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Hot Coal Gas Desulfurization With Manganese-Based Sorbents

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PB.12 Hot Coal Gas Desulfurization With Manganese-Based Sorbents

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ABSTRACT

The primary major deposit of manganese in the United States which can be readily mined by an in situ process is located in the Emily district of Minnesota. The U. S. Bureau of Mines Research Centers at both the Twin Cities and Salt Lake City have developed a process for extracting and refining manganese in the form of a high-purity carbonate product. This product has been formulated into pellets by a multi-step process of drying, calcination, and induration to produce relatively high-strength formulations which are capable of being used for hot fuel gas desulfurization. These pellets, which have been developed at the University of Minnesota under joint sponsorship of the U. S. Department of Energy and the U. S. Bureau of Mines, appear superior to other, more expensive, formulations of zinc titanate and zinc ferrite which have previously been studied for multi-cycle loading (desulfurization) and regeneration (evolution of high-strength SO₂ and restoration of pellet reactivity). Although these other formulations have been under development for the past twelve years, their prices still exceed \$7 per pound. If manganese pellets perform as predicted in fixed bed testing, and if a significant number of utilities which burn high-sulfur coals incorporate combined-cycle gasification with hot coal gas desulfurization as a viable means of increasing conversion efficiencies, then the potential market for manganese pellets may be as high as 200,000 tons per year at a price not less than \$3 per pound. This paper discusses the role of manganese pellets in the desulfurization process with respect to the integrated gasification combined-cycle (IGCC) for power generation.

OBJECTIVES

The objective of this study is to develop manganese-based sorbent pellets for the effective desulfurization of coal-derived fuel gases at high temperature (700-1200 °C). A number of formulations are prepared and screened first by testing in a thermogravimetric apparatus (TGA) in which individual pellets are weighed in mixtures of simulated fuel gases at atmospheric pressure and high temperatures, and then in a bench-scale fixed bed reactor. Sorbent screening criteria include measurement of sorbent (fresh, used, and regenerated) crush strength, chemical reactivity by thermogravimetric analysis, surface area, porosity, etc... The superior formulation is tested for long-term durability and chemical reactivity in the TGA apparatus and the bench-scale unit.

BACKGROUND INFORMATION

The rationale for desulfurizing coal-derived fuel gases at high temperature is a result of concerns within the U. S. Department of Energy to burn coal to produce electrical power more efficiently and also to meet government regulations for sulfur emissions which have become progressively more stringent. Conventional technology of power generation is inherently inefficient and consists of reacting coal in a burner system which exchanges heat to a boiler to generate steam (essentially the Rankine Cycle). This steam then passes through a turbine to drive a generator and produce electricity.

This conventional process for power generation is shown in Figure 1. The efficiency for conversion of heat into useful electrical power ranges from 30 to 35%. In addition, a portion of this power (up to 3%) is used internally in the plant to operate

environmental cleanup systems.

The sulfur in the coal is released in the form of sulfur dioxide (SO₂) in the flue gas. The removal of SO₂ from the flue gas prior to discharge into the atmosphere is essential to prevent air pollution. Conventional processes for sulfur removal are well established and require the coal gas be cooled to less than 100 °C in order to contact it with scrubbing reagents. The loss of thermal efficiency in the cooling process lowers the energy available for electrical conversion compared with the higher efficiencies which would be obtained if the coal gas were desulfurized while hot. Also, the primary scrubbing technique for sulfur removal entails the generation of gypsum which must be disposed of in increasingly expensive landfill space. For example, about one ton of limestone is required to make the lime needed to scrub the stack gas from each five tons of coal burned. A large 10,000-ton per day power plant requires 2,000 tons per day of limestone. The lime wastes from the scrubber are in the form of a watery sludge and are stored in holding ponds which are environmentally undesirable. Furthermore, although the wet limestone process and other flue gas cleaning systems help the utilities comply with new, more stringent environmental requirements, they lower plant operating efficiency and reliability, while increasing both capital and operating costs. Such limitations have been the main driving force behind technological innovations which aim at improving both the efficiency and environmental performance of power generation.

Figure 2 is a schematic diagram of an Ideal Integrated Gasification Combined Cycle (IGCC) system (the Brayton Cycle). The addition of a sorbent operating on a coal gasifier is shown in this diagram. This hot gas cleanup technique is needed to remove sulfur

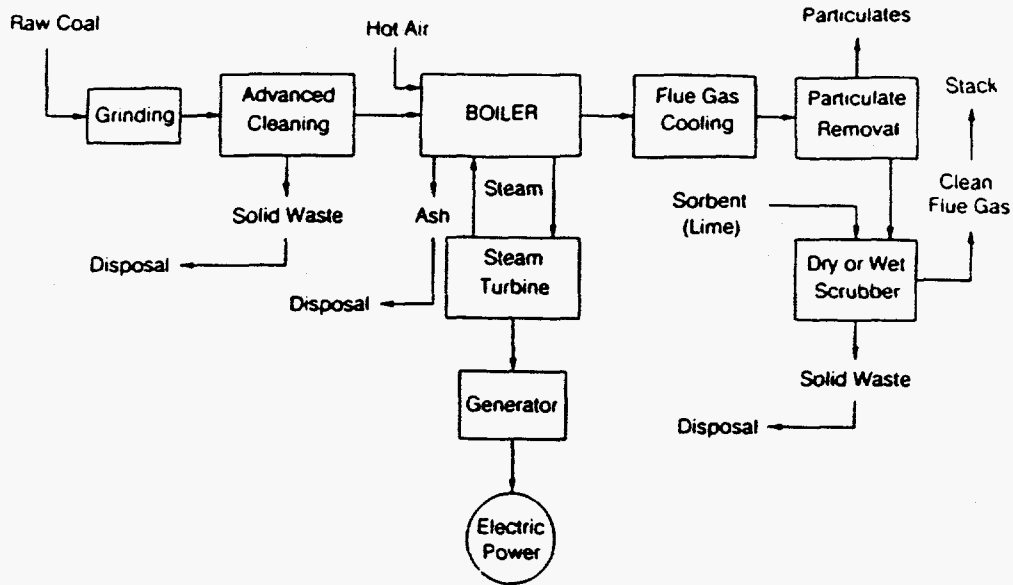


Figure 1. Schematic of a Conventional Power Generation System with pre- and post-combustion Physical and Chemical Cleaning.

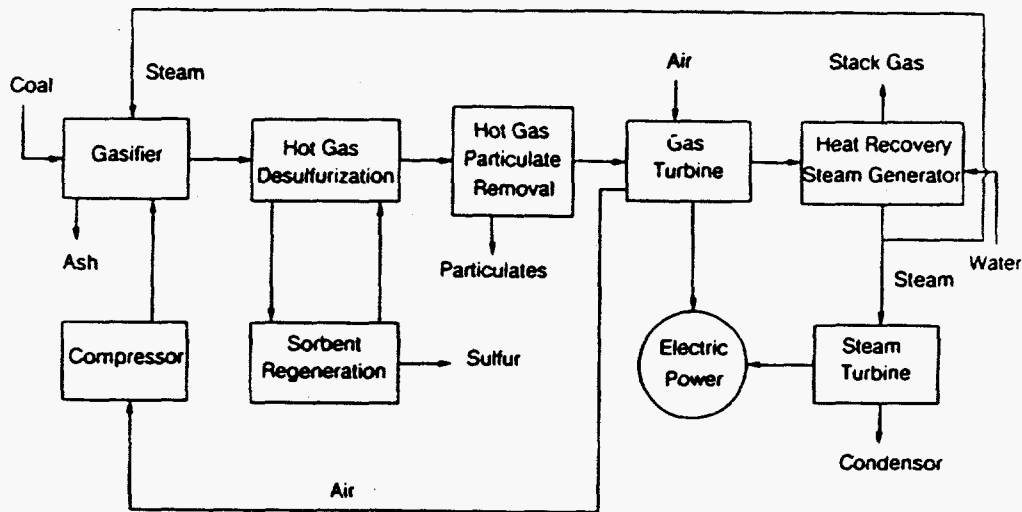


Figure 2. Schematic of an Ideal Integrated Gasification Combined Cycle (IGCC) System.

and other impurities in the fuel gas stream, mainly to meet stringent government regulations for sulfur emissions and also to protect system components from the corrosive action of H_2S (the main form in which sulfur exists in the fuel gas). Hydrogen sulfide 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, and the subsequent reheat of cleaned gas which gives this design a better overall efficiency and reduces the capital costs associated with expensive heat recovery systems. In addition, since the volume of the fuel gas is significantly less than that of the flue gas stream, particularly since it is usually also at elevated pressure, the removal of sulfur-bearing species at high temperature results in considerably lower hardware costs. Also, conventional SO_2 scrubbing results in the formation of gypsum sludge, which requires costly management. A regenerable sorbent avoids this problem since the sulfur can be recovered as sulfur dioxide or other sulfur products. Since hot gas desulfurization is a dry process, it does not require expensive waste water treatment plants to handle process condensate from quenching processes. The desulfurizing agent (e.g. sorbent) is reusable over many sulfur capture cycles which, in turn, improves process economics and reduces the amount of solid waste generated and ultimately landfilled.

In addition to IGCC systems, the cleaned hot fuel gas may be useful in a number of applications such as the molten carbonate fuel cell (MCFC) and the pressurized fluidized-bed combustor (PFBC). Efficiencies of heat conversion to useful electrical power approaching 50 percent are feasible with IGCC systems. However, in the

longer range future, power generation may be rendered more efficient by using the generated fuel gases in fuel cells for the direct conversion of heat into electricity.

Desulfurization with sorbents is essentially a process of removal of the species H_2S from the gas phase. As H_2S is removed, the other minority sulfur-bearing species, such as COS, equilibrate in the gas phase and also are proportionately reduced. The high temperature desulfurization can be successfully accomplished by using solid sorbents such as oxides of those metals that form stable sulfides. The effectiveness of a desulfurizing agent in treating coal 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 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 or lower is sought.¹ The focus of much current work on hot coal-derived fuel gas desulfurization is primarily in the use of zinc ferrite and zinc titanate sorbents. The choice of zinc oxide is typically based on the thermodynamic considerations that indicated very low concentration levels of H_2S in equilibrium with ZnO , ZnS , and H_2O vapor.²

To improve the process economics further, an easily regenerable sorbent is required which would not only reduce sorbent costs but also costs associated with frequent loading and unloading of the desulfurization reactors with sorbent and disposal of the spent sorbent. Furthermore, the sulfur produced by regeneration of the sorbent should be recoverable in a form which is readily saleable, storable, or disposable. This means that the regeneration step should be flexible

and be able to produce elemental sulfur, sulfur dioxide, or sulfuric acid depending upon the demand at the location of the gasification plant.

With these restrictions in mind, research has focused almost entirely on making the zinc-based sorbents durable. However, extensive research, carried out mainly by the Morgantown Energy Technology Center (METC), casts doubt³ that zinc ferrite or zinc titanate can be utilized even for the mild conditions associated with fixed-bed operation. Given the limited success of the zinc-based sorbents, interest has been shown in formulating and testing manganese-based sorbent pellets.

PROJECT DESCRIPTION AND RESULTS

Thermodynamic Arguments Supporting the Consideration of Manganese To substantiate the potential superiority of manganese-based pellets, a systematic approach toward the evaluation of the desulfurizing power of single-metal sorbents was developed based on thermodynamic considerations.⁴ This novel procedure considered several metal-based sorbents (Fe, Ni, Mg, Ca, Mn, Cu, and Zn) 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.

The thermodynamic feasibility of using such sorbent pellets for the removal of H_2S from hot coal-derived fuel gases and the subsequent regeneration of loaded (sulfided) pellets with air was then established.^{5,6} It was determined that the objective of reducing the H_2S concentration in the fuel gas below 150 ppmv to satisfy the IGCC system requirement is thermodynamically feasible using a Mn-

based sorbent. Although desulfurization at temperatures below 800 °C is possible, thermodynamic guidelines indicate that regeneration with air must be carried out above 900 °C to avoid sulfate formation.

Experimental A novel process was 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. The procedures for sorbent pellet making, drying, and induration are fully documented in a patent application filed by the authors.⁷

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 $\text{H}_2\text{S}-\text{H}_2$ gas mixtures in a thermogravimetric apparatus (TGA, Figure 3)⁵ 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, as shown in Figure 4 at 1000 °C. 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,¹ as indicated in Figure 5.

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 conducted in the TGA apparatus, up to 5 consecutive cycles.⁶ One important finding was that the capacity of the pellets for sulfur pickup from fuel gas and the kinetics of reduction, sulfidation, and

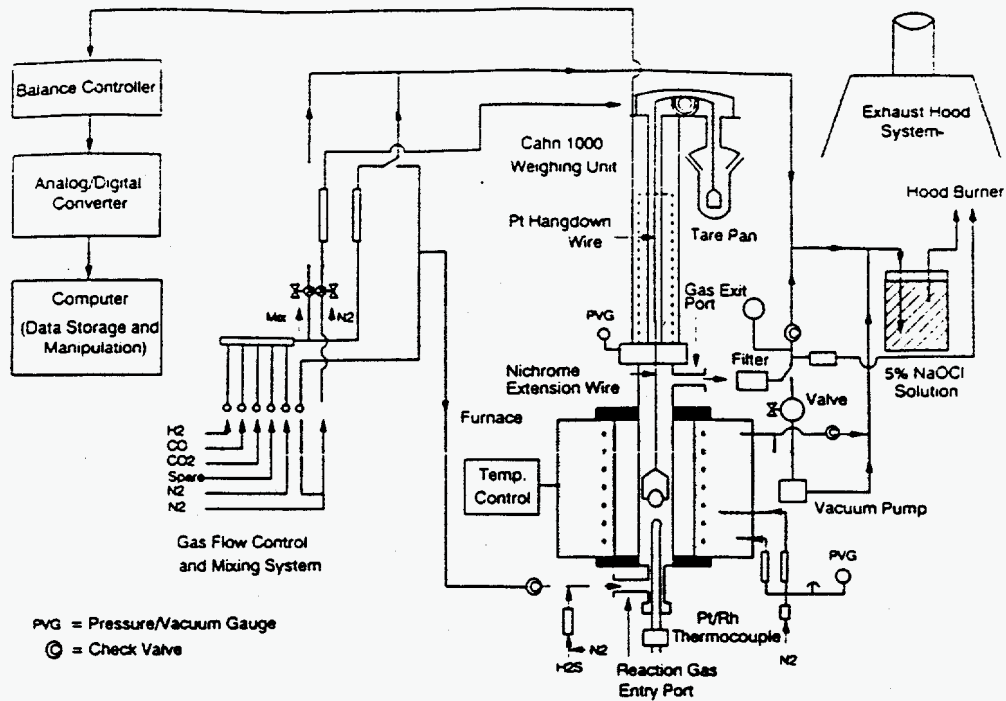


Figure 3. Schematic of the ASTRO Thermogravimetric (TGA) Apparatus.

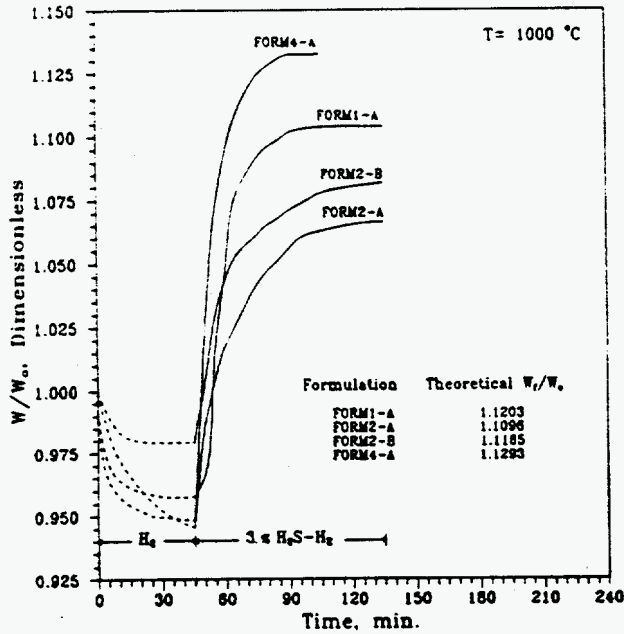


Figure 4. Comparison between Several Formulations of Manganese-Based Pellets upon Loading with Sulfidizing Fuel Gas.

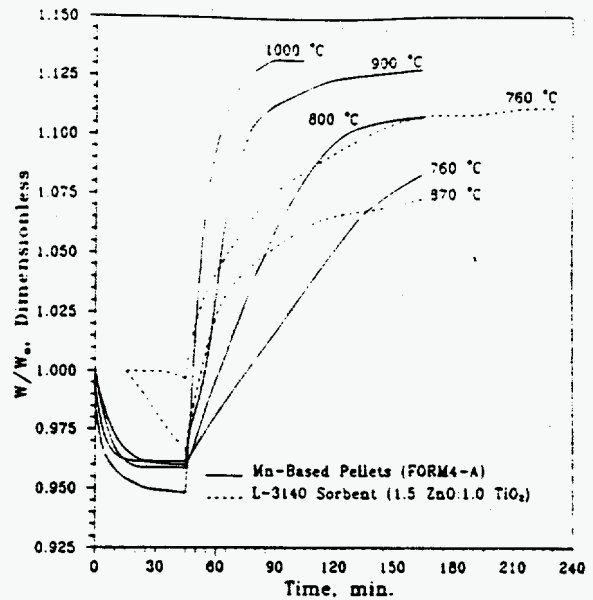


Figure 5. Comparison between Loading Behavior of Manganese-Based Pellets (FORM4-A) and Zinc Titanate Pellets.

regeneration reactions improved with recycling without compromising the strength. These results are reproduced in Figure 6. This desirable phenomenon was attributed to radial micro-crack formation which reduced the solid-state diffusion path within 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 stream.⁸ With the Mn-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.

While the results reported earlier^{5,6} were obtained using thermogravimetry, the potential usefulness of Mn-based pellets may be more realistically assessed by simulating practical processes of fuel gas desulfurization, which fall into three main categories: fixed-bed, fluidized-bed, or moving-bed technology. The main focus of this paper is to report on fixed-bed testing of the leading Mn-based sorbent pellet formulation (i.e., FORM4-A). Experiments were carried out to test the long-term (up to 50 cycles) durability and regenerability of the sorbent using a simulated fuel gas (Tampella-U) for sulfidation and air for regeneration. A more thorough description of these results is provided in a recent paper published by the authors.⁹

Experimental Results on Fixed Bed Tests

The leading formulation, FORM4-A, 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 2.6% TiO_2), 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. The pellets 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 g S/100 g of indurated pellet.

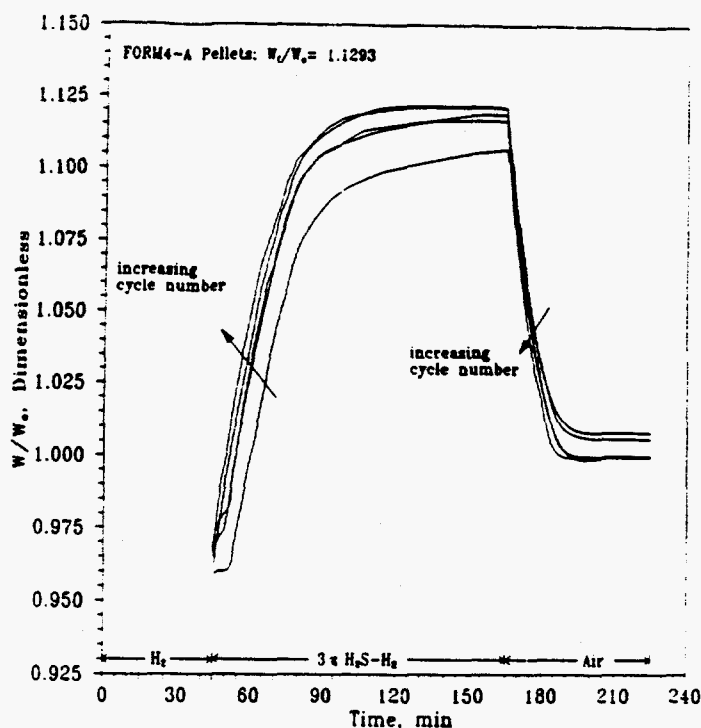


Figure 6. Effect of Repeated Cyclical Loading and Regeneration on the Reaction Kinetics and Capacity of FORM4-A Pellets.

The schematic diagram of the overall experimental arrangement for fixed-bed tests is shown in Figure 7. The split or two-zone furnace was positioned with respect to the bed to accomplish gas preheating and careful control of the bed temperature. Gas combinations for flows were produced via control of bottled gases through the valves and flowmeters shown in the diagram. The water content of the system was controlled by a metering pump acting on distilled water which was discharged into a heated stainless

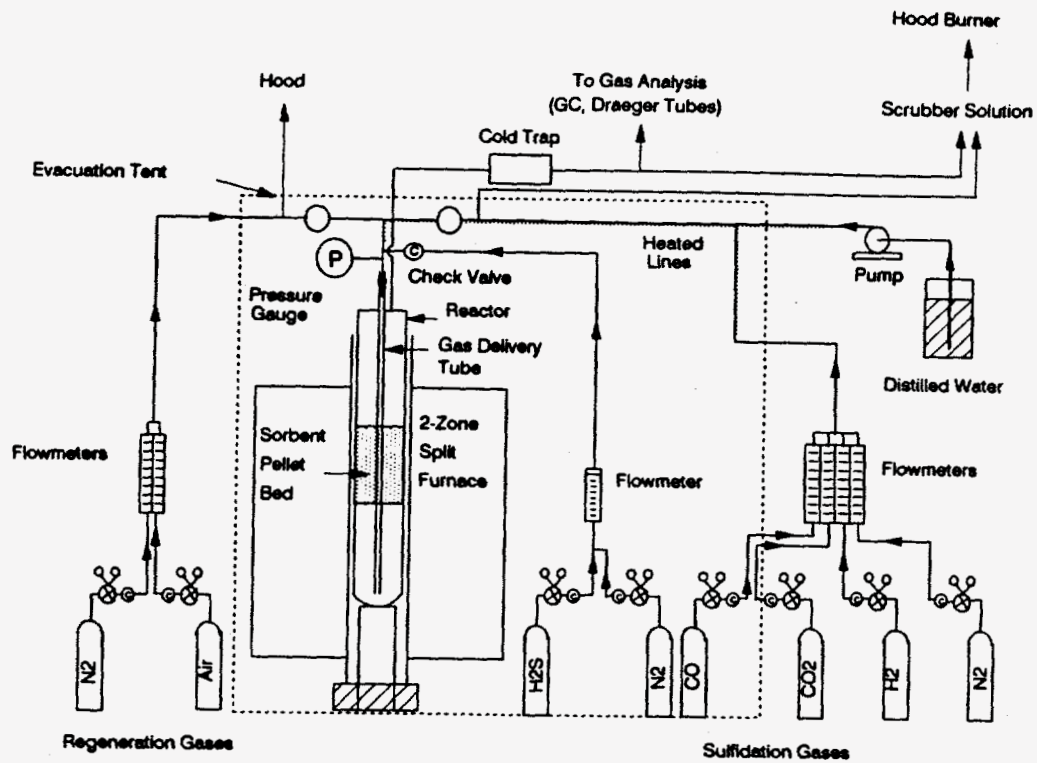


Figure 7. Schematic of Overall Experimental Arrangement for Fixed-Bed Tests.

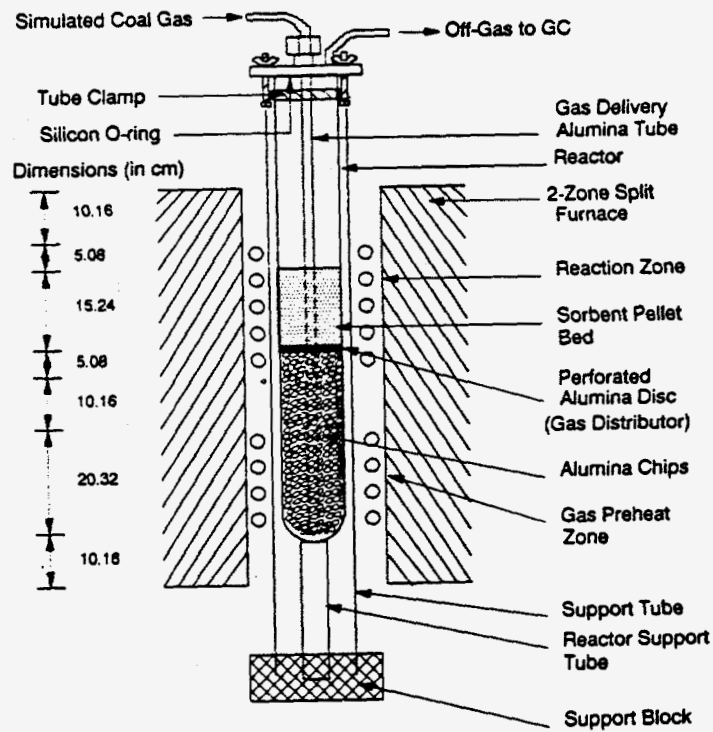


Figure 8. Schematic Diagram of Reactor Details.

steel tube to induce the vaporization of liquid water and provide the gas composition required for the simulation of a slightly modified form of the Tampella-U gas composition (13% H₂; 50% N₂; 24% CO; 5% CO₂; 5% H₂O; and 3% H₂S). The hydrogen sulfide level was about three times higher than that which would actually be produced by a gasifier to accelerate breakthrough. The hydrogen sulfide is mixed with the other gases and water vapor immediately before the introduction of the complete mixture into the reactor to minimize corrosion of system components. The reactive gas feed line was heat-traced to prevent subsequent condensation. In addition, the exhaust gas line was also heated from the top of the reactor to the cold trap to prevent any formation and subsequent freezing of elemental sulfur. Breakthrough of hydrogen sulfide gas was arbitrarily defined at a concentration of 500 ppmv in the exit gas.

The fixed-bed was made with 292.7 grams of FORM4-A pellets packed to a height of 15.24 cm (6 inches) in the 2-in (I.D.) reactor tube (Figure 8). In a typical test, the reactor was purged with nitrogen to expel air. During the purge, reactive gas flows were adjusted and routed directly to the scrubber solution. The reactive gases were then introduced into the reactor and the loading test timed. In such a fixed-bed desulfurization reactor H₂S removal would first occur near the bottom of the bed where reduction of Mn₃O₄ to MnO and the immediate conversion of MnO to MnS occur. The majority of the unreacted pellets are then exposed to the sulfur-free reducing gas for varying times as the reaction front progressed through the bed.

At the conclusion of the sulfidation test, the bed is flushed with nitrogen in order to expel remaining combustible gases and a regeneration gas consisting of air is initiated

with the product gas being periodically analyzed for SO₂ using detector tubes. The regeneration step is discontinued when the concentration of SO₂ is measured below 500 ppmv.

The breakthrough curve for sulfidation at 900 °C on the first cycle is shown in Figure 9. The concentration of H₂S in the exhaust gas (on wet basis) appears to reach a steady state value of approximately 222.5 ppmv for at least the first 7 hours of the loading test. This value is close to that of the MnO/MnS equilibrium. The vertical dashed line corresponds to the theoretical time required for breakthrough and is a function of the quantity of sorbent pellets in the reactor, the loading gas flowrate or space velocity, and the equilibrium pH₂O/pH₂S in the exhaust gas, i.e. reaction temperature since the amount of water vapor in the feed gas is fixed at 5% by volume. If breakthrough is arbitrarily defined at 500 ppmv in the exhaust gas, then breakthrough occurred after a total reaction time of 8 hours which corresponds to 21.12% loading or 81.86% bed utilization.

The concentration of SO₂ in the regeneration product gas is shown in Figure 10 as a function of reaction time. Again, the theoretical time for complete regeneration is displayed as a vertical dashed line which is a function of air flowrate, the quantity of pellets in the reactor, and temperature to a lesser extent since the reaction occurs essentially to completion. In addition, the theoretical maximum SO₂ concentration in the product gas (before mixing with after-burner gas) is shown in Figure 10 as a horizontal dashed line. This 13.76% value corresponds to regeneration with air and the complete consumption of oxygen in the air, and is calculated based on the stoichiometry of the overall regeneration reaction, as previously outlined in detail.⁶ As can be seen in Figure

10, the breakthrough occurred rapidly when the bed was almost completely regenerated.

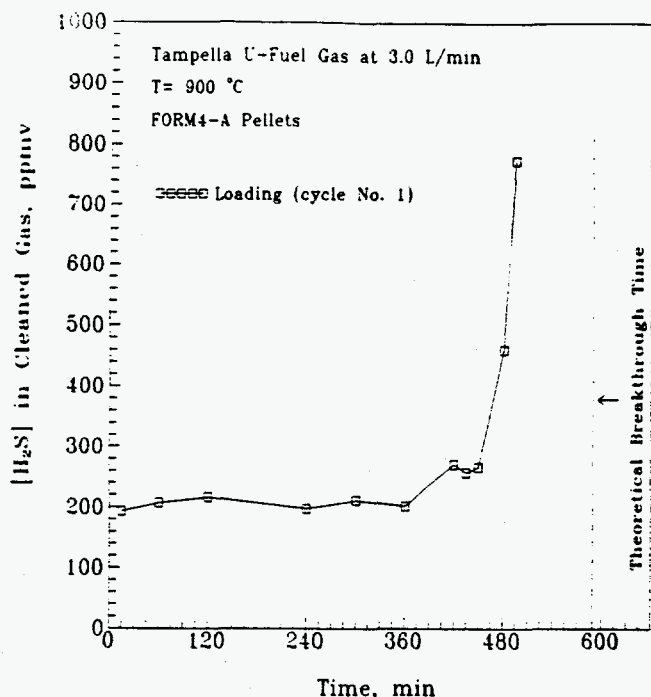


Figure 9. Breakthrough Curve for First-Cycle Sulfidation at 900 °C.

A relatively short series of complete sulfidation/regeneration cycles was then carried out at 900 °C to verify the sorbent as a viable candidate for a fixed-bed fuel gas desulfurization. Six consecutive cycles over a 15-day period were deemed adequate for this purpose. The results of sulfidation tests from cycles 1,2,3, and 6 are reported in Figure 11. Before breakthrough the H_2S concentration in the cleaned gas approaches more closely the equilibrium value, which is an indication of an improvement in pellet reaction kinetics with increasing cyclic loading. These results are consistent with the previous results from TGA tests on individual pellets.⁶

A fifty-cycle series of tests was then completed to demonstrate the durability and regenerability of FORM4-A sorbent

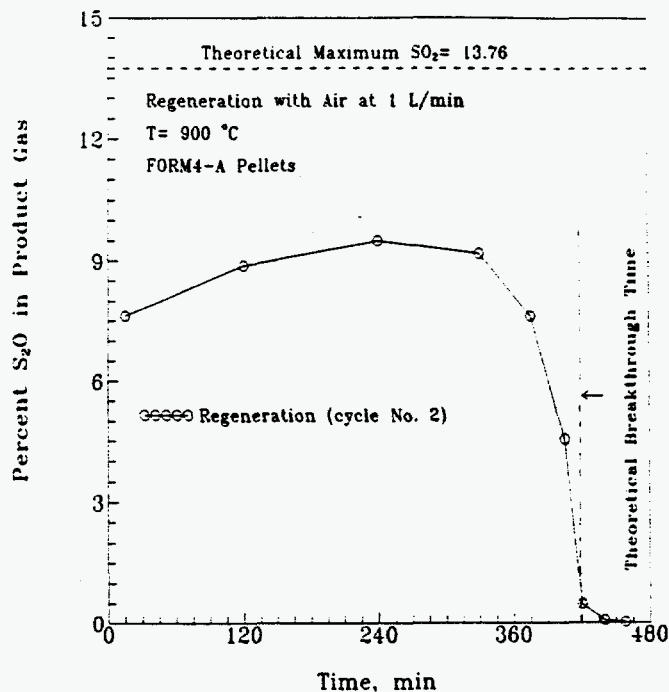


Figure 10. Concentration of SO_2 in Regeneration Product Gas.

formulation. Each sulfidation and regeneration repeated the initial run conditions. The results are reported in Figure 12 which shows the effect of cycling on the sulfur capacity of FORM4-A pellets at 900 °C upon repeated loading and regeneration. The sulfur loading capacity (defined as grams of sulfur per 100 grams of original pellet mass) shows a slight improvement with each cycle up to the fourteenth cycle. This effect is noticeable in the second cycle, but is much less pronounced in subsequent cycles. The sulfur capacity in the first eighteen cycles (except for cycle fifteen) ranged from 21.12% to 23.12%, which corresponds to approximately 90% sorbent bed utilization. This sulfur capacity is calculated using mass balances, based upon gas analyses for H_2S entering and leaving the reactor. At the fifteenth cycle, a equipment failure caused that test to be aborted. Upon removing the

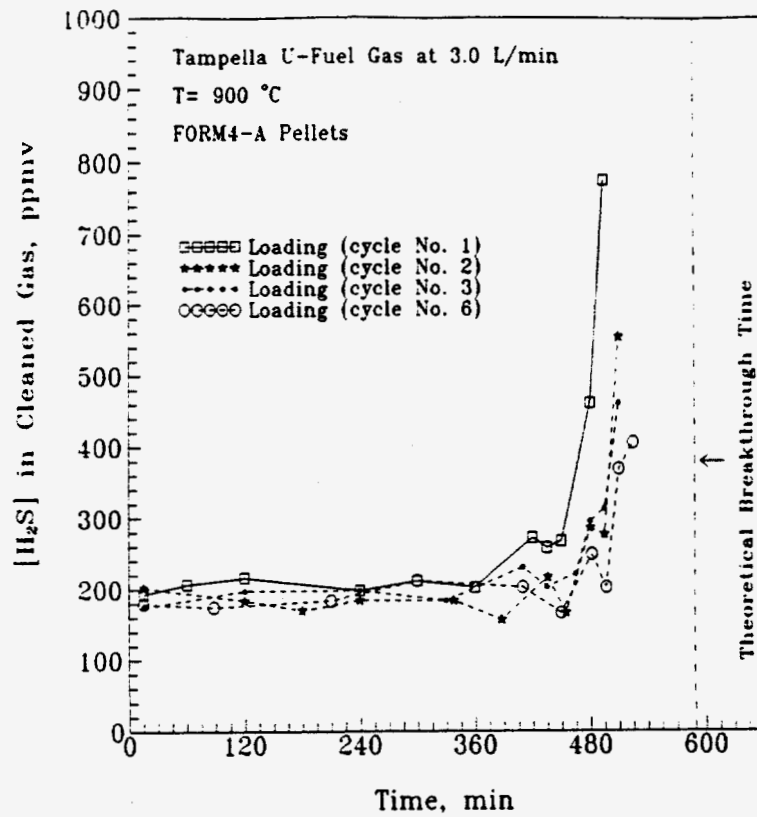


Figure 11. Series of Six Loading Cycles at 900 °C to Determine Sorbent Viability for Subsequent Fixed-Bed Testing (Cycles 1, 2, 3, and 6 are shown).

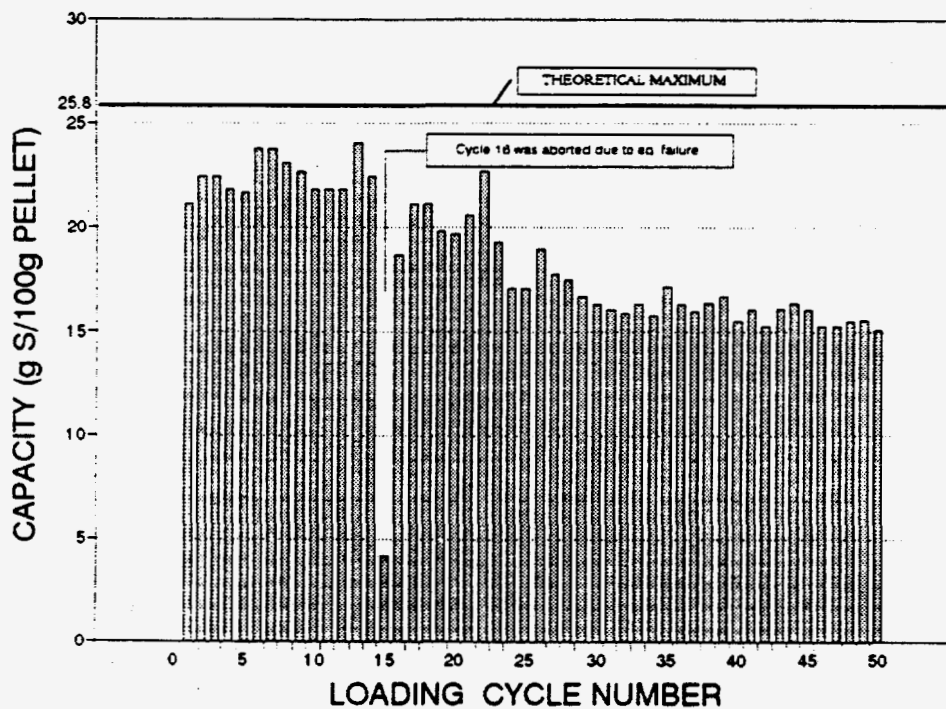


Figure 12. Capacity Tests via Multicyclic Loading and Regeneration of FORM4-A Pellets.

bed and examining the pellets, they were free-flowing and exhibited very little attrition (about 1% of their weight were in the form of fines). After the twenty-second cycle a drop off in bed performance is observed through the twenty-ninth cycle to about 17% capacity. (Studies are still in progress on this sorbent). These results can be compared with those on zinc titanate where the initial capacity on the first cycle is only 10 percent dropping to values as low as 2 percent after twenty-five cycles.¹⁰

STATUS OF PROGRAM

About five years ago, the U. S. Bureau of Mines, Twin Cities Research Center and the University of Minnesota entered into a joint program to study in situ leaching of manganese from Minnesota deposits. We decided to examine the Emily deposit since it was a high grade manganese oxide with minimal amounts of other carbonates or soluble oxides which would consume the lixiviant, sulfur dioxide. The Bureau both at Minneapolis and in Salt Lake City developed a continuous piloting process for purification of the leach solutions and the production of a pure manganese carbonate. (see Figures 13 and 14) About three years ago, the University secured funding for undertaking the use of manganese pellets as regenerable sorbents for hot fuel gas desulfurization. This application was included in the Bureau's economic overall evaluation and was found to be the most favorable candidate for development. The high manganese purity and low iron levels of their product are necessary in order to achieve the required properties of cyclic loading and regeneration.

Simultaneous with the development of the piloting process, the University continued to study pellet formulations and to engage in long term cyclic testing. The program with the

Department of Energy, initially begun with support from the Morgantown Energy Technology Center has been extended for three more years by the Pittsburgh Energy Technology Center. These future studies are to examine the kinetics of loading and regeneration and also to determine if loading can proceed at lower temperatures by changes in the pellet formulation.

In the past year, the Minnesota Manganese Resources Company has shown an interest in these studies and has encouraged our efforts to develop a value-added application for in situ mined manganese. Their ore body has been the one which the Bureau was exploring with respect to leach tests on core samples to produce leach liquors for their purification pilot plant. Although the tests we reported in this paper were for reagent-grade manganese carbonate, we are planning to determine the reproducibility of the pellet formulations made with in-situ mined-product (ISMP) with respect to its: strength, effectiveness in loading and regeneration and resistance to degradation upon multiple cycle loading. Preliminary results indicate that pellets from ISMP is equivalent to the commercial grade manganese and has a potential value ranging from \$3 to \$7 per pound. (The latter value is that generally assigned to the zinc titanate product which is considered for use in IGCC systems).

As a final note for those of us which are more familiar with taconite pellet production, it might be useful to think of the future potential of manganese pellets in these terms:

The manganese pellet product has the potential for one hundred times the value of taconite pellets, but will have a market demand less than one-half of

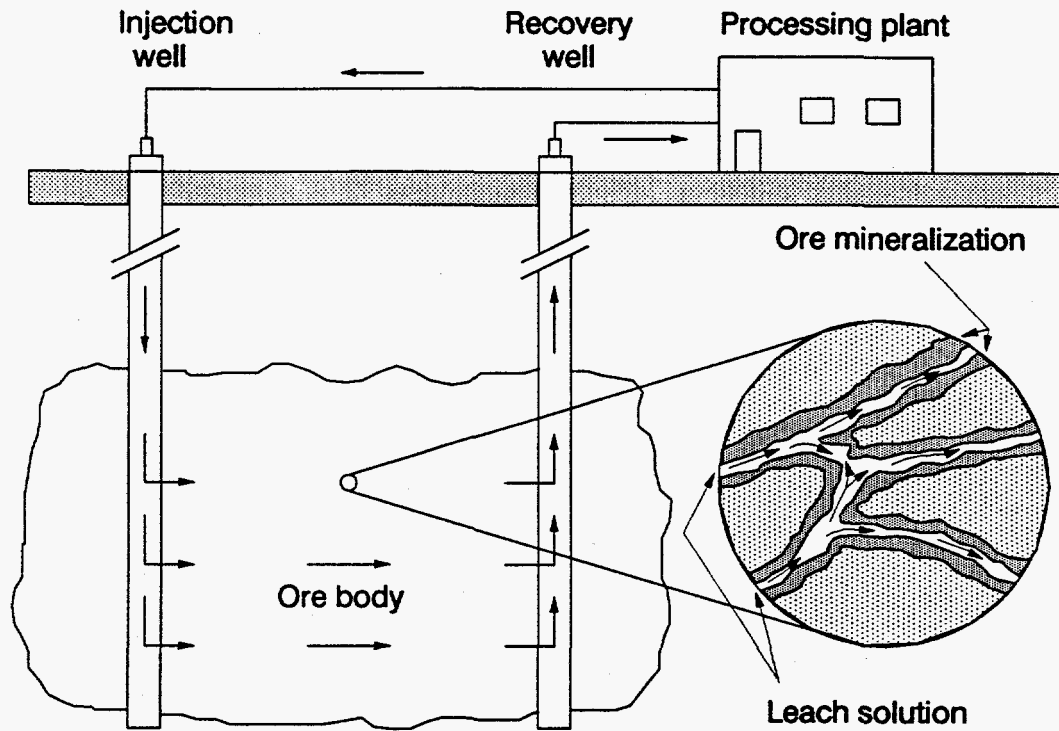


Figure 13. Cross Section of an In Situ Leach Mining System in which the Core is Leached via a System of Vertical Wells.¹¹

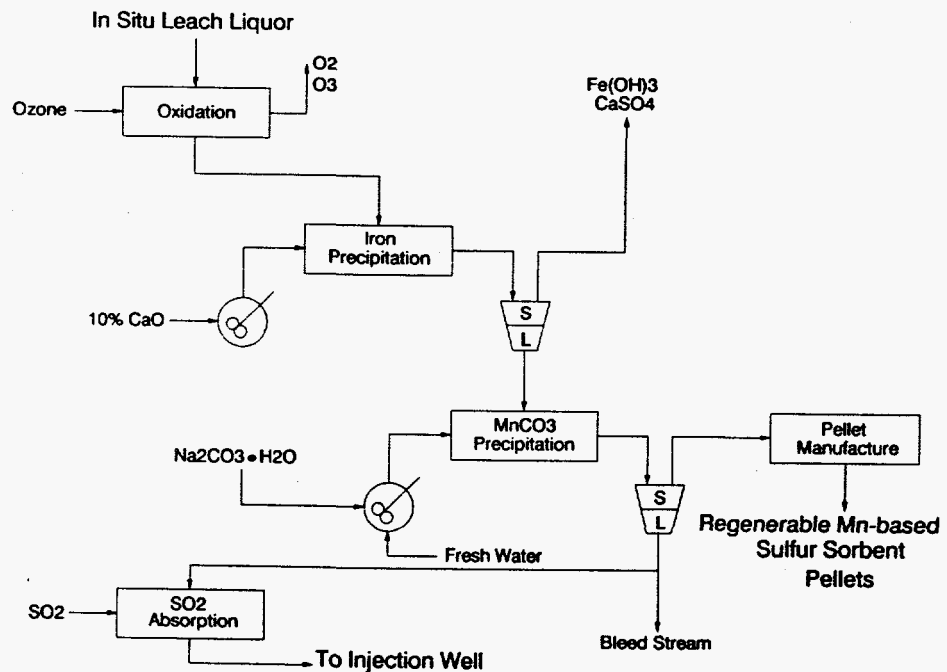


Figure 14. Simplified Flow Diagram for a Manganese Carbonate Recovery Process Developed at the the Salt Lake City Research Center of the U.S. Bureau of Mines.¹²

one percent of the taconite tonnage. This leads one to hope that if all factors are favorable, a new industry for north-central Minnesota may be in the offing: a product to improve the environment produced by a mining process with minimal impact on the environment.

What are the "ifs"? At present the requirements for this product to move forward are dependent upon the willingness of the power industry to shift to combined cycle operation and avoid gypsum sludge by use of a regenerable sorbent. Zinc titanate appears to be inferior to manganese; however, most of the research work conducted by the U.S. DOE and its contractors has been done on zinc titanate. Consequently, a body of information must be assembled to support manganese as an alternative.

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