Sorbent Testing and Commercialization of Transport Reactors For Hot Gas Desulfurization

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Introduction

Under DOE/METC sponsorship, as part of the hot gas cleanup program, Kellogg carried out experiments to test regenerable mixed metal oxide sorbents in a transport reactor to remove H_2S from high temperature gases for use in commercial IGCC plants. A spray-dried version of ZnO-based sorbent, EX-SO3, on a zinc titanate matrix (ZnTi) developed by Research Triangle Institute (RTI) and Intercat Development, Inc. was tested and the results obtained on this sorbent are presented in this paper.

The attrition resistance, sulfur absorption capacity, regeneration initiation temperature, regeneration behavior, tendency for sulfate formation and change of these properties with number of cycles were studied in a Transport Reactor Test Unit (TRTU) located at the Kellogg Technology Development Center. These test parameters were evaluated with respect to the design and operation of Sierra Pacific Power Company (SPPC) Piñon Pine plant desulfurizer. Kellogg has designed a commercial-scale High Temperature Desulfurization System (HTDS) for SPPC Piñon Pine plant at Tracy Station, Nevada, which is nearing startup. Plans on commissioning and operating this unit are outlined here.

Some of the attributes of transport reactors such as low sorbent inventory, low sorbent exposure time to a reactive environment and passage of char fines through the absorber are discussed. The advantages of transport reactors over fluidized bed and moving bed reactors for desulfurization and the implications of using transport reactors for a commercial desulfurizer are presented. Based on the extensive sorbent testing performed to date in the TRTU, the requirements on sorbent properties regarding attrition behavior, sulfur capacity and regeneration characteristics as applied to a commercial desulfurizer are discussed.

Objectives

The objectives of the program were:

- To identify the required and preferred sorbent characteristics for a transport desulfurization system,

- To perform testing on potential candidate sorbents in a transport reactor at conditions simulating commercial operation,

- To develop criteria for sorbent acceptance for a commercial desulfurizer,

- To commission and operate the commercial desulfurizer, and

- To test sorbent inat the commercial desulfurizer and correlate the commercial desulfurizer data with pilot plant results.

Experimental

A description of the test facility, located at the Kellogg Technology Development Center, and the procedures used in operating the TRTU are given in this section. The operating conditions used in testing the RTI-formulated sorbents in the TRTU are shown in Table 1.

A simplified sketch of the reactor system is shown in Figure 1. The reactor system consists of a mixing zone, a riser, a cyclone, and a standpipe. The mixing zone of the reactor, which can be operated either as a dense-phase fluid bed or as an entrained reactor, consists of a 10-foot tall section of 1-1/2 inch Schedule 160 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 mixing zone through a specially-designed gas distributor. During the absorption cycles, the gas was a mixture of H_2S and N_2. During regeneration, the mixture of H_2S and N_2 to the mixing zone was replaced with air.

Above the mixing zone is a 32-foot tall riser made of one inch Schedule 160 pipe. At the base of the riser is an injection nozzle that was used for feeding H_2 and 8 mol% H_2S/N_2 mixture. Dilution of this feed with gas from the mixing zone resulted in a desired H_2S concentration at the injection point. At a typical gas velocity of 12.8 ft/s used during absorption, the gas residence time was about 2.5 sec in the riser section. 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. Gas leaving the top of the cyclone is cooled, measured, and sampled.

The standpipe consists of a 33-foot tall section of 1-1/2 inch Schedule 160 pipe. The use of a relatively small diameter standpipe results in a low solids inventory requirement and minimal solids holdup time. Make up solids are added, if necessary, to 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 that is aerated.

During absorption, outlet H_2S concentration was measured every five minutes with a Varian 3300 gas chromatograph (GC) that employs a flame photometric detector. The leakage of H_2S of < 20 ppm as measured by this GC was verified with Draeger tubes. SO_2 concentration during regeneration was continuously monitored using a Bovar 721-M photometric analyzer. The regeneration outlet gas

was also monitored for O_2 concentration by means of an MSA model 4000 O_2 analyzer to determine if a breakthrough occurred. This instrument uses an electro-galvanic cell to detect and quantify O_2 (O_2 reacts with a reducing catalyst which then reacts with lead). All the thermocouple readings and pressure drop measurements were continuously recorded by a computer data logging system.

Project Description

The objective of the project was to test suitable candidate sorbents for absorbing H_2S from product gas from a gasifier and identify suitable sorbents for use in the commercial desulfurizer, shown in Figure 2, and to correlate the results from the HTDS with those obtained in the pilot plant. In addition to sorbent testing, the operating parameters for transport reactors for desulfurization and regeneration of sorbents for satisfactory operation have been developed. The benefits of transport reactors in absorbing H_2S and in regenerating sulfided sorbents compared to fluidized bed and moving bed reactors are outlined below.

Benefits of Transport Reactors

The advantages of transport reactors over fluidized and moving bed reactors are the following:

- Sorbent inventory is low since transport reactors take advantage of the fast H_2S absorption reaction by employing low riser densities (one to two seconds residence time in the riser). The requirement of sorbent inventory in fluidized or moving beds is much higher.
- Time of sorbent exposure to a reactive environment is low both in absorption and regeneration.
- Char fines pass through the absorber without accumulating, thus eliminating the need to have a barrier filter upstream of the HTDS.
- A slipstream of circulating solids is used for regeneration and hence control of temperature rise is easier and no diluent is required to absorb heat.
- The amount of sulfur absorbed and regenerated per cycle is about 2 wt%. This minimizes the stresses imposed on sorbent particles which, in turn, improves attrition resistance.

Results and Discussion

The operating conditions used for multi cycle testing of RTI-formulated sorbents in the TRTU and the results from this testing are presented in this section. RTI has been developing these ZnO-based sorbents under DOE project DE-AC21-88MC25006. In 1995, RTI and CMP, Inc. provided the CMP-107 zinc titanate sorbent, which was produced by spray drying, for TRTU testing. TRTU testing of this sorbent at Kellogg indicated that the sorbent readily removed H2S to <5 ppmv (the analytical detection limit), but its attrition rate was twice the target value that Kellogg used in the design of transport reactor for Piñon Pine. Recently, RTI and Intercat Development, Inc. developed the EX-SO3 formulation. This zinc titanate formulation was produced at Intercat in its commercial manufacturing facilities at Savannah, GA. This formulation was recently tested in TRTU at KTDC and results of this testing are presented below.

Table 1 - Operating Conditions for TRTU Testing

Operating pressure, psia	100
Operating temperature, °F	1000-1200
Mixing zone density, lb/ft^3	8 - 32
Mixing zone velocity, ft/s	3.0-6.7
Riser density, lb/ft^3	0.5 - 4.0
Riser velocity, ft/s	10.0 - 18.2
H_2S conc. at riser inlet, %	0.16 - 1.22
Sorbent inventory, lb	8 to 20
Solid circulation rate, lb/hr	220 - 950

One of the absorption cycles was operated at near SPPC Piñon Pine desulfurizer conditions, i.e., 1000 to 1050ºF and at an inlet H_2S concentration of 1,600 ppm. These conditions correspond to an H_2S partial pressure that is 35 percent higher compared to the Piñon Pine desulfurizer (400 ppm at 300 psia). This was a long duration cycle test conducted to demonstrate the suitability of the sorbent for application to the Piñon Pine desulfurizer. This cycle was conducted for about 13 hr at an H_2S inlet concentration of 1,600 ppm and then for 10 hr at an H_2S inlet concentration of 2,000 ppm. The H_2S breakthrough behavior in this cycle, shown in Figure 3, shows excellent H_2S absorption.

The temperatures in the mixing zone (TE-200 and TE-201) and SO_2 and O_2 concentration profiles obtained during sorbent regeneration in a typical cycle are shown in Figures 4 and 5 to illustrate sorbent behavior. Regeneration was successful at about 1000ºF, with a proprietary RTI additive, with the mixing zone density at 20 lb/ft^3 in this cycle. The peak SO_2 concentration of 6.5 vol% measured compares well with a theoretical value of about 6 vol%, based on the gas flowrates used. No oxygen leak was observed until there was O_2 breakthrough toward the end of the regeneration as the sorbent was fully regenerated in the cycle. Figures 4 and 5 clearly show that the sorbent was regenerated very well as depicted by the repeatable peak SO_2 concentration and expected temperature rise without any significant O_2 breakthrough.

One of the nice features of the EX-S03 sorbent is its high bulk density compared to other sorbents. A comparison of EX-SO3 with a sorbent with lower bulk density for application to the Piñon Pine regenerator is shown in Table 2 to illustrate the advantage of higher bulk density.

Table 2 - Comparison of Two ZnO-based Sorbents for Piñon Pine Regenerator

Sorbent	Hypothetical	EX-SO3
Bulk density of sorbent, lb/ft^3	50	100
Solid circulation rate, ft^3/hr	180	180
Sulfur removal rate, lb/hr	120	120
Solid circulation rate to	9,000	18,000

regenerator, lb/hr		
Sulfur absorption capacity, wt%		9
Sulfur removal, lb/ft^3 of sorbent		9
lb of solid circulated/lb of S	75	150
Temperature rise in regenerator, °F	400	145
Estimated attrition rate, lb/hr*		
Fines defined as < 11 µm	-	0
Fines defined as < 22 µm	-	4.5

* Preferred specification for the Piñon-Pine HTDS < 10 lb/hr.

Based on the results of the testing, the EX-SO3 sorbent is well suited for use in the Piñon Pine desulfurizer. The implications of using this sorbent versus a sorbent with a lower bulk density are discussed below. The design of the regenerator is based on the volume of the sorbent it holds and not the weight of the sorbent. The EX-SO3 sorbent resulted in significantly lower than an acceptable attrition rate. For the same sulfur removal duty, the temperature increase in the regenerator can be reduced from about 400°F to 145°F with the EX-SO3 sorbent due to the increase in sorbent mass flowrate. For a new design, this reduction in temperature rise may permit the operation of the desulfurizer at a higher temperature with a consequent increase in thermal efficiency; or for the same regenerator, the sulfur removal capacity can be increased by a factor of about two for the same temperature rise. The latter results in improved capital cost for a new design.

Based on the extensive testing performed in the TRTU, the following are the preferred sorbent properties at the Piñon Pine desulfurizer:

- Absorption of H_2S over an appreciable number of cycles at an inlet concentration of 5000 ppm to less than 5 ppm,

- No significant deterioration of sorbent with respect to sulfur capacity and attrition rate with the progression of absorption/regeneration cycles,

- Regeneration of sorbent over several cycles at about 1000 to 1200°F should be satisfactory with no O_2 breakthrough (as the sorbent is partially sulfided and regenerated) and with minimal or no sulfate formation, and

- Initiation of sorbent regeneration at 1000°F (the temperature in the commercial regenerator is not higher than this level).

Application of Sorbent Testing in the TRTU

The results obtained in the TRTU on various sorbents were utilized to develop criteria to accept a sorbent and to identify the preferred sorbent characteristics for the commercial desulfurizer in addition to developing design and operating data. The operating conditions of the Piñon Pine desulfurizer are

given in Table 3. In this desulfurizer, air is used as the oxidant and sulfur recovered as 14%SO_2 which is disposed of in the sulfator (SO_2 reacts with CaO to form Ca SO_4).

Table 3 - Piñon Pine Desulfurizer Operating Conditions

Absorber riser density, lb/ft^3	1.0
Absorber riser velocity, ft/s	22
Sorbent inventory, lb	25,000
Sorbent circulation rate, lb/hr	600,000
Solid circulation rate to regenerator, lb/hr	9,000
Sulfur capacity, lb/hr	120
H_2S leakage through absorber, ppm	< 20

Desulfurizer Commissioning

Future activities on commissioning and operation of the Piñon Pine desulfurizer are given below to describe the application of the results obtained in the pilot plant.

- Sorbent will be loaded after establishing purge/fluffing gas flows, while the pressure is essentially atmospheric.
- The system will be pressurized to initial operating pressure by admitting hot air (at 750°F) from air booster system. Gas flow will be directed through the filter to stack. The regenerator is isolated from the absorber during pressurization and pressurized independently.
- After the downstream filter is heated above the dewpoint, flow through the absorber is initiated. Sorbent circulation is started around the absorber circuit resulting in heat up of the same.
- Initially the regenerator can be heated using hot air, but it needs hot sorbent circulation from the absorber to reach operating temperature.
- Some time is required to integrate the sorbent flows from the absorber to the regenerator and back to the absorber.
- Sorbent flows through the absorber will be minimized at about a riser density of one lb/ft^3. Sorbent flowrate through the regenerator will be set near the design point to affect uniform heat up of HTDS Train and to avoid excessive thermal stresses.

Desulfurizer Operation

- After satisfactory performance of the HTDS system, including cyclones, has been demonstrated, the gasifier will be commissioned. While the gasifier is being commissioned, the HTDS system stays on line and is heated.
- After gasification is established and the throughput increased to 60% of design capacity, the HTDS system will begin to regenerate sorbent and send resulting SO_2 to the sulfator where it is reacted with CaO to form $CaSO_4$.

- Air flow to the regenerator is set based on net gasifier sulfur production. Sorbent flow to the regenerator is set based on sulfur loading and the regenerator overhead temperature.
- Absorber inlet temperature is controlled to affect a 1000°F fuel gas temperature at the gas turbine fuel gas inlet. Absorber inventory is maintained by periodic makeup through a lockhopper arrangement allowing for online addition of sorbent.
- Regenerator overhead temperature is held above 1200° F to ensure proper sorbent regeneration. Temperature is controlled by a combination of air addition and sorbent flow to the regenerator. Sorbent loading is maintained close to 6 wt% sulfur. Regeneration per pass is controlled to result in a sorbent temperature rise of about 300°F and a regenerator overhead temperature of at least 1200°F.

The performance of the desulfurizer will be characterized in terms of H_2S leakage and control of solid flowrates from the absorber to the regenerator. General sorbent properties during absorption and regeneration will be studied and correlated with the pilot plant results.

Contract Information

Contract Number:	DE-AC21-88MC-25006
Cooperative Agreement No:	DE-FC21-92MC29309
Contractor Name Address:	The M.W. Kellogg Company, 601 Jefferson Avenue, Houston, Texas 77002-7990
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References

(1) Subcontract Report "Zinc Titanate Sorbent Testing in the Transport Reactor Test Unit," submitted by The M. W. Kellogg Company to Research Triangle Institute (January 15, 1997).

(2) Subcontract Report "RTI/CMP-107 Zinc Titanate Sorbent Testing in the Transport Reactor Test Unit," submitted by The M. W. Kellogg Company to Research Triangle Institute (October 30, 1995).

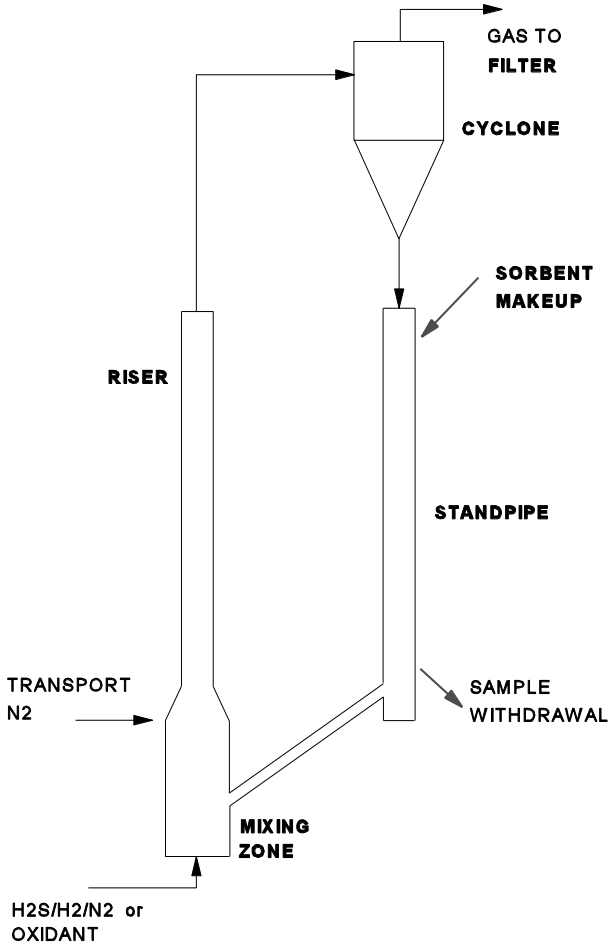

Figure 1. Transport Reactor Test Unit

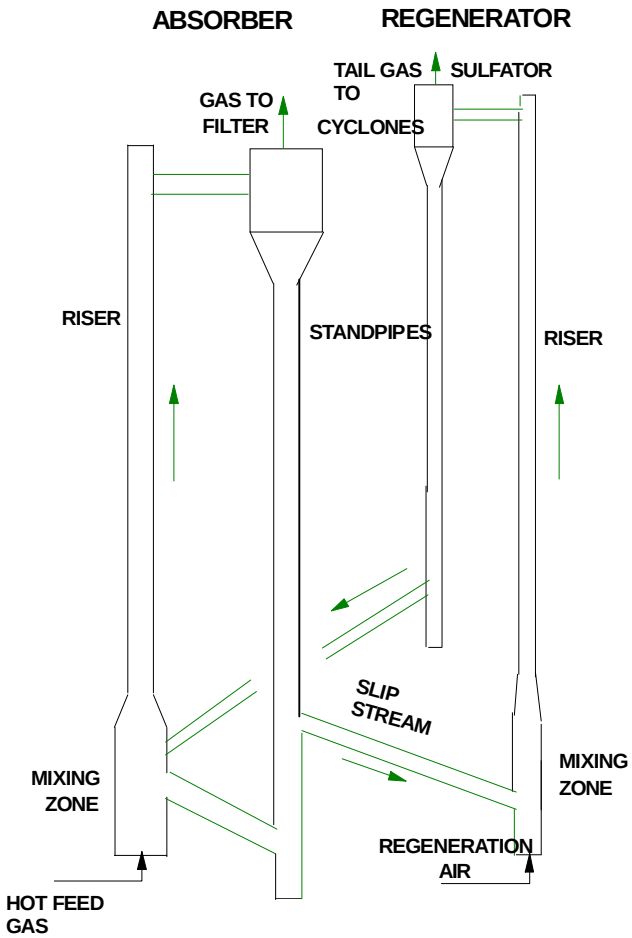

Figure 2. Piñon Pine Desulfurizer

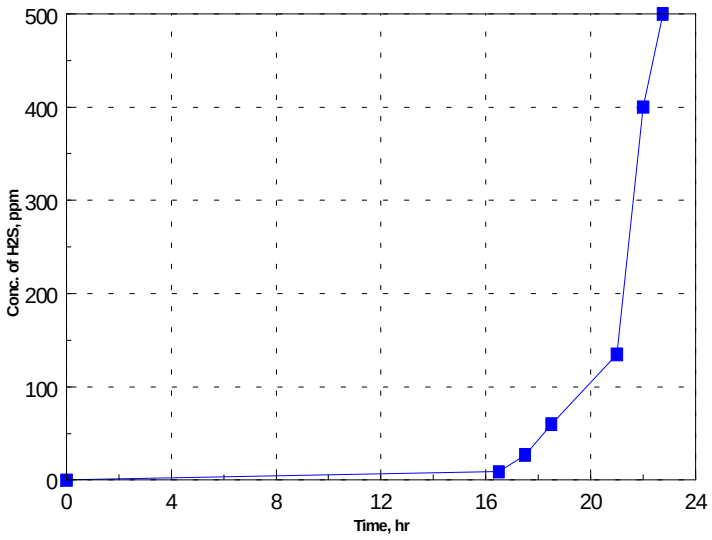

Figure 3. H_2S Breakthrough in Absorption

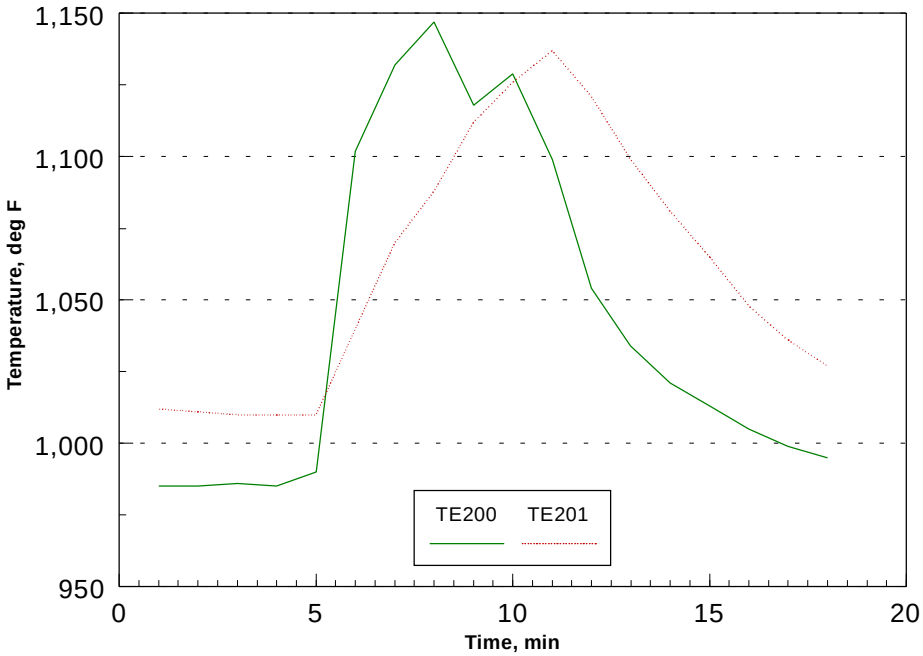

Figure 4. Temperatures in Mixing zone - Regeneration with 5% RTI additive.

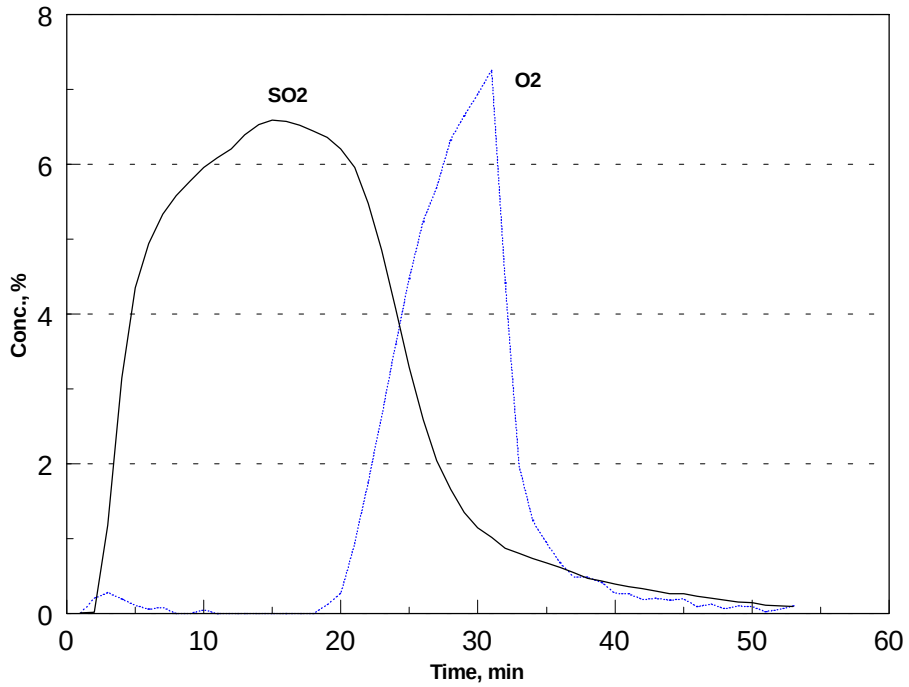

Figure 5. SO_2 and O_2 Conc. Profiles in Regeneration