

## 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-1 and 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. During these desulfurization tests, the RVS-1 sorbent maintained an effluent H<sub>2</sub>S concentration of <5 ppmv at temperatures from 260 to 600 °C (500-1100 °F) and pressures of 203-2026 kPa (2 to 20 atm) with a feed containing 1.2 vol% H<sub>2</sub>S. The types of syngas tested ranged from an oxygen-blown Texaco gasifier to biomass-generated syngas. The RVS-1 sorbent has demonstrated high crush strength and attrition resistance, which, unlike past sorbent formulations, does not decrease with extended testing at actual operating conditions. The sulfur capacity of the sorbent is roughly 17 to 20 wt.% which has been shown to remain constant during extended testing (>25 cycles). In addition to H<sub>2</sub>S, the RVS-1 sorbent has also demonstrated the ability to remove dimethyl sulfide and carbonyl sulfide from syngas. It was also possible to obtain sulfur levels in the parts per billion by volume range with the modified RVS-1 sorbent.

During regeneration, the RVS-1 sorbent has been regenerated with dilute oxygen streams (1 to 7 vol% O<sub>2</sub>) at temperatures as low as 370 °C (700 °F) and pressures of 304-709 kPa (3 to 7 atm). Although regeneration can be initiated at 370 °C (700 °F), regeneration temperatures in excess of 538 °C (1000 °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.

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A number of commercial tests employing 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 Inc. (MTI), 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. This RVS-1 sorbent is also being tested as a candidate for a new high performance integrated gasification combined cycle system being developed by Texaco Global Gas and Power.

## 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 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 demonstrated an excellent sulfur capacity, even at 260°C (500°F).

A systematic study to understand the effect of temperature, pressure, gas composition, and H<sub>2</sub>S 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 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 Inc. (MTI), 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. In the Navy application, 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 fuel cell electric generator. Research Triangle Institute conducted laboratory-scale testing, and the results showed the capability of the sorbent 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.

RVS-1 sorbent was also tested as a potential candidate for the new IGCC system at Texaco Global Power. A 20-cycle test was conducted on RVS-1 to explore its desulfurization performance utilizing Texaco syngas with extremely high steam content. The presence of high percentage of steam ( 63%) in the sulfidation gas and low temperature 350 °C(600 °F) required for the Texaco gasification process is not favorable for sulfidation reaction. The results of the 20-cycle test under Texaco test conditions are also described in the paper. Despite the detrimental conditions utilized during the tests, the RVS-1 sorbent performed well during the 20-cycle test.

## **II Experimental**

The RVS-1 sorbent was developed by NETL in-house researchers. This is a zinc oxide based sorbent and preparation procedure is described in previous literature (Siriwardane 1996, 1997, 1999). 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**

Parametric 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 °C (1,000 °F) and 260 °C (500 °F) using simulated TECO coal gas (35.8% vol. CO, 12.2% CO<sub>2</sub>, 26.8% H<sub>2</sub>, 18.1% steam, and 5.95% nitrogen). The pressures were varied during sulfidations at 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<sub>2</sub> at 566 °C (1,050 °F). Space velocity was maintained at 2,000 hr<sup>-1</sup> during sulfidation and regenerations. 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 to 6.7 lb/ft<sup>3</sup> during sulfidations, but the last sulfidation cycle was conducted until breakthrough (2000 ppmv H<sub>2</sub>S) occurred.

## **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 °C (600 °F), and at 2026 kPa(20 atm) utilizing syngas with a composition of 35.8% CO, 11% CO<sub>2</sub>, 44.9% H<sub>2</sub>, and 6.3-8.1% N<sub>2</sub>, and containing 2000-20,000 ppmv of H<sub>2</sub>S. During the first 19 cycles, syngas with 2000 ppm H<sub>2</sub>S was utilized for 4 hours at 1000 hr<sup>-1</sup> STP, followed by syngas with 20,000 ppmv H<sub>2</sub>S at 2000 hr<sup>-1</sup>, until the effluent sulfur content exceeded 100 ppmv. The increase in H<sub>2</sub>S concentration after 4 hours was conducted to expedite the breakthrough (saturation of the sorbent). In cycle 20, syngas with 2000 ppm of H<sub>2</sub>S was maintained for 8 hours. A 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 °C (1200 °F), at 230 kPa(2 atm), at 2000 hr<sup>-1</sup> and with 98% N<sub>2</sub> and 2% O<sub>2</sub>.

## **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 diesel feeds at MTI. The composition of the gases used for sulfidation was 8.0 vol.% CO, 8.0% CO<sub>2</sub>, 25% H<sub>2</sub>, 36% steam, 800-10000 ppm H<sub>2</sub>S and 22-22.92% N<sub>2</sub>. Regeneration was performed with 10% CO<sub>2</sub>, 19% H<sub>2</sub>O, 68-68.5% N<sub>2</sub> and 2.5-3% O<sub>2</sub>. The sulfidation was conducted at both 315 and 482 °C, at space velocities of 2000 and 6000 hr<sup>-1</sup> and at 412 kPa(4 atm). Regeneration was performed at 565 °C, 239 kPa(3.3 atm), 2000 hr<sup>-1</sup> at STP.

## **II.D RVS-1 Sorbent Tests for Texaco Inc. Gasification Program**

The sorbent was also tested at conditions suitable for the Texaco IGCC process. A bed temperature of 316 °C (600 °F) under 3039 kPa(30 atm) of pressure was used during sulfidation. Syngas (18.9% CO, 3.9% CO<sub>2</sub>, 13.2 % H<sub>2</sub>, 1% H<sub>2</sub>S, and 63% H<sub>2</sub>O) containing 10,000 ppmv of H<sub>2</sub>S at a space velocity of 2000 h<sup>-1</sup> was fed to the sorbent test facility. A concentration of 100 ppmv of H<sub>2</sub>S (sulfur leak) or greater in the effluent gas stream from the reactor was used as the criterion for the end of sulfidation. After sulfidation, the sorbent bed temperature was increased to 649 °C (1200 °F) at 344 kPa (3.4 atm) with 100% N<sub>2</sub> and the sorbent bed was regenerated at 2000 h<sup>-1</sup> with a depleted oxygen stream containing 3 vol% O<sub>2</sub>. Duration of regeneration was determined by the SO<sub>2</sub> concentration in the reactor effluent. A concentration of 2000 ppmv of SO<sub>2</sub> or smaller marked the end of regeneration.

### III Results and Discussion

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

The effects of H<sub>2</sub>S concentration, pressure and temperature on the performance of sulfidation of RVS-1 sorbent are discussed below. Prior to the breakthrough (200 ppmv H<sub>2</sub>S) the sulfur removal efficiencies in all these experiments were below 5 ppmv.

##### *Effect of H<sub>2</sub>S Concentration on Sulfidation*

The breakthrough (200 ppmv H<sub>2</sub>S) times for the third sulfidation and the calculated sulfur loading values at the breakthrough with varying H<sub>2</sub>S 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<sub>2</sub>S concentration. The RVS-1 sorbent is designed (Siriwardane 1999) to have sufficient porosity inside the pellet to facilitate diffusion of gases. It appears that better diffusion of H<sub>2</sub>S inside the sorbent pellet can be achieved with lower H<sub>2</sub>S concentration.

**Table 1**  
**Breakthrough Times for Third Sulfidations**  
**and Calculated Sulfur Loading of the Reactor Bed at 243 kPa and 538 °C**

H <sub>2</sub> S 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 the sorbent pellets. At higher pressures (1,134 and 2,026 kPa), the sulfur uptake values with 12,000 ppm H<sub>2</sub>S are considerably higher than those at 243 kPa. This indicates that the diffusion of H<sub>2</sub>S 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<sub>2</sub>S**

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 °C (1,000 °F) and 260 °C (500 °F) with 12,000 ppm H<sub>2</sub>S at 2,026 kPa are shown in Table 3.

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

Temperature (°C)	H <sub>2</sub> S 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 °C (500 °F) than at 538 °C (1,000 °F) when the concentration of H<sub>2</sub>S is 12,000 ppmv. However, at 260 °C (500 °F) a higher sulfur uptake can be achieved at a lower concentration (2000 ppmv) of H<sub>2</sub>S. At 538 °C (1,000 °F) the sulfur uptake was only sensitive to the H<sub>2</sub>S 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<sub>2</sub>S even at high pressure (2,026 kPa) when the sulfidation was performed at 260 °C (500 °F). The sorbent pellets were better utilized for sulfidation with 2,000 ppmv of H<sub>2</sub>S at 260 °C (500 °F), and it was possible to achieve a sulfur loading of about 17 wt. %. This indicates that there was a higher diffusional resistance at lower temperature when the H<sub>2</sub>S concentration was high, but sulfur uptake similar to that at 580 °C (1,000 °F) can be achieved at 260 °C (500 °F) by lowering the H<sub>2</sub>S concentration to 2,000 ppmv.

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

RVS-1 sorbent was tested at different temperatures to determine the sulfur removal efficiency. Since it is zinc oxide-based sorbent, ppbv level sulfur removal efficiency was obtained around 316 °C(600 °F). The sorbent had sufficient sulfur capacity at 316 °C(600 °F) even though it was lower than that at 482 °C(900 °F).

The effluent concentration of H<sub>2</sub>S for the first 4 hours of sulfidation with 2000 ppm H<sub>2</sub>S at 316 °C(600 °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<sub>2</sub>S 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. 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<sub>2</sub>S 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 Inc. (MTI) 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<sup>-1</sup> and sulfidation temperature range of 316-482 °C (600-900 °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. A typical sulfidation test result utilizing simulated diesel reformat with 800 ppmv H<sub>2</sub>S is shown in Figure 2. During the multi cycle test, the RVS-1 sorbent successfully removed the sulfur to 10 ppm level from the reformat gas stream. Since the RVS-1 sorbent was designed to have high sulfur capacity, it performed well even in the presence of a large amount of steam. For good process operability, 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.

### III.D RVS-1 Sorbent Tests for Texaco Inc. Gasification Program

The main sulfur species in the reactor effluent was H<sub>2</sub>S. Pre-breakthrough H<sub>2</sub>S concentrations were small during all the cycles in the 20-cycle test and were always lower than 10 ppmv. The H<sub>2</sub>S leak was very low from cycles 1 through 4 and ranged from 1 to 3 ppmv. However, from cycles 5 to 20 there was a gradual increase in the H<sub>2</sub>S leak as the number of cycles increased that ranged from about 5 to 10 ppmv. COS concentrations in the reactor effluent were below 13 ppmv during the entire 20-cycle run, while pre-breakthrough COS concentrations were even smaller on the order of 6 ppmv.

During the 20-cycle run the breakthrough time (H<sub>2</sub>S in the reactor effluent is greater than 100 ppmv) continually decreased as the number of cycles increased. The breakthrough time of each cycle is shown in Figure 3. During Cycles 1 through 8, the breakthrough time ranged from 276 to 393 minutes. From Cycle 8 through Cycle 11 there was a significant decrease in breakthrough time from 342 minutes in Cycle 8 to 181 minutes in Cycle 11. However, from Cycle 11 through Cycle 20 the breakthrough time was stabilized and ranged from 138 to 203 minutes. This behavior may be attributed to a process of stabilization of the RVS-1 sorbent that occurred around Cycle 10.

The sulfur loading values for the entire 20-cycle run on RVS-1 are shown in Figure 4. During the first eight cycles the sulfur loading values ranged from 13.8 wt.% in Cycle 2 to 9.6 wt.% in Cycle 6. From Cycle 8 through Cycle 11 there was a significant decrease in the sulfur loading (12.1 wt.% in Cycle 8 to 6.4 wt.% in Cycle 11). However, from Cycle 11 through Cycle 20, a stable sulfur loading value averaging around 6.5 wt.% was observed. This behavior was similar to that was observed with the sulfidation time.

## IV Conclusions

RVS-1 sorbent performed well at various experimental conditions. Pressure, temperature and concentration of H<sub>2</sub>S affected the performance of the sorbent. High pressure, high temperature and low concentration of H<sub>2</sub>S are desirable in obtaining high sulfur loadings. The concentration of H<sub>2</sub>S and pressure did not affect the sulfur loading at 538 °C. However, at lower temperatures (260 °C) and at lower pressures (243 kPa) a high sulfur loading can be achieved only at low concentrations (2000 ppmv) of H<sub>2</sub>S.

It was possible to modify the RVS-1 sorbent to achieve ppbv level sulfur removal efficiency at 315 °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 MTI for sulfur removal from syngas produced from diesel fuel. The RVS-1 desulfurization sorbent also performed well during a 20-cycle test conducted utilizing Texaco syngas with high steam content. Despite the detrimental conditions of high percentage of steam (63%) in the Texaco syngas and low temperature 316 °C (600 °F) utilized during the tests, the RVS-1 sorbent performed well during the 20-cycle test.

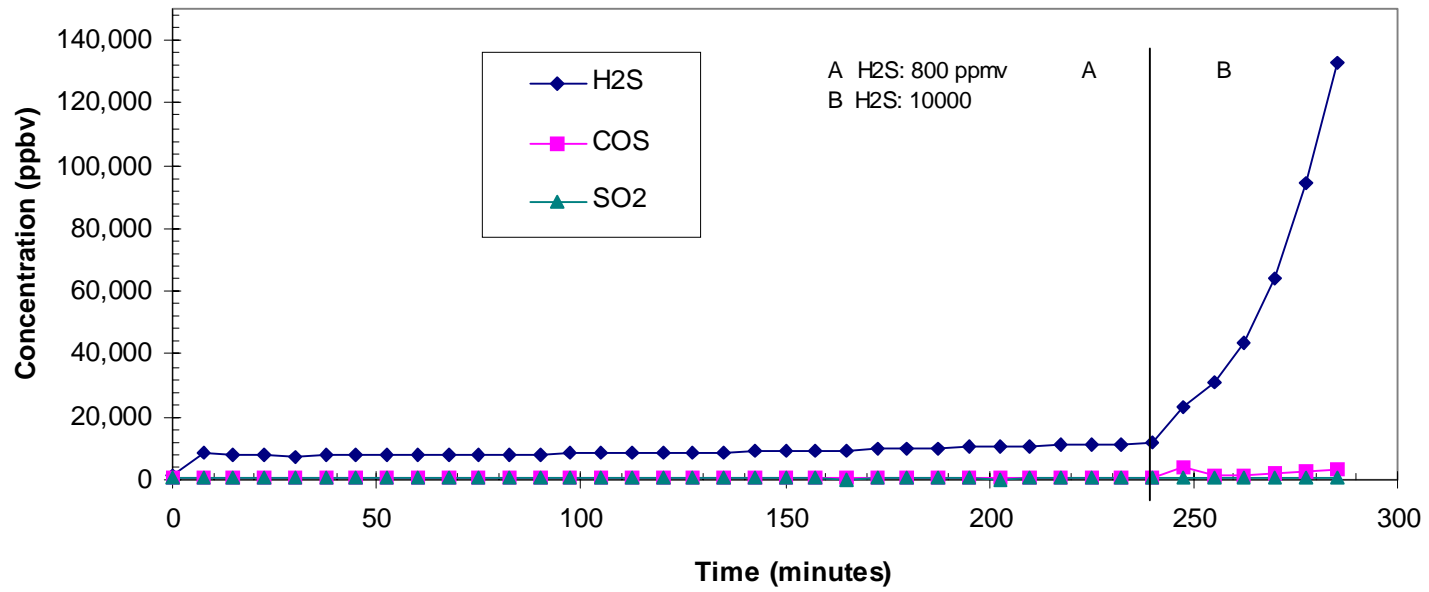


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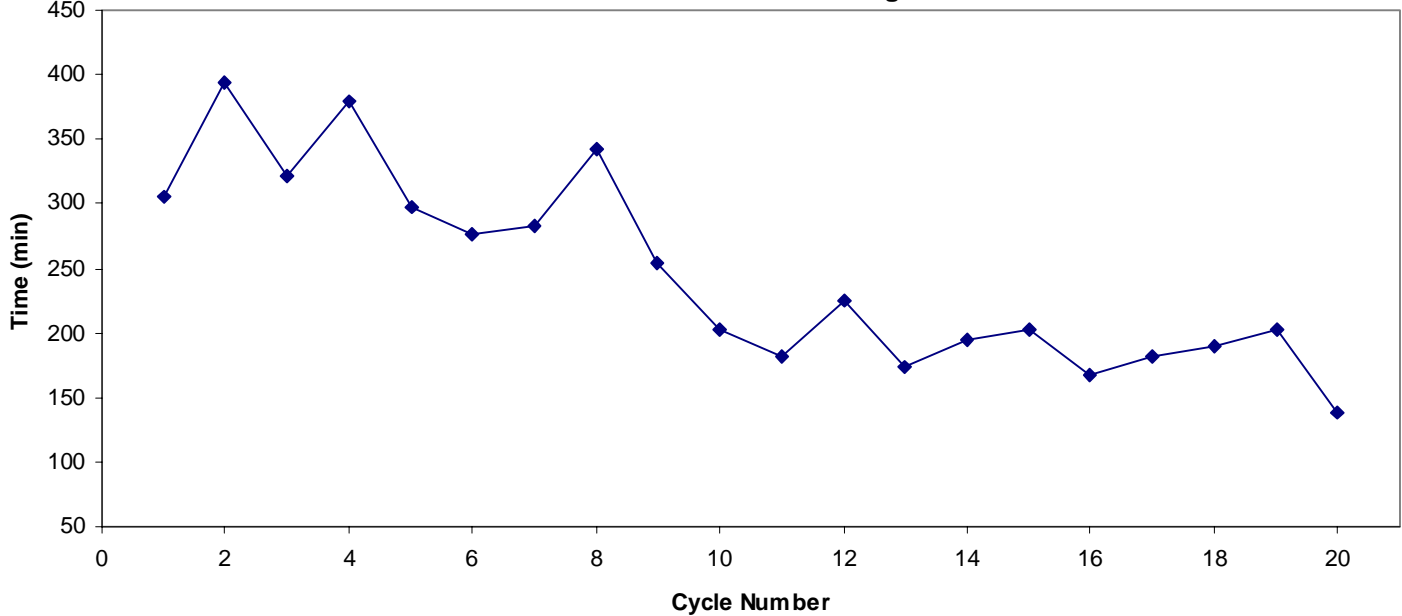
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**Figure 2**  
**Sulfidation of RVS-1 with Syngas Produced by Hydrocarbon Liquid Feed**



**Figure 3**  
**Breakthrough Times of the 20-Cycle Bench Scale Test**  
**- Texaco Inc. Gasification Program**



**Figure 4**  
**Sulfur Removal Efficiency and Sulfur Loading Values of the 20-Cycle Bench Scale Test**  
**-Texaco Inc. Gasification Program**

