Development of Advanced Hot-Gas Desulfurization Processes

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ABSTRACT

Advanced integrated gasification combined cycle (IGCC) power plants nearing completion, such as Sierra-Pacific, employ a circulating fluidized-bed (transport) reactor hot-gas desulfurization (HGD) process that uses 70-180 μm average particle size (aps) zinc-based mixed-metal oxide sorbent for removing H_2S from coal gas down to less than 20 ppmv. The sorbent undergoes cycles of absorption (sulfidation) and air regeneration. The key barrier issues associated with a fluidized-bed HGD process are chemical degradation, physical attrition, high regeneration light-off (initiation) temperature, and high cost of the sorbent. Another inherent complication in all air-regeneration-based HGD processes is the disposal of the problematic dilute SO_2 containing regeneration tail-gas. Direct Sulfur Recovery Process (DSRP), a leading first generation technology, efficiently reduces this SO_2 to desirable elemental sulfur, but requires the use of 1-3 % of the coal gas, thus resulting in an energy penalty to the plant. Advanced second-generation processes are under development that can reduce this energy penalty by modifying the sorbent so that it could be directly regenerated to elemental sulfur.

The objective of this research is to support the near and long term DOE efforts to commercialize the IGCC-HGD process technology. Specifically we aim to develop:

- optimized low-cost sorbent materials with 70-80 μm average aps meeting all Sierra specs.
- attrition resistant sorbents with 170 μm aps that allow greater flexibility in the choice of the type of fluidized-bed reactor e.g. they allow increased throughput in a bubbling-bed reactor.
- modified fluidizable sorbent materials that can be regenerated to produce elemental sulfur directly with minimal or no use of coal gas.

The effort during the reporting period has been devoted to development of an advanced hot-gas process that can eliminate the problematic SO_2 tail gas and yield elemental sulfur directly using a sorbent containing a combination of zinc and iron oxides.

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Introduction

Advanced integrated gasification combined cycle (IGCC) power plants are being developed to produce electricity from coal due to their potential for superior environmental performance, economics, and efficiency in comparison to conventional coal-based power plants. The U.S. Department of Energy (DOE), Federal Energy Technology Center (FETC) Clean Coal Technology program has led to the successful construction of two such advanced plants--Sierra Pacific and TECO, with shakedown and commissioning currently in progress. A key component of these advanced IGCC plants is a hot-gas desulfurization (HGD) process employing efficient regenerable zinc-based mixed-metal oxide sorbents that can remove the hydrogen sulfide (H_2S) in coal gas to <20 ppmv and that can be regenerated with air for multi-cycle operation as shown below for zinc oxide:

$$ZnO + H_2S \rightarrow ZnS + H_2O \qquad \text{(Sulfidation)}$$

$$ZnS + (3/2)O_2 \rightarrow ZnO + SO_2 \qquad \text{(Regeneration)}$$

For economic reasons, the sorbent must be able to maintain an acceptable level of reactivity over numerous absorption (sulfidation)-regeneration cycles.

This study is directed towards the development of sorbents for fluidized-bed reactors. The Sierra-Pacific plant employs the M.W.Kellogg (Kellogg) circulating fluidized-bed (transport) HGD process whereas the TECO plant employs the General Electric (GE) moving-bed HGD process. The key barrier issues facing the successful development of a fluidized-bed HGD process are chemical degradation, physical attrition, high regeneration light-off (initiation) temperature compared to sulfidation temperature, and high cost of the sorbent. Current leading first generation sorbents such as zinc titanate (ZT-4) typically prepared with an average particle size (aps) of 170 μm using a granulator and Phillips Petroleum=s Z-Sorb III (175 μm aps) undergo significant chemical degradation, losing their reactivity and capacity by as much as 50 % in just 50 cycles and they cost as much as \$8-10 per lb. These sorbents also have very low attrition resistance compared to bench-mark fluid catalytic cracking (FCC) catalysts (70-80 μm aps) prepared by spray drying and employed in a petroleum refinery. The larger aps of 170 μm results in reduced entrainment and allows greater throughput and flexibility in a bubbling-bed, but has not to date been successfully made using a spray drier. Also the regeneration light-off temperature of first generation zinc titanate sorbents is around 630-650^{o}C, which is unacceptably higher than the 480-550^{o}C sulfidation temperature being employed at Sierra. To allow efficient heat integration, the sulfidation and regeneration light-off temperatures need to be close to each other.

Another inherent complication associated with all HGD processes is the disposal of a problematic dilute SO_2 containing tail gas produced by air-regeneration of the zinc-based sorbent. The higher the oxygen concentration in the regeneration gas, the higher will be the SO_2 concentration in the tail gas. However, the highly exothermic air regeneration reaction imposes an upper limit on the oxygen concentration that can be used. The GE moving bed reactor HGD process at TECO uses recycled SO_2 as the diluent to moderate the reaction and produce a 12-14 volume % SO_2 tail gas. The Kellogg transport reactor HGD process at Sierra represents a major advancement in this regard because it enables efficient temperature control by rapidly circulating the sorbent and limiting the degree of regeneration, thus allowing the use of neat air as regeneration gas without recycle. However, higher O2 concentrations in the regeneration gas can promote sulfate formation in the sorbent which is undesirable. Even with neat air, a dilute SO_2 tail gas containing a maximum of 14 volume % SO_2 is produced which needs to be disposed. Production of elemental sulfur from the SO_2 is the most attractive option because it can be readily disposed, sold, stored and transported over long distances. The Direct Sulfur Recovery Process

(DSRP) is a leading first generation process for converting the SO_2 in the tail gas to elemental sulfur. In DSRP, the SO_2 is catalytically reduced to elemental sulfur using a small slip stream of coal gas:

$$SO_2 + 2H_2 \text{ (or } 2CO) \rightarrow 2H_2O \text{ (or } 2CO_2) + (1/n)S_n$$

For each mole of sulfur, 2 moles of H2+CO are consumed. This represents an energy penalty to the IGCC plant. The higher the sulfur content of the coal, the higher is the consumption of coal gas by DSRP to produce elemental sulfur. Advanced second generation sulfur recovery processes are under development that aim to produce elemental sulfur rather than SO_2 during sorbent regeneration by using SO_2 itself as the regeneration gas. These advanced processes aim to develop and use a modified mixed-metal oxide sorbent in which one of the metals (M1) has favorable thermodynamics for regeneration by SO_2 and yielding elemental sulfur directly where as the other metal (M2) is air regenerable to produce the SO_2 needed for the first metal:

$$2M1S + SO_2 \rightarrow 2M1O + (3/n)S_n$$

$$M2S + (3/2)\, O_2 \rightarrow M2O + SO_2$$

with the net reaction being:

$$2M1S + M2S + (3/2)O_2 \rightarrow 2M1O + M2O + (3/n)S_n$$

This advanced process avoids the energy penalty associated with the coal gas consumption in the DSRP, however, the appropriate mixed metal oxide sorbent combination needs to be developed that yields the above overall stoichiometry during regeneration and at the same time can reduce the H_2S in the coal gas to less than 20 ppmv during sulfidation.

In our previous work, an attrition resistant form of MCRH-61 was tested in the 2.0 inch HTHP fluidized-bed reactor simulating the Sierra-Pacific conditions for 10 cycles at sulfidation conditions of simulated Kellogg gasifier gas with 0.4 % H_2S at 18.8 atm pressure, 480-510^oC, and 15 slpm through a 145 g sorbent bed. The regeneration was conducted with pure air with an initial temperature of 480-510^oC. The H_2S breakthrough results indicated essentially complete removal of H_2S until a sharp breakthrough in all 10 cycles. The sorbent lost some capacity after the first cycle presumably due to pure air regeneration that increased the bed temperature to around 700^oC. After the first cycle, the capacity stabilized even with temperature excursions to 675-700^oC and no attrition of the sorbent occurred in the 10 cycle test. Due to pure air regeneration, some sulfate formation did occur as seen from the SO_2 evolution curves for cycles 2-10 during sulfidation. The sorbent lighted-off nicely at 482^oC. Overall the test is a success with potential for an optimized MCRH-61 to be a candidate for Sierra-Pacific. The cause of the reactivity drop during the first cycle and stabilization thereafter needs to be evaluated. The sulfate formation on the sorbent needs to be minimized during pure air regeneration and the overall preparation needs to be optimized to reduce cost down to less than $3.00 per lb.

To summarize, the short-term and long-term DOE research and development needs in fluidized-bed HGD processes include:

- optimized sorbents with 70-80 μm aps meeting all Kellogg specifications for their transport reactor HGD process at the Sierra-Pacific power plant
- 170 μm aps attrition resistant sorbents to allow greater flexibility, reduced entrainment, and increased throughput in bubbling-bed reactors.
- fluidizable sorbent materials that can not only reduce H_2S to <20 ppmv but at the same time be directly regenerable to elemental sulfur without coal gas consumption as in DSRP

RESULTS AND DISCUSSIONS

The project consists of four experimental tasks (Tasks 1-4) addressing the contract objectives described above.

Task 1: Development of Sorbent for Sierra-Pacific

Task 2: Bubbling-Bed Reactor Sorbents

Task 3: Advanced Sulfur Recovery Sorbents

Task 4: Sorbent Characterization

Task 1: Development of Sorbent for Sierra-Pacific

Several zinc-based sorbents have been prepared and tested. The sorbent surface were modified to prevent sintering during pure air regeneration. Modifications were made to the sorbent to increase its ability to withstand high temperature and prevent loss of capacity by utilizing various textural promoters. These sorbents are designated as FHR sorbents. Based on the screening study, the FHR-32 sorbent showed the best suifidation performance. Currently, plans are underway to test this sorbent for about 50 cycles in a multicycle run.

Task 2: Bubbling-Bed Reactor Sorbents

Several zinc-based sorbents have been prepared and tested. The FHR-33 sorbent was prepared using spray drier. Sulfidation performance of the FHR-33 sorbents showed that the pre-breakthrough level was less than 60 ppm. There is no decline in activity in 5-cycles tested.

Task 3: Advanced Sulfur Recovery Sorbents

A number of sorbents based on iron and zinc oxides were prepared and tested for SO_2 regeneration. The sulfided sorbent that was based purely on ZnO as the active sorbent showed essentially no regeneration with 3 % SO_2 in N_2 at up to 800^{o}C and 1.0 MPa. However, sulfided iron-and zinc-based sorbents showed good regeneration with SO_2.

Based on the preliminary study, two attrition resistant candidate materials in larger batches, designated AHI-1 and AHI-2 was prepared and tested. The attrition indices for AHI-1 and AHI-2 were 0.5 and 1.2, respectively. The sulfidation performance of AHI-1 and AHI-2 sorbents are shown in Figures 1 and 2. The protocol for the sulfidation using simulated coal gas consisted of a 20-minute initial reduction, with no H_2S present, followed by the introduction of 4000 ppm of H_2S into the feed gas. AHI-1 generally achieved better than 20 ppm H_2S outlet concentration, and always less than 40 ppm. AHI- 2 performed slightly better than AHI-1 and achieved approximately 10ppm H_2S concentration. These initial testing did not include SO_2 regeneration.

A longer test program, 27 cycles, was conducted with the addition of the SO_2 regeneration. As shown in Figure 3 excellent activity in terms of low outlet H_2S concentration was observed; concentrations below 20 ppm were consistently obtained, with many runs below 10 ppm. Interestingly, the later runs showed higher activity than the initial runs; starting at cycle 19, the initial concentrations were undetectable (below 1 ppm). No H_2S or SO_2 was detected during reductive regeneration indicating the absence of sulfation.

The SO_2 regeneration consisted of 3.5 hours of 10% SO_2 in nitrogen at 630^{o}C. There are no analytic data from this step, nor was elemental sulfur recovered from the small scale apparatus involved. The amount of regeneration accomplished with the SO_2 was estimated by difference from the O_2 regeneration data. Integration of the values for outlet SO_2 concentration gave an estimate of the amount of residual sulfur in the sorbent that was regenerated by the dilute air stream. By these calculations, the SO_2 regeneration resulted in up to 50 % regeneration to elemental sulfur.

Task 4: Sorbent Preparation and Characterization

This task provides support to each of the previous tasks. The following analytical techniques are used to characterize the fresh, sulfided and regenerated sorbents on an as needed basis.

1. X-ray Diffraction (XRD) for crystalline phase.
2. Surface area measurement using BET method.
3. Hg-porosimetry for pore volume, bulk density, average pore diameter and pore size distribution determination.
4. Atomic Absorption (AA) Spectrometry for elemental composition analysis.
5. 3-hole attrition tester for attrition measurement

FUTURE WORK

Work will continue to develop attrition-resistant zinc-oxide based sorbents for fluidized bed applications.

PUBLICATION/PRESENTATION

1. K. Jothimurugesan and S.K. Gangwal " Advanced Hot-Gas Desulfurization Sorbents for Transport Reactor" 1998 Spring National AIChE Meeting, New Orleans, LA, March 8-12, 1998.

2. K. Jothimurugesan and S.K. Gangwal., "Development of Advanced Hot-Gas Desulfurization Processes," Advanced Coal-Based Power and Environmental Systems '98 Conference, Morgantown, WV, July 21-23, 1998.

3. S.K. Gangwal, J.W. Portzer, T.P. Dorchak and K. Jothimurugesan, “Advanced Hot Gas Desulfurization Process with Sulfur Recovery,” Gas Cleaning at High Temperatures, Karlsruhe, Germany, September 22-24, 1999. Abstract Accepted.

Time Schedule for Year 3 (October 1, 1999 -September 30, 1999)

TASK	**Quarter**			
	1	2	3	4
Task1: Development of Sorbent For Sierra-Pacific	━	━	━	━
Task 2: Bubbling-Bed Reactor Sorbent				━
Task 3: Advanced Sulfur Recovery Sorbents		━	━	━
Task 4: Sorbent Characterization	━	━	━	━
Semi-Annual Report		✍		✍

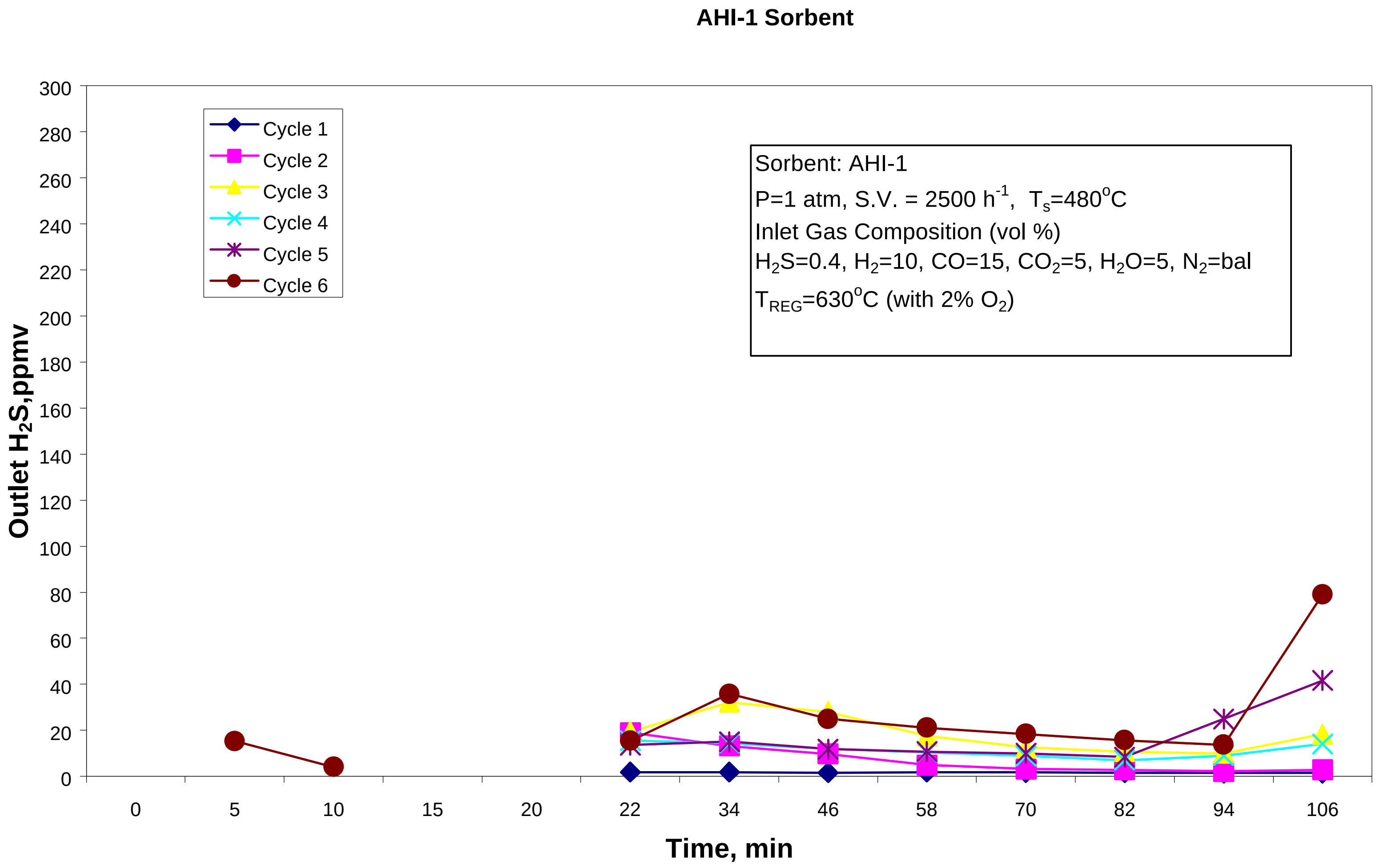

Figure 1. H_2S Breakthrough Curves in Successive Sulfidation Cycles of AHI-1 Sorbent

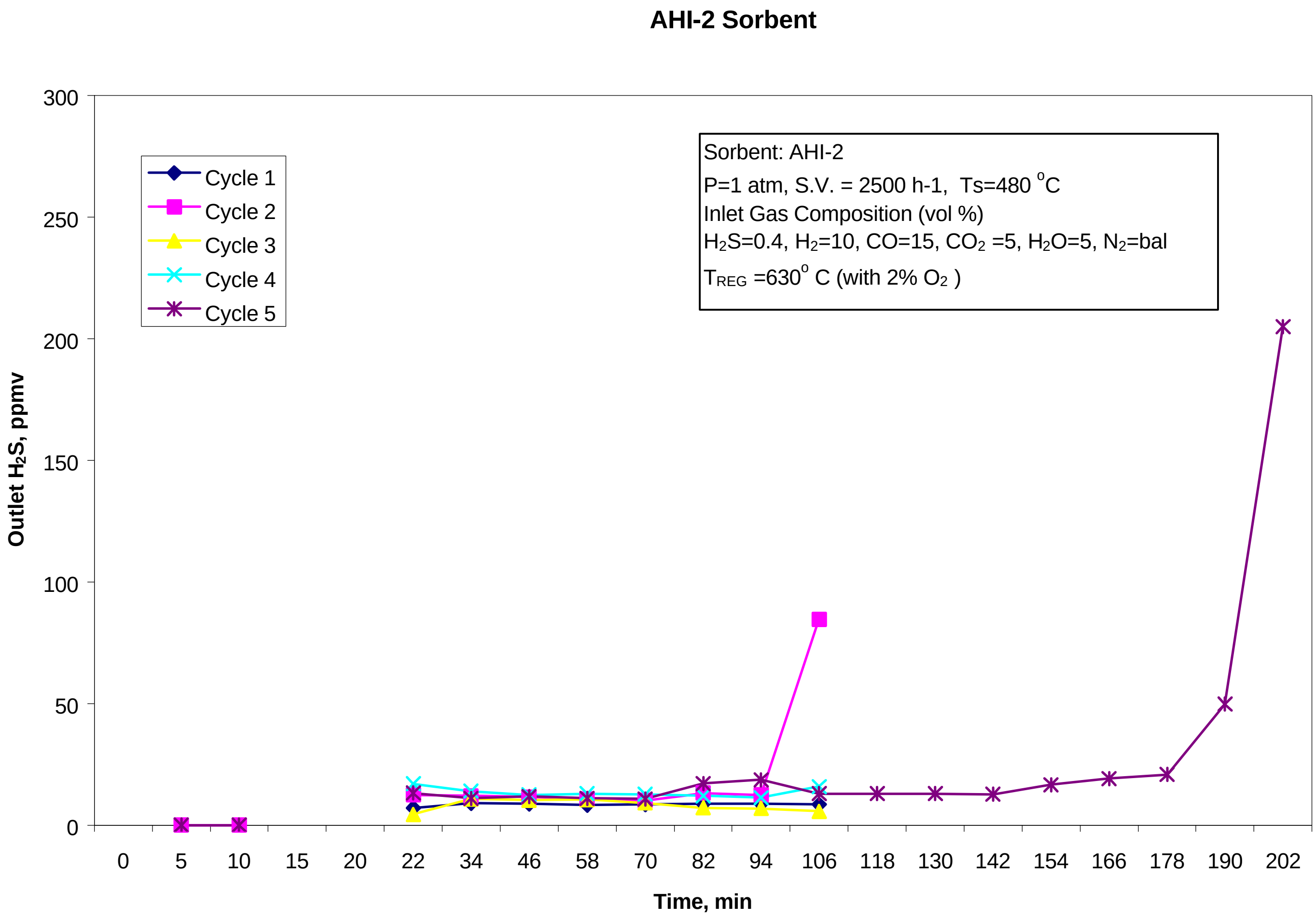

Figure 2. H_2S Breakthrough Curves in Successive Sulfidation Cycles of AHI-2 Sorbent

Figure 3. H_2S Breakthrough Curves in Successive Sulfidation Cycles of AHI-2 Sorbent