PHILLIPS SORBENT DEVELOPMENT FOR TAMPA ELECTRIC COMPANY AND SIERRA PACIFIC POWER COMPANY

Gyanesh P. Khare (gpkhare@bvemx.ppco.com; 918-661-9435)
Gary A. Delzer (gad@bvemx.ppco.com; 918-661-7995)
Gil J. Greenwood (gjgreen@bvemx.ppco.com; 918-661-3693)
Donald H. Kubicek (918-661-3148)
Phillips Petroleum Company
Corporate Technology
Bartlesville, OK 74004

ABSTRACT

Phillips Z-Sorb® sorbent will be used for startup at both Tampa Electric Company and Sierra Pacific Power Company Integrated Gasification Combined Cycle (IGCC) demonstration projects. Commercial preparations for these two applications required additional development to meet specific client needs. Tampa Electric required a presulfiding of the sorbent to facilitate startup. Sierra Pacific desired emphasis on operational flexibility and attrition. Procedures and test results from these commercial developments will be discussed.

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CONTRACT INFORMATION

Contract Number N/A

Contractor N/A

Other Funding Sources N/A

Contractor Project Manager N/A

Principal Investigators G. P. Khare
G. A. Delzer
G. J. Greenwood
D. H. Kubicek

METC Project Manager N/A

Period of Performance N/A

INTRODUCTION

Research and Development in IGCC technology will come to fruition in 1996 as two commercial demonstration projects undertake their startup operations. Tampa Electric Company has its Polk Power Station in Tampa, Florida, scheduled for August; Sierra Pacific Power Company's Piñon Pine station near Reno, Nevada, will begin in November. Phillips Z-Sorb® sorbent has been selected as the first load for each of these units. In the first case, a moving-bed sorbent Z-Sorb® III-M will be used in the TECO plant. This material is designed as a sphere with an average pellet diameter of about 4 mm. In the second case, the Piñon Pine site will use a fluid-bed sorbent with an average particle size of 175 μm.

APPROACH

Previous publications from us have disclosed the efforts in preparing and testing these two formulations of sorbent (1). The goal of the present paper is to discuss final development of each of these sorbents as commercially manufactured materials for use in the respective demonstration projects. From this scenario, it will be clear that commercial quantities of Phillips sorbent for hot gas cleanup systems are available in whatever forms are required. There are numerous options available to the end-user, depending on the particular need to remove hydrogen sulfide from a

coal gasification stream. A conclusion we have reached from our experience is that no single sorbent will suffice for every situation, and it is our goal to have a suite of sorbents available.

TECHNOLOGY

Phillips Petroleum Company has been engaged in testing its proprietary Z-Sorb® sorbent for a number of applications in which the removal of hydrogen sulfide is important. A new class of regenerable zinc based sorbents has been developed for the removal of hydrogen sulfide in the fuel gas that is produced in a clean coal technology power plant at moderate pressure (5-20 atm) and a broad range of operating temperatures (600-1000°F). Tests have been carried out in fixed-, moving-, and fluid-bed applications. All formulations have been successfully produced by commercial vendors.

ACCOMPLISHMENTS

Z-Sorb® Sorbent for Tampa Electric Company Polk Station

Sulfur capacity and mechanical strength were important parameters in the design of the moving-bed sorbent for the TECO Polk Station. Z-Sorb® III-M sorbent was tested by Phillips in a fixed bed unit under the guidelines of a protocol established by General Electric. Table 1 shows the relevant parameters for the test.

Table 1

Fixed Bed Testing of Z-Sorb® III-M Sorbent

Absorption
Bed Temp. (°F)	900
Absolute Pressure (atm)	20
Space Velocity (h^{-1})	1000 to 2000
Inlet H_2S (%)	3.3 to 3.6

Regeneration
Initial Bed Temp. (°F)	1050
Absolute Pressure (atm)	7
Oxygen Concentration (%)	2.2 to 3.3

Figure 1 depicts the loading curve that was measured during this test of fifteen cycles. There is a slight fall-off of sulfur capacity with cycle number, but the loading stayed above the design limit of 6 lb/ft^3 at the top of the bed. The low level at cycle 2 was attributed to incomplete regeneration after cycle 1. Once the regeneration scheme was adjusted, the loading recovered.
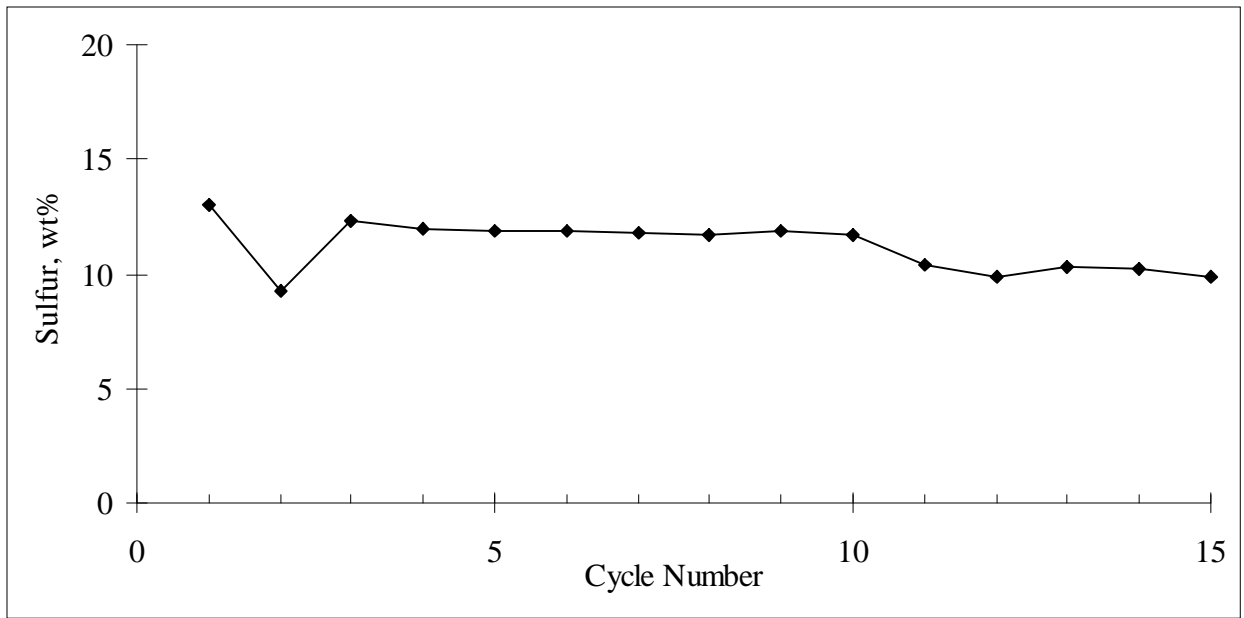
Figure 1. Loading curve of Z-Sorb® III-M Sorbent in Fixed-Bed Testing under GE Protocol.

The excellent performance of the sorbent is shown in Figure 2, which shows the breakthrough curves of hydrogen sulfide. Loadings are based on a 200 ppm breakthrough. Even after fifteen cycles, hydrogen sulfide stays low until just before breakthrough.
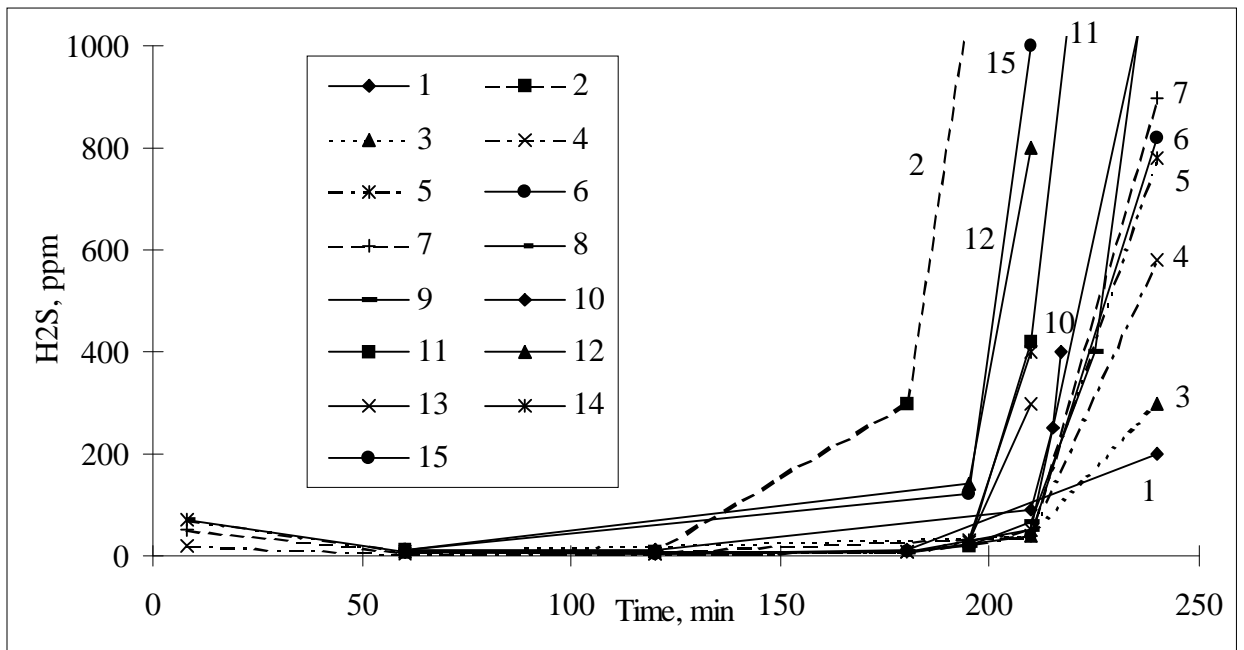

Figure 2. Breakthrough curves of Z-Sorb® III-M Sorbent in Fixed-Bed Testing under GE Protocol.

An additional critical feature of the sorbent was the attention given to dealing with the methanation reaction that may occur on the nickel-promoted Z-Sorb® sorbent when synthesis gas passes over it the first time. An exotherm approaching 200°F can take place (2). However, testing in the moving-bed pilot plant at the General Electric Corporate Research and Development site in Schenectady, New York, (3) did not show such an exotherm, but it was deemed desirable to make sure that such a heat release would not be a problem in the commercial plant. Initial pilot plant and lab tests at Phillips showed that using a low absorption temperature would keep this exotherm under control. An example of such a case is illustrated in the study mentioned above in which Z-Sorb® III-M sorbent was tested by Phillips in a fixed-bed unit. The sorbent was sulfided in-situ at 500°F in the first cycle, and there was no temperature rise in that cycle and only minor temperature increases in subsequent cycles at 900°F. Note, too, that at 500°F, the sulfur loading was 14 wt%. Secondly, since sulfur is a poison for the methanation reaction, we also verified that presulfiding the sorbent would minimize the methanation reaction. Table 2 illustrates the results that were found for controlling the methanation reaction and, hence, the exotherm. We examined cases in which the sorbent was presulfided ex-situ by treating with hydrogen sulfide at room temperature, incorporating a sulfur containing poison in the preparation procedure, and presulfiding using two different proprietary commercial techniques. The off-gas from a lab reactor was sampled and analyzed using mass spectrometry during the first cycle absorption run at 900°F using a simulated fuel gas.

Table 2

Control of Methanation Reaction in Z-Sorb® III-M Sorbent

Method	Methane, ppm	Sulfur Capacity, wt%
No pretreatment	1100	>10
Sulfiding with H_2S at room temperature	20	>10
Incorporation of sulfur poison during preparation	5	>10
Commercial method A	10	>10
Commercial method B	15	>10

It was judged not to be possible to sulfide the sorbent in-situ at ambient conditions while it was in the TECO reactor, so an ex-situ presulfiding route was chosen. In the final commercial preparation, we let the manufacturers develop their proprietary procedure to presulfide the sorbent, hence poisoning the methanation reaction. The reduced methane level translates into a lower exotherm for the large quantities of sorbent used in a commercial reactor. From the time of our initial discussions of the need to presulfide the sorbent until the time of delivery to TECO of the commercially presulfided material, only seven months had elapsed.

Z-Sorb® Sorbent for Sierra Pacific Power Company Piñon Pine Plant
Development of a fluid-bed sorbent for the Sierra Pacific Power Company plant initially centered on the issue of flexible operation, that is, ease of transporting the sorbent in the reactor. Once that matter had been settled, two additional characteristics evolved, namely attrition and low regeneration temperature. The attrition had to be fine-tuned so that proper transport control and

minimum make-up rate could be achieved. Regeneration temperature was an issue because it was desired to initiate the regeneration without requiring additional heat input to raise the sorbent temperature. By comparison, a moving-bed sorbent is heated at least 100°F in going from the absorption zone to the regeneration zone. Because of the nature of the work that was required, all testing was done at the Kellogg Technical Development Center. However, we tested several formulations of the fluid-bed sorbent in a bench scale reactor, and the sulfur capacities of two of these are given in Table 3. Formulation B is the one chosen for loading at the Piñon Pine plant, which provides an obvious advantage over the first fluid-bed formulation.

Table 3

Sulfur Capacities and Attrition Resistance of Fluid-bed Z-Sorb® Sorbent

Fluid-bed Sorbent	Sulfur Capacity[a], wt%	Attrition Resistance[b], %
Formulation A	12.8	91
Formulation B	18.0	99

[a]Average sulfur capacity over 20 cycles
[b]Measured in a 3-hole attrition tester (4)

FUTURE ACTIVITIES
We have earlier noted the adverse effect of steam regenerations at high temperatures (1400°F) on Z-Sorb® III sorbent (2). Phillips has undertaken an R&D program to develop enhanced steam resistant sorbents. The bench scale test results of one new fluid-bed formulation at atmospheric pressure and 1000°F temperature are shown in Figure 3. The activity of the new sorbent and Z-Sorb® III sorbent are compared. It is evident from this data that the new sorbent does not show any sulfur loading capacity loss when regenerated in air diluted with 42 vol% steam at 1200°F. At 1400°F, however, there is a 30% loss in capacity, but the residual capacity is still very high, estimated to be 16-17 wt% sulfur, in contrast to the Z-Sorb® III sorbent where a similar treatment resulted in a capacity of only about 6 wt%.
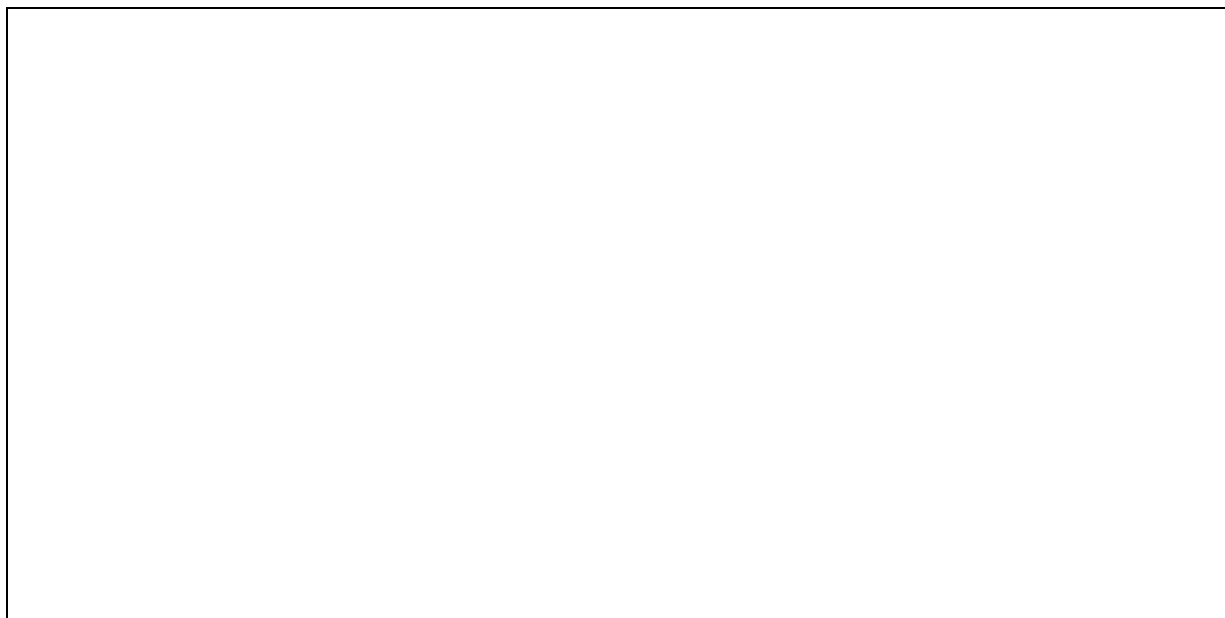
Figure 3. Sulfur Loading of Fluid-Bed New Generation Sorbent; Regeneration: 7.6% O_2/42.4% H_2O/50% N_2.

Figure 4 shows the reactivity of a 4 mm spherical sorbent at 900°F and 4 atm pressure. The sulfidation feed contained 3.4% H_2S, 20% water and the balance CO_2/N_2. Regenerations were conducted with a gas containing 4.6, 42.8, 52.4 vol% O_2, N_2 and H_2O, respectively and at 4 atm pressure. The new sorbent again exhibited superior resistance to steam and suffered no sulfur capacity loss in 1200°F steam regenerations while Z-Sorb® III sorbent lost a major portion of its capacity under the same conditions.
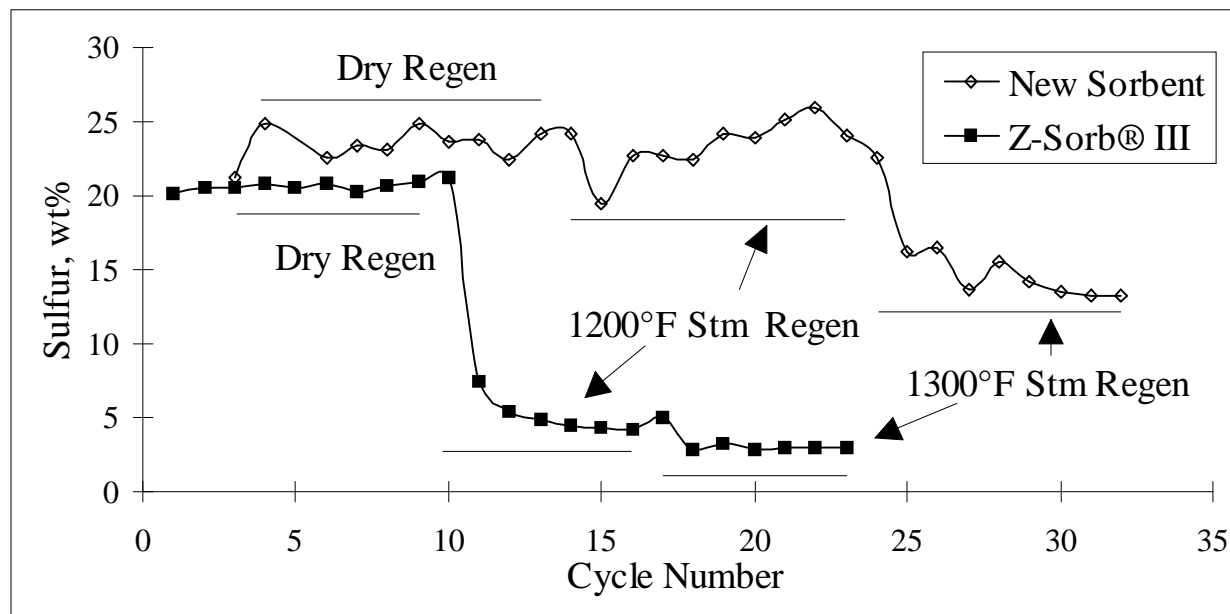

Figure 4. Effect of Steam Regeneration on Sorbents; Absorption: 900°F, 4 atm, 3.4% H_2S/20% H_2O/bal. CO_2-N_2; Regeneration: dry - 4.6% O_2; stm - 4.6% O_2/52.4% H_2O.

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4. Attrition resistance measured using a procedure similar to that described in USP 4,010,116.