Hot Gas Desulfurization Using Transport Reactors

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Abstract

Sierra Pacific Power Company is building a 100 MW_e IGCC power plant based on KRW fluid bed gasifier technology that utilizes transport reactors for hot gas desulfurization and sorbent regeneration. Use of a transport absorber avoids the need for pre-filtration of dust-laden gasifier effluent, while a transport regenerator allows for the use of 100% air without the need for heat exchange equipment.

Selection of transport reactors for hot gas desulfurization using a proprietary sorbent, based on testing performed in a transport reactor test unit (TRTU) at the M. W. Kellogg Technology Development Center and in a fixed bed reactor at Morgantown Energy Technology Center (METC), is outlined in the paper. The results obtained in these two test facilities and reasons for selecting transport reactors for the above IGCC power plant in preference to either fixed bed reactors or fluidized bed reactors are discussed. This paper reviews the evolution of the hot gas desulfurization system designs and includes selected results on H_2S absorption and regeneration of sulfided sorbent over several absorption/regeneration cycles conducted in the TRTU and the METC fixed bed reactor.

The original design for the Sierra Pacific Project was based on fixed bed reactors with zinc ferrite as the sorbent. Owing to high steam requirements of this sorbent, zinc titanate was selected and tested in a fixed bed reactor and was found unacceptable due to loss of strength on cyclic absorption/regeneration) operation. Another sorbent evaluated was Z-Sorb® sorbent, a proprietary sorbent developed by Phillips Petroleum Company. This sorbent was found to have excellent sulfur capacity, structural strength and regenerability. Steam was found unsuitable as fixed bed regenerator diluent, this results in a requirement for a large amount of inert gas, whereas a transport regenerator requires no diluent. The final Sierra design features transport reactors for both desulfurization and
 regeneration steps using neat air.

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INTRODUCTION

The Hot Gas Desulfurization (HGD) Unit for the Sierra Pacific Power Company (SPPCo) Piñon Pine Project has evolved almost continually since the start of the project. Originally, the design was based on a fixed bed cyclic reactor unit, using zinc ferrite as the sorbent. Although this sorbent is very effective in capturing H_2S, it has the undesirable characteristic of promoting carbon formation unless a large quantity of steam is added to the process gas. This requirement of process steam was not practical for the specific application at Sierra Pacific. To satisfy the specific requirements at Piñon Pine, a program was initiated to evaluate and identify an alternative HGD sorbent.

The first alternative sorbent selected for evaluation was a zinc titanate formulation reputed to have both good absorption capacity and durability. However, tests on this material showed that it was unable to withstand the repeated cycling between absorption and regeneration, experiencing both physical and chemical deterioration (1) .

The second sorbent evaluated was a proprietary material developed by the Phillips Petroleum Company, Z-Sorb ® sorbent (2). Extended fixed bed testing conducted at METC demonstrated that the sorbent has outstanding physical durability, but its initial high capacity decreased significantly with repeated cycling. Steam, used as a diluent during regeneration, was identified as a major cause of this deterioration. Although this sorbent is satisfactory for the proposed fixed bed commercial system, its use requires the addition of a large and expensive nitrogen system for supplying the diluent required during regeneration.

In order to reduce the cost of the desulfurization system, The M. W. Kellogg Company proposed the use of a transport reactor design, using Z-Sorb® sorbent. This concept was demonstrated in Kellogg's pilot plant in mid-1993 and appeared to be a viable alternative to the fixed bed design. A transport reactor system has the advantage of not requiring dilution gas for regeneration, and has the additional advantage of limiting the exposure of the sorbent to high temperatures. The latter is also suspected of contributing to loss in sorbent capacity in a fixed bed reactor system..

OBJECTIVE

The objective of the project to be discussed was to obtain the necessary design data for the transport system, and to answer some of the technical questions which arose from the fixed bed test results, a comprehensive test program was developed and carried out at Kellogg's Technology Development Center (KTDC).

APPROACH

I.   METC Testing of Z-Sorb® Sorbent

In order to evaluate and qualify Z-Sorb® sorbent for application in original fixed bed cyclic reactor design of the Piñon Pine desulfurization reactor system, METC conducted a total of forty absorption tests (3). The test apparatus used in this study was a 2" ID fixed bed reactor. These tests investigated sorbent performance in terms of sulfur capacity and durability under a variety of absorption conditions. Parametric tests were done to determine optimum operating conditions for the commercial reactor and included evaluation of superficial gas velocity, absorption temperature, HCl in the feed gas, diluents for use in sorbent regeneration, and various regeneration techniques.

The key conclusions from the testing at METC were:

1.   The sulfur absorption capacity for Z-Sorb® sorbent averaged about 11-15 wt.% sulfur, with good reproducibility. The sorbent also showed excellent physical stability, with no loss of physical integrity.

2.   At absorption temperatures of 900-1100°F the absorption rate is essentially independent of temperature. Superficial gas velocity was varied between 0.5 fps and 2.0 fps, and results indicate that the reaction wave front is quite short, approximately the depth of the experimental bed (16 cm) at velocities of 1.0-1.5 ft/s.

3.   At temperatures of 900-1100 ^{o}F, sulfur sorbent capacity declined as a function of the number of regeneration cycles. In these tests the capacity reached a final lower level of 4-6 wt.% sulfur. During regeneration, the use of either steam or nitrogen is required for minimizing sorbent bed exotherms.

4.   At regenerator temperatures below 1100 ^{o}F, the sorbent is partially sulfated, leading to lower sulfur absorption capacities.

5.   Regeneration at temperatures around 1350°F results in complete regeneration of the sorbent. No metal sulfates were observed using these higher regeneration temperatures.

6.   The physical stability of the sorbent is affected by the use of high regeneration temperatures.

On the basis of these test data, a process design was proposed for the Piñon Pine HGD unit. This proposed HGD unit for Piñon Pine, required a large amount of diluent nitrogen to be available during regeneration. The production of this nitrogen required the installation of an air separation unit at Piñon Pine. The capital cost for the air separation unit was found to be too high for inclusion in this project.

The need to identify an alternative process for using Z-Sorb® sorbent at Piñon Pine that will meet the technical and financial objectives of this project led to the application of a transport

reactor for this service. The major advantage that the transport reactor was believed to offer was that the heat balance of the absorption (riser) and regeneration could be established such that there was no need for a large volume of a diluent nitrogen stream. By limiting the sulfur regeneration per cycle to a level such that the heat liberated during regeneration does not lead to excessive exotherms, the need for the diluent nitrogen stream is eliminated.

Simplified Transport Reactor System
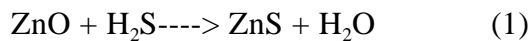
II.   Features of the Transport Reactor

For the purposes of this discussion, a transport reactor is defined as a dilute phase, fluid bed reactor. In its simplest form, the transport reactor is analogous to a modern day riser reactor commonly used in the fluid catalytic cracking unit of a modern day refinery. Figure 1 presents a simplified process flow diagram of a generic transport reactor system.

In this system, there is a riser absorber and a regenerator that are coupled such that circulating solids continually pass from the riser standpipe to the regenerator back to the riser absorber.
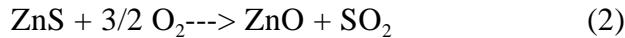For hot gas desulfurization applications, the riser absorber is used for the absorption of H_2S , and the regenerator is used for oxidation of the metal sulfide to generate SO_2.

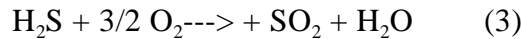The simplified stoichiometry for these two basic reactions are presented below:

Riser Reactor

$ZnO + H_2S ----> ZnS + H_2O$ (1)

Regenerator Reactor

$ZnS + 3/2\ O_2 ---> ZnO + SO_2$ (2)

Overall Reaction

$H_2S + 3/2\ O_2 ---> + SO_2 + H_2O$ (3)

In general, the residence times for the riser reactors are significantly shorter then the residence times for regeneration. In addition, the linear velocities of the solids being transported in the riser are significantly higher than those for the regenerator. Table 1 summarizes typical ranges for residence times and solids velocities commonly used in a typical transport reactor system.
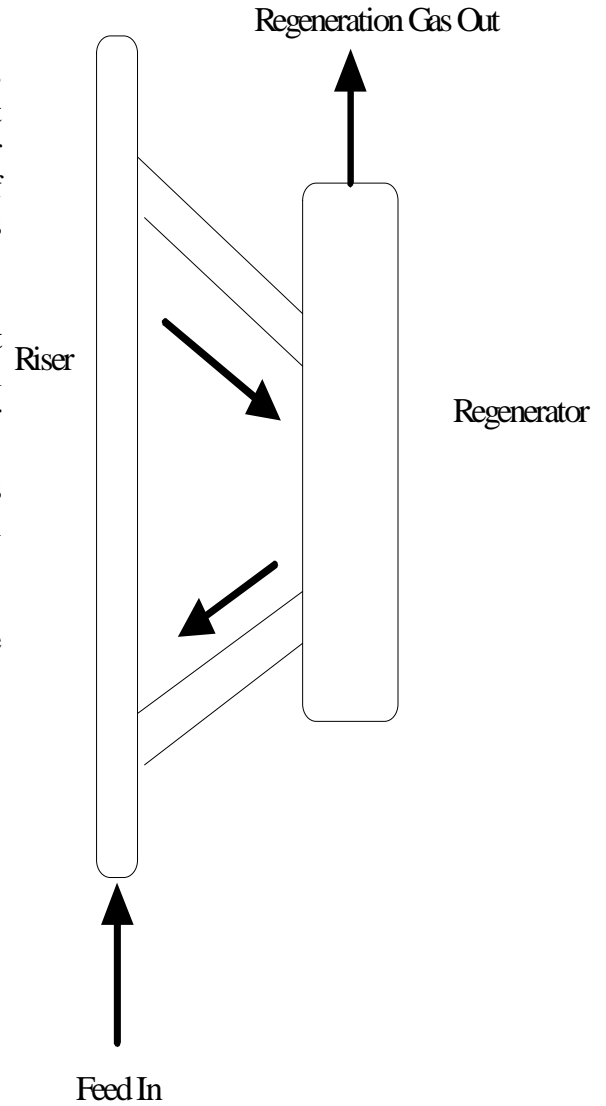
Table 1: Characteristics of Riser and Regenerator Reactors		
	Residence Time	**Linear Velocity**
Riser	1-10 seconds	10-30 ft/sec
Regenerator	1-10 minutes	< 15 ft/sec

The successful application of a transport reactor in the place of fixed bed reactors for hot gas desulfurization at Piñon Pine demands that the following requirements be addressed:

- The rate of H_2S absorption must be significantly fast such that no sulfur breakthrough from the riser to the regenerator is observed.

- Regenerator must be capable of operating using neat air as oxidant. Sorbent must be capable of initiating regeneration at 1000 ºF, temperature at which sulfided sorbent enters the regenerator.

- Sorbent must be operated at partial loading, as regeneration requires only a small amount of the sulfide is oxidized per pass to reach maximum operating temperature.

- The successful sorbent must be able to retain its activity over multiple cycles.

- Attrition rate of the sorbent must be low, preferably in line with chemical deactivation rate.

- Fines emissions from absorber require that the transport absorber be located ahead of the absolute filter, this in turn means that char fines from the gasifier must pass through the absorber without interfering with the operation of the absorber and/or regenerator.

As discussed further in this paper, the transport reactor system designed by The M. W. Kellogg Company in combination with the proprietary sorbent developed by Phillips Petroleum Company, meets all of these requirements.

Heat Balance Considerations

A key feature of the transport reactor for HGD, is the coupling of the sulfur absorption and sorbent regeneration. Circulation of sulfided sorbent from absorber standpipe to regenerator is such only a small amount of the sulfide is oxidized per pass. This oxidation heat is absorbed by the sorbent and given up in the riser absorber.

III.   Transport Reactor Development at Kellogg

The results from the fixed bed testing at METC clearly demonstrated that Z-Sorb® sorbent was an effective sorbent for HGD application using a cyclic fixed bed reactor system. To use a transport reactor for this service however, requires that the absorption rate of H_2S be exceedingly high. Given the short residence times of transport reactors (Table 1), the absorption of H_2S must occur within a few seconds.

In 1993, Kellogg modified its pilot plant sized transport reactor test unit (TRTU) that was supporting gasification studies, in order to demonstrate the application of this reactor technology for HGD (3). The results from this study, summarized in Table 2, clearly demonstrated that the rates of H_2S absorption were very high. On the basis of these results, the development of the transport reactor HGD unit for Piñon Pine was formally initiated.

In support of this development activity, three different reactor systems were used.

Reactor 1:   A small fluidized bed quartz reactor was used to determine sorbent capacity.

Reactor 2:   A larger fluidized bed unit (BRU) was used for a long term multi-cycle test.

Reactor 3:   Transport reactor conditions required for adequate absorption and regeneration were evaluated in the TRTU. This unit, as well as a plastic cold flow model corresponding in design to the TRTU, were used to investigate the capture and interaction of fines with circulating sorbent.

Sulfur capacity tests were conducted with fresh sorbent as well as samples exposed to steam and an inert environment (N_2) at temperatures of 1000-1400°F. In all tests, the physical form of Z-Sorb® sorbent was consistent with that required for use in a transport reactor. In particular, the particle size was in the range of 40-300 microns.

RESULTS

I.   Sulfur Capacity

Using Reactor 1, the sulfur absorption capacity of fresh Z-Sorb® sorbent was measured at 12.0-12.3 wt.%. This sulfur capacity is consistent with the results reported by METC for the pelleted form of Z-Sorb® sorbent. (Table 2)

Table 2: Summary of Z-Sorb® Sorbent Sulfur Capacities		
Temperature, °F	Atmosphere	Sulfur capacity, wt.%
1000	nitrogen	12.8
1400	nitrogen	12.0
1000	steam	12.1
1400	steam	3.2

Exposure to steam at temperatures above 1000°F reduced the sorbent capacity significantly, with the capacity falling to about 3 wt.% after a 1400°F steam soak. Exposure to N_2 at temperatures as high as 1400°F had no apparent effect.

II.   Multi-Cycle Tests

The multi-cycle test in the BRU (Reactor 2) consisted of 20 absorption and regeneration cycles, with H_2 pretreatment, before the absorption cycle, being included in about half of the runs. The absorption cycles, primarily done at 1000°F, loaded the sorbent to nominally 1 wt.% sulfur using a feed gas containing 1 mole% H_2S. Regenerations were done with N_2-diluted air (1.5, 3.5 mole% O_2), with the key variable being the regeneration temperature. The following observations were made based on the results from 20 cycles of testing in the BRU:

Absorption

- Absorption of H_2S was very good with no H_2S in the outlet gas during the absorption cycles.

- When no pretreatment step was used prior to absorption, SO_2 evolution exceeded conc. of 1000 ppm during absorption. This indicated that the sulfate formed during regeneration was reduced to ZnO with SO_2 evolution.

- With pretreatment in 5 to 15% H_2, SO_2 is evolved, but does not react with H_2 to form H_2S. Subsequent absorption gives off no SO_2.

Regeneration

- In all the tests done in the quartz reactor and the BRU, sulfate was formed during regeneration. The amount varied depending upon the temperature.

- Heating the sorbent to 1370°F prior to regeneration and a peak temperature of 1400°F yielded the least amount of SO_2 during pretreatment.

- For the initial and peak temperatures of 1370 and 1400°F during regeneration, the amount of sulfur (present on the sorbent) converted to sulfate during regeneration is about 0.43%.

These tests showed complete absorption of H_2S over the entire multi-cycle period. Sulfur capacity dropped slightly, to 11 wt.% after 17 cycles and to 10 wt.% after the final cycle. During the initial absorption cycles, as well as the hydrogen pretreatment periods, SO_2 (not H_2S) evolved due to the reduction of sulfate formed during the prior regeneration per reaction (4). The SO_2 leakage observed during the absorption cycles may be attributed either to the stripping of SO_2 from the reactor wall/piping or to the following reaction of sulfate formed during regeneration:

$$ZnSO_4 + H_2 \text{ ---> } ZnO + SO_2 + H_2O \qquad (4)$$
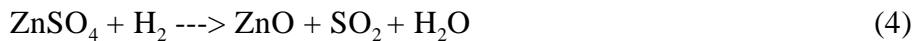
The concentration of SO_2 was minimized by running the regenerations at nominally 1400°F. At this temperature, residual sulfate on the regenerated sorbent was less than 0.5 wt.%.

III. Transport Reactor Pilot Plant Testing

Description of Transport Reactor Test Unit

The TRTU at Kellogg's Technology Development Center (KTDC) was originally built for developing a new coal gasification technology. A simplified schematic of the TRTU is presented in Figure 2.

The general features of the TRTU include 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. Solids from the standpipe are returned to the bottom of this zone. Fluidization gas which can be N_2, air, steam, O_2, or any combination of these, is fed to the bottom of the mixing zone through a specially designed gas distributor.
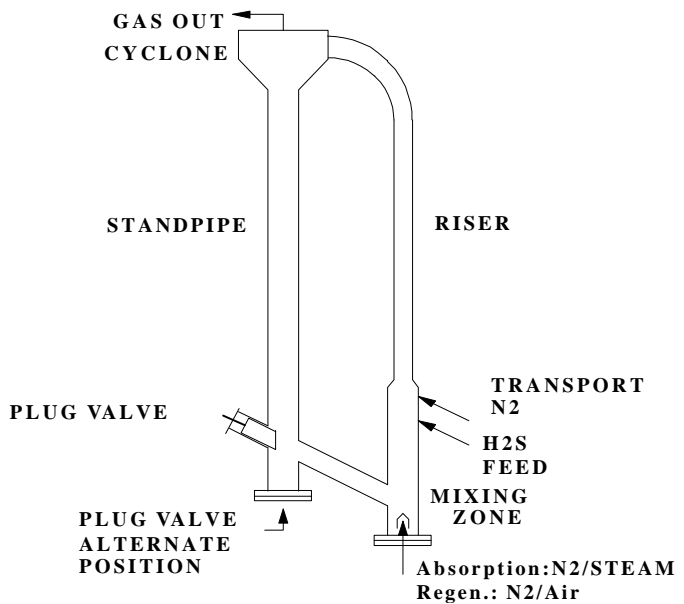

Figure 2 Simplified Process Flow Diagram of Kellogg's TRTU

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Above the mixing zone is a 32-foot tall, 1" riser. At the base of the riser is an injection nozzle that is used for introducing feed gases, which include H_2 and H_2S/N_2 blend. Dilution of the this feed gas with the mixing zone fluidization gas resulted in actual H_2S concentration of 1-2 mole %. At the velocity of 12.8 ft/s used during many of the runs, the gas residence time was about 2.5 seconds in the riser section.

Gas and solids (sorbent) leave the top of the riser and flow directly to a high efficiency cyclone. Gas leaving the cyclone is cooled and the volume and composition are measured.

Solids from the cyclone enter the top of the standpipe. The standpipe consists of a 33-foot tall, 1.5" pipe. Solid samples may be withdrawn at any time from the bottom section of the standpipe. Makeup solids are added to the top of the standpipe as needed. Solids flow from the bottom of the standpipe to the mixing zone of the riser via a lateral transfer line.

The testing with the TRTU focused primarily on sulfur absorption and sorbent regeneration studies.

Sulfur Absorption Tests

The sulfur absorption tests in the TRTU included 5 complete cycles, with multiple regenerations being done during 2 of the cycles. Absorptions were done typically at 1000°F with a nominally 1 mole % H_2S feed gas. Regenerations were done using air, with the regeneration temperature being varied from 1000°F to 1200°F to study its effect.

The following observations were made based on the TRTU testing:

- Z-Sorb® sorbent was loaded to as high as 8.3 wt.% sulfur. H_2S was not detected in the outlet gas throughout the absorption cycles.

- Hydrogen pretreatment resulted in very low SO_2 release in subsequent absorption cycles.

- During regeneration, oxygen breakthrough resulted below 1200°F temperature.

- Residual sulfate existed and was highest at lowest regeneration initiation temperature. Chemical analyses of samples after regeneration showed sulfate contents of 0.1-0.2 wt.%.

Regeneration Studies

The effect of oxygen partial pressure and temperature on the regeneration of pre-sulfided Z-Sorb® sorbent was studied in the TRTU. This test was run to determine the most favorable regeneration conditions for the multi-cycle Z-Sorb® sorbent test runs. The Z-Sorb® sorbent was

pre-sulfided in the absence of steam to a nominal 6 wt.% and regenerated to a nominal 4 wt.%. The reactor was operated at 85 psig pressure and at three riser temperatures namely, 1000, 1100 and 1200°F. Two oxygen partial pressures equivalent to 40% and 60% by volume of oxygen in the oxidant stream were used. The oxidant stream was injected into the riser for a sufficient time to reduce the sulfide sulfur consistent with the heat balance requirements of the commercial unit.

The most favorable regeneration temperature for oxidant partial pressures of 40 to 60 psi was found to be 1200 °F. The sulfate sulfur content in the Z-Sorb® sorbent at the end of the five regeneration runs was 0.09 wt.%. The maximum capacity of the sorbent for sulfur absorption decreased from 14 wt.% for the virgin sorbent to 13 wt.% at the end of the last regeneration run.

Subsequent Z-Sorb® sorbent formulations have resulted in the manufacture of an improved sorbent capable of initiating regeneration at 950 °F to 1000 °F. This is the formulation that will be used at SPPCo.

CONCLUSIONS

The results of the bench scale and pilot plant testing conducted at KTDC confirmed that a transport reactor, using a proprietary sulfur sorbent from Phillips Petroleum (Z-Sorb® sorbent), could be used for HGD application at Sierra Pacific. The basic design of the Transport Reactor for this service provides a very efficient, low cost option that will meet the technical and financial requirements of this facility. Figure 3 provides a simplified process flow diagram of the HGD Unit for Sierra Pacific.
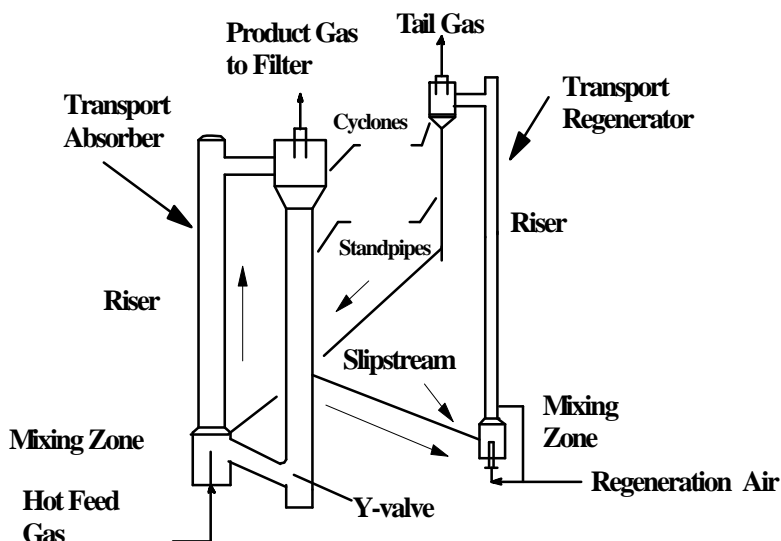

Figure 3 Simplified Process Flow Diagram of the HGD Unit for Sierra Pacific

The causes of sorbent capacity deterioration, observed during these tests, are not specifically known. Since regeneration with steam diluent is suspected as a potential problem, it should be avoided in the commercial design unless additional test data prove it satisfactory.

The major conclusions from this study can be summarized as follows:

- Complete absorption of H_2S was obtained under all conditions tested. No problems are expected with H_2S leakage in the commercial reactor, even at low riser density.

- BRU tests show a decline in Z-Sorb ® sorbent sulfur capacity with repeated cycling, but the final capacity at the end of the multi-cycle test was still well above the intended sulfur loadings for the commercial absorber.

- Exposure of the Z-Sorb® sorbent to steam at temperatures above 1100-1200°F results in an unacceptably high loss in sulfur capacity.

- Exposure of the Z-Sorb® sorbent to nitrogen (inert atmosphere) at temperatures up to 1400°F had no apparent effect on sulfur capacity.

- Testing in the TRTU, performed to determine the effect of char fines on sorbent absorption/regeneration, showed that the HGD unit could be located ahead of the current absolute filter and does not require additional filters.

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