

**CHAPTER V: DESULFURIZATION OF HOT COAL-DERIVED FUEL GASES
WITH MANGANESE-BASED REGENERABLE SORBENTS.**

2. REGENERATION AND MULTICYCLE TESTS

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

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In a previous paper, the reduction and sulfidation thermodynamic and kinetic characteristics of four manganese-based high-temperature desulfurization sorbents were investigated. A formulation, FORM4-A, which consisted of Mn carbonate, alundum, and bentonite exhibited the best combination of capacity and reactivity; whereas, FORM1-A, which consisted of Mn ore, alundum, and dextrin exhibited the best combination of strength, capacity, and reactivity. In this paper the thermodynamic feasibility of regeneration is discussed. The kinetics of regeneration of sulfided (loaded) pellets with air is studied in the 800 to 1000 °C temperature range. Repeated cycling of the leading sorbent formulation (FORM4-A) was then conducted in a thermogravimetric apparatus (TGA), 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 improved with recycling without compromising the strength. This appears to be a result of radial micro-crack formation which reduced the solid-state diffusion path within the pellet.

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5.1 Introduction

Current methods for the conversion of chemical energy to electrical energy tend to be cumbersome, wasteful, and environmentally unsound. In a typical system, depicted in Figure 5.1, coal is burned in a boiler to generate steam which passes through a turbine to drive a generator and produce electricity. This process wastes more than 60% of the energy originally present in the coal.¹ Energy is also lost in transmitting the generated electricity through power lines to users causing the process to be, overall, only 30 to 35% efficient. In addition, solid waste streams are generated and must be disposed of in increasingly expensive landfill space.

Stricter government regulations on pollutant emissions and the need to improve process efficiency led to the development of advanced power generation systems. For example, in the Clean Air Act of 1990 legislation is directed toward cleanup of coal gases by development of processes for removal of sulfur and particulates from coal combustion products. Since such cleanup is expensive, more efficient utilization of coal is required to offset these costs. One approach toward the more efficient use of coal is via combustion in gasification processes to produce a fuel gas which can be used in combined cycle operations in which a gas turbine utilizes the gasifier product; however, to achieve maximum efficiency by this approach, the fuel gases should not be cooled to remove sulfur, but rather, they must be desulfurized when still hot to conserve their sensible heat. Another approach is directed toward the development of processes in which coal gases can be used directly in fuel cell applications to avoid the inefficiencies inherent in the Rankine cycle (conversion of heat into electricity). In this latter application, sulfur must be removed from the gasification products to avoid deterioration of the cell. An approach to cleanup of gasification products which conserves their sensible heat is to contact the hot coal gases with a sorbent capable of removing the sulfur.

Emerging technologies which are reaching the commercial stage include the integrated gasification combined cycle (IGCC), the molten-carbonate fuel cell (MCFC), and the pressurized fluidized-bed combustor (PFBC). These technologies are principally based on coal gasification, i.e. the production of gaseous fuels from coal. During gasification, coal containing carbon, hydrogen, and oxygen, as well as impurities such as sulfur, nitrogen, ash, and trace metals reacts with steam and either air or oxygen to produce a fuel gas. To obtain the desired product, gasifier operating conditions must be carefully controlled. The proportion of the various gaseous components exiting the reactor (CO , H_2 , CH_4 , N_2 , etc.) is influenced by the type of coal, the composition of the feed gases (steam + air/oxygen), the type of reactor (fixed-bed, fluidized-bed, or entrained flow), and operating conditions (temperature, equivalence ratio,^{2,3} flow, and pressure). The compositions of some commercially-produced fuel gases were previously reported.⁴

One of the most promising and attractive new technologies being considered by the electric utility industry is the IGCC process.⁵ A configuration of

an ideal* system is depicted in Figure 5.2. In this emerging technology the mixture of carbon monoxide and hydrogen produced through gasification is burned; the very hot exhaust is routed through a gas turbine to generate electricity; and the residual heat in the exhaust is used to boil water for a conventional steam-turbine generator thus producing more electricity. In a coal gasifier, unlike coal combustion processes, the sulfur in coal is released in the form of hydrogen sulfide, H_2S , rather than sulfur dioxide, SO_2 . The IGCC process must employ hot gas cleanup techniques to remove sulfur and other impurities in the fuel gas stream, principally to meet stringent government regulations for sulfur emissions and also to protect turbine components from the corrosive action of H_2S . The H_2S should be removed by purifying the product gas while it is still hot so that the gas can be used directly without loss of heat values. This completely eliminates the more costly, less efficient method of low-temperature, liquid-based, fuel gas scrubbing systems. In addition, since the volume of the fuel gas stream is a lot smaller than that of the flue gas stream, the removal of H_2S at high temperature results in considerably lower hardware costs than would be required by a conventional SO_2 scrubbing method at low temperature.

The focus of current work being performed by the Morgantown Energy Technology Center (METC) of the Department of Energy (DOE) on hot coal-derived fuel gas desulfurization is primarily in the use of zinc ferrite and zinc titanate sorbents; however, prior studies by Turkdogan and Olsson⁶ indicated that an alternate sorbent, manganese dioxide-containing ore in mixture with alumina, may be a viable alternative to zinc-based sorbents. Manganese, for example, has a significantly 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. A more thorough comparison of Mn-based sorbents and Zn-based sorbents has been given by Ben-Slimane and Hepworth.⁴ In addition, the following thermodynamic analysis of the manganese-sulfur-oxygen (Mn-S-O) system shows it to be much less amenable to sulfation than zinc-based sorbents. Potential also exists for utilization of manganese at higher temperatures than zinc ferrite or zinc titanate which would boost the efficiency of power generation from coal.

In a previous paper,⁴ the thermodynamic feasibility for the use of manganese-based sorbents for the removal of hydrogen sulfide (H_2S) from hot coal-derived fuel gases was established. Screening sulfidation tests were carried out on individual sorbent pellets via thermogravimetric analysis (TGA). It was concluded that sorbents prepared with the organic binder, dextrin, on Moanda manganese ore offered the best combination of strength, reactivity, and capacity.

* An ideal IGCC system is one in which there are *no* designed changes in gas pressure or temperature as the gas flows through the system.

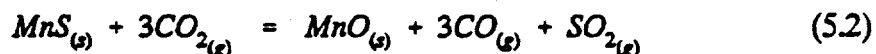
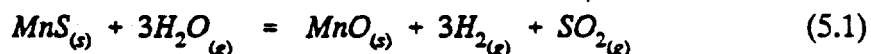
Sorbents prepared with bentonite on manganese carbonate possessed the best combination of capacity and reactivity. The loading characteristics of these two leading Mn-based pellets were shown to be superior to those obtained using Zn-based sorbents.

Economics dictates that the sulfur sorbent employed be regenerable, i.e. the loaded sorbent may be restored to its original (fresh) condition. The regeneration step is indicated on Figure 5.2 as a process in parallel with the hot gas desulfurization step. In this paper, the feasibility of regeneration of manganese-based pellets is discussed from thermodynamic considerations. Experimental tests, utilizing the best formulation, FORM4-A, were carried out to study the kinetics of regeneration. The reaction parameters which were varied included temperature and oxygen content in O₂-N₂ gas mixtures. Repeated sulfidation and regeneration tests were then carried out to investigate the effect of pellet recycling on its chemical reactivity, physical durability, and capacity for sulfur pickup from fuel gases.

5.2 Thermodynamic Considerations

The goal of regeneration is to restore the loaded (sulfided) sorbent to its original fresh condition. Hence, regeneration involves the oxidation of manganese sulfide to manganese oxide using an oxidizing gas. Regeneration conditions (temperature and nature of regeneration gas) must be carefully controlled to maintain the reactivity and physical durability of the sorbent pellets. Excessive temperatures may lead to sintering, causing the pellet reactivity to diminish considerably through substantial loss of porosity. Relatively low temperatures and the presence of SO₂ in the regeneration product gas may lead to sulfate formation. Sulfation must be avoided because once sulfate is formed, its decomposition is slow. In addition to the above restrictions, the SO₂ concentration in the regeneration product gas must be high enough to meet the requirement of a sulfuric acid plant ($\approx 6\%$ SO₂ by volume).

Sulfur sorbents may be regenerated after sulfidation by reacting the sulfide with H₂O-containing gas mixtures. This is desirable because, in the case of zinc ferrite or zinc titanate, for example, steam addition provides a highly effective oxygen diluent to limit the maximum sorbent temperature reached during regeneration.⁵ If the regeneration gas consisted of pure H₂O or CO₂, the regeneration of Mn-based pellets may be represented by the following reactions:



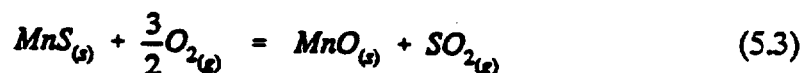
However, these two routes may be thermodynamically unlikely and also not practical because of the low SO₂ concentration in the product gases.

The regeneration of MnO must be oxidative, i.e. involving air, pure oxygen, oxygen-enriched air, oxygen-deficient air, or SO₂-O₂ mixtures. Further discussion

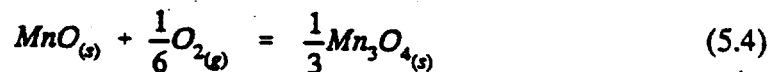
of regeneration thermodynamics must thus be made with reference to the phase equilibria in the Mn-S-O system in the temperature range of interest. Figure 5.3 is a stability equilibrium diagram for the Mn-S-O system at 800, 1000, and 1200 °C. The phase equilibria among the various solid compounds involved are shown as a function of the logarithms of the equilibrium partial pressures of two components in the gas phase, namely SO₂ and O₂. In this diagram each phase is stable within a predominance region, bordered by lines that represent the coexistence with other phases.⁷ The slope of each curve is determined by the stoichiometry of the corresponding reaction. As the temperature increases, the equilibrium lines shift up and to the right, further constricting the region of stability of the sulfate.

The effect of temperature is best displayed by plotting Log(P_{O₂}) versus reciprocal temperature at constant SO₂ partial pressure, as shown in Figure 5.4. In this figure the solid lines are for P_{SO₂} = 1 atm and the dashed lines are for P_{SO₂} = 0.14 atm. This latter value was selected because it represents the maximum SO₂ partial pressure attained during the early stages of regeneration with air. As the SO₂ partial pressure decreases, the regions of oxide stability expand while those of the sulfide and sulfate diminish. It is also clear that MnO/Mn₃O₄ and Mn₃O₄/Mn₂O₃ equilibria are independent of the SO₂ partial pressure, as expected. Theoretical guidelines may be deduced from Figure 5.4 to avoid the possibility of sulfate formation during regeneration. For example, for a regeneration product gas containing 10% SO₂, it can be shown that sulfate formation is not thermodynamically feasible above approximately 915 °C. The location of this operating point on the diagram is marked with a circle and is probably the lowest possible temperature to avoid sulfate formation.

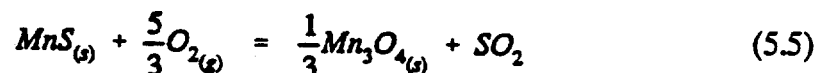
The regeneration reaction proceeds initially according to the following reaction:



Then MnO is readily converted to Mn₃O₄ because of the availability of O₂ in the gas:



Consequently, under these conditions the overall regeneration reaction is given by



The above reaction is thermodynamically favorable and proceeds essentially to completion in the temperature range 800 to 1200 °C. Thus, the

oxygen in the reactant gas is virtually converted to SO_2 . The regenerated manganese oxide would be in the form of Mn_3O_4 which would be immediately reduced to MnO upon exposure to the hot reducing fuel gas during the sulfidation stage. The maximum temperature of both sulfidation and regeneration may be as high as 1232°C , the eutectic temperature of the pseudo-binary MnO-MnS system.⁶

It should be noted, however, that the oxidative regeneration of the oxide is highly exothermic. Reaction (5.5), for example, has a heat of reaction of -527.2 kJ per mole of MnS reacted in the temperature range 900 to 1200°C .⁸ Accordingly, practical problems may be encountered in the control of the reactor temperature. Turkdogan and Olsson⁶ suggested that 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 , a number of endothermic reactions may occur. By appropriate adjustment of the composition of the feed gas $\text{CO}_2\text{-H}_2\text{O-O}_2$, it is possible to control the reactor temperature at the desired level during regeneration. Consequently, a thermodynamic model was developed to calculate the composition of the feed gas for the operation of the reactor at a desired temperature of regeneration with an exhaust gas containing sufficient SO_2 for recovery in the sulfuric acid plant. This was done by combining SOLGASMIX⁹ and THERBAL,¹⁰ mass balance and heat balance software packages, respectively. The calculation procedure using these computer programs is outlined in Figure 5.5. 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 . Pure oxygen or air is added to the product gas above the bed to convert all sulfur-bearing species to SO_2 . At the same time, the H_2 and CO present are oxidized so that the final product gas contains only SO_2 , H_2O , and CO_2 . With the assumption of complete equilibrium in the reactor, the calculated data in Figure 5.6, for the feed gas preheated to 800°C and regeneration carried out isothermally at 1100°C , give the concentration of SO_2 in the product gas (wet and dry basis) as a function of the composition of the feed gas. The additional amount of oxygen needed for complete combustion of the regeneration product gas above the bed is also given. Similar plots may readily be made for other combinations of preheat and regeneration temperatures.

The above thermodynamic model is useful in making predictions which may be essential prior to the design of a regeneration reactor. For example, it may be estimated that for a feed gas at 800°C containing equimolar amounts of CO_2 and H_2O , the composition of the feed gas required to maintain the regeneration isothermal at 1100°C is 6.08% O_2 , 46.96% (i. e., $[100-6.08]/2$) CO_2 , and 46.96% H_2O . In addition, the diagram shows that to ensure complete combustion of the regeneration product gas, 2.59 mols of O_2 per 100 mols of feed gas (or 2.52%) must be added in the after burner above the bed. The final regeneration product gas will contain 11% and 5.78% SO_2 on a dry and wet basis, respectively. Both of these SO_2 concentrations satisfy the requirements of a typical sulfuric acid plant.

5.3 Experimental Investigations and Results

The test work reported here was directed to formulation FORM4-A which was shown to possess the most favorable loading characteristics of the four formulations selected for screening sulfidation tests. This formulation is made up of 81.31% by weight manganese carbonate (containing 93-95% MnCO_3), 16.73% alundum (containing 96.6% Al_2O_3), and 1.96% bentonite (an inorganic binder). Upon forming pellets, they were first dried to a constant weight at 110 °C, then heated to 350 °C to allow for dissociation of the manganese carbonate.* They were then heated to 1250 °C and indurated for 2 hours in an air atmosphere before removal from the furnace. The average size of the pellets was 4.8 mm and they had an average strength of 23.8 N/mm of diameter (5.4 lbs/mm). The final manganese assay of the indurated pellets was 44.22% by weight, which corresponds to a theoretical sulfur capacity of 25.8%, i.e., 25.8 gS/100g of indurated pellet.

5.3.1 Regeneration Tests

The equipment used in the thermogravimetric (TGA) experimental work has been previously described in detail.⁴ The TGA tests focused on studying the effects of regeneration parameters (temperature and O_2 content) and on repeated loading and regeneration of the selected FORM4-A pellets. Since up to fifteen pellets may be used in each reduction/sulfidation test, various tests were needed to provide enough fully-loaded pellets for the various regeneration tests planned. This provided an opportunity to determine the reproducibility of the sulfidation tests. The reduction and sulfidation were carried out under standard conditions of 950 °C and 3% $\text{H}_2\text{S-H}_2$ gas mixtures at 500 cc/min delivery for a total of approximately 2 grams of pellets. Reduction was carried out with pure hydrogen for the first 45 minutes and then the hydrogen sulfide was added.

Figure 5.7 shows the reproducibility of loading tests resulting from five separate tests on fresh pellets (i.e., first loading cycle) at 950 °C with 3% by volume hydrogen sulfide in hydrogen. This figure gives the error bars on the data to indicate the range of the results. In all subsequent figures, W_0 refers to the mass of the indurated pellet and W to the mass of the reacting pellet as a function of time. Although not shown for the reduction portion of the curve the reproducibility is particularly good, with reduction essentially completed in fifteen minutes. Figure 5.7 shows that deviations in extent of loading occur even though during each test the macroscopic properties (mass and size) of the pellets were kept as constant as possible. These deviations may be due to the difficulty associated with controlling temperature, flow rates, etc. However, the reproducibility of sulfidation is excellent beyond the first 30 minutes after the initial reduction period (total lapse time of 75 minutes). The solid line represents the average values and therefore serves as an indication for future test results.

A total of five regeneration tests were then carried out using five pellets

* MnCO_3 dissociates to MnO and CO_2 at 343 °C with CO_2 evolving at 1 atm.

during each test. The regeneration gas was air flowing at 500 cc per minute and regeneration temperature varied between 800 and 1000 °C in increments of 50 °C. The purpose was to determine the temperature at which loaded pellets could be fully regenerated in reasonable time. The results from these tests are reported in Figure 5.8. The loading curve corresponds to the solid line shown in Figure 5.7; however, the right-hand portion of this figure shows the regeneration portion after a total time lapse of 165 minutes. These results appear to be in strict accordance with thermodynamic predictions which were outlined above, viz.: at 800 °C the loaded pellets first oxidize (and hence lose weight) for about 3 minutes at which time sulfation with an concurrent weight gain becomes predominant. When approximately 60% of the MnS is converted to MnSO₄, sulfate decomposition starts and the pellets begin to show a weight loss. Continuing at higher temperatures, at 850 °C, the same trend is observed; however, the oxidation of the pellets appears to be faster than sulfation; this is reasonable since the driving force for the decomposition of sulfate is greater. Regeneration kinetics appear to be a weak function of temperature over the range 900 to 1000 °C. In this range regeneration is essentially complete in 10 to 15 minutes and sulfation does not occur, as concluded from the prior thermodynamic analysis of the Mn-S-O system. It must be noted, however, that full regeneration (i.e., $W/W_0 = 1$) apparently requires a temperature of 1000 °C or higher.

Figure 5.9 shows the effect of oxygen content in N₂/air gas mixtures on regeneration kinetics for four oxygen levels: 5, 10, 15, 21% (air) by volume. Even for the lowest oxygen level, the flow rates and mass of samples were chosen so that the rate of gas delivery was not rate-limiting. The results are as expected, with the regeneration rate increasing with the O₂ content of the regeneration gas. It appears that a duration of 10 minutes is required for full regeneration with air, while at the 5% O₂ level the reaction is essentially complete in 50 minutes. These results are of consequence to the operation of a fixed-bed where temperature control may be essential to prevent overheating and resulting sintering and deterioration of pellet reactivity during regeneration.

5.3.2 Multicycle Tests

Over a five-day period, one loading and regeneration cycle was completed each day at 950 °C for reduction and sulfidation and 1000 °C for regeneration. The TGA data for these five tests are shown in Figure 5.10. The arrows show the direction of increasing cycle sequence numbers, i. e. for loading, the capacity and reaction kinetics improve for each of the five cycles with the change between the first and second cycles being the most pronounced. For the tail of the curve terminating the regeneration step, the weight loss drop is steepest for the fifth cycle: again showing that the rate of regeneration increases with pellet re-use. An optical examination at 30 magnifications with a binocular microscope as well as petrographic thin sections examined at 100x showed the presence of radial cracks. The penetration distance of the sulfur as exhibited by the higher reflectivity of the manganese sulfide phase was densest adjacent to these cracks, indicating that the

diffusion distance for permeation of sulfur (and counter-transport of oxygen) was decreased by the change in diffusion geometry occasioned by the cracking. Whereas the original pellet experiences diffusion for a gross pellet size of ≈ 2.5 mm in radius; upon cracking of the pellet, the solid-state diffusion distance is somewhat reduced. This permits gaseous species to be transported by the relatively faster mechanism of gaseous diffusion into the cracks compared with the slower process of solid state counter diffusion of oxygen out of the pellet to exchange for sulfur into the pellet. This diffusional kinetics will be developed subsequently.

This is a unique feature of manganese-based pellets, i. e. their retained strength upon micro-cracking and improved kinetics compared with competing sorbents, e. g., zinc titanate, in which the reaction kinetics and sorbent loading capacity and pellet strength decrease upon cyclic loading.

5.3.3 Discussion

The results reported here and in a previous paper⁴ relate to the use of manganese-based sorbent pellets for the desulfurization of H_2S-H_2 gas mixtures in the 700 to 1000 °C temperature range, and the subsequent regeneration of the loaded pellets with air. It must be noted that the use of a very aggressive reduction period (in pure H_2) is intended to ensure complete reduction of Mn_3O_4 to MnO ; the reduction of MnO to elemental Mn is not feasible, as was previously explained in detail⁴. The use of an H_2S plus H_2 mixture may seem unrealistic as a process simulation, and further work should be carried out to see if the same results could be obtained with a different gas mixture that approximates more closely the composition of a coal-derived fuel gas. The authors realize that currently 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.

Both the desulfurization and regeneration processes should desirably be carried out at a level somewhat above gas turbine combustor pressures so that further and very significant equipment cost savings can result. Since the regeneration process must take place above 900 °C (which is reasonable) and since the overall oxidation reaction is highly exothermic, the ability to efficiently recover the released heat of regeneration offers a potential system performance enhancement. This is particularly true if a so-called after-burner becomes part of the regeneration process. The ability to accomplish this heat recovery is also normally improved to the degree the sorbent's crush strength is improved (e.g., producing an ability to use fluidized beds and enhanced sorbent/heat transfer

media or surface contacting).

While the results reported in this paper are obtained using thermogravimetric (TGA, widely recognized as a good research tool) testing on small batches of pellets, practical processes aim to minimize required reactor and sorbent volume. This translates to the processes of most potential interest having a need to "move" the sorbent in some fashion between the desulfurization and regeneration vessels. Consequently, both the crush strength of the sorbent and its sorption capacity after repeated cycling are of critical interest. Normally, and especially in the 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 stream). With the manganese-based sorbents the presence of these small cracks apparently led to improvement in the reaction rate for sulfidation and regeneration without adversely affecting the strength. At the conclusion of each of the five consecutive cycles reported earlier, the weight of the regenerated pellets was almost identical to the original weight of pellets indicating that no spalling took place. In addition, the crush strengths of five separate pellets ranged from 21.2 to 23.6 N/mm of pellet diameter (4.8 to 5.2 lbs/mm).

5.4 Kinetic Considerations

Previously,⁴ the shrinking-unreacted core model was found to approximate the kinetic behavior of Mn-based sorbent pellets during the sulfidation stage. Rate equations (time-fractional conversion) were derived for diffusion through gas film control, diffusion through product layer control, and surface reaction control. Kinetic analysis of thermogravimetric experimental data determined that beyond approximately 35% reaction completion, the sulfidation rate was controlled primarily by countercurrent diffusion through the porous MnS product layer.

The regeneration reaction is irreversible; in addition, its highly exothermic nature makes it even more likely to be controlled by countercurrent diffusion of oxygen and sulfur through the porous Mn_3O_4 product layer. For these reasons, only the derivation of the equation when diffusion through product layer is rate-limiting is deemed worthwhile. As was established in the previous thermodynamic analysis, the overall regeneration reaction is represented by equation (5.5). The symbols used in the following equations and their units are as follows: t : time (s); J : total molar flux ($mol/cm^2\cdot s$); J_i : molar flux of gaseous component i ($mol/cm^2\cdot s$); D_e : effective diffusivity (cm^2/s); C_i : molar concentration of gaseous component i (mol/cm^3); r : arbitrary position within radius of pellet (cm); y_i : mole fraction of component i in the gas phase (dimensionless); F_{MnS} : fractional conversion of MnS in loaded pellet (dimensionless); P : total pressure (atm); R : universal gas constant ($cm^3\cdot atm/mol\cdot ^\circ K$); T : absolute temperature ($^\circ K$); ρ_{MnS} : molar density of component MnS in pellet (mol/cm^3); R_p : radius of loaded or sulfided pellet (cm); superscript e : equilibrium value of parameter; superscript o : initial value of parameter; P_i : partial pressure of gaseous component i (atm); and C_1 : constant of integration.

The molar flux of O_2 through the newly-formed Mn_3O_4 layer is expressed by Fick's law, as follows:

The first term on the right-hand side of the above equation is termed molecular

$$J_{O_2} = -D_s \frac{dC_{O_2}}{dr} + y_{O_2} J \quad (5.6)$$

diffusion flux and is produced by a concentration gradient; the second term represents the flux resulting from the bulk motion of the regeneration gas. J is the total flux, and is given by:

$$J = J_{O_2} + J_{SO_2} \quad (5.7)$$

From the stoichiometry of the overall regeneration reaction, the following relation applies:

$$J_{SO_2} = -\frac{3}{5} J_{O_2} \quad (5.8)$$

Substituting for J in terms of J_{O_2} in equation (5.6) and rearranging, we get:

$$\left(1 - \frac{2}{5} y_{O_2}\right) J_{O_2} = -D_s \frac{dC_{O_2}}{dr} \quad (5.9)$$

Using mass balance considerations, it can be shown that:

$$3 - 2F_{MnS} - 3(1 - F_{MnS})^{2/3} = \frac{9D_s P}{RT\rho_{MnS} R_p^2} \ln \left[\frac{5P - 2P^*_{O_2}}{5P - 2P^*_{O_2}} \right] t + C_1 \quad (5.10)$$

The rate data for the regeneration reaction of FORM4-A pellets with air at 1000 °C are plotted in Figure 5.11 in accordance with equation (5.10). The results follow the limiting rate equation closely, indicating that diffusional product layer is present and controls the rate of reaction. Also shown in Figure 5.11 are rate data for the sulfidation reaction at 1000 °C (with 3% H₂S-H₂ as previously described). For example, for a 90% reaction completion, the sulfidation reaction requires about 30 minutes; whereas, regeneration requires about 10 minutes.

5.5 Summary and Conclusions

Sorbent pellets composed of high purity manganese carbonate, alundum, and bentonite as a binder were found to be potentially highly effective for the removal of sulfur from simulated fuel gases at high temperature (800 to 1000 °C). These sorbents were also found to be capable of being regenerated after sulfidation by reacting the sulfide with air or oxygen-deficient air. Pellets which underwent loading and regeneration over five consecutive cycles showed a slight improvement in capacity and reaction kinetics. This unique phenomenon is attributed to the formation of radial cracks which reduced the diffusion distance required for transport of sulfur into the pellet and oxygen out of the pellet. These cracks did not have a significant effect upon pellet strength which continued to be

no less than 21.2 N/mm of pellet diameter (4.8 lbs/mm). Although the pellets may be loaded at temperatures below 800 °C, regeneration must be accomplished above 900 °C to avoid sulfate formation.

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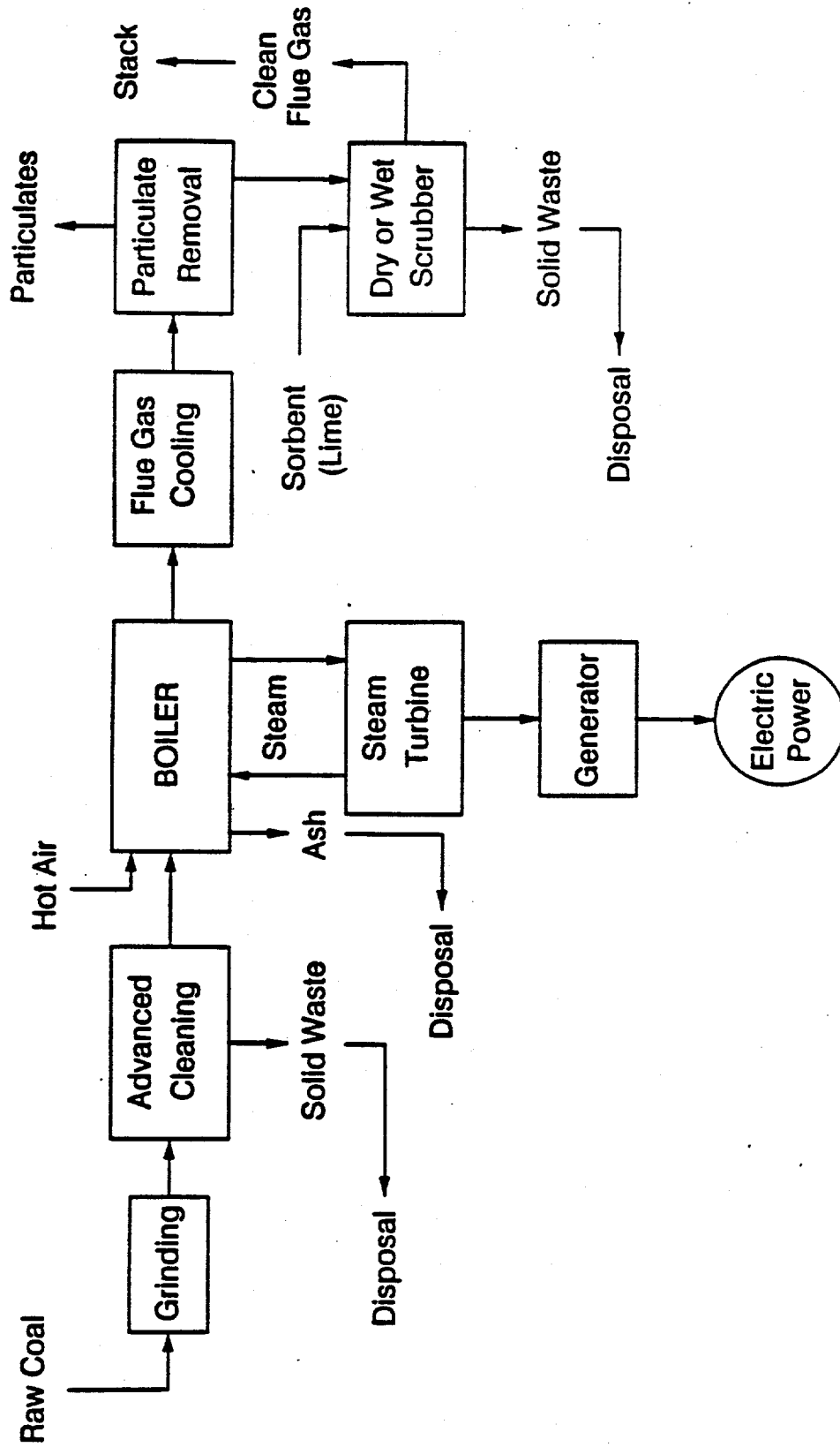


Figure 5.1 Schematic of a conventional power generation system with pre- and post-combustion physical and chemical cleaning.

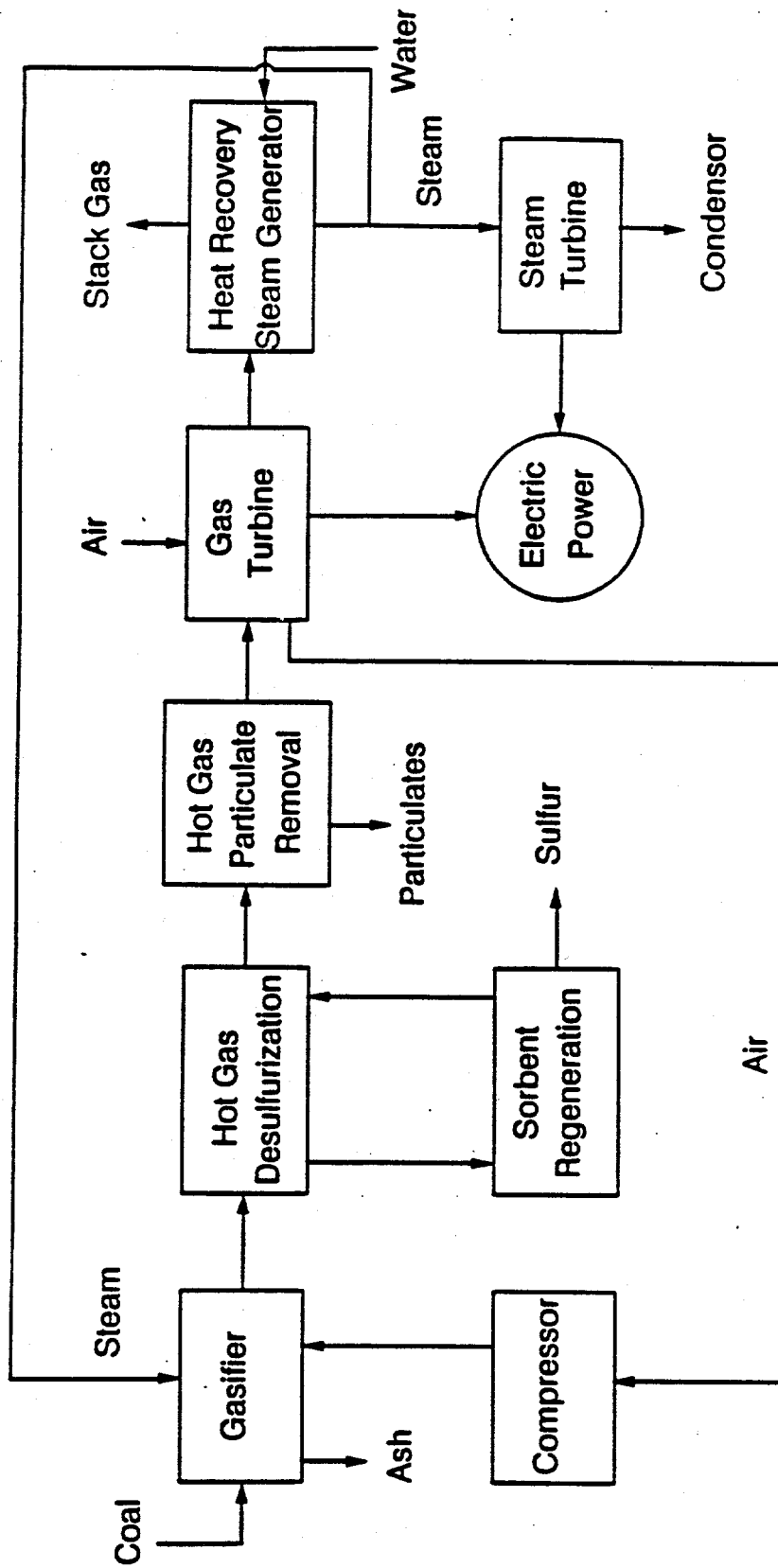


Figure 5.2 Schematic of an ideal integrated gasification combined cycle (IGCC) system.

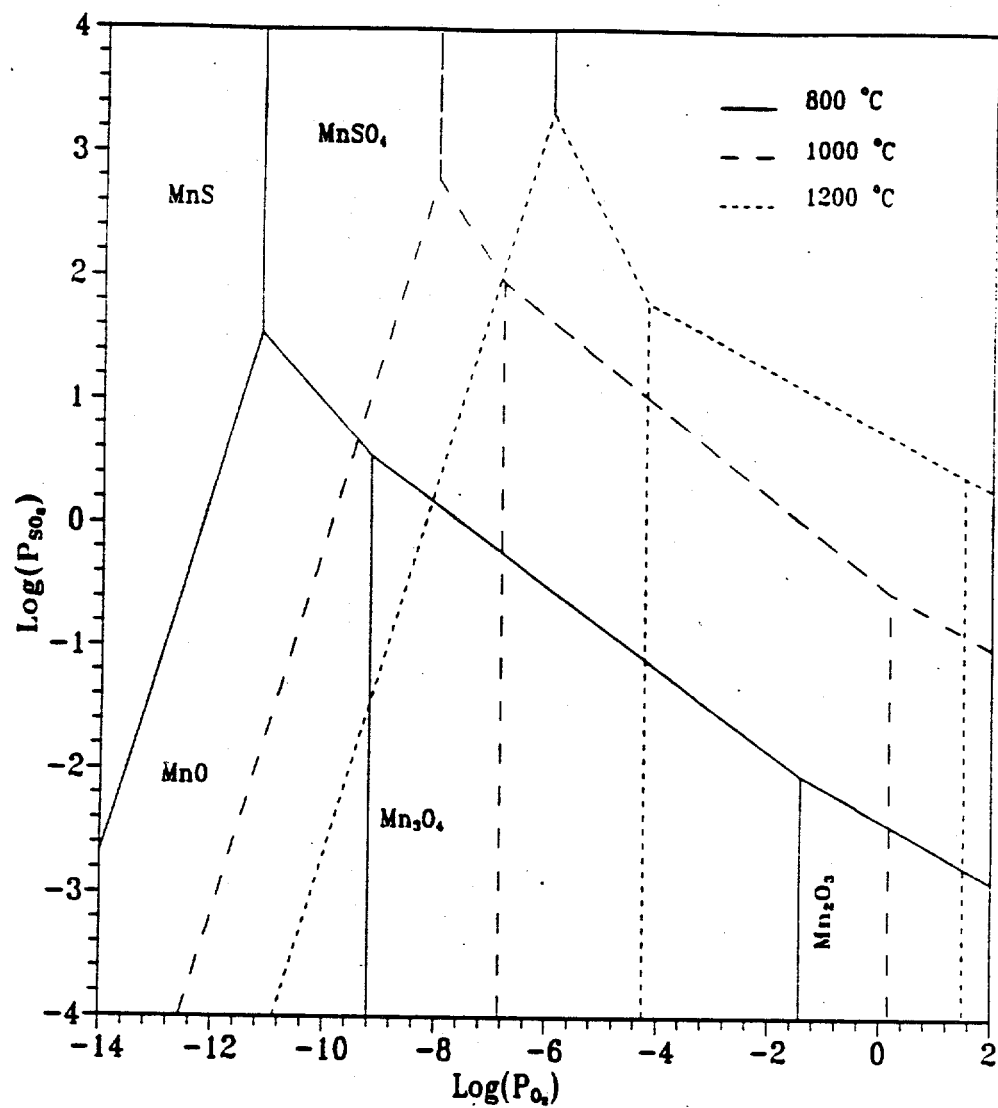


Figure 5.3 Predominance area diagram for the Mn-S-O system at 800, 1000, and 1200 °C.

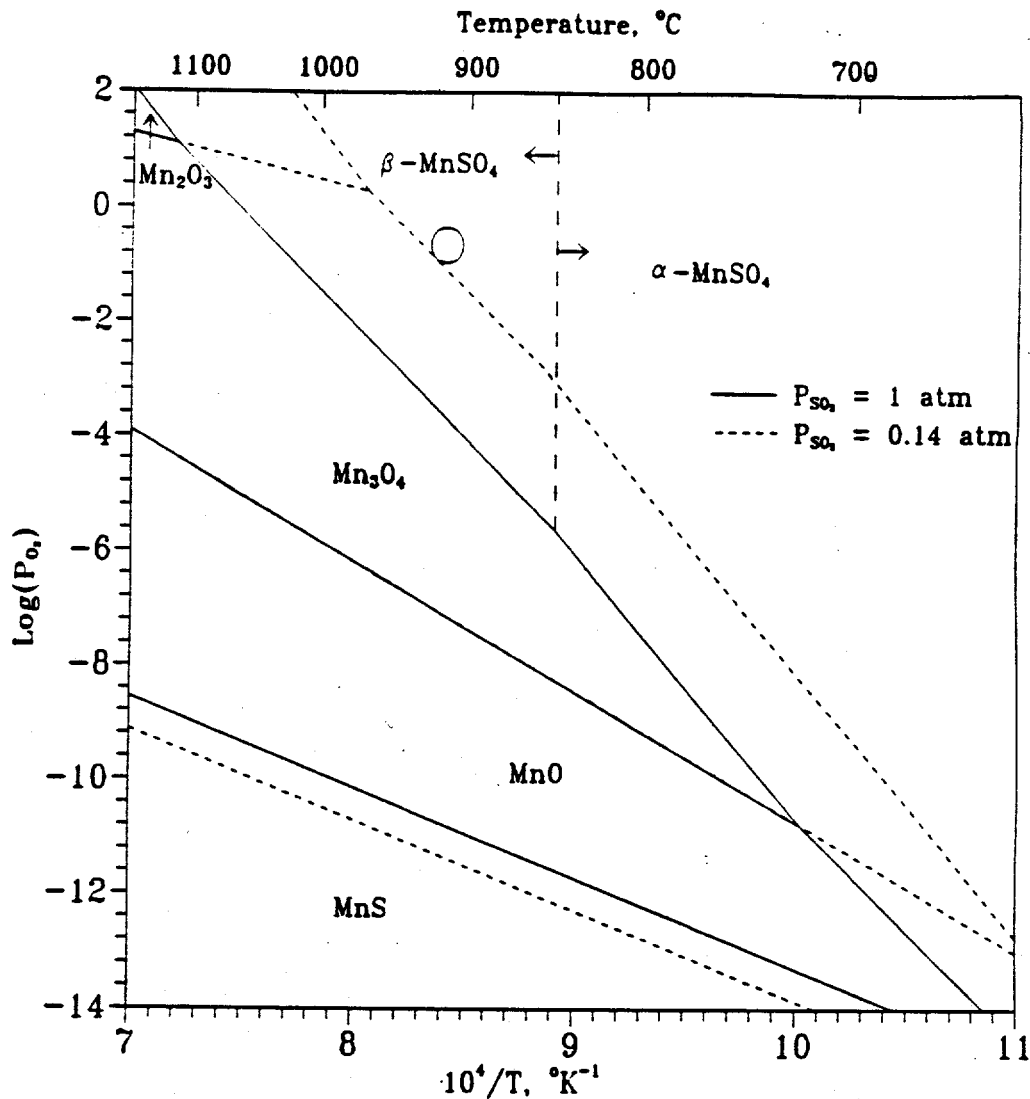


Figure 5.4 Effect of temperature on phase equilibria in the system Mn-S-O at constant SO_2 partial pressure. $P_{\text{total}} = 1 \text{ atm}$.

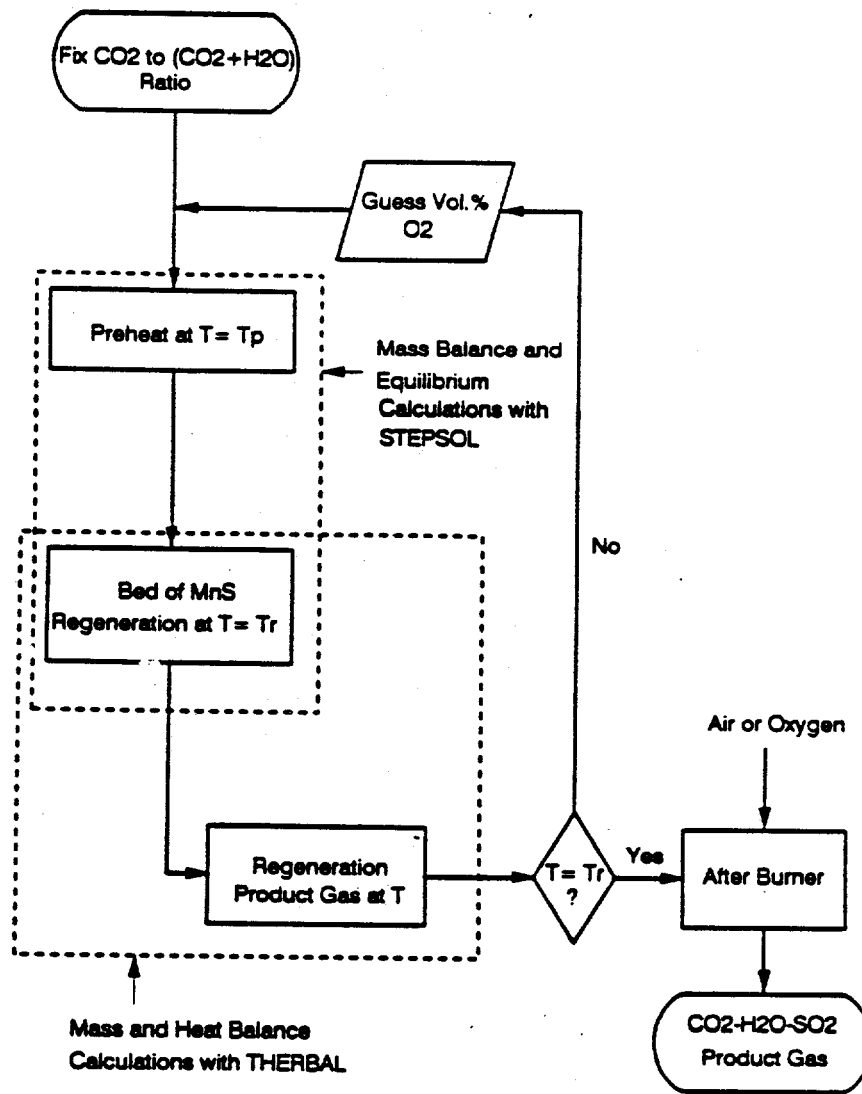


Figure 5.5 Schematic of heat and mass balance calculations on the isothermal regeneration of manganese oxide from sulfide.

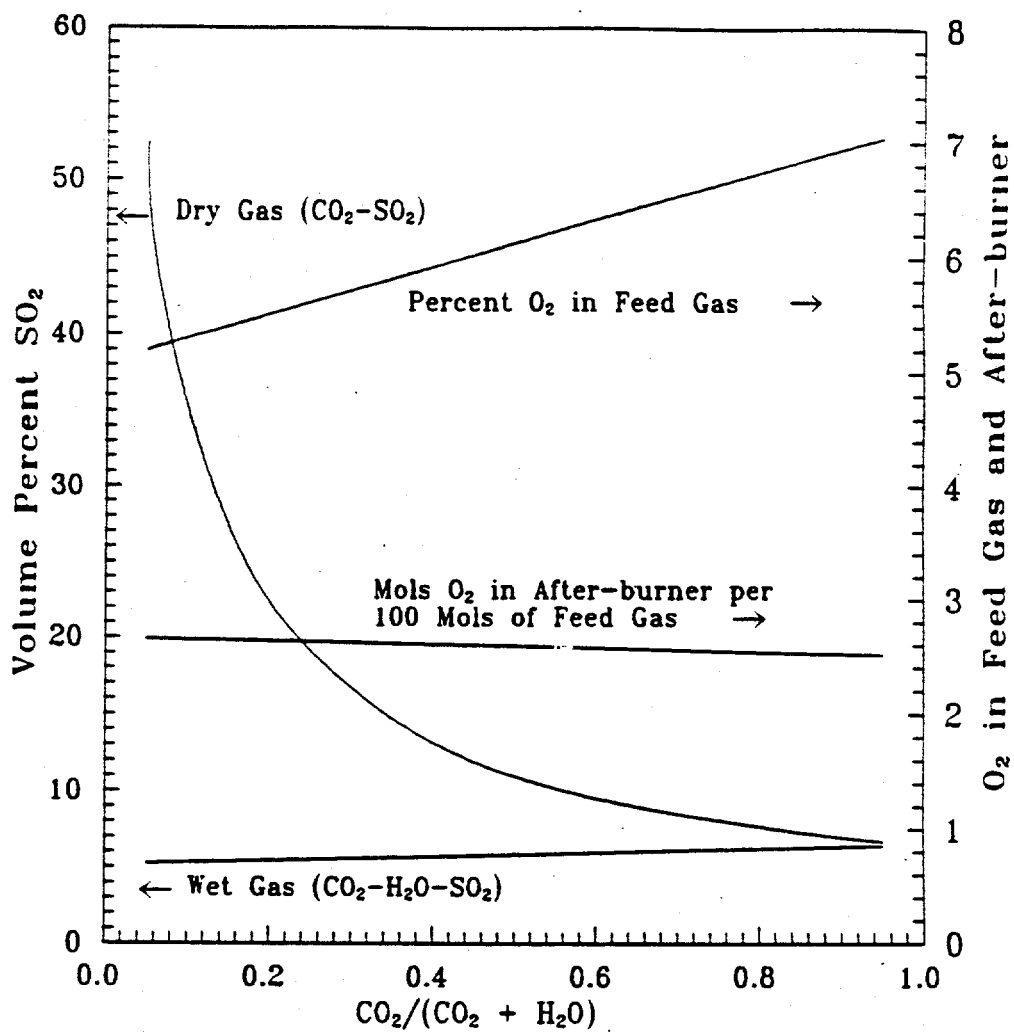


Figure 5.6 SO₂ content of regeneration product gas (on wet and dry basis) as a function of feed gas composition. Regeneration gas is fed at 800 °C and regeneration is carried out at 1100 °C.

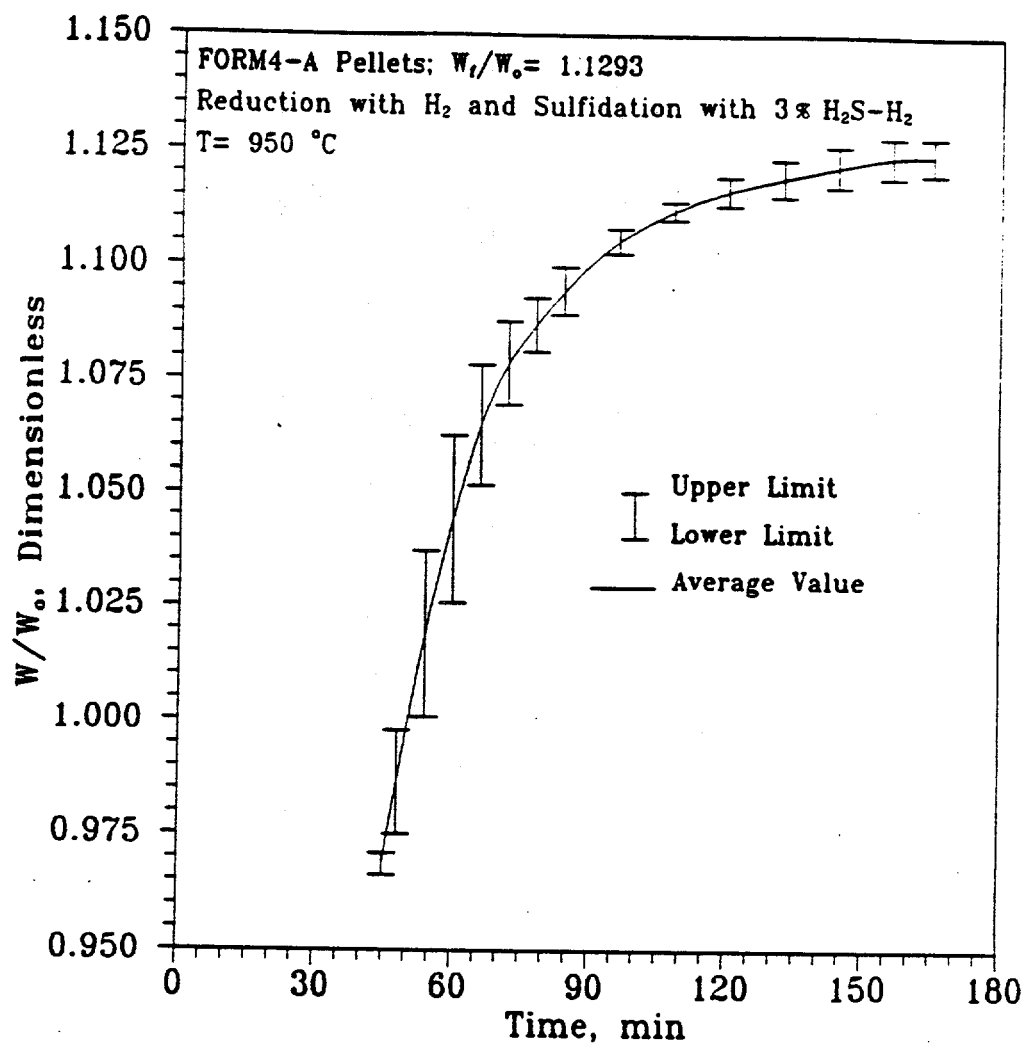


Figure 5.7 Reproducibility of loading tests at $950\text{ }^\circ\text{C}$ with $3\% H_2S-H_2$ gas mixtures showing average value and error bars.

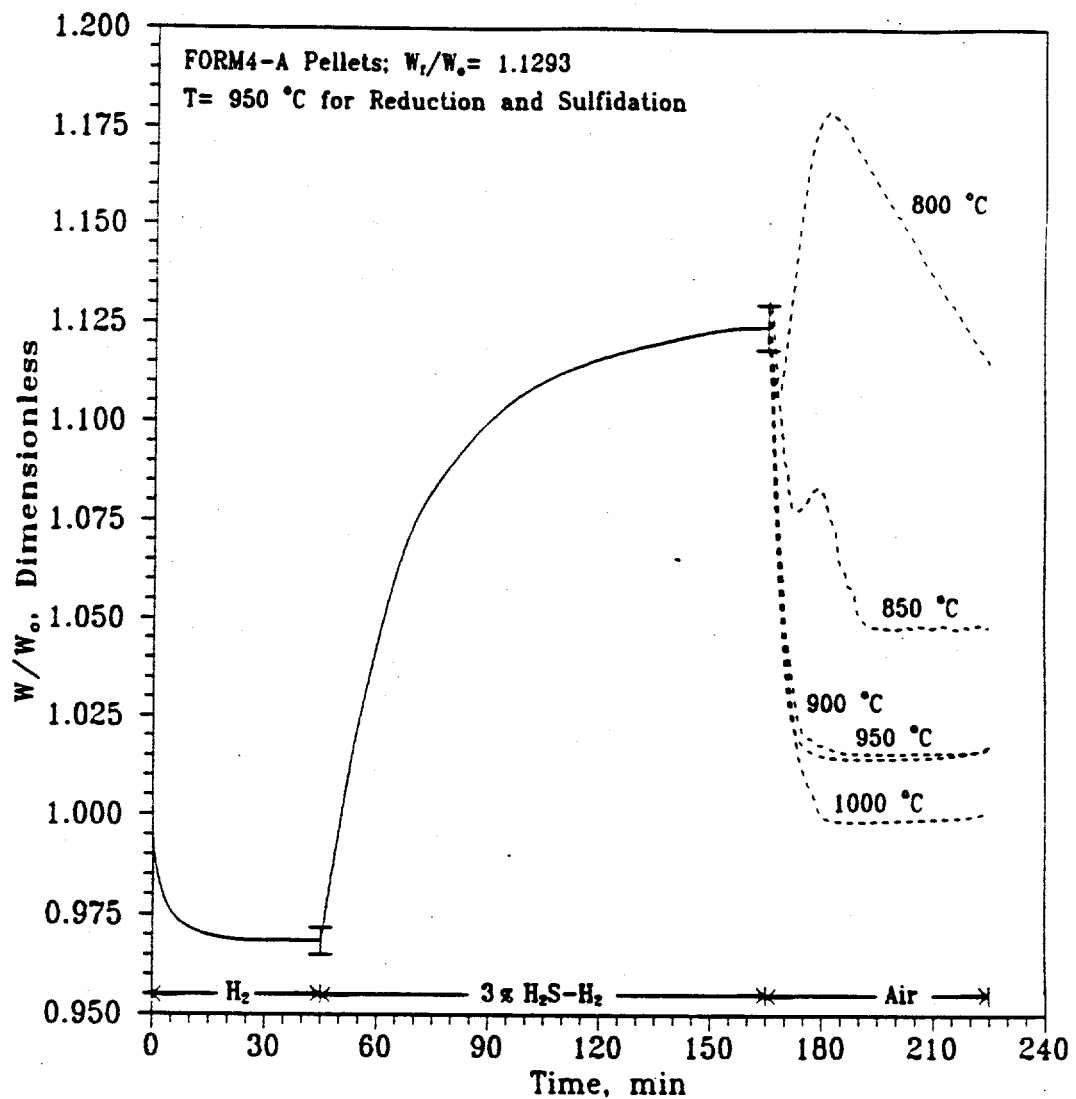


Figure 5.8 Effect of temperature on regeneration kinetics of FORM4-A Mn-based pellets. Reduction and sulfidation were carried out at $950 \text{ }^\circ\text{C}$ in H_2 and $3\% \text{ H}_2\text{S-H}_2$ gas mixtures, respectively.

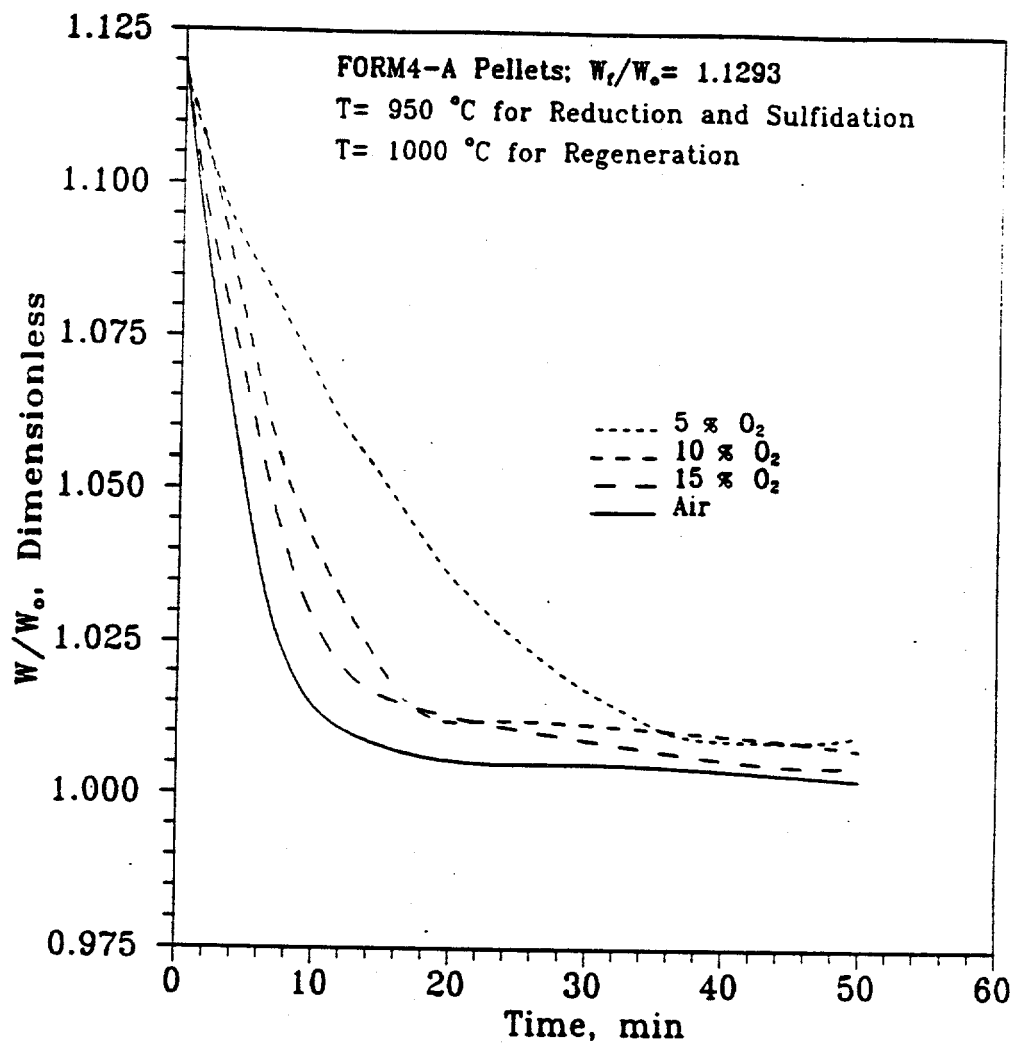


Figure 5.9 Effect of O_2 concentration in $\text{O}_2\text{-N}_2$ gas mixtures on regeneration kinetics of FORM4-A pellets at $1000\text{ }^\circ\text{C}$.

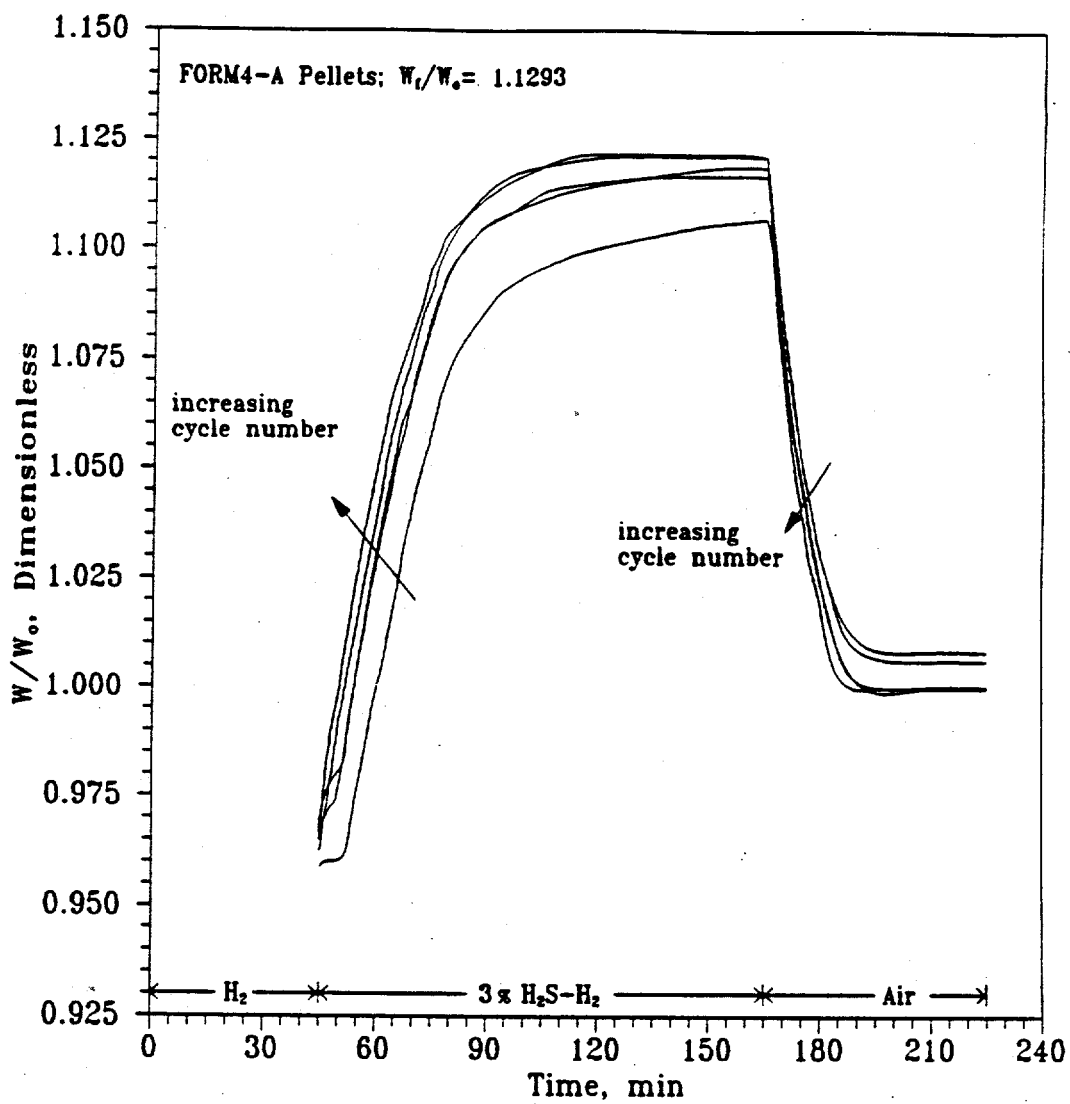


Figure 5.10 Effect of repeated cyclical loading and regeneration on the reaction kinetics and capacity of FORM4-A pellets.

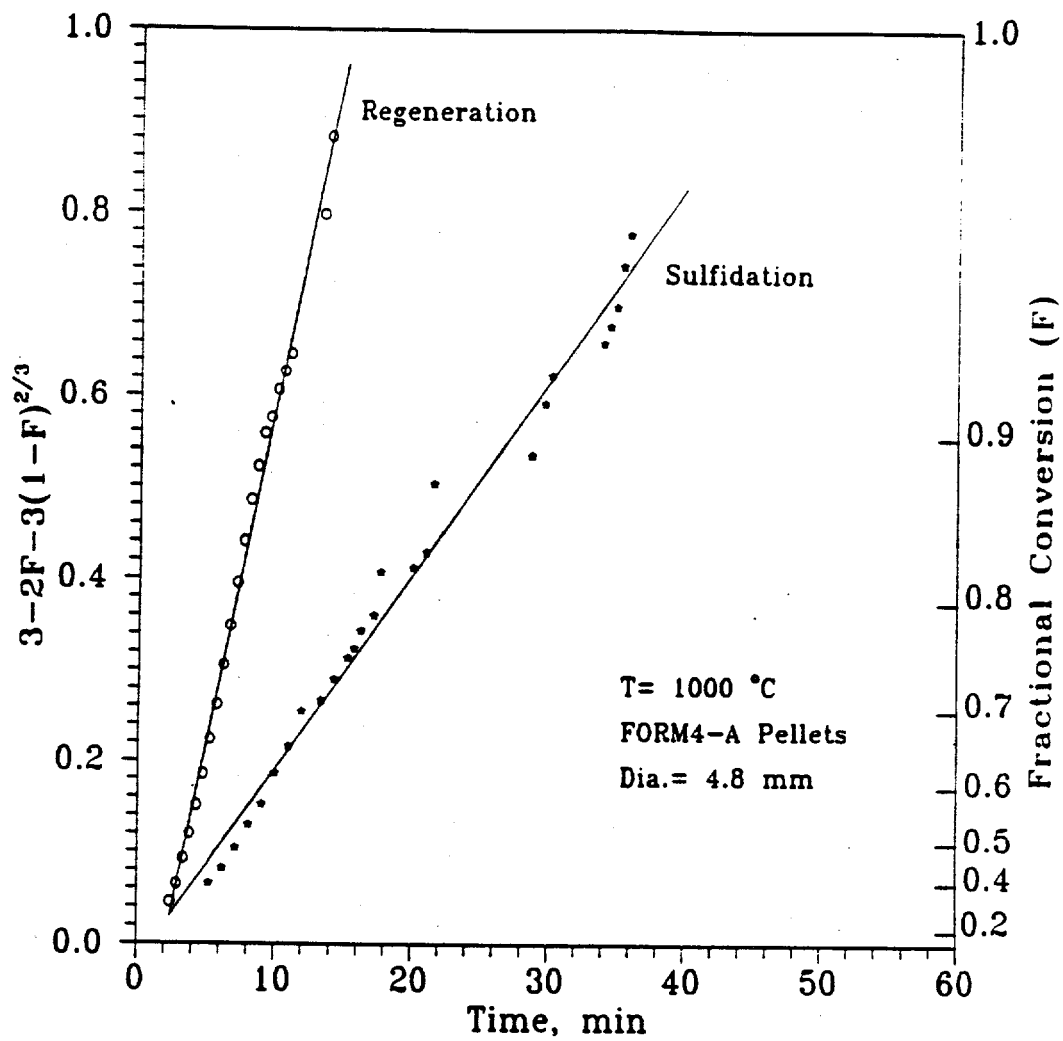


Figure 5.11 Reaction rate data for sulfidation and regeneration of FORM4-A pellets at 1000 °C.