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Spray-Dried Fluid-Bed Sorbents Tests - CMP-5

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CONTRACT INFORMATION

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Period of Performance September 1, 1993 to September 30, 1995

Schedule and Milestones

FY95 Program Schedule

| | S | O | N | D | J | F | M | A | M | J | J | A | S |
|------------------------------|-------|---|---|-------|---|---|---|-------|---|-------|---|---|-------|
| Sorbent Characterization | _____ | | | | | | | | | | | | |
| Sorbent Testing | | | | _____ | | | | | | | | | |
| Sorbent Production | | | | | | | | _____ | | | | | |
| TRTU Testing at M.W. Kellogg | | | | | | | | | | _____ | | | |
| Topical Report | | | | | | | | | | | | | _____ |

OBJECTIVES

The objective of this study is to determine the feasibility of manufacturing highly reactive and attrition-resistant zinc titanate sorbents by spray drying, suitable for bubbling (conventional) as well as transport-type fluidized-bed reactor systems.

BACKGROUND INFORMATION

RTI has been pursuing the sorbent development work with the objective of producing highly reactive and attrition-resistant sorbent particles for fluidized-bed applications since 1988. A number of techniques have been investigated in this program, including granulation and spray drying, to produce fluidizable particles. Earlier efforts in

this project were focused on the development of the reactive and durable sorbents using a granulation technique as described in various RTI publications (Gupta and Gangwal, 1992; Gupta et al., 1993; Gupta and Gangwal, 1994). This effort has led to the development of the ZT-4 sorbent which has been tested in both laboratory and bench-scale reactors with simulated coal gas as well as in pilot-scale semicommercial systems employing real coal gas in the United States as well as in various European countries (Gupta and Gangwal, 1995).

Alternatively, a spray-drying process 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 scale 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 simply be added to a slurry prior to spray drying. Furthermore, spray drying provides particles of highly uniform size and shape.

During earlier stages of this contract (FY 1991-1992), attempts were made to prepare reactive and attrition-resistant zinc titanate sorbents by spray drying. United Catalysts, Inc. (UCI) prepared four preliminary formulations by spray drying with and without addition of a silica binder. Testing of these formulations at RTI indicated that the formulations that contained the silica binder had good attrition resistance, but essentially no chemical reactivity. Consequently, the formulations that did not contain the silica binder had reasonable chemical reactivity, but extremely poor attrition resistance (Gupta and Gangwal, 1992). Joint efforts between RTI and DuPont to prepare attrition-resistant particles using DuPont's polysilicic acid technology were not suc-

cessful, primarily due to the presence of free silica in the sorbent (Gupta and Gangwal, 1992).

Despite these unsuccessful attempts, the knowledge gained in these trials was useful and led to the successful development of the CMP-5 sorbent, which is the subject of investigation in this paper.

PROJECT DESCRIPTION

This project is a collaborative effort with the Contracts Materials Processing (CMP), Inc., a small specialty catalyst manufacturing company in Baltimore, MD. CMP, a subcontractor to RTI in this project, is responsible for preparing various zinc titanate formulations using a pilot-scale spray drier. As noted previously, the zinc titanate sorbents suitable for fluidized-bed applications must demonstrate high chemical reactivity, as measured by the rate of sulfur absorption and the sulfur loading capacity, as well as good fluidizing characteristics and mechanical strength characterized by low attrition losses.

Sorbent Preparation and Characterization

In the beginning of this program, CMP prepared 14 zinc titanate formulations designated by CMP-X series (CMP-1 to CMP-14). These formulations were prepared by varying the binders, binder amount, Zn-to-Ti atomic ratio, and spray-drier operating conditions. The particle size range of these formulations varied between 40 and 150 μm —typical for commercial FCC catalysts used in the petroleum industry. All of these 14 formulations were characterized for their chemical reactivity and regenerability in a thermogravimetric analyzer (TGA), pore size distribution, particle size distribution, bulk density, BET surface area, and the attrition-resistance (in RTI's three-hole airjet attrition tester). Based on these physical and chemical characterization tests, two superior formulations (CMP-1 and CMP-5) were identified for further testing.

Table 1 shows a comparison of the physical and chemical properties of CMP-1 and CMP-5 formulations. Also included in this table are the properties of the ZT-4L sorbent (a benchmark fluidized-bed sorbent prepared using a granulation technique as noted previously). The properties of CMP-1 and CMP-5 formulations are comparable with the exception of the attrition resistance. The attrition resistance of the CMP-5 formulation is far superior compared to that of the CMP-1 formulation. It is to be noted here that the average particle size (APS) of ZT-4 and CMP formulations is 180 and 80 μm , respectively, primarily due to the different methods of manufacturing. The superior attrition properties of the CMP-5 formulation are attributed to the presence of additional proprietary additives and know-how to spray dry and impart unusually high attrition resistance to the sorbent. A patent application is pending on the method of manufacturing these spray-dried zinc titanate formulations.

Bench-Scale Testing

Following the physical and chemical characterization, the CMP-5 formulation was tested in RTI's high-temperature, high-pressure (HTHP) bench-scale test facility. A detailed description of RTI's HTHP test facility is provided elsewhere

Table 1. Physical and Chemical Properties of Spray-Dried Formulations

| | ZT-4L | CMP-1 | CMP-5 |
|---|-------|-------|-------|
| Average particle size (μm) | 180 | 80 | 80 |
| Attrition resistance | | | |
| 5-h loss (%) | 17 | 86.6 | 13.4 |
| 20-h loss (%) | 71 | 94.0 | 14.2 |
| Surface area (m^2/g) | 3.53 | 3.24 | 2.83 |
| Chemical composition | | | |
| ZnO/TiO ₂ (molar) | 1.5 | 1.5 | 1.5 |
| % Binder | 5 | 5 | 5 |
| TGA sulfur capacity (wt.%) | 22 | 22.5 | 22.5 |

(Gupta and Gangwal, 1992; Gupta and Gangwal, 1993). Two HTHP tests, each consisting of 10 sulfidation-regeneration cycles, were performed on the CMP-5 sorbent. The first 10-cycle test was conducted similar to RTI's previous multicycle tests with the ZT-4 sorbent in which the sorbent was sulfided until the breakthrough followed by complete regeneration. In the second 10-cycle test, sulfidation-regeneration cycles were carried out to operate the system in a window of sulfur loading, mimicking the operation of a commercial hot-gas desulfurization system employing a fluidized-bed reactor.

First 10-Cycle HTHP Testing

Table 2 lists the operating conditions for this run. The sorbent was prescreened in the 80- to 150- μm particle size range. A charge of 200 g of the sorbent was loaded in the 2-in. I.D. cage. Because the bench unit was not equipped with a gas-particle separation device (such as a cyclone), the superficial gas velocity was kept below the terminal velocity for the smallest particle. The sulfidation was carried out at 600 °C (1,112 °F) and at a pressure of 250 psig (18 atm). The coal gas composition used in this test simulated the fuel gas produced from an air-blown fluidized-bed gasifier (as shown in Table 2) and had a reducing power of about 3.0 [determined as a ratio of (CO + H₂) to (CO₂ + H₂O)]. The regeneration of the sulfided sorbent was initiated at 600 to 650 °C (1,112 to 1,202 °F) with 3 to 4 percent O₂ in N₂. Regeneration was continued until the SO₂ concentration in the regeneration off-gas fell below 500 ppm.

Figure 1 shows the breakthrough data for the 10 cycles. As can be seen, following initial activation in Cycles 1 and 2, the breakthrough curves for Cycles 3 to 10 were essentially the same, indicating a stable performance of the sorbent. From these breakthrough data, sulfur capacity values at breakthrough (500 ppm of H₂S in the outlet gas) were estimated and are shown as a function of the

Table 2. Operating Conditions for First 10-Cycle Run

| | |
|--|--|
| Sorbent particle size | 80 to 150 μm |
| Sorbent charge | 200 g |
| Reactor diameter | 5.08 cm (2 in.) |
| Reactor L/D | 4 |
| Gas flow rate | 25 std L/min (53 std ft ³ /h) |
| Operating pressure | 18 atm (250 psig) |
| Superficial gas velocity | 4.4 cm/s (0.15 ft/scc) |
| Terminal velocity for 80- μm particle | 9.6 cm/s (0.3 ft/scc) |
| Minimum fluidization velocity | 0.20 cm/s |
| U/U_{mf} | 22 |
| Sulfidation | |
| Temperature = | 600 °C (1,112 °F) |
| Gas Composition | |
| CO | 24.0 |
| H ₂ | 14.0 |
| CO ₂ | 5.0 |
| N ₂ | 48.0 |
| H ₂ S | 1.0 |
| H ₂ O | 8.0 |
| Reducing power = | 3.0 (severely reducing coal gas) |
| Breakthrough ppm = | 500 ppm H ₂ S in outlet gas |
| Regeneration | |
| Temperature | 600 to 650 °C (1,112 to 1,202 °F) |
| Regeneration gas | 3 to 4% O ₂ in N ₂ |
| End point | 500 ppm SO ₂ in outlet gas |

cycle number in Figure 2. The sulfur capacity was essentially constant from Cycles 3 to 10 at a value of about 24 g S/100 g fresh sorbent. This indicates greater than 95 percent utilization of the sorbent's sulfur capture capacity. The theoretical sulfur capacity of the CMP-5 sorbent was 24.9 g S/100 g sorbent.

Regenerability of this sorbent was found to be extremely good. Figure 3 shows the temperature and SO₂ and O₂ concentration profiles for Cycle 2 (arbitrarily chosen for illustration purposes). In

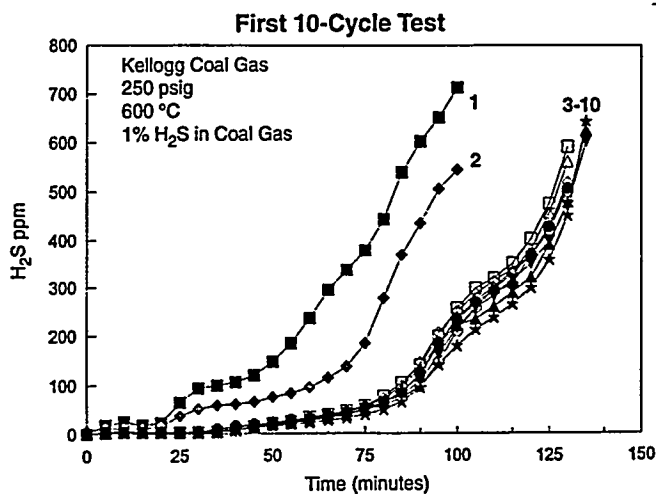


Figure 1. Breakthrough data for CMP-5 sorbent.

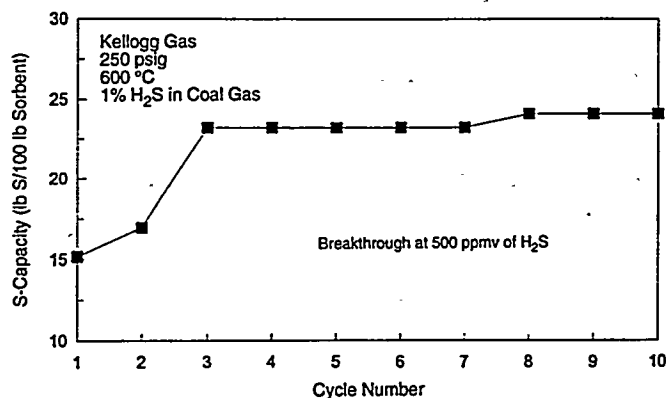


Figure 2. S-capacity for CMP-5 sorbent at breakthrough.

this case, the regeneration was initiated at 640 °C (1,184 °F) using 3 percent O₂ in N₂. As expected, in the beginning the SO₂ concentration and the sorbent bed temperature increased rapidly to a steady-state value of about 20,000 ppmv (2% v/v) for SO₂ concentration and about 690 °C (1,275 °F) for temperature. This SO₂ concentration corresponds to the stoichiometric value for 3 percent O₂ used (it will be two-thirds of the O₂ concentration). As shown in Figure 3, the O₂ con-

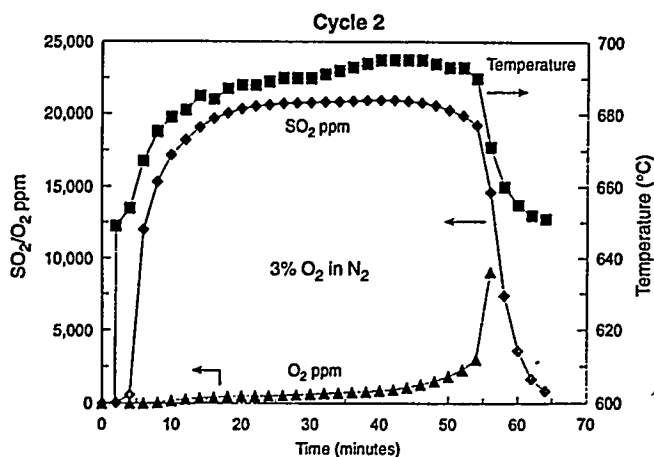


Figure 3. Regeneration of CMP-5 sorbent.

centration during the steady-state SO_2 evolution is essentially zero and it exhibited a breakthrough when regeneration was nearly complete. The sulfur capacity values obtained from H_2S breakthrough data were also compared with the SO_2 evolution data obtained during the subsequent regeneration and they matched within ± 2 percent, indicating that this sorbent can be easily regenerated without any sulfate formation.

At the end of the 10-cycle run, the reactor was opened and the sorbent was removed. Out of 200 g of the sorbent loaded, 1.8 g of the sorbent elutriated during initial heating. Out of the remaining 198.2 g, 197.8 g were collected from the cage after 10 cycles of testing, resulting in a net loss of 0.4 g (0.2 percent). No deposits were found on the sulfidation and regeneration filters.

A sample of the reacted sorbent was characterized for its physical and chemical properties to determine any changes in the sorbent structure. Table 3 compares the properties of fresh and reacted sorbents. As can be seen, about 7 percent increase is observed in the APS, which can be within the error of experimental measurement. No changes are evident in either the mercury pore volume or x-ray diffraction phases. Despite the severely reducing nature of the coal gas, the Zn-

Table 3. Comparison of Physical and Chemical Properties of Fresh and 10-Cycle Regenerated Sorbent in the First 10-Cycle Test

| | Fresh | 10-cycle reacted |
|--|--|--|
| Particle size distribution (wt.%) | | |
| Mesh | | |
| +100 | 6.2 | 11.6 |
| -100 + 140 | 33.6 | 43.7 |
| -140 + 170 | 34.1 | 23.2 |
| -130 + 230 | 24.9 | 21.5 |
| -230 + 270 | 1.2 | 0.0 |
| Total | 100.0 | 100.0 |
| Average particle size (μm) | 99.6 | 106.9 |
| Mercury pore volume (cm^3/g) | 0.4061 | 0.3930 |
| Attrition resistance | | |
| 5-h loss (wt.%) | 12.0 | 52.8 |
| 20-h loss (wt.%) | 13.6 | 76.2 |
| Bulk density (lb/ft^3) | 38.3 | 42.8 |
| XRD ^a phases | Zn_2TiO_4 , traces of ZnTiO_3 | Zn_2TiO_4 , traces of ZnTiO_3 |
| ICP ^b analysis | | |
| Zn | 42.8 | 42.4 |
| Ti | 19.4 | 20.0 |

^a XRD = x-ray diffraction.

^b ICP = inductively coupled plasma.

to-Ti ratio remained essentially unchanged. However, a decline in the sorbent attrition resistance as measured in a three-hole air-jet attrition tester was noticed due to cycling. The causes for this decline are currently being investigated.

To summarize the pertinent findings of this 10-cycle test, the CMP-5 sorbent exhibited excellent chemical reactivity and sulfur capacity. Nearly complete (>95%) capacity utilization was obtained with this sorbent. The sulfur capacity remained constant over 10 cycles at about 24 g S/100 g of the fresh sorbent. Sorbent was found to have excellent regenerability as evidenced by nearly stoi-

chiometric SO_2 formation at steady state. No sorbent loss was observed from the reactor. No significant changes were evident in the physical and chemical properties of the sorbent, except for a decline, as yet unexplained, in the attrition resistance.

Second 10-Cycle HTHP Testing

Following the excellent desulfurization performance of the CMP-5 sorbent in the first 10-cycle run, the second 10-cycle run was carried out to determine the sorbent performance when operated in a window of sulfur loading. Table 4 shows the test conditions for this run, which was made at a pressure of 20 atm (294 psi) and at a sulfidation temperature of 550 °C (1,022 °F) with a simulated air-blown gasifier gas. As indicated in Table 4, in Cycle 1, the sorbent was sulfided until breakthrough followed by a complete regeneration, similar to the first 10-cycle run.

Table 4. Test Conditions for the Second 10-Cycle Test

| | |
|-------------------------|---|
| Sulfidation temperature | = 550 °C (1,022 °F) |
| Pressure | = 20 atm (294 psi) |
| Coal gas composition | |
| CO | : 21% |
| H ₂ | : 15% |
| CO ₂ | : 7% |
| H ₂ O | : 9% |
| H ₂ S | : 1% |
| N ₂ | : 47% |
| Operation Mode | |
| Cycle 1: | Sulfidation until breakthrough followed by complete regeneration |
| Cycles 2-10: | Sulfidation up to 7.5 wt.% S-capacity and regeneration until S-level reaches 1 wt.% |
| Regenerations | |
| 1-5: | 5 to 6% O ₂ in N ₂ |
| 6-10: | 5% O ₂ , 45% N ₂ and 50% steam |

However, during Cycles 2 to 10, the sorbent was sulfided to a sulfur loading of 7.5 wt.% and regenerated until the sulfur level of the regenerated sorbent reached 1 wt.%. These sulfur loading values for sulfidation were estimated from the inlet H₂S concentration and the breakthrough data obtained in Cycle 1, while during regeneration this estimation was based on the SO₂ evolution data. Also in this test, the effect of O₂ concentration and the presence of steam in the regeneration gas were investigated.

Figure 4 shows the breakthrough behavior of the sorbent for this 10-cycle run. As shown, following the activation of the sorbent in Cycle 1, no change in the chemical reactivity is evident during Cycles 2 to 7. However, when 50 percent (v/v) steam was present in the coal gas, some degradation in the sorbent performance, as indicated by higher prebreakthrough H₂S levels shown in Figure 4, was noticed in the subsequent sulfidation cycles. Previous testing at RTI with ZT-4 sorbent did not exhibit performance degradation due to the presence of steam in the regeneration gas. More tests are necessary to understand this degradation.

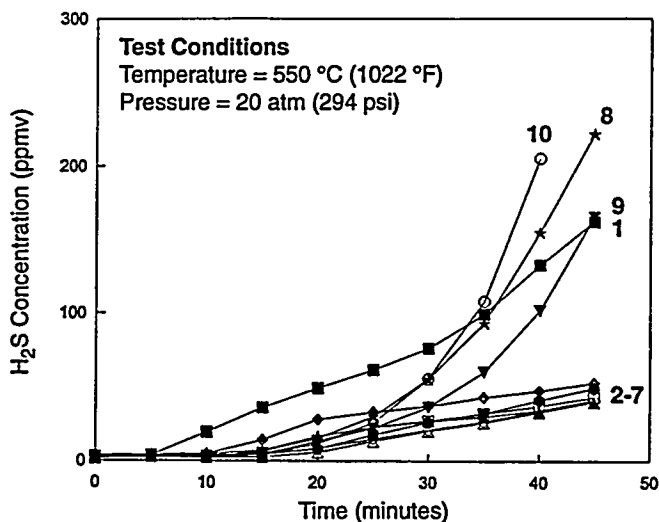


Figure 4. Breakthrough behavior for the second 10-cycle run.

Table 5 shows a comparison of physical and chemical properties of the fresh and 10-cycle reacted sorbents. Except for the attrition resistance, hardly any change is observed in particle size distribution, APS, pore volume, and bulk density of fresh and reacted sorbent samples.

Production of Sorbent with Larger Particle Size

As noted previously, the APS of the CMP-5 sorbent tested in this study was about 80 μm with a particle size range of 40 to 150 μm . This particle size distribution may be suitable for a riser type reactor; however, for a conventional bubbling-bed reactor, the desired particle size of the sorbent is slated to be between 100 and 300 μm (with an APS of 180 μm). Incidentally, the transport reactor system contemplated by M.W. Kellogg for the hot-gas desulfurization for the Pinon Pine Clean Coal Technology Demonstration plant will use 100- to 300- μm particle size for the sorbent.

Table 5. Comparison of Physical and Chemical Properties of Fresh and 10-Cycle Regenerated Sorbent in the Second 10-Cycle Test

| | Fresh | 10-cycle reacted |
|--|--------|------------------|
| Particle size distribution (wt.%) | | |
| Mesh | | |
| +100 | 6.2 | 0.0 |
| -100 + 140 | 33.6 | 31.9 |
| -140 + 170 | 34.1 | 31.3 |
| -170 + 230 | 24.9 | 34.7 |
| -230 + 270 | 1.2 | 1.4 |
| -270 | 0.0 | 0.7 |
| Total | 100.0 | 100.0 |
| Average particle size (μm) | 99.6 | 93.4 |
| Mercury pore volume (cm^3/g) | 0.4061 | 0.4120 |
| Attrition resistance | | |
| 5-h loss (wt.%) | 12.0 | 53.0 |
| 20-h loss (wt.%) | 13.6 | 55.4 |
| Bulk density (lb/ft^3) | 38.3 | 38.1 |

With a subcontract from RTI, CMP modified their pilot-scale spray drier to produce larger particle size of the sorbent. Recently, after a series of trials, CMP successfully produced large particles by spray drying. This formulation designated as CMP-107 and prepared using the recipe of CMP-5 had a particle size distribution in the 80- to 250- μm range with an APS of 165 μm . The yield in the 100- to 300- μm range varied between 70 and 90 percent. Preliminary screening of this sorbent indicated good TGA reactivity and attrition resistance of this sorbent.

A 200-lb batch of this sorbent was produced to demonstrate the scaleup. Out of this, 100 lb sorbent was shipped to M.W. Kellogg for testing in their transport reactor test unit (TRTU). A 20-lb batch was shipped to the U.S. Department of Energy/Morgantown Energy Technology Center (DOE/METC) for testing in METC's Modular Gas Cleanup Rig (MGCR).

FUTURE WORK

Future work in this project includes testing of the CMP-107 sorbent in M.W. Kellogg's TRTU system and 10-cycle HTHP testing at RTI.

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