Durable Zinc Oxide-Based Regenerable Sorbents for Desulfurization of Syngas in a Fixed-Bed Reactor

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Abstract

A fixed-bed regenerable desulfurization sorbent, identified as RVS-1and developed by researchers at the U.S. Department of Energy's National Energy Technology Laboratory, was awarded the R&D 100 award in 2000 and is currently offered as a commercial product by Süd- Chemie Inc. An extensive testing program for this sorbent was undertaken which included tests at a wide range of temperatures, pressures and gas compositions both simulated and generated in an actual gasifier for sulfidation and regeneration. This testing has demonstrated that during these desulfurization tests, the RVS-1 sorbent maintained an effluent H_2S concentration of <5 ppmv at temperatures from 260 to 600 ^{0}C (500-1100 ^{0}F) and pressures of 203-2026 kPa(2 to 20 atm) with a feed containing 1.2 vol% H_2S. The types of syngas tested ranged from an oxygen-blown Texaco gasifier to biomass-generated syngas. The RVS-1 sorbent has high crush strength and attrition resistance, which, unlike past sorbent formulations, does not decrease with extended testing at actual at operating conditions. The sulfur capacity of the sorbent is roughly 17 to 20 wt.% and also remains constant during extended testing (>25 cycles). In addition to H_2S, the RVS-1 sorbent has also demonstrated the ability to remove dimethyl sulfide and carbonyl sulfide from syngas.

During regeneration, the RVS-1 sorbent has been regenerated with dilute oxygen streams (1 to 7 vol% $O_{2)}$ at temperatures as low as 370^{0}C (700^{0}F) and pressures of 304-709 kPa(3 to 7 atm). Although regeneration can be initiated at 370 ^{0}C (700^{0}F), regeneration temperatures in excess of 538 ^{0}C (1000 ^{0}F) were found to be optimal. The presence of steam, carbon dioxide or sulfur dioxide (up to 6 vol%) did not have any visible effect on regeneration or sorbent performance during either sulfidation or regeneration.

A number of commercial tests involving RVS-1 have been either conducted or are planned in the near future. The RVS-1 sorbent has been tested by Epyx, Aspen Systems and McDermott

Technology (MTI), Inc for desulfurization of syngas produced by reforming of hydrocarbon liquid feedstocks for fuel cell applications. The RVS-1 sorbent was selected by MTI over other candidate sorbents for demonstration testing in their 500-kW ship service fuel cell program. It was also possible to obtain sulfur levels in the ppbv range with the modified RVS-1 sorbent.

I Introduction

Development of a suitable regenerable sorbent is one of the major barrier issues in the gas cleanup program for Integrated Gasification Combined-Cycle (IGCC) systems (Lew et al. 1989). A series of novel sorbents containing zinc oxide were developed at NETL to address these problems (Siriwardane 1996, 1997, 1999). These NETL-developed sorbents showed excellent performance during 20-cycle high-pressure fixed-bed tests with steam regeneration, and a 50-cycle high-pressure fixed-bed test with dry regeneration. In addition, one of the sorbents (RVS-1) was tested in the moving bed reactor at the General Electric (GE) pilot plant. Despite several operational problems at the facility, promising results were obtained during the testing. The RVS-1 sorbent was tested in a fixed bed for 25 sulfidation/regeneration cycles at Research Triangle Institute (RTI) under regeneration conditions that closely simulated those encountered at the Tampa Electric Co./Clean coal technology (TECO/CCT) project (Siriwardane et al. 1998). The performance of the sorbent was excellent under these conditions, and it exceeded all the performance criteria required for the TECO/CCT project. The RVS-1 sorbent was tested at lower temperatures to determine whether it was suitable for low-temperature applications (Siriwardane 1998). The sorbent had an excellent sulfur capacity, even at 260EC (500EF).

A systematic study to understand the effect of temperature, pressure, gas composition, and H_2S concentration on the performance of RVS-1 sorbent was conducted, and the results of this study are discussed in this paper.

With increased interest in fuel cells and in co-production of chemicals and electricity, the need to reduce sulfur levels to ppbv(sub ppmv) range in the syngas has increased. Several compositional modifications were made to the RVS-1 sorbent and the modified sorbent was tested to evaluate the potential for achieving sulfur removal to ppb level (Turk and Gupta, 2000). Successful test results of a 20-cycle test conducted at RTI, with the modified sorbent will be discussed in this paper.

The RVS-1 sorbent has shown promising results with many commercial applications. McDermott Technology (MTI), Inc is developing a new form of power generation utilizing fuel cells for shipboard applications under a contract from the Office of Naval Research and the Naval Sea Systems Command. The diesel fuel is combusted and reformed as the fuel for the fuel cell. Since the diesel fuel contains sulfur and fuel cell components are extremely sensitive to even minute levels of sulfur a desulfurization sorbent was critically required. A regenerative desulfurizer was important for meeting aggressive size and weight targets for the generator. Research Triangle Institute conducted laboratory-scale testing, and the results showed its capability in reducing the sulfur concentration to <5 ppmv under MTI conditions (Privette et al. 1999). The tests showed that the sorbent easily met the MTI specifications and some of those successful test results are discussed in this paper. As a result, RVS-1 sorbent was incorporated into the MTI:S 2.5 kWe fuel cell design and a demonstration test was conducted by MTI. Test results from the 100-hour demonstration of the regenerable desulfurizer with RVS-1 sorbent showed effective removal of hydrogen sulfide from the synthesis gas and effective regeneration of the sorbent.

II Experimental

The RVS-1 sorbent was developed by NETL in-house researchers. Süd Chemie prepared the RVS-1 sorbent under guidance from NETL using equipment large enough to produce a sorbent batch with the physical and chemical characteristics that would be obtained for a commercially prepared sorbent batch. This sorbent was supplied as 3-mm ellipsoidal pellets. The RVS-1 sorbent is commercially available from Süd Chemie.

II.A Effect of Various Experimental Parameters on the Performance of the RVS-1 Sorbent

The fixed-bed tests were conducted at RTI to understand the performance of the sorbent at various temperatures, pressures and gas compositions. Sulfidations were performed at both 538 EC (1,000 EF) and 260 EC (500 EF) using simulated TECO coal gas (35.8% vol. CO, 12.2% CO_2, 26.8% H_2, 18.1% steam, and 5.95% nitrogen). The pressures during sulfidations were 243, 1,134, and 2,026 kPa (2.4, 11.2, and 20 atm). Regeneration was performed at 243 kPa (2.4 atm) with 3.5% O_2 at 566 EC (1,050 EF). Space velocity during sulfidation and regeneration was 2,000 hr^{-1}. Two and half cycle tests were conducted, and physical and chemical characteristics of the solid samples were determined after the third sulfidation. The sorbent was loaded up to 6.7 lb/ft^3 during sulfidations, but the last sulfidation cycle was conducted until the breakthrough (2000 ppmv H_2S).

II.B Performance of the modified RVS-1 Sorbent for ppb level sulfur removal efficiency

RVS-1 sorbent was modified to obtain sulfur removal efficiency in the ppb range. The modified sorbent was tested at RTI for 20 cycles. Sulfidation was conducted at 350 ^{0}C (600 ^{0}F), and at 2026 kPa(20 atm) utilizing syngas with a composition of 35.8%CO, %11CO_2, 44.9%$H_{2,}$and 6.3-8.1%$N_{2,}$ and containing 2000-20,000 ppmv of H_2S. During the first 19 cycles, syngas with 2000 ppm H_2 S was utilized for 240 min at 1000 hr-1 STP, followed by syngas with 20,000 ppmv H_2S at 2000 hr-1, until the effluent sulfur content exceeded 100 ppmv. The increase in H_2S concentration after 240 min was conducted to expedite the breakthrough (saturation of the sorbent). In cycle 20, syngas with 2000 ppm of H_2S was maintained for 480 min. Hewlett Packard 6890 gas chromatograph equipped with a model 355 Sievers sulfur chemiluminescence detector was used to measure the sulfur concentration. Regeneration was performed at 649 ^{0}C (1200 ^{0}F), at 230 kPa(2 atm), at 2000 hr-1 and with 98% N_2 and 2% O_2.

II.C RVS-1 Sorbent tests for McDermott Technology (MTI), Inc. Ship Service Fuel Cell Program

The fixed bed sorbent tests were also conducted at RTI at conditions suitable for the desulfurization of syngas produced by reforming of hydrocarbon liquid feeds at McDermott Technology (MTI), Inc. The composition of the gases usedfor sulfidation was 8.0 vol.% CO, 8.0% CO_2, 25% H_2, 36% steam, 800-10000 ppm H_2S and 22-22.92% N_2. Regeneration was performed with 10% CO_2, 19% H_2O, 68-68.5% N_2 and 2.5-3% O_2. The sulfidation was conducted at both 315 and 482 ^{0}C, at space velocities of 2000 and 6000 hr^{-1}and at 412 kPa(4 atm). Regeneration was performed at 565 ^{0}C, 239 kPa(3.3 atm), 2000 hr-1 at STP.

III Results and Discussion

III. A Effect of Various Experimental Parameters on the Performance of the RVS-1 Sorbent

The effects of H_2S concentration, pressure and temperature on the performance of sulfidation of RVS-1 sorbent are discussed below. Prior to the breakthrough (200 ppmv H_2S) the sulfur removal efficiencies in all these experiments were below 5 ppmv.

Effect of H_2S Concentration on Sulfidation

The breakthrough (200 ppmv H_2S) times for the third sulfidation and the calculated sulfur loading values at the breakthrough with varying H_2S concentrations at 243 kPa are shown in Table 1. It is interesting to see that the concentration of the inlet gas has a major effect on the breakthrough time and the sulfur loading at 243 kPa. It was possible to obtain a higher sulfur loading at lower H_2S concentration.

Table 1
Breakthrough Times for Third Sulfidations
and Calculated Sulfur Loading of the Reactor Bed at 243 kPa and 538 ^{0}C

H_2S Concentration (ppm)	Breakthrough Time (min)	Calculated Sulfur Loading of the Bed (wt.%)
2,000	2,100	13.9
7,000	350	7.5
12,000	222	7.7

Effect of Pressure on Sulfidation

The breakthrough times and the calculated sulfur loading values from the breakthrough curves at different pressures are shown in Table 2. It is evident that the pressure has a significant effect on the sulfur uptake of these sorbent pellets. At higher pressures (1,134 and 2,026 kPa), the sulfur uptake values with 12,000 ppm H_2S are considerably higher than those at 243 kPa. This indicates that the diffusion of H_2S to the interior of the pellet is enhanced at higher pressure.

Table 2
Breakthrough Times and Calculated Sulfur Loading Values
at Different Pressures with 12,000 ppm H_2S

Pressure (kPa)	Breakthrough Time (min)	Calculated Sulfur Loading (wt.%)
243	222	7.7
1,134	450	17.1
2,026	400	15.3

Effect of Temperature on Sulfidation

The breakthrough times and calculated sulfur loading values at both 538 EC (1,000 EF) and 260 EC (500 EF) with 12,000 ppm H_2S at 2,026 kPa are shown in Table 3.

Table 3
Breakthrough Times and Calculated Sulfur Loading Values
at Different Temperatures

Temperature (EC)	H_2S Concentration (ppm)	Breakthrough Time (min)	Calculated Sulfur Loading (g)
260	2000	2,500	16.5
260	7000	400	8.3
260	12,000	250	8.6
538	12,000	400	15.3

It is clear that the sulfur uptake is lower at 260 EC (500 EF) than at 538 EC (1,000 EF) when the concentration of H_2S is 12,000 ppmV. However, at 260 EC (500 EF) a higher sulfur uptake can be achieved at a lower concentration (2000 ppmv) of H_2S. At 538 EC (1,000 EF) the sulfur uptake was only sensitive to the H_2S concentration when the sulfidation was performed at lower pressure, but not at higher pressure (1,134 and 2,026 kPa). However, the sulfur uptake is sensitive to concentration of H_2S even at high pressure (2,026 kPa) when the sulfidation was performed at 260 EC (500 EF). The sorbent pellets were better utilized for sulfidation with 2,000 ppmv of H_2S at 260 EC (500 EF), and it was possible to achieve a sulfur loading of 17 wt. %. This indicates that there was a higher diffusional resistance at lower temperature when the H_2S concentration was high, but sulfur uptake similar to that at 580 EC (1,000 EF) can be achieved at 260 EC (500 EF) by lowering the H_2S concentration to 2,000 ppmv.

III.B Performance of the modified RVS-1 Sorbent for ppb level sulfur removal efficiency

The effluent concentration of H_2S for the first 240 min of sulfidation with 2000ppm H_2S at 316 ^{0}C(600 ^{0}F) for each of the 20 cycles with the modified RVS-1 sorbent are shown in Figure 1. During the first 30 min of sulfidation, the H_2S effluent concentration increased to a short maximum of 1.2 ppmv and dropped below 500 ppbv for the remainder of the sulfidation. Recent tests have indicated that these initial small ppmv level sulfur spikes can be eliminated by incorporating a reductive regeneration step prior to the sulfidation as shown in Figure 2. The total sulfur loaded (calculated from breakthrough curves) during sulfidation were between 24 and 26 g for the first six cycles, but decreased to a stable value of 20 g after cycle 6. The sulfur content of the sorbent measured with a LECO sulfur analyzer at the gas inlet location was 6.0 wt.%. Higher sulfur loadings may be achieved if the inlet H_2S concentration was not increased to 2% in order to get a faster breakthrough. The crush strength of the fresh sorbent was 14.7 lb/pellet and it increased to 22.7 lb/pellet after sulfidation.

III.C RVS-1 Sorbent tests for McDermott Technology (MTI), Inc. Ship Service Fuel Cell Program

Muti-cycle sulfidation and regeneration tests were performed with RVS-1 sorbent to understand the performance of the sorbent over a range of sulfidation space velocities as high as 6000 hr-1 and sulfidation temperature range of 316-482 ^{0}C (600-900 ^{0}F) at a pressure of 412 kPa (4 atm). The sulfidation gas consisted of a large amount of water (36%) which is not favorable for the sulfidation equilibrium. During the multi cycle test, the RVS-1 sorbent successfully removed the sulfur to 10 ppm level from the reformate gas stream. It is crucial to have the regeneration time faster than the sulfidation time for a two-bed regenerable desulfurizer. The regeneration time was about 2 hours, which was considerably lower than the sulfidation time. Thus, the regeneration time was suitable for a two-bed operation.

As a result of the successful bench scale tests conducted at RTI, RVS-1 sorbent was incorporated into the MTI:S 2.5 kWe fuel cell design and a demonstration test was conducted at MTI. The results from the 100-hour demonstration test of the regenerable desulfurizer with RVS-1 sorbent at MTI showed effective removal of hydrogen sulfide from the synthesis gas and effective regeneration of the sorbent during 10 cycles.

IV Conclusions

RVS-1 sorbent performed well at various experimental conditions. Pressure, temperature and concentration of H_2S affected the performance of the sorbent. High pressure, high temperature and low concentration of H_2S are desirable in obtaining high sulfur loadings. The concentration of H_2S and pressure did not affect the sulfur loading at 538 ^{0}C. However, At lower temperatures (260 ^{0}C)and at lower pressures (243 kPa) a high sulfur loading can be achieved only at low concentrations(2000 ppnv) of H_2S. It was possible to modify the RVS-1 sorbent to achieve ppbv level sulfur removal efficiency at 315 ^{0}C. The modified RVS-1 sorbent maintained ppbv level sulfur removal efficiency during a 20-cycle test. The RVS-1 showed promising results during tests conducted at McDermott Technology (MTI), Inc. for sulfur removal from syngas produced from diesel fuel.

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Figure 1 - Effluent concentration of sulfur during 20-cycle test with ppb sulfur sorbent

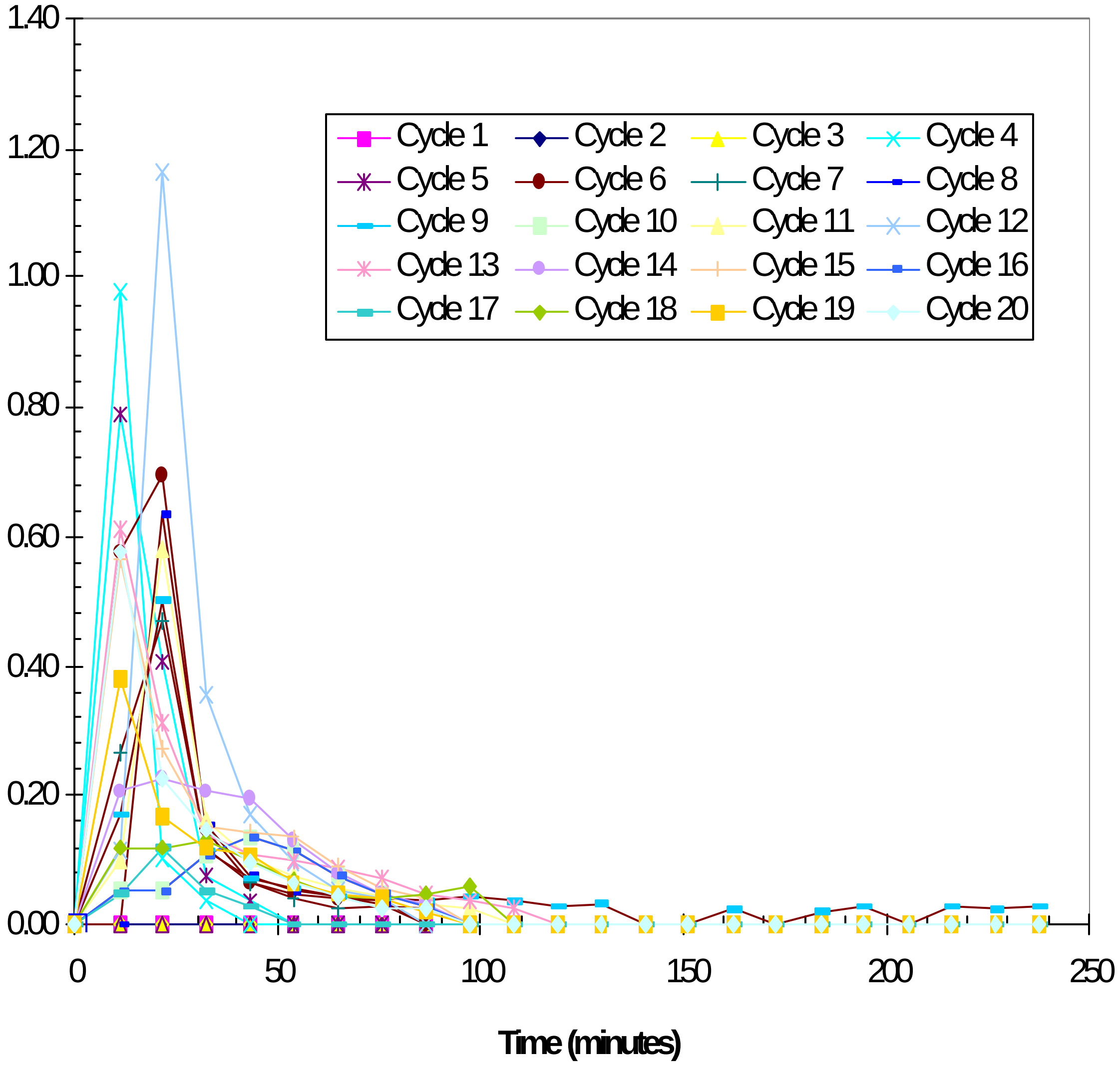

Figure 2 - Effluent concentration of sulfur with the ppb desulfurization sorbent after incorporation a reductive regeneration step