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Desulfurization of Hot Fuel With Z-Sorb III Sorbent

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4.7 Desulfurization of Hot Fuel Gas With Z-Sorb III Sorbent

CONTRACT INFORMATION

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Period of Performance	February 1, 1993 to July 6, 1993

Schedules and Milestones

FY92 Program Schedule

	F	M	A	M	J	J
Test Plan	—					
Phase I	—					
Phase II		—				
Phase III			—			
Phase IV				—		
Data Analysis					—	

OBJECTIVES

The objective of this project is to evaluate regenerable sorbents for potential use in desulfurization of integrated gasification combined cycle (IGCC) fuel gas in a fixed bed operating at temperatures of 900-1200°F (482-649°C) and pressures up to 300-400 psia (2068-2758 kPa). Important evaluation criteria are adequate sulfur

absorption capacity, physical and chemical durability, and complete regenerability.

BACKGROUND

The Pinon Pine Power Project (Sierra Pacific Power Company) is one of the demonstration projects selected by the U.S. Department of Energy in their Clean Coal Technology Round IV program. The facility will be an integrated gasification combined

cycle (IGCC) plant which employs an air-blown KRW gasifier to produce a low-BTU fuel gas for combustion in a gas turbine. Detailed engineering design of the plant, which will be built near Reno, Nevada, is just beginning, with start-up anticipated in 1997.

As part of the design, a fixed-bed desulfurization system will be used to treat the fuel gas from the gasifier prior to combustion. Fuel gas feed to this unit will be at about 300 psia (2068kPa) and, nominally, 1000°F (538°C), although the actual absorption temperature can be varied somewhat to satisfy the final design constraints.

The original design of the desulfurization system was based on the use of zinc ferrite as the sorbent. In order to prevent carbon formation in the desulfurizer, a large quantity of steam must be added to the fuel gas. This has two major drawbacks. First, the heating value of the fuel gas is significantly reduced, making the gas more difficult to burn. Second, since the volume of gas is increased, the size and cost of the desulfurization system, as well as downstream equipment, also increases.

Experimental testing was begun to investigate potential alternatives to zinc ferrite. The first sorbent selected for evaluation was a zinc titanate formulation reputed to have the required characteristics. However, this material proved unable to withstand repeated cycling between absorption and regeneration, experiencing both physical and chemical degradation. Results of this phase of the project are reported by Mei et al, 1993.

Since the zinc titanate formulation tested was shown to be unsuitable for the intended application, a second alternative was sought for testing. The sorbent selected was Z-Sorb III, a proprietary material developed by the Phillips Petroleum Company. This sorbent has undergone extensive development through successful commercial

testing, albeit for a different application, and a specific formulation was immediately available for our test unit. The test program was begun in February and was completed in late May of this year.

PROJECT DESCRIPTION

The experimental tests were conducted at the Morgantown Energy Technology Center in their high pressure bench-scale hot gas desulfurization unit, which contains a 2" (5.1 cm) ID reactor system. A complete description of this unit is contained in Mei et al, 1993.

Like zinc ferrite and zinc titanate, Z-Sorb III is also a zinc oxide-based sorbent wherein zinc oxide and a promoter are supported on a proprietary matrix designed to provide stability and prolong the sorbent life. Phillips supplied the sorbent in cylindrical form, the pellets being somewhat variable in size but generally 1/8" (0.32 cm) diameter by 1/4-3/8" (0.64-0.95 cm) long. The sorbent is surprisingly light, having a bulk density of roughly 55 lb/ft³ (0.88 gms/cc), or about 1/3 less than the zinc titanate sorbent.

In general, the test procedures and conditions paralleled those used in the zinc titanate test program. A 16" (0.41 m) deep fixed bed of sorbent was subjected to alternating periods of sulfidation and regeneration. Sulfidation was accomplished by feeding a gas, which simulated the expected KRW fuel gas composition, in a downflow mode through the reactor. The gas was produced by blending of individual, metered components upstream of the reactor system. Sorbent regeneration was done in the reverse direction (upflow), using air diluted with nitrogen or nitrogen/steam to control the regeneration exotherm and limit regeneration temperatures to less than 1400°F (760°C).

The test program was divided into four phases. Phase I was essentially a screening or feasibility study and consisted of a relatively

short series of complete sulfidation-regeneration cycles. The intent was merely to verify the sorbent as a viable candidate for the intended application. Phase II was a longer term multi-cycle test designed to demonstrate durability and regenerability of the sorbent. A fifteen-cycle test was deemed adequate for this purpose. During this phase, a variety of regeneration techniques were tried, including substitution of steam for a portion of the nitrogen, which was used exclusively in Phase I, as the diluent.

Parametric tests of sulfidation variables were done in Phase III. The major variables investigated were gas velocity (0.5-2.0 fps) (0.15-0.61 mps) and absorption temperature (900-1100°F) (482-593°C). Work continued on regeneration techniques during this phase with the purpose of identifying the most cost-effective method for the commercial reactor. This phase ended with an abbreviated absorption for the last cycle to measure the sulfur loading profile along the reactor length.

Phase IV of the test program was included to examine the effects, if any, of small quantities of HCl in the feed gas. A total of seven cycles were completed.

The test program ended with a single sulfidation at the same conditions run during Phase I. This permitted a direct comparison of a relatively fresh sorbent with one that had been subjected to a wide variety of test conditions over an extended period of time. Differences in sulfur capacity as well as physical characteristics are an indication of sorbent durability.

RESULTS

Phase I

The screening runs consisted of 4 complete sulfidation/regeneration cycles, followed by a final sulfidation. Each

sulfidation and regeneration repeated the initial run conditions.

The sulfidations were run at, nominally, 1000°F (538°C) and 150 psia (1034kPa), using a feed gas containing 800ppmv H₂S. This concentration yields a partial pressure of H₂S equivalent to what is expected in the commercial reactor, which is expected to operate at an inlet H₂S concentration of 400ppmv but at twice the total pressure (300psia) (2068kPa). The lower pressure was selected for these tests to simplify operation and to minimize gas consumption. The superficial gas velocity for all sulfidations was maintained at 1.0 fps (0.30 mps).

The outlet H₂S concentration was monitored using detector tubes, and each test was run for several hours beyond the point where the concentration reached approximately 800ppmv, to ensure high sorbent utilization. The final sulfidation was run for an even longer time at the 800ppmv exit H₂S concentration to fully saturate the sorbent.

All regenerations were done at 25 psia (172 kPa), which is the pressure to be used in the commercial design. Gas velocity was maintained constant at 1.0 fps (0.30 mps). A multi-stage technique, from the prior zinc titanate work, was used initially. With nitrogen as the diluent gas, the oxygen concentration was increased in discreet increments from 0.5 mole % to 21 mole % while simultaneously increasing the bed temperature from 1000 to 1400°F (538-760°C). The exit gas was monitored for SO₂, using detector tubes. All regenerations were run until the SO₂ concentration dropped to less than 50ppmv.

During the first stage of regeneration, at an oxygen concentration of 0.5 mole % and an initial bed temperature of 1000°F (538°C), there was very little evolution of SO₂. Almost all of the SO₂ was evolved during the second stage of regeneration, in which the initial bed temperature was raised

to approximately 1100°F (593°C) while increasing the oxygen concentration to 2.5 mole %. This is clearly indicated not only by the rapid increase in SO₂ concentration to 1.3-1.5 mole %, but also by a large exotherm which is propagated along the bed. Subsequent regeneration stages, in which both bed temperature and oxygen concentration were increased, showed flat bed temperature profiles as well as very low outlet SO₂ concentrations. However, ramping of oxygen concentration and bed temperature ensured as complete a sorbent regeneration as possible.

Results of the five sulfidation runs (1-S1 to 1-S5) are shown in Figure 1, where outlet H₂S concentration is plotted against time. For all of these runs, H₂S removal was virtually complete for at least 6 hours. After the first sulfidation, which showed slightly higher sulfur capacity, the sorbent stabilized and demonstrated good, reproducible performance. This is also an indication of complete regeneration.

The sorbent was removed from the reactor after the fifth sulfidation. The pellets were intact, showing no visible signs of dusting or any other kind of physical deterioration. Analysis of the sorbent by Phillips showed sulfur loadings of 14.3% and 13.6% on pellets from the top (inlet) and bottom (outlet) of the reactor, respectively. This is more than 60% of the theoretical loading of about 22% and is significantly higher than the maximum loadings achieved with the zinc titanate sorbent previously tested.

These tests also identified other sorbent characteristics worth noting. For this series of tests only, a small quantity (100 ppmv) of carbonyl sulfide (COS) was added to the feed gas. Gas chromatograph data show that the COS is also effectively removed from the gas. Outlet COS concentrations paralleled the H₂S concentrations.

The gas analytical data also indicate little or no sorbent catalytic activity towards

Figure 1. Sulfidation Breakthrough Curves - Test Series 1

the water gas shift reaction. The simulated fuel gas feed corresponds to an equilibrium composition near gasifier conditions, but little change in gas composition was seen across the Z-Sorb bed.

Phase II

Phase II tests were primarily intended to demonstrate sorbent durability over an extended number of cycles. A second objective was to investigate various regeneration techniques, especially the use of steam as a diluent. Regeneration with steam is highly desirable since it is readily available in a commercial unit and represents the least costly option for regeneration.

Tests were begun with a fresh batch of sorbent loaded into the reactor. In order to expedite testing and reduce the cycle time, two changes were made to the test conditions used in Phase I. For the sulfidation runs, the inlet H_2S concentration was increased to 2000ppmv to load the sorbent faster.

Additionally, the regeneration cycle was simplified to a single stage, with the oxygen concentration maintained at 2.5 mole %, since prior tests showed that virtually all of the SO_2 was evolved at this concentration. The initial bed temperature was set at 1075°F (579°C), giving a peak temperature of about 1350°F (732°C) as the regeneration exotherm passed through the bed. At the end of each regeneration, the bed temperature was increased and held at 1400°F (760°C) for several hours to ensure complete regeneration.

The first six complete cycles were run essentially in this manner. Plots of exit H_2S concentrations for these sulfidation runs (2-S1 to 2-S6) are shown in Figure 2. Although not conclusive, sorbent performance appeared to deteriorate throughout these runs. For example, H_2S leakage at 200ppmv in run 2-S6 occurred about one hour earlier than in run 2-S1. Regeneration during these cycles used nitrogen dilution.

Figure 2. Sulfidation Breakthrough Curves - Test Series 2: Performance at 2000 ppmV Inlet Concentration

In order to get a direct comparison with Phase I results, and to determine whether or not the sorbent capacity had been reduced, it was decided to lower the inlet H_2S concentration back to 800 ppmv. This concentration was used for the remainder of the test program.

Beginning with the seventh regeneration (2-R7), and continuing for six regeneration cycles, steam was added to the regeneration gas. For experimental reasons, it was limited to 50 mole %, whereas in the commercial unit it would be the sole diluent used. During this group of tests, the regeneration conditions were varied to include a lower oxygen concentration (1.5 mole %) as well as a lower initial bed temperature (1000°F) (538°C). The final high temperature (1400°F) (760°C) period was abandoned, since prior tests showed adequate regeneration could be achieved without this "soaking" period.

2-S15 are presented in Figure 3. Also plotted are the data from the first sulfidation in Phase I, run 1-S1. Comparing the latter with 2-S7, it is clear that the sorbent capacities are the same, indicating that the sorbent had not deteriorated during the first six sulfidations in Phase II.

Comparison of runs 2-S7 through 2-S13 show a definite and consistent loss in sorbent capacity. This can be attributed to the steam used during regeneration. Steam at high temperatures is known to have a detrimental effect on metal oxides (Leach, 1984). Moderating the regeneration conditions by lowering initial bed temperature and oxygen concentration (2-R10,11,12) did not stabilize the sorbent. Capacity continued to decrease in successive runs.

Following run 2-S13, the sorbent was regenerated without steam present. Two additional sulfidation tests, 2-S14 and 2-S15, were done. The results of these tests, also shown in Figure 3, show a constant, stabilized

Results from sulfidations 2-S7 through

Figure 3. Sulfidation Breakthrough Curves - Test Series 2: Effect of Steam Regeneration on Sulfidation Performance

sorbent capacity, thus confirming that steam in the regeneration gas is detrimental.

Phase III

Phase III consisted of a series of parametric tests to evaluate the effects of two primary sulfidation variables: bed temperature and superficial gas velocity. Bed temperature was varied between 900°F (482°C) and 1100°F (593°C) and gas velocities of 0.5-2.0 fps (0.15-0.61 mps) were used. The inlet H₂S concentration was maintained at 800 ppmv for all of these tests. In addition, some work was done on variations in regeneration conditions, primarily to see if regeneration could be accomplished at initial bed temperatures significantly lower than the 1075°F (579°C) temperature normally used during the tests.

A fresh batch of sorbent was loaded into the reactor and used for the remainder of the test program. After Phase III was completed, the sorbent was removed from the

reactor for sampling, and then returned to the reactor.

A series of twelve cycles were included in Phase III. Sulfidation tests were generally run until the outlet H₂S concentration exceeded 400 ppmv. The last sulfidation, 3-S12, was deliberately abbreviated when the outlet concentration exceeded 20 ppmv.

Most of the sulfidation tests were done at a gas velocity of 1.0 fps (0.30 mps). Results of tests at this velocity in which temperature was varied are given in Figure 4, where the outlet H₂S concentration is plotted against an adjusted time. At a fixed velocity, the quantity of H₂S flowing through the reactor is inversely proportional to the absolute temperature. Consequently, the time coordinate has been adjusted by the ratio of absolute temperatures to show results on a common basis.

Comparison of the adjusted curves shows that temperature, over the range of

Figure 4. Sulfidation Breakthrough Curves - Test Series 3: Effect of Bed Temperature on Sulfidation Performance

900°F (482°C) to 1100°F (593°C), has little effect on the absorption rate of H₂S. This implies that the rate is diffusion limited, as might be expected. This is a useful result, since it allows flexibility in selection of the absorption temperature for the commercial reactor to match other design criteria.

Results of several tests at 1100°F (593°C), at varying superficial velocities, are shown in Figure 5. Noticeable breakthrough of H₂S for the two higher velocities (1.5, 2.0 fps) (0.46, 0.61 mps) occurs fairly rapidly, indicating that the wave front (variable sorbent loading and gas concentration through the reactor) exceeds the reactor depth of 16" (0.41 m). Data from the lower velocity runs (0.5, 1.0 fps) (0.15, 0.30 mps) show much longer breakthrough times, indicating that the sorbent at the reactor inlet may be saturated, or close to saturation. It should be kept in mind that these data correspond to a 16" (0.41 m) deep experimental bed. At breakthrough, the experimental bed represents essentially the

end segment of the bed in a commercial reactor, which is expected to have a bed depth on the order of 20 feet (6.1 m). The remainder of a commercial reactor bed would be fully loaded at some saturation value.

Test 3-12 was run at 1000°F (538°C) and a gas velocity of 1.0 fps (0.30 mps). As mentioned, this test was deliberately stopped at a low outlet H₂S concentration (actual final detector tube reading was 70 ppmv). This was done in order to get a sorbent loading profile across the experimental bed. The depth of this profile is useful for estimating overall sorbent utilization in a commercial system. A sharp loading profile (short wave front) indicates that a high overall sorbent utilization, approaching saturation, can be used for design.

Analyses by Phillips of sulfur loadings on sorbent samples taken after this test were completed are plotted in Figure 6. Sulfur loadings vary from 11-12% at the reactor inlet to 2.5% at the outlet, and the variation

Figure 5. Sulfidation Breakthrough Curves - Test Series 3: Effect of Gas Velocity on Sulfidation Performance

Figure 6. Sorbent Loading Profile - 3-S12

is almost linear. The high loading at the inlet shows that the sorbent is virtually saturated. Thus, the wave front appears to be approximately equal to the reactor depth (16") (0.41 m), at this velocity.

Two regenerations were done at low initial bed temperatures, 900°F (482°C) and 975°F (524°C). Peak temperatures did not reach 1300°F (704°C) during either run. Although the initial regeneration period was similar to those done at higher bed temperatures, regeneration was incomplete. After the initial, but relatively short, period of high outlet SO₂ concentrations, the concentration decayed quite slowly, and it is suspected that a significant amount of sulfur remaining in the bed was oxidized to zinc sulfate, rather than SO₂. However, since the sorbent was not removed from the reactor after this test, this could not be confirmed by sorbent analysis.

Phase IV

The final phase of the test program was included primarily to investigate the effects of small quantities of HCl in the fuel gas feed. A series of seven sulfidation tests were run with 50 ppmv HCl in the gas. A bed temperature of 1000°F (538°C) and a gas velocity of 1.5 fps (0.46 mps) were used for all tests. The inlet H₂S concentration of 800 ppmv was continued. Sorbent regenerations were done at a gas velocity of 1.0 fps (0.30 mps), using a 2.5 mole % oxygen concentration and an initial bed temperature of 1075°F (579°C).

Measurements were made for chloride in the condensates from the sulfidations and are summarized in Table 1. Virtually all of the chloride in the feed gas passes through the reactor. Material balance closures are quite good, within 20%.

The condensates were also analyzed for zinc, and these measurements are also included in the table. It appears that zinc

**Table 1. Chloride and Zinc Measurements
Tests 3-S1 to 3-S19**

Run No	Cl in (g)	Cl out (g)	Total out(g)	% Closure		Zn in condensate (ppm)
3-S13	5.70	6.68	6.70	117		17.3
3-R13	-	0.02				-
3-S14	5.17	5.28	5.30	102		4.4
3-R14	-	0.02				-
3-S15	5.27	5.96	5.99	114		5.0
3-R15	-	0.03				-
3-S16	4.60	5.27	5.28	115		3.9
3-R16	-	0.01				-
3-S17	4.89	4.13	4.14	85		0.94
3-R17	-	0.01				-
3-S18	4.09	4.37	4.37	107		1.7
3-R18	-	0.01				-
3-S19	4.42	3.80	3.81	86		7.4
3-R19	-	0.01				-
3-S1 to 3-S12 (no HCl)					avg	1.04

losses during these runs might be higher than losses during runs in which no HCl was present in the gas. Spent sorbent samples are being analyzed for zinc content and distribution to confirm this observation.

The final run in the test program, 3-S20, was a duplicate of the runs in Phase I, to allow direct comparison between fresh sorbent and sorbent that had been exposed to a wide variety of test conditions. A comparison of 3-S20 with the Phase I sulfidation tests is given in Figure 7. It is apparent that there is a significant loss in sorbent capacity as a result of extended cycling under varying conditions.

Sorbent removed from the reactor after the final test was analyzed by Phillips for sulfur content. Loadings were 9.0% at the reactor inlet and 3.8% at the outlet. Additional analyses are being done to confirm these values.

On the basis of detector tube readings, average sulfur loadings were calculated for each of the 20 runs with this batch of sorbent. Results are shown in Figure 8. Although the absolute values calculated on this basis are only approximate, it is believed that the trend shown is correct. There was a continual decline in loading as the runs proceeded and, in general, this appears to be independent of the run conditions. The lack of dependence on run conditions may be due to the fact that all of these tests were continued until the outlet H₂S concentration exceeded 400 ppmv, thereby approaching sorbent saturation. The reason for the low loadings for runs 5 and 6, both of which were done at 0.5 fps (0.15 mps), is not known. The low loading in run 10 resulted from incomplete regeneration during the prior regeneration step as well as the high velocity (2.0 fps) (0.61 mps) used during this absorption.

It is not clear whether the sorbent had stabilized by the end of the test program. The last run, which was continued for about 4

Figure 7. Sulfidation Breakthrough Curves - Test Series 1 & 3: Comparison of Fresh vs. Aged Sorbent

Figure 8. Change in Sorbent Performance During Test Series 3

hours after the sorbent appeared to be saturated (leakage of H_2S of 800ppmv), produced only a 3.8% loading on the sorbent at the reactor outlet.

FUTURE WORK

It is recommended that the following areas be explored in future work:

1. Improved steam resistance
2. New formulations with different promoters
3. Absorption tests on larger pellets
4. Reactor modeling studies.

Additionally, it would be worthwhile to consider Z-Sorb III as a candidate sorbent material in some of the fluid bed and entrained reactor systems now being developed for hot fuel gas desulfurization.

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