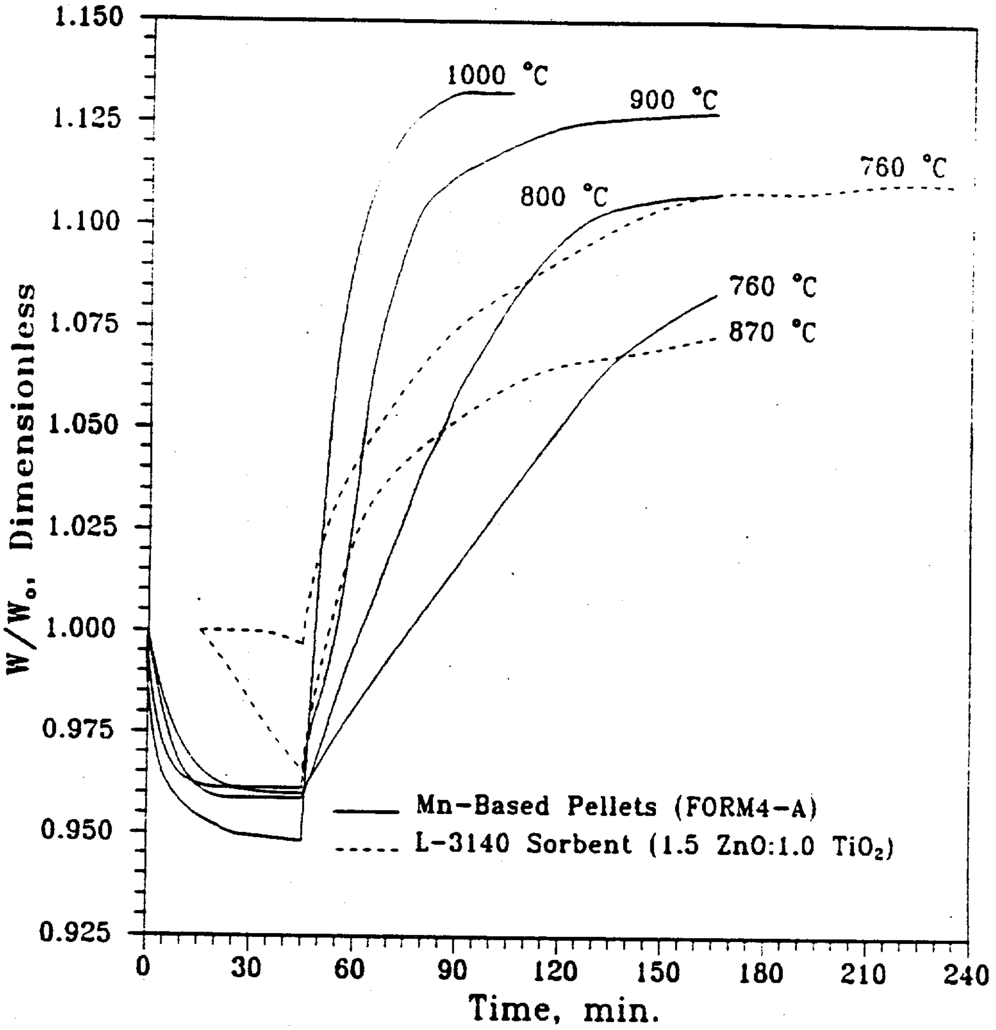

Figure 4.13 **Comparison of sulfidation kinetics via thermogravimetric analysis of FORM4-A Mn-based pellets and L-3140 Zn-based sorbents.**