

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

**Final Report  
September 1992 - December 1994**

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

**For  
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**November 1994**

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## ACKNOWLEDGEMENT

*Credit for the original conception of manganese as a regenerable sorbent is given to Dr. E. T. Turkdogan, whose assistance in formulating the initial stages of this work proved invaluable. The support and encouragement of members of the staff of the Morgantown Energy Technology Center is acknowledged. In particular, the author wishes to express thanks to Dr. Venkat K. Venkataraman for his help as the technical monitor and Mr. Suresh Jain who originally participated in the formulation of the program. In addition, the patience of Ms. Dianne Manilla, who guided the author in the process of satisfying report requirements is acknowledged. The support of the staff of the U. S. Bureau Mines, Twin Cities Research Laboratories, in particular, Dr. Dianne Marozas, is acknowledged and also Dr. Lewis Wade, Director, for permission to use the Cahn micro balance and gas train at that laboratory. Finally, and not least, the author wishes to express his thanks to the personnel at METC who carried out the complex tasks of arranging contractors's meeting which proved especially valuable in maintaining current awareness for the author and his students on developments in the field of sorbent development. These contributions of METC have provided a rich background for instruction to graduate and undergraduate students in recognizing the importance of clean coal combustion. By this means, the efforts of the METC staff are multiplied by their willingness to provide technical reports and encouragement to the academic community. When one realizes that up to one billion tons of new coal combustion facilities in China are being scheduled for construction up-wind of our continent, the importance of technical advances in clean coal combustion cannot be under-estimated. The wise provision of Congress in funding Clean Coal Programs shows their concern for the preservation of our environment for future generations.*

The focus of much current work being performed by the Morgantown Energy Technology Center (METC) of the Department of Energy on hot coal-derived fuel gas desulfurization is in the use of zinc-based sorbents. Extensive research, however, casts doubt that these sorbents can be utilized even for the mild conditions associated with fixed-bed operation. Accordingly, METC has shown interest in formulating and testing manganese-based pellets as alternative effective sulfur sorbents in the 700 to 1200 °C temperature range.

To substantiate the potential superiority of Mn-based pellets, a systematic approach toward the evaluation of the desulfurizing power of single-metal sorbents is developed based on thermodynamic considerations. This novel procedure considered several metal-based sorbents and singled out manganese oxide as a prime candidate sorbent capable of being utilized under a wide temperature range, irrespective of the reducing power (determined by  $\text{CO}_2/\text{CO}$  ratio) of the fuel gas. Then, the thermodynamic feasibility of using Mn-based pellets for the removal of  $\text{H}_2\text{S}$  from hot-coal derived fuel gases, and the subsequent oxidative regeneration of loaded (sulfided) pellets was established. It was concluded that MnO is the stable form of manganese for virtually all commercially available coal-derived fuel gases. In addition, the objective of reducing the  $\text{H}_2\text{S}$  concentration below 150 ppmv to satisfy the integrated gasification combined cycle system requirement was shown to be thermodynamically feasible.

A novel process is developed for the manufacture of Mn-based spherical pellets which have the desired physical and chemical characteristics required during the long-term cyclic sulfidation and regeneration in a high-temperature desulfurization operation. Screening sulfidation tests on a number of formulations, consisting of a Mn-containing compound (ore or  $\text{MnCO}_3$ ), alundum ( $\text{Al}_2\text{O}_3$ ), and organic or inorganic binders, were carried out using  $\text{H}_2\text{S}$ - $\text{H}_2$  gas mixtures in a thermogravimetric (TGA) apparatus at temperatures ranging from 700 to 1000 °C. A formulation, designated FORM4-A, was found to possess the best combination of sulfur capacity, reactivity, and strength. Regeneration tests determined that for  $T \geq 900$  °C, loaded pellets can be fully regenerated with air in 10 to 15 minutes, without sulfate formation, in strict accordance with thermodynamic guidelines. Repeated cycling of the leading sorbent formulation (FORM4-A) was then conducted in the TGA apparatus, up to 5 consecutive cycles. One important finding was that the capacity of the pellets for sulfur pickup from fuel gas and the kinetics of reduction, sulfidation, and regeneration reactions improved with recycling without compromising the strength.

Testing of the leading Mn-based sorbent pellets was carried out in a 2-inch fixed-bed reactor to evaluate the long-term durability and regenerability of the sorbent using a Tampella-U fuel gas for sulfidation and air for regeneration. Consistent with TGA results on individual pellets, the fixed-bed tests show small improvement in capacity and kinetics with the sulfur capacity being about 22% by weight of the original pellet, which corresponds to approximately 90% bed utilization. In addition, the effect of temperature on sulfidation reaction equilibrium is determined in the range 800 to 1000 °C. A re-assessment of the equilibrium states of reactions in the Mn-S-O system is then presented based on the results obtained and a recent study by Turkdogan.

The shrinking unreacted-core model was found to approximate the kinetic

behavior of Mn-based pellets during both the sulfidation and regeneration stages. Kinetic analysis of TGA experimental data determined that beyond approximately 35% reaction completion, sulfidation and regeneration reaction rates were controlled primarily by gaseous counter-diffusion through the porous product layer.

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