Bench-Scale Development of Fluidized-Bed Spray-Dried Sorbents

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Introduction

Successful development of regenerable mixed-metal oxide sorbents for removal of reduced sulfur species (such as H_2S and COS) from coal-derived fuel gas streams at high-temperature, high-pressure (HTHP) conditions is a key to commercialization of the integrated-gasification-combined-cycle (IGCC) power systems. Among various available coal-to-electricity pathways, IGCC power plants have the most potential with high thermal efficiency, simple system configuration, low emissions of SO_2, NO_x and other contaminants, modular design, and low capital cost. Due to these advantages, the power plants of the 21st century are projected to utilize IGCC technology worldwide. Sorbents developed for sulfur removal are primarily zinc oxide-based inorganic materials, because of their ability to reduce fuel gas sulfur level to a few parts-per-million (ppm).

Although desulfurization and regeneration reactions can be carried out using fixed-, moving-, or fluidized-bed reactors, fluidized-bed reactors offer several potential advantages including excellent gas-solid contact, ability to add or remove sorbent continuously, excellent temperature control of the highly exothermic regeneration reaction, faster overall kinetics associated with using smaller particles, and continuous steady-state operation. However, highly attrition-resistant sorbents with high reactivity capable of withstanding the stresses induced by rapid temperature swings, chemical transformations, and fluidization and transport are required before fluidized-bed hot-gas desulfurization systems can be commercialized.

Pure zinc oxide sorbents are not suitable because they are prone to undergo reduction in coal gas resulting in zinc vaporization. Similarly, zinc ferrite sorbents have limited applicability due to excessive attrition, iron carbide formation, and carbon deposition (Gupta and Gangwal, 1992). Zinc titanate sorbents do not suffer from these problems and therefore have emerged as alternatives to zinc ferrite sorbents.

Earlier in this study, efforts focused on development and testing of highly reactive and durable zinc titanate sorbents with a 100- to 300-μm particle size range for bubbling fluidized-bed reactors. These efforts led to the development of ZT-4 prepared using a granulation technique (Gupta et al., 1993). A number of life-cycle tests were performed on the ZT-4 sorbent to demonstrate its long-term chemical reactivity and attrition resistance using simulated coal gas

mixtures (Gupta and Gangwal, 1995b). Tests were also conducted using fuel gas produced directly from coal gasifiers at three pilot plant sites: Enviropower in Finland, U.S. Department of Energy/Morgantown Energy Technology Center (DOE/METC) at Morgantown, West Virginia, and Coal Technology Development Division (CTDD) in England. The superior performance exhibited by the ZT-4 sorbent in all three tests is reported elsewhere (Gupta and Gangwal, 1995b).

As an alternative to granulation, a spray-drying process to prepare zinc titanate sorbent is being investigated. Spray drying is extensively employed in the production of various catalysts, particularly fluid catalytic cracking (FCC) catalysts, for use in fluidized-bed reactors. Spray drying offers a number of advantages over a granulation process. For example, spray drying is a commercial process that can be readily scaled to industrial production using existing technology to produce large quantities of a product. Spray drying facilitates the addition of other additives and reagents to the composition since additional reagents can be simply added to a slurry prior to spray drying. Furthermore, spray drying provides particles of uniform spheroidal shape in the desired size range.

Objectives

This project extends the prior work on the development of fluidizable zinc titanate particles using a spray-drying technique to impart high reactivity and attrition resistance. Specific objectives are:

- Develop highly reactive and attrition-resistant zinc titanate sorbents in 40- to 150-μm particle size range for transport reactor applications using semicommercial- to full commercial-scale spray driers;

- Transfer sorbent production technology to private sector; and

- Provide technical support for Sierra Pacific's Clean Coal Technology Demonstration plant and METC's hot-gas desulfurization process development unit (PDU), both employing a transport reactor system.

Project Description

This study is a collaborative effort with Contract Materials Processing (CMP), Inc., a small speciality catalyst manufacturing company in Baltimore, Maryland, the M.W. Kellogg Company of Houston, Texas, that developed the transport reactor technology for hot-gas desulfurization, and Intercat, Inc., another catalyst manufacturing company located in Savannah, Georgia. Both CMP and Kellogg are subcontractors to the Research Triangle Institute (RTI) on this project. RTI and Intercat have entered into a teaming agreement to jointly develop and commercialize spray-dried zinc titanate sorbents.

Development and Testing of CMP-5 Sorbent

In FY 1994-95, CMP made a series of spray-dried zinc titanate sorbents in the 40- to 150-µm particle size range (average particle size [APS] = 80 µm). Screening of these spray-dried sorbents led to the development of CMP-5 sorbent which had excellent chemical reactivity and good initial attrition resistance as measured using a three-hole airjet attrition apparatus (13.4% 5-h loss). Twenty cycles of HTHP testing were performed on this sorbent at RTI. Results of this testing indicated that, unlike the ZT-4 sorbent, this sorbent did not undergo capacity reduction; however, it lost its attrition resistance. Attrition resistance of the sorbent after testing was 53 wt% 5-h loss compared to 13.4 wt% loss for the fresh sorbent (Gupta and Gangwal, 1995a).

Development and Testing of CMP-107 Sorbent

In preparation for operation of the transport hot-gas desulfurization reactor at Sierra Pacific's Clean Coal Technology Demonstration plant, Kellogg had investigated Z-Sorb III sorbent in a particle size range of 100- to 300-μm with an APS of about 180 μm (Campbell et al., 1995). Z-Sorb III is a proprietary ZnO-based sorbent developed by the Phillips Petroleum Company and contains Ni and additional activators and promoters. Kellogg recommended production of CMP-107 in comparable particle size range as Z-Sorb III to obtain a direct comparison of the performance of these two sorbents.

RTI and CMP worked jointly to produce a spray-dried zinc titanate sorbent with the appropriate particle size distribution. In the summer of 1995, a CMP-107 sorbent with an APS of 165 µm was developed.   Table 1 shows a comparison of physical and chemical properties of CMP-5 and CMP-107 sorbents. Chemical composition of both formulations was similar in terms of relative amounts of ZnO and TiO$_2$. The primary difference between these two was in the APS, as noted above.

Table 1. Properties of CMP-5 and CMP-107 Sorbents

	CMP-5	CMP-107
Particle size range (μm)	40-150	80-250
APS (μm)	80	160
Surface area (m^2/g)	2.83	14.2
Bulk density (lb/ft^3)	38.3	34.4
Thermogravimetric analyzer (TGA) sulfur capacity (wt%)	22.5	16.6
Attrition loss (wt%)		
5-h	13.4	5.8
20-h	14.2	12.0

TRTU Testing of CMP-107 Sorbent

In order to qualify a sorbent as a potential candidate for the Sierra system, Kellogg designed and built a bench-scale transport reactor test unit (TRTU). This facility is located at the M.W. Kellogg Technology Development Center in Houston. Figure 1 shows a simplified sketch of the TRTU system.

Description of TRTU

As shown in Figure 1, Kellogg's TRTU system consists of a mixing zone, a riser, a cyclone, and a standpipe. The lower mixing zone of the reactor, which can be operated either as a dense phase fluidized-bed or as an entrained-bed reactor, consists of a 10-ft tall section of 1.5-in. Schedule 160 stainless steel (SS) pipe. Solids from the standpipe are returned to the bottom of this zone. Fluidization gas, which can be air, oxygen, steam, nitrogen, or any combination of these, is fed to the bottom of the zone through a specially designed gas distributor.

Above the mixing zone is a 32-ft tall riser made of 1 in. Schedule 160 SS pipe. Gas and solids leaving the top of the riser flow to a high-efficiency cyclone, which separates the solids from the gas and returns them, via a standpipe, to the reactor. The standpipe is a 33-ft tall 1.5-in. Schedule 160 SS pipe. Use of a relatively small diameter standpipe results in a low solids

Figure 1. Schematic Sketch of Kellogg's TRTU System.

inventory requirement and minimal solids holdup time. Make-up solids are added, if necessary, at the top of the standpipe to compensate for attrition losses. Solid samples may be withdrawn at any time from the bottom section of the standpipe. Solids are returned to the bottom of the mixing zone via a lateral return leg, with solids flow rate controlled by means of a plug valve located at the base of the standpipe. This system is a prototype of the hot-gas desulfurization system being built at Sierra Pacific.
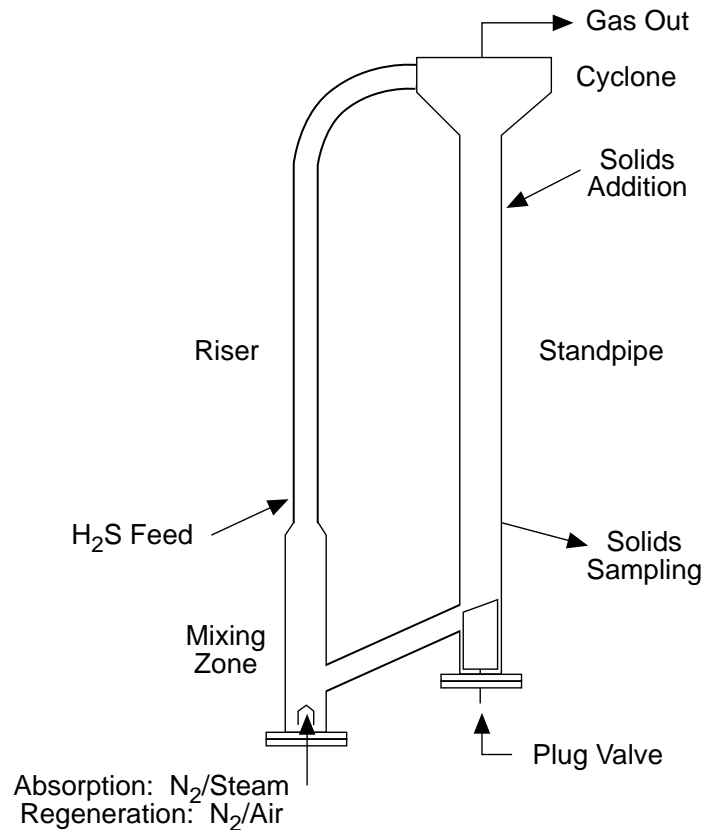
Experimental Procedure

Both sulfidation and regeneration were carried out at nominally 1,200 °F and at a system pressure of 100 psia.

During sulfidation, outlet H_2S concentration was measured every 5 min with a Varian 3300 gas chromatograph (GC) that employs a flame photometric detector (FPD). The H_2S concentration measured by this GC was verified by Dräeger tubes. SO_2 concentration during regeneration was monitored continuously using a Bovar 721-M ultraviolet (UV) photometric analyzer. The O_2 concentration in the regeneration outlet gas was continuously measured with an MSA model 4000 O_2 analyzer. This instrument uses an electrogalvanic cell to detect and quantify O_2. All

thermocouple readings and pressure drop measurements were continuously recorded by a computer data logging system. Table 2 shows the sulfidation gas composition used during the TRTU testing.

Before starting either sulfidation or regeneration, N_2 flow to the unit was divided between the mixing zone and the riser to match the velocities intended for the individual steps. During sulfidation, the mixing zone was maintained at a velocity of 1.6 ft/s, and the riser velocity was maintained at about 12.8 ft/s. During regeneration, these velocities were slightly lower as given in Table 3.

At the beginning of sulfidation, steam was introduced into the mixing zone. A small amount of H_2 was then added to the riser to ensure a reducing atmosphere in the sulfidation zone. An H_2S/N_2 mixture was then added to the riser, giving an H_2S inlet concentration of 1.2 mol%. As the H_2 and H_2S streams were added, N_2 flow was reduced accordingly to maintain constant riser velocity. After sulfidation was complete, these steps were reversed to bring the unit back to purge conditions.

Air was introduced to replace the N_2 feed into the mixing zone to begin regeneration. At the end of regeneration, air was replaced with N_2 to return to purge conditions. Gas flow rates were monitored and carefully controlled during the test. An adequate purge period was maintained between sulfidation and regeneration steps of each cycle.

Table 2. Gas Composition Used During Sulfidation

Gas Component	Vol%
H_2S	1.2
H_2	4.1
H_2O	7.8
N_2	86.9
Total	100.0

Table 3. Operating Conditions for the Multicycle TRTU Test

Sorbent	RTI/CMP-107 ZnTi
Operating pressure (psia)	100
Operating temperature (°F)	1,160 to 1,225
Sulfidation time (min)	26 to 98
Regeneration time (min)	7 to 30
Mixing zone density (lb/ft^3)	13 to 24
Mixing zone velocity (ft/s)	1.1 to 1.6
Riser density (lb/ft^3)	0.6 to 0.9
Riser velocity (ft/s)	11.5 to 12.8
Gas residence time for sulfidation (s)	2.5
H_2S concentration at riser inlet (%)	1.2
Solid inventory (lb)	8.0
Solid circulation rate (lb/h)	90 to 150

Prior to the multicycle test, several cold flow tests were conducted with the CMP-107 sorbent in the TRTU to determine optimum operating conditions required in the mixing zone and riser, and the solids plug valve position in order to achieve reliable operation at extremely low riser densities. The initial test plan called for a riser density of about 2 lb/ft^3, but, due to problems encountered with the solids plug valve, a riser density of 0.6 to 0.9 lb/ft^3 was found to provide a steady circulation of sorbent.

Results

TRTU Testing

Sulfidation. For the first two cycles, the sorbent was sulfided until the H_2S leakage was >1,000 ppmv to determine sulfur loading of the fresh sorbent at breakthrough. During Cycles 3 to 48, the sorbent was sulfided for a predetermined period of 26 min to obtain a sulfur loading of about 2 wt%. Figure 2 shows the maximum H_2S leakage as a function of cycle number during the 50-cycle test. Except for seven cycles, the maximum H_2S leakage was below the detection limit of GC, indicating excellent chemical reactivity of the CMP-107 even with extremely low riser density.

During the 9th and 35th sulfidation cycles, H_2S concentration exceeded 1,000 ppmv. This was primarily attributed to flow maldistributions resulting from system upsets (unstable solids circulation). Similarly, small H_2S leakage during the other five cycles was also associated with flow problems in the TRTU.
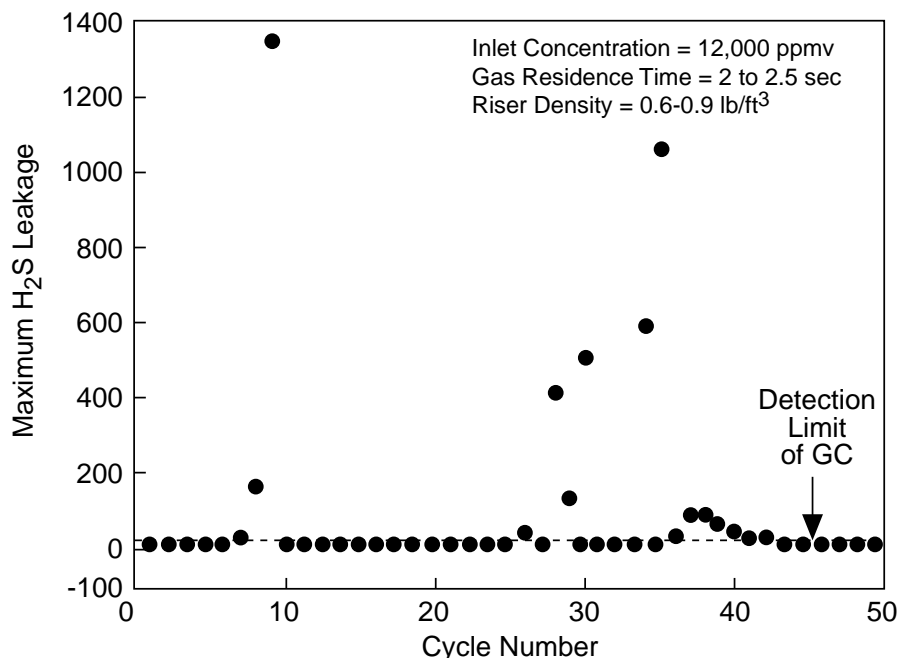

Figure 2. Maximum H_2S Leakage During the 50-Cycle TRTU Test.

Regeneration. Sorbent performance during regeneration, as represented by SO_2 and O_2 concentration profiles and temperature exotherms recorded by two thermocouples, namely TE201 (temperature of the upper portion of the mixing zone) and TE200 (temperature of lower portion of the mixing zone) from Cycle 8 to Cycle 27 (selected randomly for illustration purposes), is shown in Figure 3. Peak SO_2 concentration measured in various cycles compared well with the theoretical value of 3.6 percent, based on gas flow rates used, as shown in Figure 3. This figure clearly shows that the sorbent regenerated very well in all the cycles as shown by the relatively constant peak SO_2 concentration and temperature exotherm. Absence of O_2 breakthrough and stoichiometric SO_2 formation demonstrated that no sulfate was formed during regeneration.

Temperatures
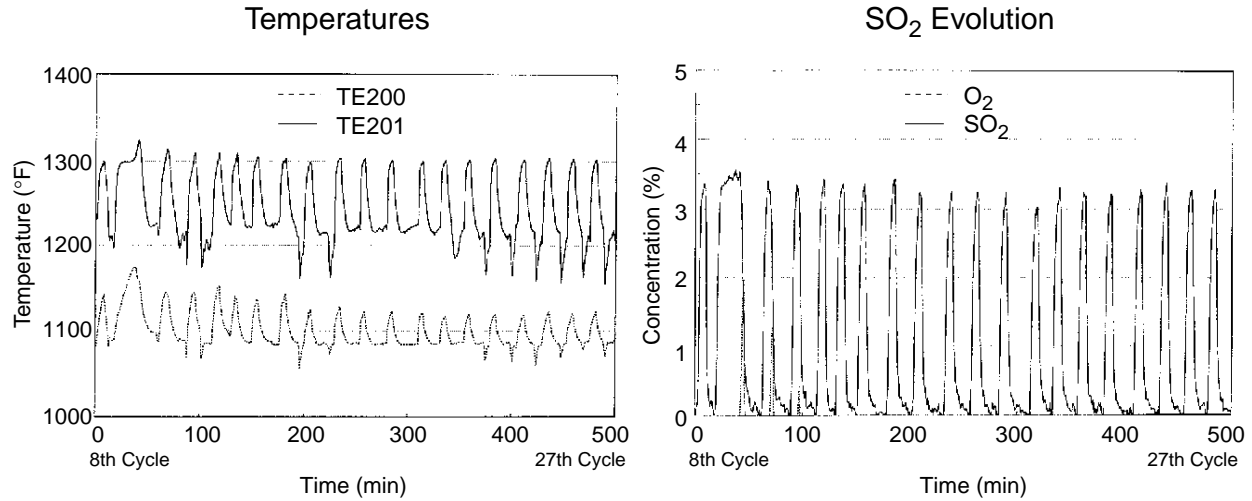

SO$_2$ Evolution

Figure 3.   Regeneration of CMP-107 in the TRTU.

Sorbent Attrition. As mentioned previously, in addition to possessing high chemical reactivity required to remove H$_2$S below detection limits in 2 to 3 sec, the sorbent must be physically strong to withstand the mechanical stresses generated in a transport reactor. To determine sorbent attrition during the 50-cycle TRTU testing, a material balance was used to estimate the amount of fines lost as a percentage of the feed. Defining fines as particles <11 μm (as <11 μm particles were not found in the feed or the bed drain), 5.13 percent of the feed was lost as fines.

The particle size distributions of the feed, bed drain, and filter fines obtained at the end of the test were measured by means of a Microtrac (laser-based particle size analyzer) and sieve analysis. Results are presented in Figure 4. It is quite evident from Figure 4 that particle size distribution has shifted toward finer size during testing. Based on the cumulative distribution shown in Figure 4, the APS (determined as d$_{50}$) changed from 160 μm for the feed to about 70

Particle Size Distribution
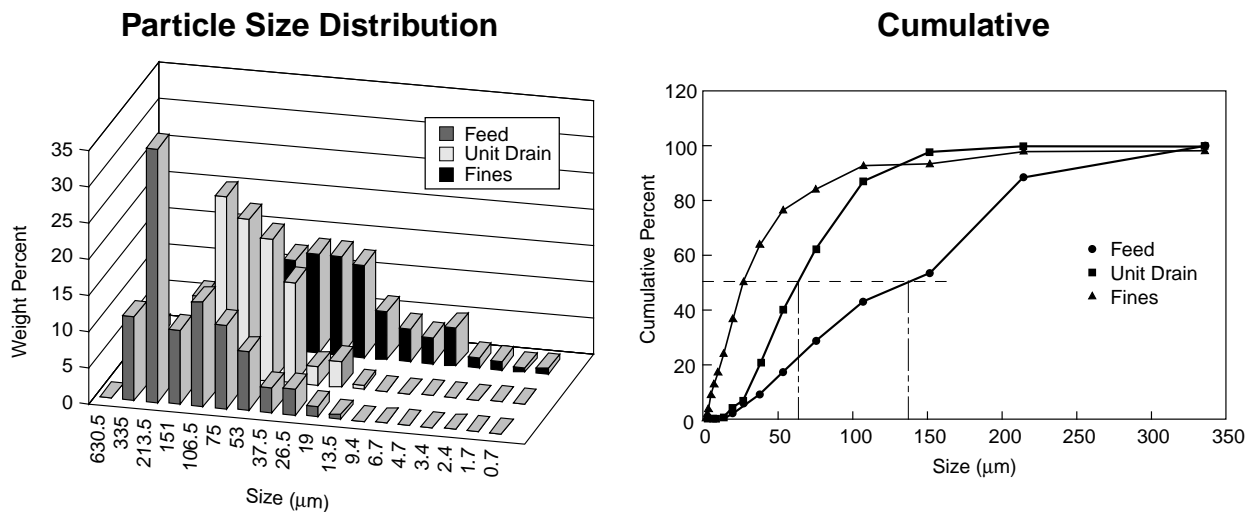
Cumulative

Figure 4.   Change in Particle Size Distribution During TRTU Testing.

μm for the unit drain. Based on additional data taken at RTI and Kellogg, it was determined that most of the particle size reduction occurred during the first cycle.

From the particle size and fines generation data, Kellogg estimated that the attrition rate was about 7×10^{-5} lb sorbent attrited per lb of sorbent circulated. The design value for the sorbent attrition rate for the Sierra plant is 3×10^{-5} based on the assumption of 15 lb of sorbent lost per hour for a circulation rate of approximately 500,000 lb/h using a commercially available Z-Sorb III sorbent from the Phillips Petroleum Company. Despite this ambitiously low attrition rate target, the attrition rate of spray-dried CMP-107 zinc titanate sorbent was sufficiently close to the design target to suggest this target could be readily met with minor improvements in the sorbent.

Post-test Characterization

Table 4 shows physical and chemical properties of fresh sorbent and sorbent removed after the 50th regeneration in the TRTU. As noted previously, during testing, the APS decreased from 160 μm to 73.4 μm. BET surface area increased by 50 percent while the bulk density increased by 30 percent. The increase in bulk density can be attributed to reduction in APS. Attrition resistance of sorbent removed after testing measured in a three-hole airjet attrition tester was quite poor compared with fresh sorbent.

Table 4. Comparison of Physical and Chemical Properties of Fresh and 50-Cycle Regenerated CMP-107 Sorbent

	Fresh	After 50th Regeneration
APS (μm)	160	73.4
Surface area (m^{2}g)	14.2	21.4
Bulk density (lb/ft^3)	34.4	44.9
TGA sulfur capacity (wt%)	16.6	15.0
Attrition loss (wt%)		
5-h	5.8	63.0
20-h	12.0	69.0
Chemical analyses		
Carbon (wt%)	0.23	0.10
Total sulfur (wt%)	<0.05	1.15
Sulfate sulfur (ppmw)	223	402

Although the sorbent lost its attrition resistance during the 50-cycle TRTU testing, its chemical reactivity remained unchanged as confirmed by TGA and TRTU testing. As listed in Table 4, TGA sulfur capacity of reacted sorbent was > 90 percent that of fresh sorbent. These results were confirmed by running a sulfidation in the TRTU on the 50-cycle regenerated sorbent. Sulfur capacity at breakthrough for 50-cycle regenerated sorbent was 93.3 percent that of fresh material, corroborating the TGA results. Therefore, the sorbent did not undergo any decline in either chemical reactivity (indicated by H_2S removal) or sulfur capacity.

MGCR Testing of CMP-107 Sorbent

In addition to testing in Kellogg's TRTU, CMP-107 sorbent was also tested in DOE/METC's modular gas cleanup rig (MGCR) during August 1995. This test was conducted using a slipstream of real coal gas generated in METC's fluidized-bed gasifier. Conditions during MGCR

testing are shown in Table 5.

Figure 5 shows H$_2$S breakthrough behavior of CMP-107 in the MGCR. As can be seen, CMP-107 reduced H$_2$S concentration to a few ppm before breakthrough. Sulfur capacity of the sorbent at breakthrough was 17.6 percent. These results indicated other impurities present in real coal gas did not affect the desulfurization performance of the sorbent.

Criteria for Commercial Sorbent Selection

Comprehensive analysis of results obtained during bench-scale testing at RTI, TRTU testing at Kellogg, and MGCR testing at DOE/METC with CMP-107 sorbent indicated that a proper combination of reactivity and attrition properties is required to minimize the impact of sorbent costs on operation of the hot gas desulfurization system at Sierra. Figure 6 depicts the interrelationship of various process parameters involved in the sorbent selection process. Every candidate sorbent should be subjected to the screening process of Figure 6 to estimate costs of operation of a hot-gas desulfurization system.

Based on the screening process of Figure 6, analysis of CMP-107 sorbent test results led to the following recommendations by Kellogg:

Table 5. Test Conditions for MGCR Testing of CMP-107

Gas flow rate	1,000 scfh
Average H$_2$S content	1,300 ppmv
Temperature	1,000 °F (538 °C)
Pressure	20 atm (280 psig)
Gas composition (vol%)	
CH$_4$	2.87
H$_2$S	0.13
H$_2$	14.14
Ar	0.48
CO$_2$	11.21
CO	11.87
N$_2$	48.50
H$_2$O	10.47
NH$_3$	0.33
Total	100.00
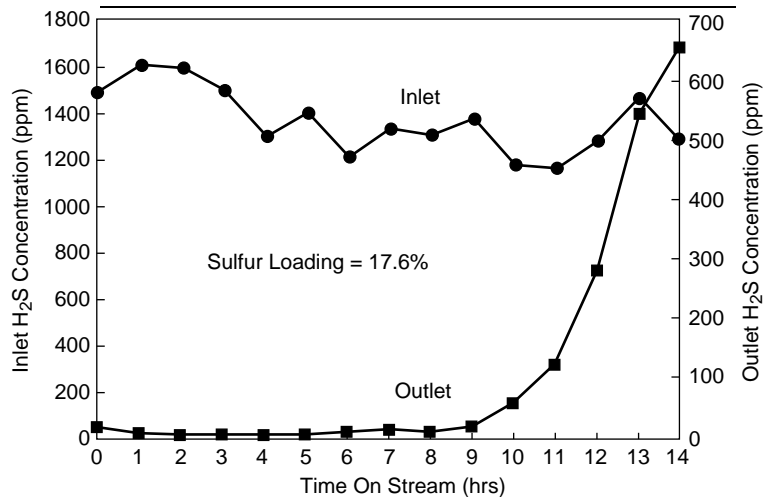
Figure 5. Testing of CMP-107 in METC's MGCR with Real Coal Gas.

- Sulfidation activity of the sorbent is quite adequate.

- Bulk density should be increased to ≥50 lb/ft^3.

- The APS should be between 80 and 90 μm with <5 percent below 40 μm and <1 percent
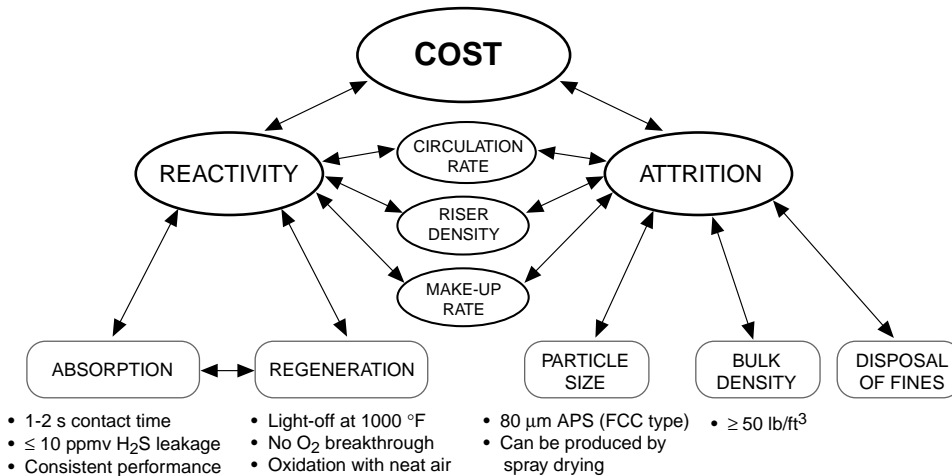
Figure 6. Criteria for Commercial Sorbent Selection.

below 20 μm.

- During regeneration, the sorbent should light off at a temperature ≤ 1050 °F (565 °C) with neat air to operate the transport reactor system is an isothermal mode with minimal sulfate formation.

- Attrition resistance of the sorbent should be improved by a factor of three to meet the 15 lb/h design target.

Regeneration Light-off Study

Of the recommendations made by Kellogg, lowering regeneration light-off temperature was the most challenging to achieve. Currently, a proprietary additive is being tested, which lowers the temperature required for regeneration light-off of zinc titanate sorbents. Figure 7 shows two temperature profiles taken during regeneration of CMP-107 sorbent in RTI's HTHP bench-scale reactor. Without additive, the minimum light-off temperature for regeneration of CMP-107 was about 1,130 °F; however, with a

Figure 7. Regeneration Light-off Additive for the CMP-107 Sorbent.

small amount of the additive, regeneration of CMP-107 was initiated at 925 °F. Details about this additive are proprietary and a patent application is being prepared.
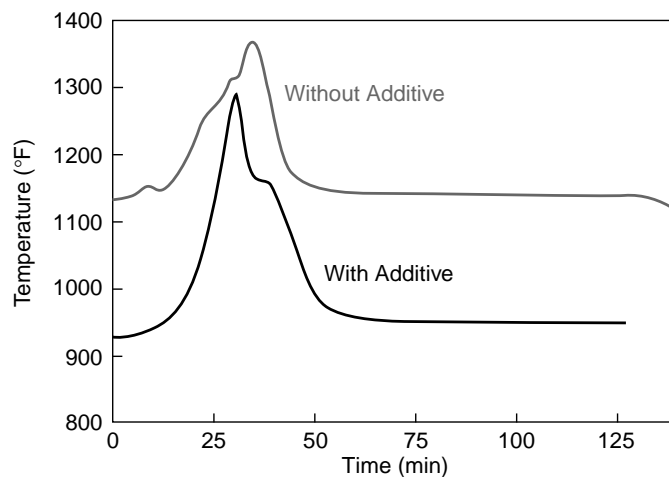
Additional Sorbent Improvements

In parallel to lowering regeneration light-off temperature, work has commenced with Intercat, Inc., to improve the attrition resistance of spray-dried zinc titanate sorbent. RTI and Intercat have entered into a teaming agreement to develop and commercialize this sorbent technology. After preparing a number of trial batches, Intercat has developed a formulation (designated as IX-SO1) that appears promising.

Figure 8 shows a comparison of properties (that were found critical for the transport reactor applications) of CMP-107 and IX-SO1 sorbents along with target values recommended by Kellogg. In this figure, K_s and K_r are kinetic constants for sulfidation and regeneration, respectively. These target values were determined by extensive experimentation in a TGA and correlation with bench-scale and TRTU testing results. IX-SO1 sorbent meets the target property values except for the APS and bulk density, which can be increased when sorbent production is scaled up from laboratory-scale to pilot or semicommercial scale.
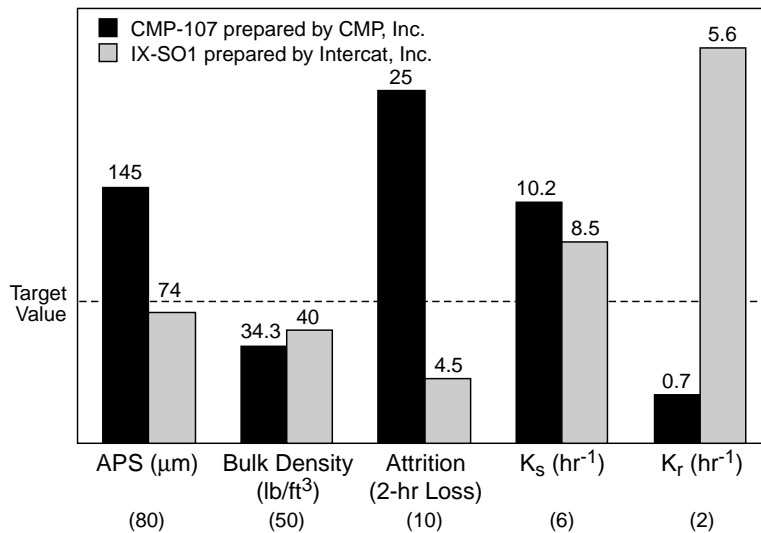

Figure 8. Properties of Current Spray-Dried Zinc Titanate Sorbents.

Applications

Near-term application of the spray-dried zinc titanate sorbents is contemplated in the transport reactor hot-gas desulfurization system in the Sierra Pacific Clean Coal Technology Demonstration plant. This 100 MWe (net) IGCC system, which will involve the KRW gasifier and transport reactor hot-gas desulfurization system developed by M.W. Kellogg, is expected to be online in early 1997. It is estimated that a 30,000 lb charge of sorbent will be needed in this system. This charge is expected to last for 2,000 h provided a sorbent with an attrition rate of ≤15 lb/h used.

With the successful demonstration of transport reactor technology at Sierra, the projected long-term IGCC market appears enormous with IGCC plants producing as much as 130 GW of electricity in the year 2040.

Future Activities

Future activities involve demonstration of zinc titanate sorbent production in a commercial-scale spray drier. A batch of the sorbent produced in the commercial-scale spray drier will be tested at M.W. Kellogg in their TRTU system to evaluate its performance, particularly chemical reactivity, attrition resistance, and regenerability.

Acknowledgments

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