

DOE/METC/C-95/7194

Fixed Bed Testing of Durable, Steam Resistant Zinc Oxide Containing Sorbents

Authors:

Ranjani V. Siriwardane (DOE/METC)

Ulrich Grimm (DOE/METC)

James Poston (DOE/METC)

Conference Title:

American Institute of Chemical Engineers 1994 Annual Meeting

Conference Location:

San Francisco, California

Conference Dates:

November 14 - 18, 1994

Conference Sponsor:

American Institute of Chemical Engineers

RECEIVED
NOV 29 1995
OSTI

MASTER

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

at

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

This report has been reproduced directly from the best available copy.

Available to DOE and DOE contractors from the Office of Scientific and Technical Information, 175 Oak Ridge Turnpike, Oak Ridge, TN 37831; prices available at (615) 576-8401.

Available to the public from the National Technical Information Service, U.S. Department of Commerce, 5285 Port Royal Road, Springfield, VA 22161; phone orders accepted at (703) 487-4650.

FIXED BED TESTING OF DURABLE, STEAM RESISTANT ZINC OXIDE
CONTAINING SORBENTS

Ranjani V. Siriwardane¹, Ulrich Grimm¹, James Poston¹,
and Steven J. Monaco²

Prepared for Presentation at the AIChE Annual Meeting
San Francisco, California
November 1994
Symposium on Gas Purification 1 & 2

The submitted manuscript has been authored by U.S. Government employees acting within their official capacities. On advice from council, a transfer of copyright form cannot be executed.

September 1994

UNPUBLISHED

AIChE shall not be responsible for statements or opinions contained in this paper or printed in its publications.

¹U.S. Department of Energy, Morgantown Energy Technology Center, Morgantown, WV 26507-0880

²EG&G Technical Services of West Virginia, Inc., Morgantown, WV 26505

SUMMARY

The U.S. Department of Energy is currently developing Integrated Gasification Combined Cycle (IGCC) systems for electrical power generation. It has been predicted that IGCC plants with hot gas cleanup will be superior to conventional pulverized coal-fired power plants in overall plant efficiency and environmental performance.

Development of a suitable regenerable sorbent is a major barrier issue in the hot gas cleanup program for IGCC systems. This has been a challenging problem during the last 20 years, since many of the sorbents developed in the program could not retain their reactivity and physical integrity during repeated cycles of sulfidation and regeneration reactions. Two promising sorbents (METC2 and METC6), which were capable of sustaining their reactivity and physical integrity during repeated sulfidation/regeneration cycles, have been developed at the Morgantown Energy Technology Center (METC) during the past year. These sorbents were tested (sulfided) both in low-pressure (260 kPa/37.7 psia) and high-pressure (1034 kPa/150 psia) fixed-bed reactors at 538 °C (1000 °F) with simulated KRW coal gas. High-pressure testing was continued for 20 cycles with steam regeneration. There were no appreciable changes in sulfidation capacity of the sorbents during the 20-cycle testing. The crush strength of the sorbent actually improved after 20 cycles and there were no indications of spalling or any other physical deterioration of the sorbents. In testing to date, these sorbents exhibit better overall sulfur capture performance than the conventional sorbents.

INTRODUCTION

The U.S. Department of Energy has funded research, development, and demonstration projects for many years in the field of advanced power generation. IGCC system is one of the most promising advanced power systems. It has been predicted that IGCC systems with hot gas cleanup will offer significant improvements in environmental performance and overall plant efficiency, compared to conventional pulverized coal-fired plants which have efficiencies of 33 to 35%. It is expected that IGCC with hot gas cleanup will achieve efficiencies of 52% by the year 2010 which will lower the cost of electricity by up to 20%, with respect to conventional plants. Furthermore, this increase in efficiency will reduce CO₂ emissions by 35%.

Development of a suitable regenerable sorbent is a major barrier issue in the hot gas cleanup program for IGCC systems. This has been a challenging problem during the last 20 years. Various formulations of zinc ferrite and zinc titanate in the form of extrudates and spherical pellets have been studied at METC for removal of sulfurous gases from coal gasification streams (Mei et al., 1993; Siriwardane et al., 1994). Problems of decrepitation and spalling have occurred after sulfidation and regenera-

tion of these sorbents. Z-Sorb, a proprietary sorbent developed at Phillips Petroleum Company, showed good physical durability during testing at METC, but there was a continuous decrease in reactivity during multiple cycle tests due to steam regeneration (Delzer et al., 1993). A series of novel sorbents containing zinc oxide have been developed at METC to address these problems. These METC-developed sorbents showed superior performance during a 20-cycle high-pressure fixed-bed test with steam regeneration conducted at METC. The results of the sorbent testing in both low- and high-pressure reactors and some sorbent analysis data are discussed in this paper.

OBJECTIVES

The overall objective of this project was to develop regenerable sorbents for hot gas desulfurization in IGCC systems. The major criteria for the development of novel sorbents included reasonable chemical reactivity and physical durability during repeated sulfidation/regeneration cycles. The sorbent should be able to withstand reducing gas atmospheres at elevated temperatures and pressures during sulfidation. During regeneration the sorbent should be able to withstand steam which is added to regeneration air to maintain temperature control.

Nine sorbents (METC1-METC9) were prepared, but only some of these sorbents were selected for initial testing. The remaining sorbents will be tested at a later time. Two of these sorbents (METC2 and METC6) have been tested both in the low-pressure and the high-pressure reactors. Results of the high-pressure testing of METC2 and METC6 and low-pressure testing of METC7 will be discussed in this paper. METC2 and METC7 were designed for fixed-bed or moving-bed applications while METC6 was designed for fluid-bed applications. However, all these sorbents were tested in a fixed bed. Twenty cycles of sulfidation reactions were completed for both METC2 and METC6 in the high-pressure reactor. Five sulfidations were completed with METC7 in the low-pressure reactor.

EXPERIMENTAL

Sorbents were prepared at METC by a solid state mixing method utilizing a mixer pelletizer. The sorbents contained about 50 wt% of zinc oxide. The solid materials were thoroughly mixed in the mixer pelletizer and sufficient amount of water was added to the mixture to form pellets. Sorbent pellets in the size ranges of both -5+8 mesh and -4+5 mesh were utilized for reactor testing.

The sorbents were initially tested in a low-pressure (272-kPa/37.7-psia) reactor. This quartz reactor had a diameter of 5.7 cm (2.2 in) and a bed height of 15.2 cm (6 in). Sorbents that showed promising results in the low-pressure unit were then tested in the high-pressure bench-scale hot gas desulfurization unit at 1034 kPa (150 psia) which contained a 5.5-cm (2.2-in)

inner diameter reactor. The reactor was constructed of Incoloy 800HT alloy steel pipe. Inside the pipe there was a removable 316 stainless steel cage for easy loading and unloading of the sorbent. The sorbent cage was suspended from the top flange of the reactor. A gas distributor was fixed at the bottom of the cage to support the sorbent. The inside of the sorbent cage was Alon-processed to prevent corrosion of stainless steel by sulfurous gases in the presence of steam. The reactor was housed inside a three-zone furnace equipped with separate temperature controllers for each zone. Quartz wool was installed on top of the sorbent bed to hold the sorbent as well as to capture particulates from the fixed bed for upflow operation. A perforated distributor was fixed at the bottom of the cage to support the sorbent pellets. The lower part of the reactor was packed with ceramic spheres and quartz wool for the purpose of heating or cooling the gases passing through the reactor and to provide a filter for particulates. The details of this system are reported by Mei et al., 1993.

Bottled gases, house nitrogen, and distilled water were used to supply the simulated coal gas. Gases were heated in an external preheater. The process water was preheated using a small boiler and then fed to the processed gas preheater along with other gases. Since hydrogen sulfide is a corrosive gas, it was added to the bulk gas stream after the preheater.

A 40.7-cm (16-in) deep fixed bed of sorbent was subjected to alternating periods of sulfidation and regeneration. Sulfidation was accomplished by feeding a gas, which simulated the KRW fuel gas composition, in a downflow mode through the reactor at 538 °C (1000 °F). KRW simulated gas was composed of 47.92% nitrogen, 9% steam, 7% carbon dioxide, 21% carbon monoxide, 15% hydrogen, and either 800 or 2000 ppmv of hydrogen sulfide. The sorbent regeneration was performed in the reverse direction (upflow) utilizing air diluted with nitrogen or nitrogen and steam in order to limit the regeneration exotherm and prevent overheating of the sorbent.

RESULTS

High-Pressure Testing

All the sulfidations in the high-pressure reactor were performed at 538 °C (1000 °F) and 1034 kPa (150 psia) utilizing a feed gas containing 800 ppmv H₂S. The superficial velocity for all sulfidations in the high-pressure reactor was maintained at 0.3 m/s (1.0 ft/s) and the space velocity was 1363 h⁻¹. The outlet H₂S concentration was monitored using detector tubes and gas chromatography.

All regenerations in the high-pressure reactor were done at 170 kPa (24.7 psia) and the gas velocity was maintained constant at 0.3 m/s (1.0 ft/s). All dry regenerations were performed utilizing a multi-stage technique. With nitrogen as a diluent

gas, the oxygen concentration was increased in discrete increments of 0.5, 2.5, 4.0, 7.0, and 21.0 mole % while simultaneously increasing the bed temperature. Temperatures at the discrete steps were 538, 579, 621, 663, and 704-760 °C (1000, 1075, 1150, 1225, and 1300-1400 °F). The exit gas was monitored for SO₂ using detector tubes and gas chromatography. All regenerations were performed until the SO₂ concentration dropped to less than 50 ppmv.

Steam regeneration was conducted in four stages. The temperatures of the four stages were 538, 579, 621, and 663 °C (1000, 1075, 1150, and 1225 °F). The steam concentration in all four stages was 50% with a varying concentration of oxygen and nitrogen. The oxygen concentration during the four stages was 0.5, 2.5, 4.0, and 7.0% respectively.

Results of the METC2 Testing in the High-Pressure Unit

The results of the six sulfidation runs for METC2 performed utilizing dry regeneration in the high-pressure reactor are shown in Figure 1. There was a continuous increase in the sorbent sulfur capacity from sulfidation cycle 1 to cycle 5 after which the capacity stabilized. A comparison of the sulfidation breakthrough curves for METC2 and for a molybdenum-containing zinc titanate from General Electric Company tested under identical conditions is shown in Figure 2. For zinc titanate, there was a decrease in the sulfur capacity up to the third cycle, and the sorbent stabilized after the third cycle. The sulfur capacity of METC2 after it stabilized at cycle 5 was significantly better than that of the zinc titanate. A comparison of the sulfidation breakthrough curves for METC2 and Z-Sorb from Phillips Petroleum is shown in Figure 3. The sulfur capacity for METC2 after it stabilized at the fifth cycle is comparable to that of Z-Sorb.

In order to understand how steam regeneration would affect the performance of the METC2 sorbent, regenerations during cycles 6 through 19 were conducted utilizing steam. The sulfidation breakthrough curves from sulfidations 7 through 20 (which all follow steam regenerations) are shown in Figure 4. There was a slight decrease in the sulfur capacity between the sixth (last sulfidation following dry regeneration) and seventh sulfidation (first sulfidation following steam regeneration). However, the breakthrough curves for sulfidations 7 to 11 overlapped, within the ±25% error of the detector tube readings, indicating that the steam regeneration did not affect the sorbent.

After sulfidation 11, some of the sorbent was removed from the reactor for total sulfur analysis. The decrease in breakthrough time between sulfidations 11 and 12 is due to the removal of this material from the sorbent bed. The sulfidation breakthrough curves from cycles 12 to 20, which also follow steam regenerations, overlapped as well, indicating that the sorbent was stable during steam regeneration. The percent total sulfur content from the solid analysis of the sorbent after the cycle 20 was similar

to that after cycle 11. This further confirmed that the decrease in sulfur capacity during cycles 11 and 12 was due to the sorbent removal. Therefore, there was no change observed in the sulfur absorption capacity caused by the steam regenerations in the sulfidation cycles 7 through 20.

The visual examination of the sorbent after 20 sulfidation cycles indicated that there was no spalling or any other physical deterioration of the sorbent. The crush strength of the sorbent after 20 cycles was higher than that of the fresh sample. Sieve analysis indicated that 92% of the material was unaffected after 20 cycles. This is even after dropping the sorbent in from the top of the reactor during the initial loading and utilizing a vacuum cleaner for sorbent removal from the bed. All of the condensates collected during the 20-cycle test were very clear, indicating that the sorbent did not decrepitate in the bed and that there was no powder lost from the sorbent as observed with zinc ferrite or zinc titanate. The zinc content detected in the condensates was negligible. The atomic absorption data indicated that there was no loss of zinc from the pellets due to volatilization.

Elemental mapping and elemental line scans of cross sections of the reacted pellets obtained utilizing scanning electron microscopy/energy dispersive analysis of X-rays indicated that the sulfur was uniformly distributed in the pellet. X-ray diffraction and Fourier transform infrared spectroscopy data indicated that there were some chemical structural changes of the sorbent during 20-cycle sulfidation/regeneration reactions. Pore diameter data obtained utilizing mercury porosimetry indicated that there was an increase in the average pore diameter of the pellets after 20 cycles of sulfidation/regeneration compared to the fresh samples. This increase in pore size of the pellets may have contributed to the increase in sulfur capacity during the first five cycles. The total sulfur contents per 100 grams of the fresh sorbent analyzed after the 11 cycles were 9.1 at the top of the bed and 5.6 at the bottom of the bed; after 20 cycles, they were 8.4 at the top of the bed and 6.3 at the bottom of the bed.

The METC2 sorbent showed a superior level of performance during the 20-cycle high-pressure fixed-bed testing. It was spalling resistant, steam resistant, and had both excellent chemical and physical durability during the 20-cycle test.

Results of METC6 Testing in the High-Pressure Unit

The chemical formulation of METC6 was designed for fluid-bed applications, but the pellets were sized for the testing which was conducted in a fixed bed. Twenty sulfidation cycles were completed with METC6 in the high-pressure unit utilizing steam regeneration. The sulfidation breakthrough curves of METC6 are shown in Figure 5. There was an increase in sorbent sulfur capacity between sulfidations 1 and 2, but the capacity decreased

again at the third sulfidation cycle. The sulfidation breakthrough curves from cycles 3 to 20 overlapped with a slight decline seen in cycles 14 and 15. This indicates that the sorbent was chemically stable during the 20 cycles of testing and was not affected adversely by the steam regeneration. The condensates collected from the reactor during this test series were very clear. Visual examination of the sorbent after sulfidation cycle 20 indicated that there was no spalling or any other deterioration of the sorbent. Even though METC6 was formulated for fluid-bed applications, it performed very well with the bigger particle sizes required in fixed-bed testing.

Results of the METC7 Testing in the Low-Pressure Unit

All of the sulfidations in the low-pressure reactor were performed at 538 °C (1000 °F) and 260 kPa (38 psia) utilizing a feed gas containing 2000 ppmv H₂S. The superficial velocity for all sulfidations in the low-pressure reactor was maintained at 0.09 m/s (0.30 ft/s) and the space velocity was 2000 h⁻¹. The outlet H₂S concentration was monitored using detector tubes and gas chromatography.

All regenerations in the low-pressure reactor were done at 272 kPa (39.7 psia) and the gas velocity was maintained constant during each stage at 0.04-0.05 m/s (0.13-0.15 ft/s). The steam regenerations were conducted in three stages. The temperatures of the stages were 538, 593, and 649 °C (1000, 1100, and 1200 °F). The steam concentration in all three stages was 50% with a varying concentration of oxygen and nitrogen. The oxygen concentrations during the three stages were 1.0, 2.5, and 3.5%, respectively.

The sulfidation breakthrough curves of METC7 in the low-pressure unit are shown in Figure 6. There was an increase in sulfur capacity from sulfidation 1 to 2, but the sulfur capacity decreased in the third sulfidation. The sulfidation breakthrough curves overlapped after the third sulfidation indicating sorbent stabilization at that point. The outlet hydrogen sulfide concentration was zero for about 15 hours during each of the 5 sulfidations indicating that the efficiency of the sorbent was excellent. A comparison of METC6 and METC7 tested in the low-pressure unit is shown in Figure 7. It is clear that the sulfur capacity of METC7 is better than that of METC6. Since METC7 was the fixed-bed version of METC6, it was expected to have a better capacity in fixed-bed testing. Visual examination of the METC7 sorbent after the fifth cycle indicated that there was no spalling or any other signs of physical deterioration during the testing.

CONCLUSIONS

Both METC2 and METC6 sorbents showed a superior level of performance during the 20-cycle high-pressure fixed-bed testing. These sorbents functioned well in the reducing gas environment at

high temperature which will be present in the coal gasification process. Both sorbents were prepared utilizing a solid state mixing method which is very inexpensive.

METC2 was designed for fixed-bed or moving-bed applications and the sulfur absorption capacity was excellent under fixed-bed testing. Steam regeneration did not adversely affect the sorbent performance during the 20-cycle testing. Crush strength of the sorbent after 20 cycles was more compared to that of the original sorbent. It was spalling resistant and had both excellent chemical and physical durability during the 20-cycle test. Overall performance of this sorbent was superior compared to other sorbents tested previously at METC.

Even though METC6 was designed for fluid-bed applications, it performed well in the 20-cycle fixed-bed testing which required bigger particle sizes. This sorbent was also spalling resistant and showed excellent physical durability and stable chemical reactivity during the 20-cycle testing. METC7, which is the fixed-bed version of METC6, showed better capacity than that of METC6 during fixed-bed testing.

ACKNOWLEDGMENTS

The authors would like to acknowledge all the members of the Sorbent Development Cluster at METC for their contributions to this project as well as the members of EG&G, the on-site support contractor at METC, who conducted the sorbent reactor testing.

REFERENCES

Delzer, G.A., G.P. Khare, and G.J. Greenwood. 1993. Z-Sorb absorbent for hot gas desulfurization, St. Louis, Missouri: AIChE Annual Meeting, Symposium on Gas Purification, Paper No. 130f.

Mei, J.S., L.D. Gasper-Galvin, C.E. Everitt, and S. Katta. 1993. Fixed-bed testing of a molybdenum-promoted zinc titanate sorbent for hot gas desulfurization, St. Louis, Missouri: AIChE Annual Meeting, Symposium on Gas Purification.

Schmidt, D.K. 1993. The systems and the developmental target for IGCC, Paper presented at Coal-Fired Power Systems Conference, June 22, at Morgantown Energy Technology Center, Morgantown, WV.

Siriwardane, R.V., J.A. Poston, and G. Evans Jr. 1994. Spectroscopic characterization of molybdenum-containing zinc titanate desulfurization sorbents, Industrial & Engineering Chemistry Research (accepted for publication, 1994).