# Development of Advanced Hot-Gas Desulfurization Processes

FINAL REPORT

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For
U.S. Department of Energy
National Energy Technology Laboratory
Pittsburgh, Pennsylvania 15236-0940

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# EXECUTIVE SUMMARY

This report describes the project "Development of Advanced Hot-Gas Desulfurization Processes" sponsored by U.S. Department of Energy, National Energy Technology Laboratory under Grant No: DE-FG26-97FT97276. The work was performed by Hampton University (prime contractor) with support by Research Triangle Institute as a subcontractor.

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:

(i) optimized low-cost sorbent materials with 70-80 $\mu$m average aps meeting all Sierra specs.

(ii) attrition resistant sorbents with 170 $\mu$m aps that allow greater flexibility in the choice of the type of fluidized-bed reactor eg they allow increased throughput in a bubbling-bed reactor.and

(iii)modified fluidizable sorbent materials that can be regenerated to produce elemental sulfur directly with minimal or no use of coal gas.

Forty Five sorbents were synthesized in this work. Details of the preparation technique and the formulations are proprietary, pending a patent application, thus no details regarding the technique are divulged in this report. Sulfidations were conducted with a simulated gas containing (vol %): $H_2$=10%, $CO$=15%, $CO_2$=5%, $H_2S$=0.4 - 1%, $H_2O$=15% and bal $N_2$ in the temperature range of 343-538$^o$C. The gas hourly space velocity for the test was about 2500 $h^{-1}$ both in sulfidation and in regeneration. Regeneration between cycles were conducted at temperatures in the range of 500-700$^o$C with pure air. To prevent sulfation, catalyst additives were investigated that promote regeneration at lower temperatures. Characterization were performed for fresh, sulfided and regenerated sorbents.

Based on fixed-bed microreactor screening of numerous sorbents, an attrition-resistant fludizable sorbent designated FHR-32 was selected for high temperature, high pressure testing. A 50 cycle test was conducted using the microreactor system. The sorbent demonstrated high reactivity over the 50 cycle test and its attrition resistance was comparable to equilibrium fluidized cracking catalyst (FCC). No sulfate formation was observed during neat air regeneration. These promising test results indicated that FHR-32 could be candidate sorbent for the Sierra-Pacific clean coal project or similar project involving transport reactor.

An advanced attrition resistant hot-gas desulfurization sorbent that can eliminate the problematic $SO_2$ tail gas and yield elemental sulfur directly has been developed. Attrition resistant Zn-Fe sorbent (AHI-2) formulations have been prepared that can remove $H_2S$ to below 20 ppmv from coal gas and can be regenerated using $SO_2$ to produce elemental sulfur.

# ACKNOWLEDGMENTS

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# 1.0  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 (Ayala, 1995, Gangwal, 1988; 1991; 1993; 1995; 1996; Harrison, 1995).  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. 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:

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

$$ZnS + (3/2)O_2 \quad ? \quad ZnO + SO_2 \qquad \text{(Regeneration)}$$
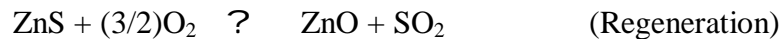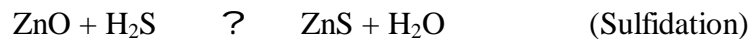
For economic reasons, the sorbent must be able to maintain an acceptable level of reactivity over numerous absorption (sulfidation)-regeneration cycles.

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 ?m using a granulator and Phillips Petroleum=s Z-Sorb III (175 ?m  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 $8-10 per lb. These sorbents also have very low attrition resistance compared to bench-mark fluid catalytic cracking (FCC) catalysts (70-80 ?m aps) prepared by spray drying and employed in a petroleum refinery.  The larger aps of 170 ?m results in reduced entrainment and allows greater throughput and flexibility in a bubbling-bed, but has not to date been successfully made using a spray drier. Also the regeneration light-off  temperature of first generation zinc titanate sorbents is around 630-650$^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 (Harrison et al., 1996; Gupta et al., 1992; 1996; Thambimuthu, 1993; Jothimurugesan et al., 1996). 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 $O_2$ concentrations in the regeneration gas can promote sulfate formation in the sorbent which is undesirable.  Even with
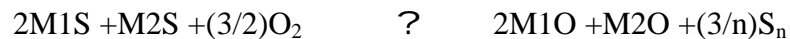
neat air, a dilute $SO_2$ tail gas containing a maximum of 14 volume % $SO_2$ is produced which needs to be disposed. Production of elemental sulfur from the $SO_2$ is the most attractive option because it can be readily disposed, sold, stored and transported over long distances. The Direct Sulfur Recovery 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:

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

For each mole of sulfur, 2 moles of $H_2$+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:

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

$$M2S + (3/2) O_2 \quad ? \quad M2O + SO_2$$
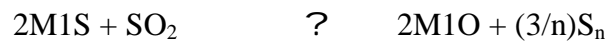
with the net reaction being:

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

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$^o$C, and 15 slpm through a 145 g sorbent bed. The regeneration was conducted with pure air with an initial temperature of 480-510$^o$C. 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$^o$C. After the first cycle, the capacity stabilized even with temperature excursions to 675-700$^o$C 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$^o$C. 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 ?m aps meeting all Kellogg specifications for their transport reactor HGD process at the Sierra-Pacific power plant

! 170 ?m 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

## 1.1   PROJECT OBJECTIVES

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 ?m average aps meeting all Sierra specs.

**!** attrition resistant sorbents with 170 ?m 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.

## 2.0   DESCRIPTION OF PROJECT TASKS

TASK 1:      Development of Sorbent for Sierra-Pacific

The objectives of this task were to develop optimized low-cost sorbent materials with 70-80 ?m average aps meeting all Sierra specs.  Several parameters were varied in the sorbent preparation to study their effects on the physical and chemical phases of the sorbents.

TASK 2:      Bubbling-Bed Reactor Sorbents.

The objectives of this task were to develop attrition resistant sorbent for bubbling-bed reactors. Coprecipitation-spray drying techniques was investigated in a systematic manner to determine the best technique to make bubbling-bed air-regenerable zincbased sorbents.

TASK 3:      Advanced Sulfur Recovery Sorbents

The objectives of this task were to modified fluidizable sorbent materials that can be regenerated to produce elemental sulfur directly with minimal or no use of coal gas.

TASK 4:     Sorbent Characterization

This task provides support to each of the previous tasks. Section 3.1 describes the various analytical techniques employed for sorbent characterization throughout the project.

## 3.0  EXPERIMENTAL APPROACH

### 3.1.Sorbent Preparation and Characterization

The method used to produce novel sorbents in this research involves both the impregnation techniques as well as coprecipitation of soluble salts of appropriate metals with an ammonium salt.  A series of zinc based mixed-metal oxide materials was prepared with various concentration of catalyst additives, such as Ni, Co, W and Mo.  The resulting materials were dried and finally calcined at the desired temperature range of 600-1000$^{o}$C.  The sorbent materials produced have surface areas which range from 10 m$^2$/g to 95 m$^2$/g depending on the calcination temperatures from 600-1000$^{o}$C.  The catalyst vendor provided the required input to keep the preparation procedure on a commercial track by making sure that the techniques were scalable.

A detailed physical and chemical characterization of the fresh, sulfided and regenerated sorbent materials was carried out using the following analytical techniques.

1.     X-ray powder diffraction patterns were obtained using a Phillips PW 1800 X-ray unit using CuK? radiation.  Analyses were conducted using a continuous scan mode at a scan rates of 0.05?2? per second.

2.     The BET Surface area of the sorbents were determined by N$_2$

Physisorption using a Micromeritics Gemini 2360 system. The samples were degassed in a Micromeritics Flow Prep 060 at 120℃ for 1 h prior to each measurement.

3. Hg-porosimetry was used for pore volume, bulk density, average pore diameter and pore size distribution determination.

4. Atomic Absorption (AA) Spectrometry for elemental composition analysis.

5. The SEM (Scanning Electron Microscopy) micrograph was taken using a Cambridge Stereoscan 100.

6. 3-hole attrition tester for attrition measurement

## 3.2. Apparatus and Procedures

The materials prepared were tested in a laboratory scale high-pressure and high temperature fixed bed reactor which is described elsewhere (Jothimurugesan et al., 1996). Briefly, the experimental setup consisted of a gas delivery system, fixed bed reactor, and a gas analysis system. In the gas delivery system, a simulated fuel gas of any desired can be generated using the bottled gases, a set of mass flow controllers and high pressure syringe pumps. Steam is added to the mixed dry gas by vaporizing liquid water injected into the gas stream at a controlled rate by a high pressure syringe pump. $NH_3$ is added to the gas mixture downstream of the generator where the temperature is high enough to avoid the formation of ammonium carbonates or sulfides. The reactor was constructed of stainless steel pipe. Inside the pipe there was a removable 316 stainless steel 1.0 cm I.D pipe with a porous alumina plate in the bottom that acts as a gas distributor. The inside of the pipe was alon-processed to prevent corrosion of stainless steel by sulfurous gases in the presence of steam. The pressure inside the reactor was measured by an electronic pressure sensor. The thermocouples are

positioned to measure the temperatures of the preheated feed gas, reactor bed temperature and the temperature of the product gas. The outlet $H_2S$ and $SO_2$ concentrations were monitored using gas chromatography.

## 4.0 RESULTS AND DISCUSSIONS

**Development of Sorbent for Sierra-Pacific**

Work has continued to improve sorbents developed in a previous DOE grant (DE-FG22-95MT05011). Modifications were made to a MCRH-61 zinc-oxide based formulation to eliminate the sulfate formation observed during bench-scale tests. Sulfidation tests were carried out with a sulfidation gas containing (vol%): $H_2$=10%, CO=15%, $CO_2$=5%, $H_2S$=0.4%, $H_2O$=15% and bal $N_2$. The gas hourly space velocity for the test was about 2500 $h^{-1}$ both in sulfidation and in regeneration. The sulfidation was carried out at 482$^o$C. Regeneration between cycles was conducted with pure air at 482$^o$C. As shown in Figure 1, microreactor tests indicated the modified formulation designated MCRH-67 showed little or no evidence of sulfate formation during second sulfidation at 482$^o$C.

MCRH-67 sorbent was tested at RTI in their 2.0 inch HTHP fludized-bed reactor simulating the Sierra-Pacific conditions for 2 cycles at sulfidation conditions of simulated Kellogg gasifier gas with 0.4 % $H_2S$ at 18.8 atm pressure. The regeneration was conducted with pure air at a temperature of 482$^o$C. Essentially complete removal of $H_2S$ was achieved until a sharp breakthrough in the 2 cycles as shown in Figure 2. However, the sorbent lost some capacity after the first cycle presumably due to pure air regeneration that increased the bed temperature to around 850$^o$C. The sorbent lighted-off nicely at 482$^o$C. The results showed no sulfation problem with this sorbent.
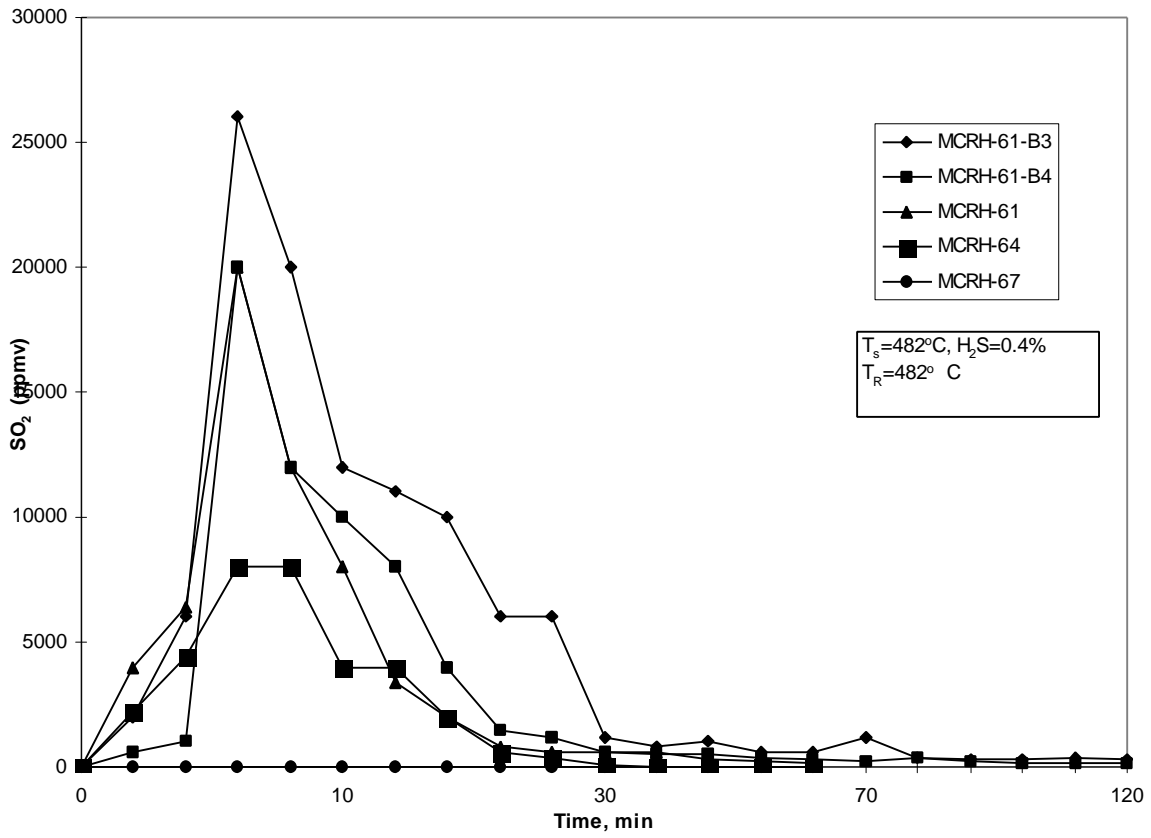
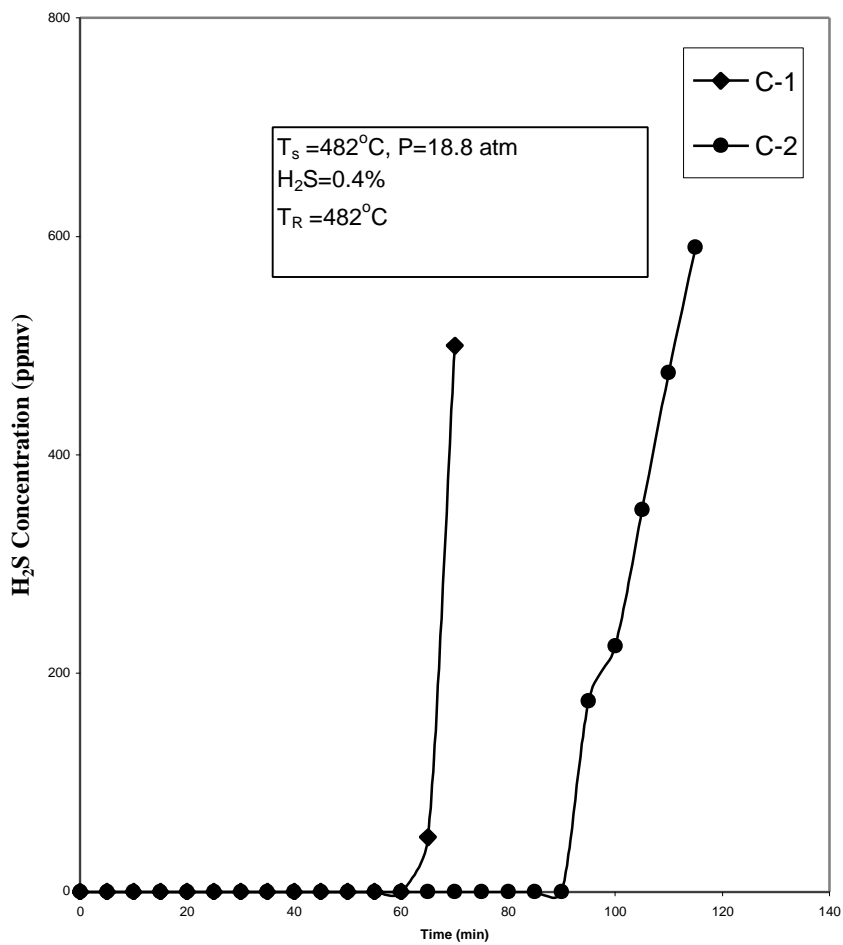Figure 1. SO$_2$ Evolution During Sulfidation Due to Sulfation

Figure 2.  Breakthrough Behavior of MCRH-67

In December of 1997, UCI (United catalysts, Inc) prepared a 100 lb batch of MCRH-67 sorbent to demonstrate commercial readiness. The properties of the sorbent are given below.

Table 1. Properties of the MCRH-67 Sorbent

| Designation | BET Surface Area $m^2/g$ | 3-hole attrition loss (wt %) | |
| --- | --- | --- | --- |
| | | 1 hour | 5 hour |
| MCRH-67 (Prepared at Hampton) | 101.1 | 1.2 | 0.7 |
| UCIMCRH-67 (Prepared at UCI) 100 lb Batch | 70.2 | 1.2 | 1.9 |

As seen in the above table, attrition properties of the both sorbents are excellent and nearly the same.

UCIMCRH-67 was also tested in the RTI 2.0 inch HTHP fludized-bed reactor simulating the Sierra-Pacific conditions for 3 cycles at sulfidation conditions of simulated Kellogg gasifier gas with 0.4 % $H_2S$, $538^oC$, at 18.8 atm pressure. The regeneration was conducted with pure air at a temperature of $538^oC$. The $H_2S$ breakthrough results indicated essentially complete removal of $H_2S$ until breakthrough in the 3 cycles. However, the pre-breakthrough level increased with cycling as shown in Figure 3. The attrition results of the fresh and used sorbents are given Table 2.

Table 2. Attrition of the Fresh and Used UCIMCRH-67 Sorbent

| Sorbent | 3-hole attrition loss (wt %) | |
| --- | --- | --- |
| | 1 hour | 5 hour |
| Fresh | 1.2 | 1.9 |
| Used, $538^oC$, 3 cycles | 0.9 | 1.3 |

$T_s = 538^o$ C, P=18.8 atm
$H_2S=0.4\%$

C-1
C-2
C-3

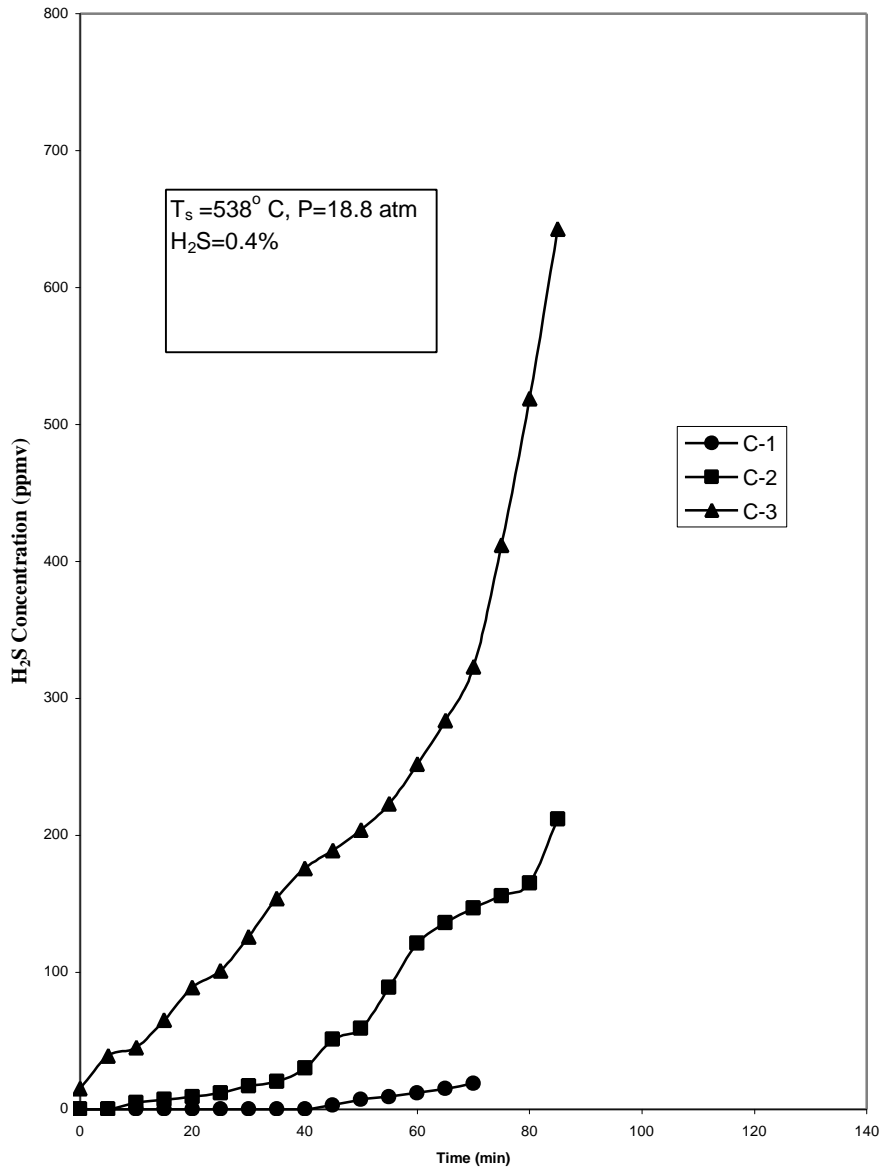**H₂S Concentration (ppmv)**

**Time (min)**

Figure 3.  Breakthrough Behavior of UCIMCRH-67

Next, the effect of calcination temperature on the sulfidation performance of UCIMCRH-67 was studied. The UCI MCRH-67 was calcined at various temperatures in the range 700-900°C for 2 h. Sulfidation tests were carried out in the microreactor with a sulfidation gas containing (vol%): $H_2$=10%, CO=15%, $CO_2$=5%, $H_2S$=1.0%, $H_2O$=15% and bal $N_2$. The gas hourly space velocity for the test was about 2500 $h^{-1}$ both in sulfidation and in regeneration. The sulfidation was carried out at 538°C. Regeneration between cycles was conducted with pure air at 538°C.

As shown Figure 4, as expected, as the calcination temperature increased from 700-900°C , the breakthrough time decreased from 140 min to 50 min. Calcining the sample beyond 800°C, resulted in sulfate formation, as seen from Figure 5.

Next, 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. Sulfidation tests were carried out with a sulfidation gas containing (vol %): $H_2$=10 %, CO=15 %, $CO_2$=5 %, $H_2S$=1.0 %, $H_2O$=15 % and bal $N_2$. The gas hourly space velocity for the tests was about 2500 $h^{-1}$ both in sulfidation and in regeneration. The sulfidation was carried out at 538°C. Regeneration between cycles was conducted with pure air at 700°C.

Figures 6-11 shows the sulfidation performance of the FHR sorbents. Of all the sorbents tested, the FHR 32 sorbent showed the best suifidation performance. The pre-breakthrough level was less than 50 ppm. The results showed no sulfation problem with this sorbent. The BET surface area of the fresh and the used sorbents are shown in Table 3.
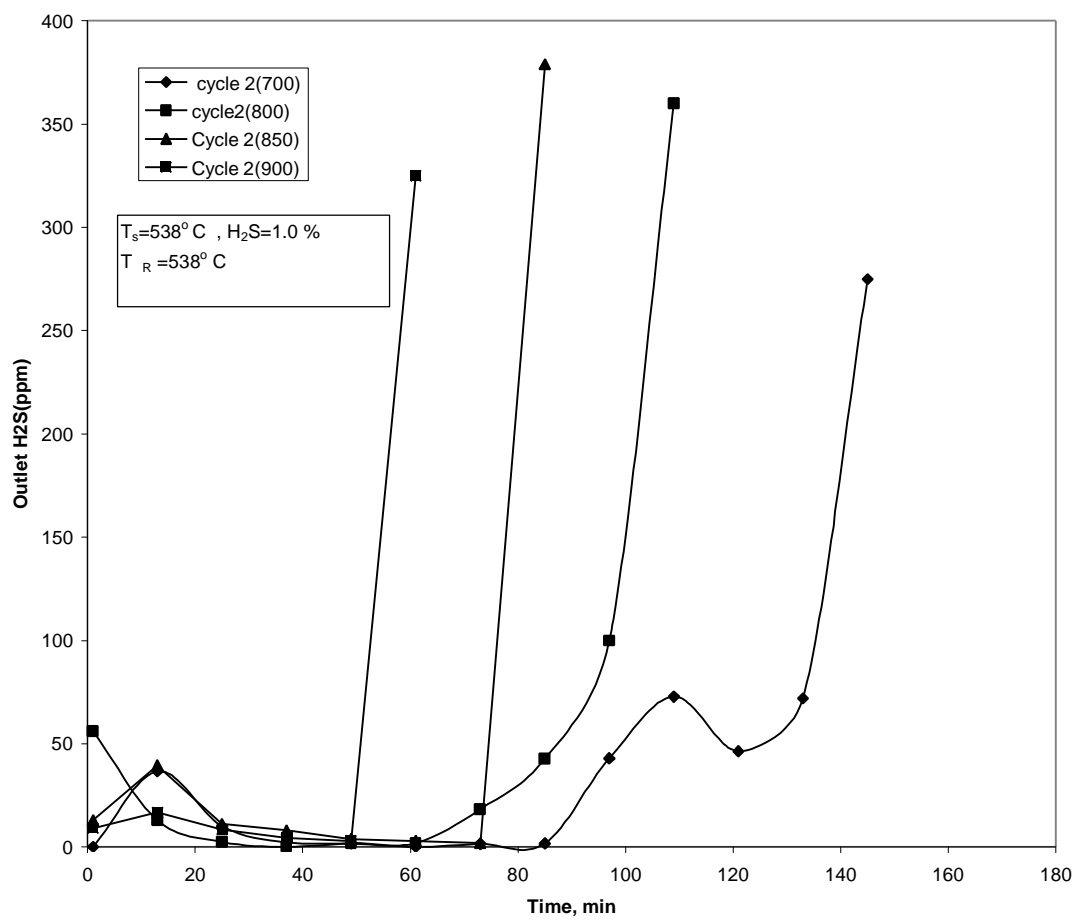
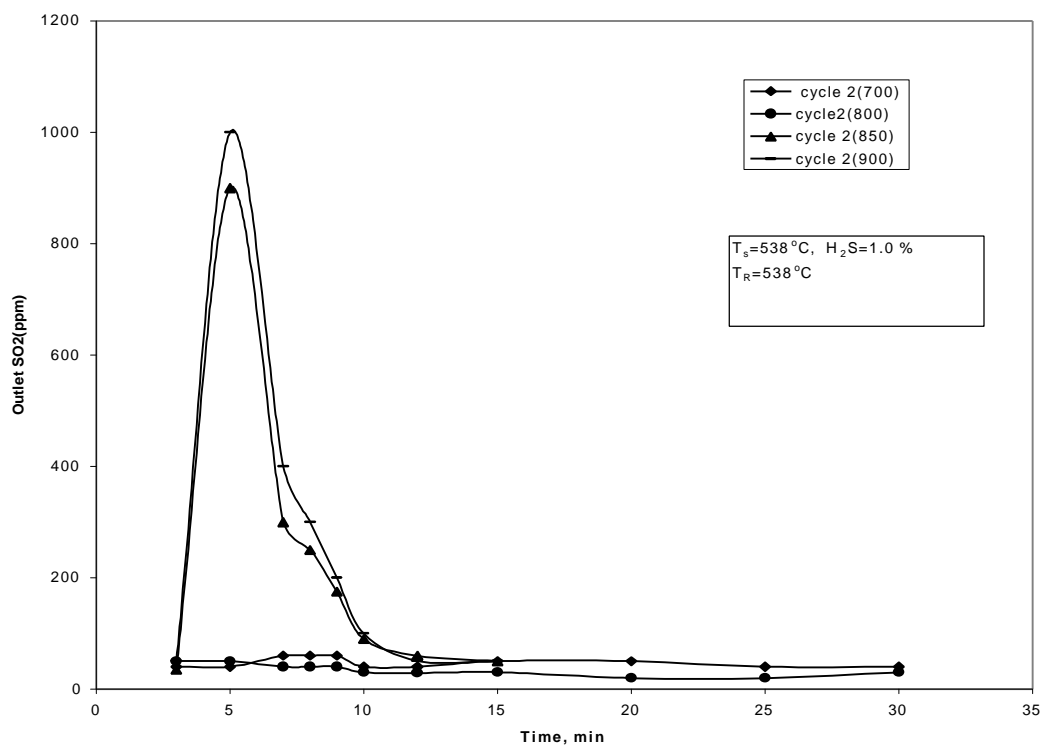Figure 4. Effect of Calcination Temperature on the Sulfidation Performance of UCIMCRH-67

Figure 5.  Effect of Calcination Temperature on the $SO_2$ Evolution During Sulfidation.

Figure 6.  H$_2$S breakthrough curves in successive sulfidation cycles of sorbent FHR 23

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Figure 7. H$_2$S breakthrough curves in successive sulfidation cycles of sorbent FHR 27
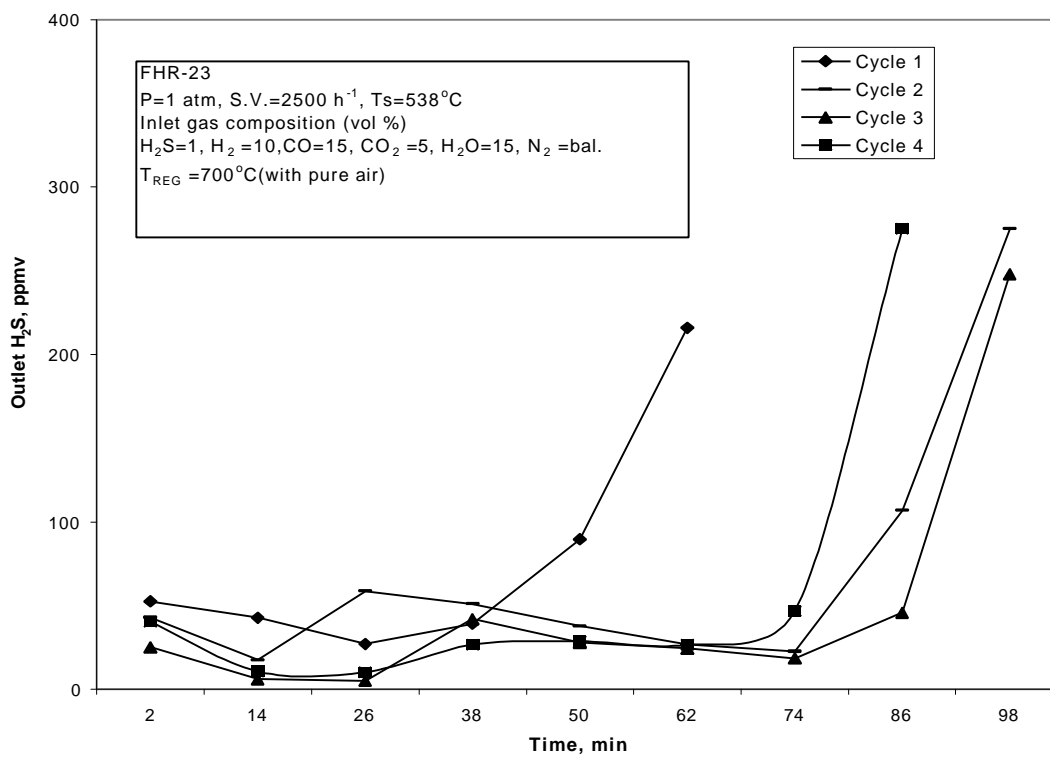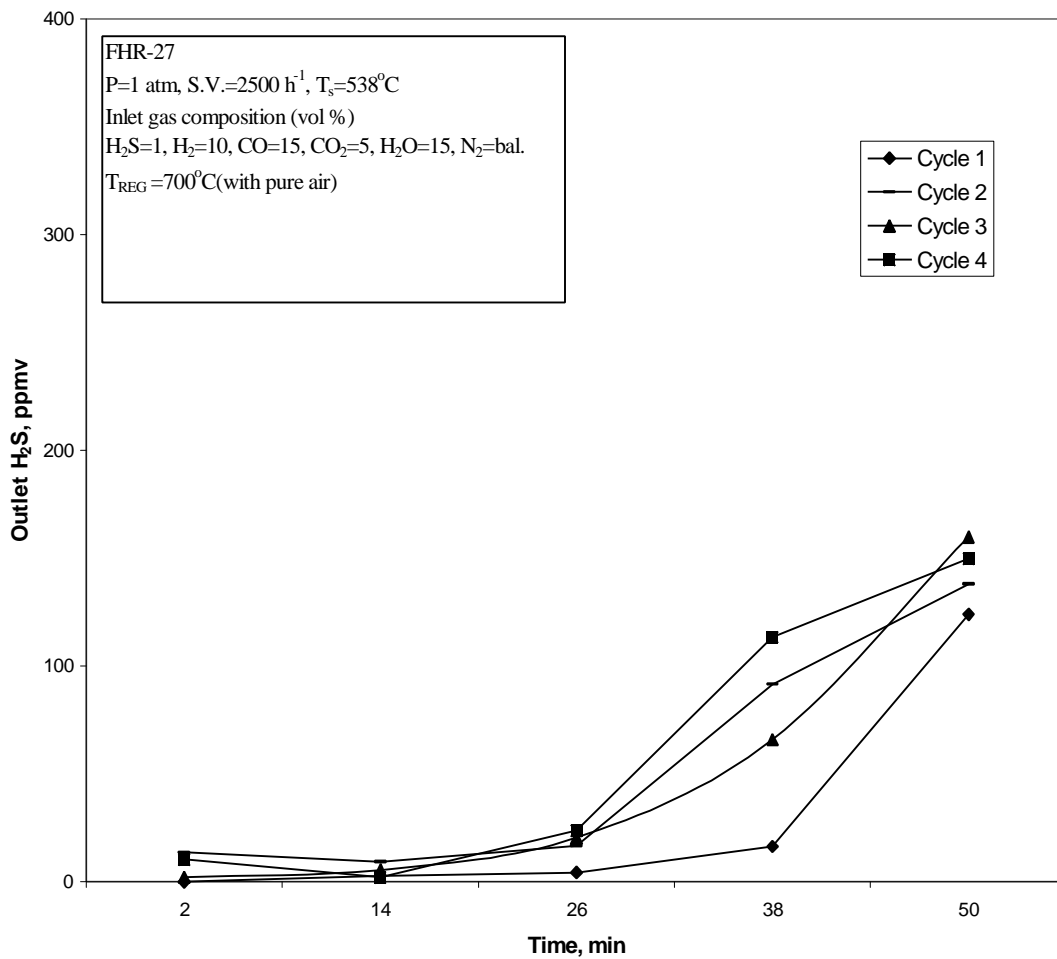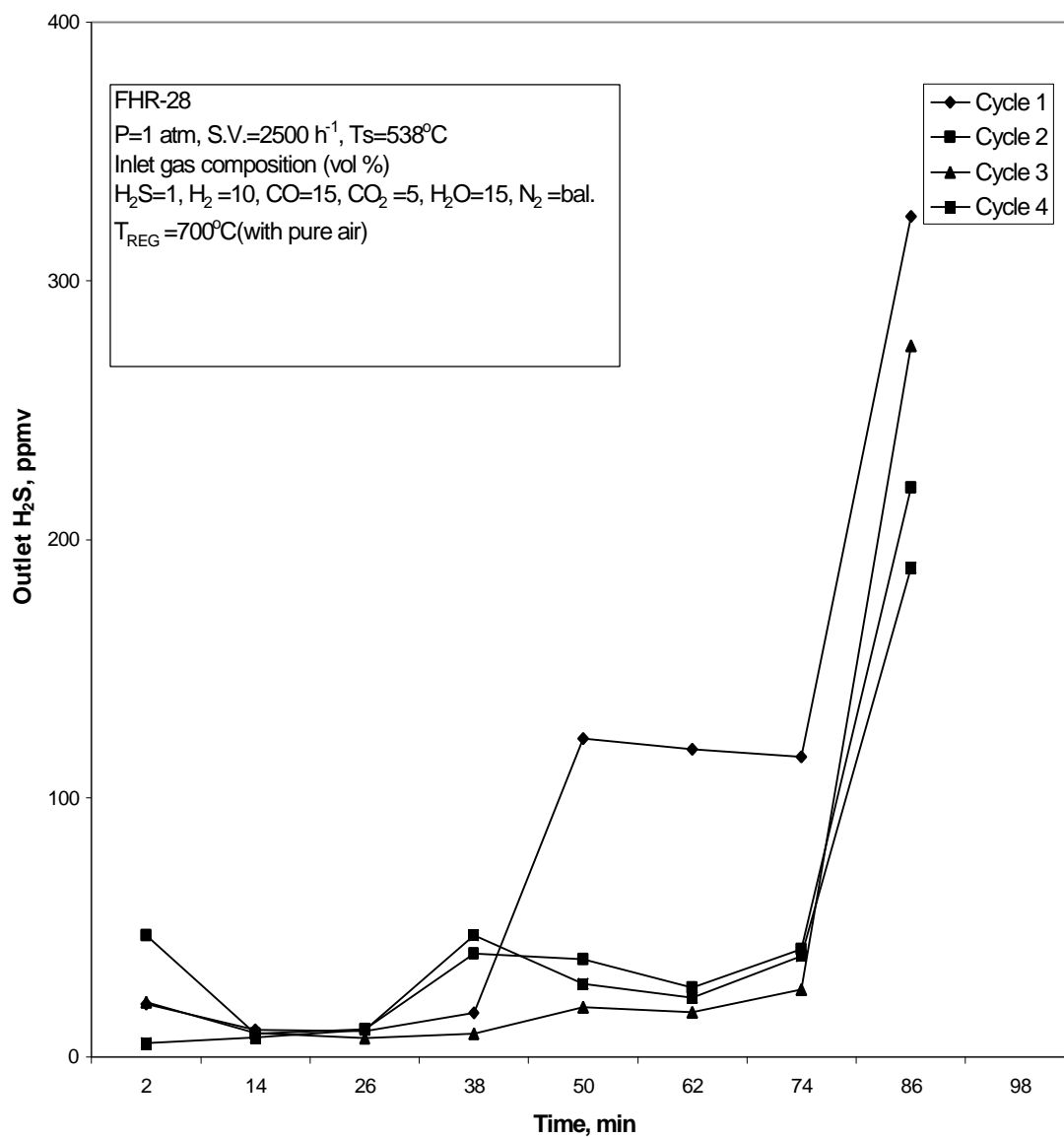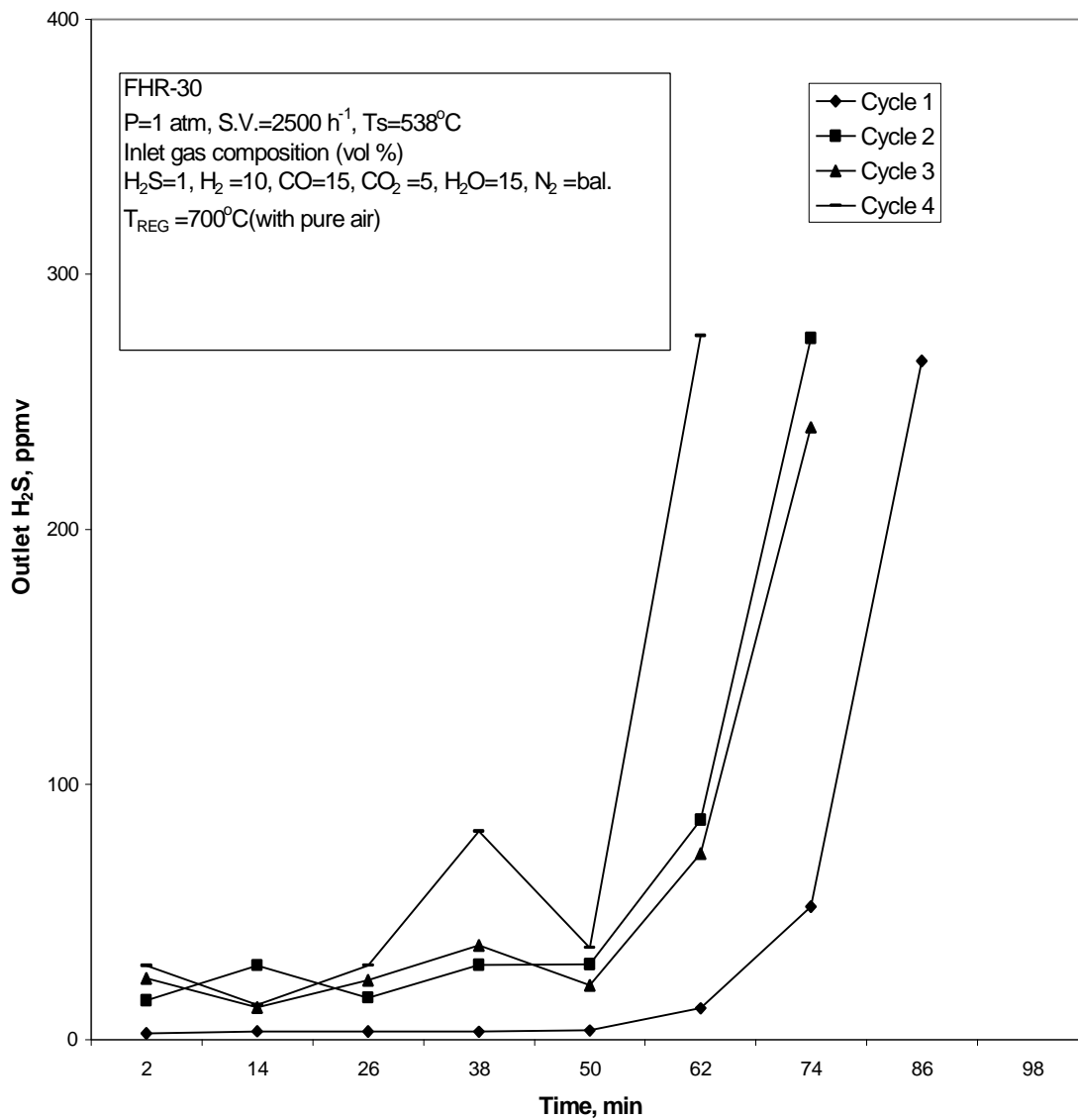
Figure 8. H₂S breakthrough curves in successive sulfidation cycles of sorbent FHR 28

Figure 9. H₂S breakthrough curves in successive sulfidation cycles of sorbent FHR 30
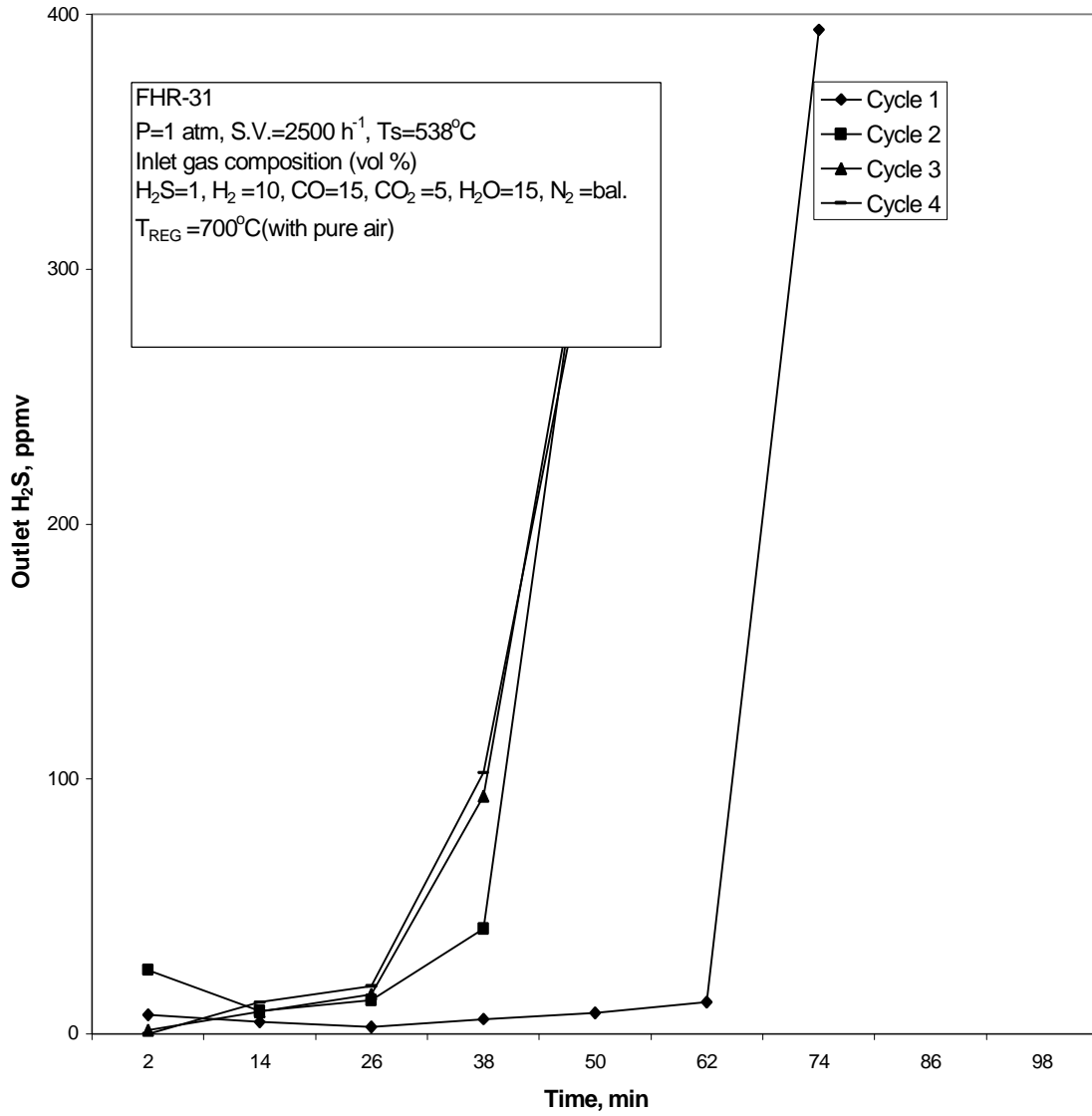
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Figure 10. $H_2S$ breakthrough curves in successive sulfidation cycles of sorbent FHR 31

Figure 11. $H_2S$ breakthrough curves in successive sulfidation cycles of sorbent FHR 32
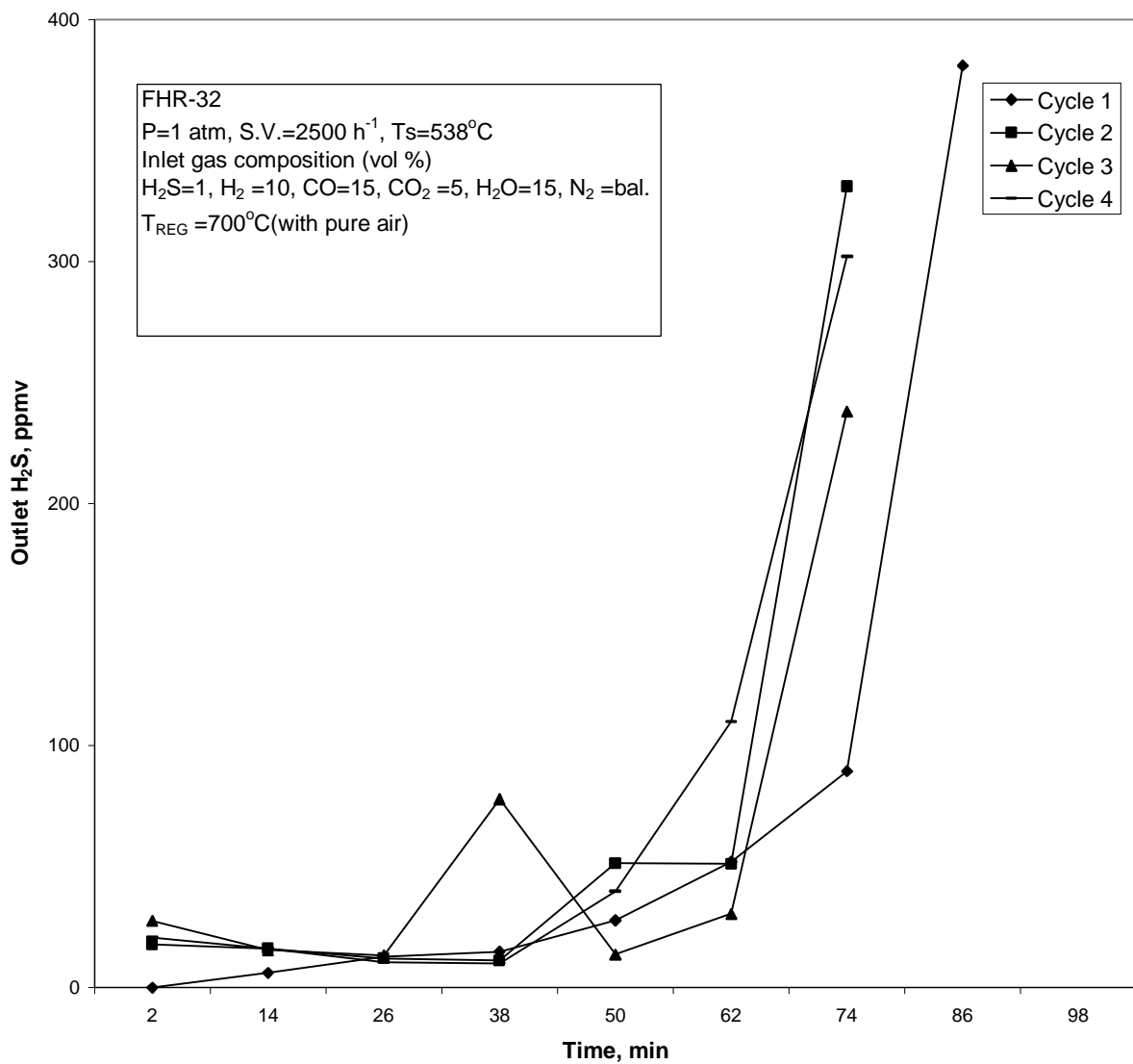
Table 3. BET surface area of the FHR sorbents

| Sorbents | BET Surface Area, $m^2/g$ | |
|----------|-------|----------|
| | Fresh | Sulfided |
| FHR-23 | 81.9 | 57.4 |
| FHR-27 | 87.0 | 53.8 |
| FHR-28 | 84.1 | 63.9 |
| FHR-30 | 83.1 | 57.2 |
| FHR-31 | 85.3 | 56.2 |
| FHR-32 | 76.8 | 54.8 |

Since, FHR-32 sorbent showed the best suifidation performance, it was tested for 50 cycles of sulfidation in the laboratory-scale reactor at 480$^o$C. Figure 12 shows the breakthrough profiles for FHR-32 sorbent. Regeneration between cycles was conducted with pure air at 480$^o$C. The gas hourly space velocity for the 50 cycles test was about 2500 h$^{-1}$ both in sulfidation and regeneration. Sulfidation tests were carried out with a sulfidation gas containing (vol %): $H_2$=10%, CO=15%, $CO_2$=5%, $H_2S$=0.4%, $H_2O$=15% and balance $N_2$. FHR-32 sorbent showed excellent sulfidation behavior. The pre-breakthrough $H_2S$ level was less than 80 ppm. **There was no deactivation in 50 cycles in this fixed bed study.**

**Bubbling-Bed Reactor Studies**

Several zinc-based sorbents have been prepared and tested. The FHR-33 sorbent was prepared using spray drier. The pore volume the sorbent is 0.37 mL/g. The attrition index is 40.9. Sulfidation tests were carried out with a sulfidation gas containing (vol %): $H_2S$=1, $H_2$=10, CO=15, $CO_2$=5, $H_2O$=15 and balance $N_2$. The gas hourly space velocity for the tests was about 2500 h$^{-1}$ both in sulfidation and regeneration. The sulfidation was carried out at 538$^o$C. Regeneration between cycles was conducted with pure air at 600$^o$C. Figure 13 shows
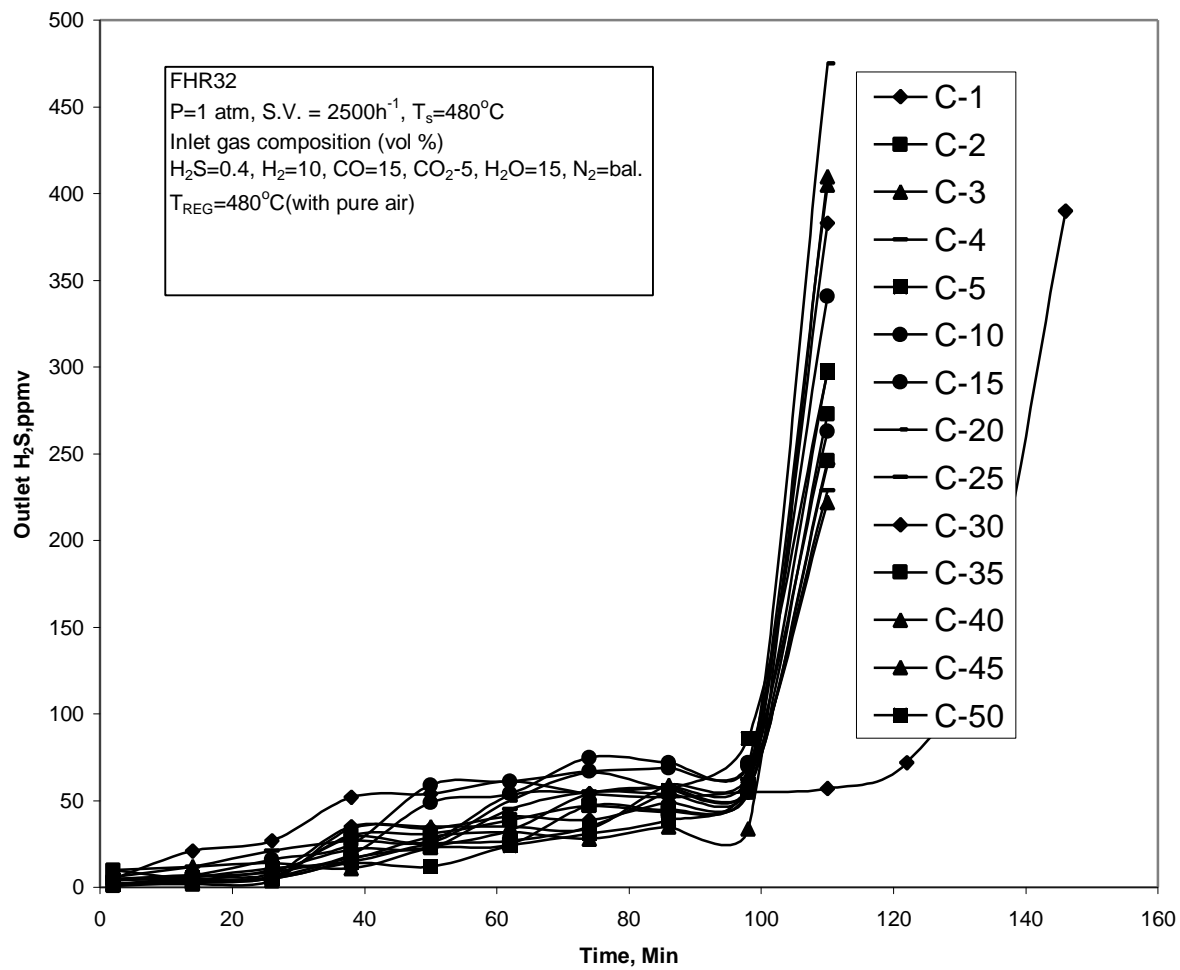
Figure 12. H$_2$S Breakthrough Curves in Successive Sulfidation of FHR-32 Sorbent
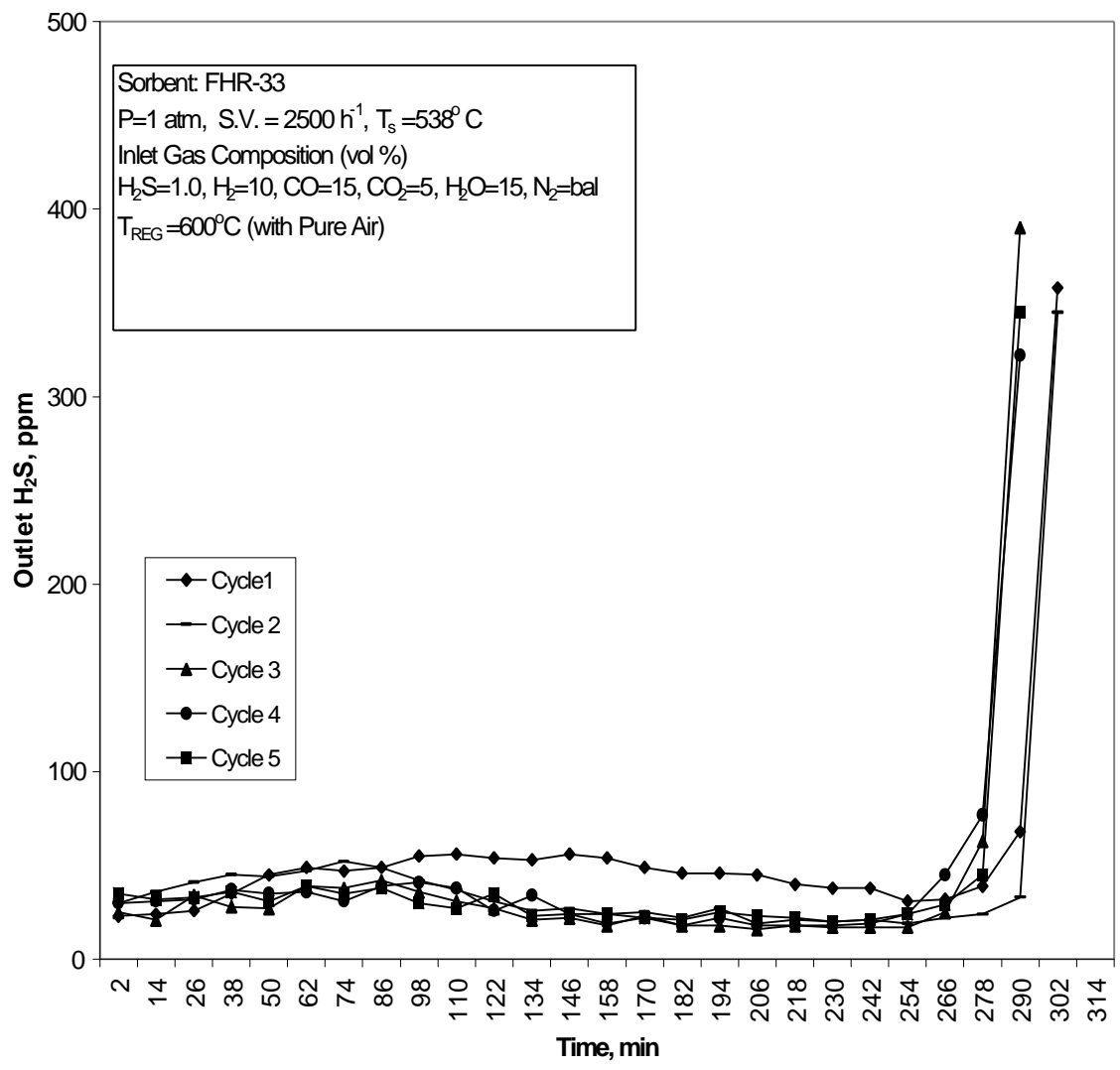
Figure 13. H₂S Breakthrough Curves in Successive Sulfidation Cycles of Sorbent FHR-33

the sulfidation performance of the FHR-33 sorbents. The pre-breakthrough level was less than 60 ppm. There is no decline in activity in 5-cycles tested.

**Advanced Sulfur Recovery Sorbents**

Several sorbents has been prepared and tested. Sulfidation tests were carried out with a sulfidation gas containing (vol %): $H_2S=0.4$, $H_2=10$, $CO=15$, $CO_2=5$, $H_2O=5$ and balance $N_2$. The gas hourly space velocity for the tests was about 2500 $h^{-1}$ both in sulfidation and regeneration. The sulfidation was carried out at $450^oC$. Figure 14 shows the sulfidation performance of the FHR sorbents. The pre-breakthrough level was less than 50 ppm. Both FHR-7 and FHR-8 showed better sulfidation performance. The BET surface areas of the fresh sorbents are shown in Table 1.

Table 4. BET surface area of the FHR sorbents

| Sorbents | BET Surface Area, $m^2/g$ |
|----------|---------------------------|
| FHR-1 | 165.1 |
| FHR-2 | 162.7 |
| FHR-3 | 165.7 |
| FHR-4 | 165.9 |
| FHR-5 | 141.9 |
| FHR-6 | 106.8 |
| FHR-7 | 120.2 |
| FHR-8 | 95.2 |

However, sulfation continued to occur on the sorbent as evidenced by the evolution of $SO_2$ during sulfidation. Sorbent FHR-8 had superior performance in terms of reduced outlet $H_2S$ concentration – less than 10 ppmv – and was selected for subsequent testing.

The formulation for FHR-8 was used as the basis for preparation of two attrition-resistant candidate materials in larger batches, designated AHI-1 and AHI-2. Both samples were tested in the atmospheric thermogravimetric analyzer (TGA) using a combination of gases
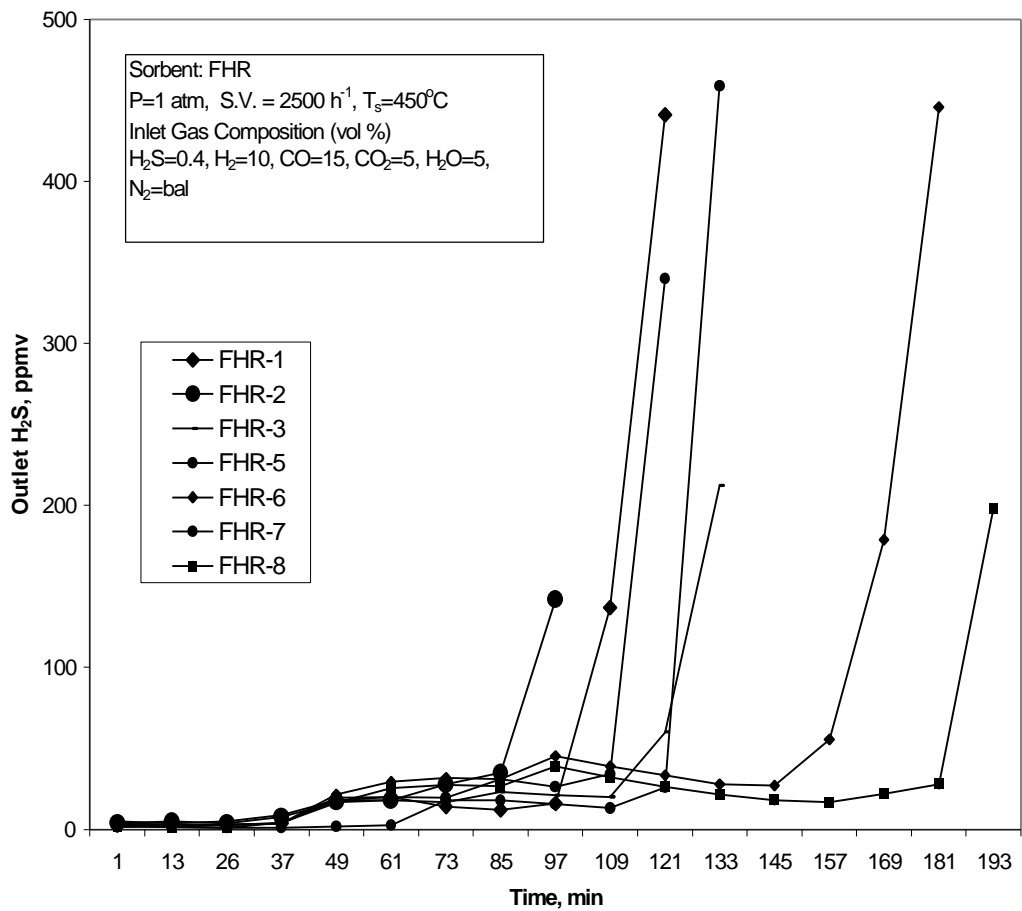
Figure 14.  $H_2S$ Breakthrough Curves in Successive Sulfidation Cycles of FHR Sorbents

and temperatures that simulated the complete AHGP: sulfidation, $SO_2$ regeneration, and $O_2$ regeneration. Variations in specific conditions, and multiple cycles with constant conditions were run in the TGA in order to determine the preferred conditions to use for further testing. The microreactor setup was modified to include $SO_2$ regeneration, as well as sulfidation and air regeneration.

Based on the 3-hole attrition test, the attrition indices for AHI-1 and AHI-2 were 0.5 and 1.2 respectively- respectively – similar to the values for the benchmark FCC catalysts.. The sulfidation performance of AHI-1 and AHI-2 sorbents are shown in Figures 15-16. 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 17 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 $630^oC$.  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
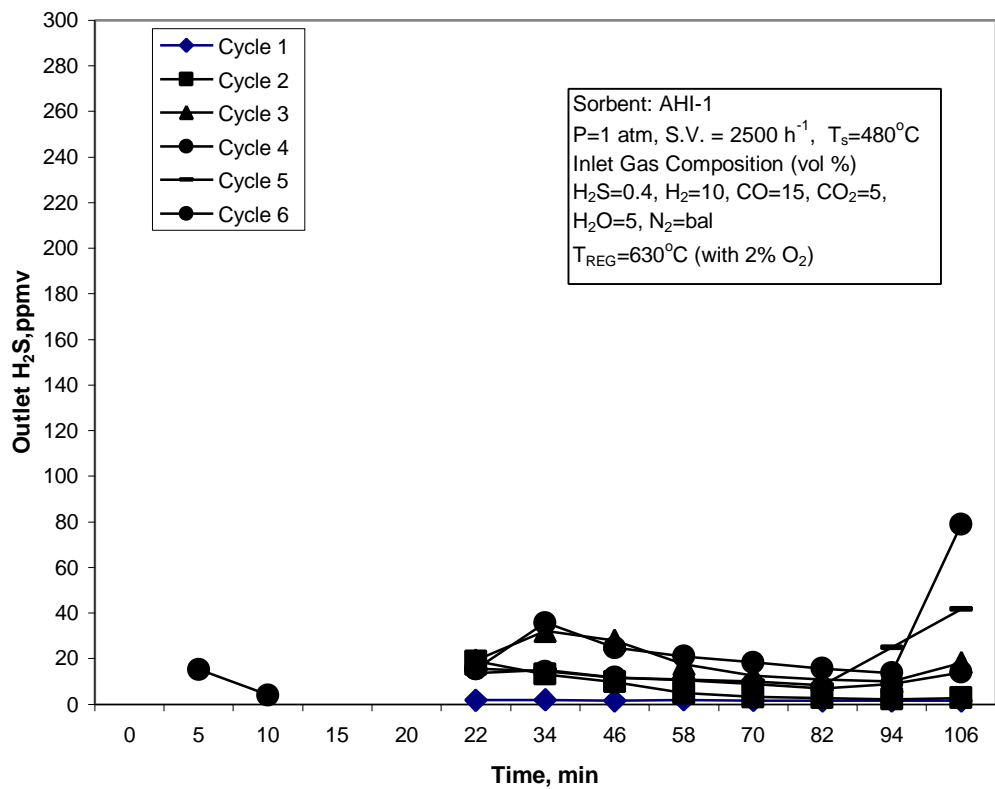
Figure 15. H₂S Breakthrough Curves in Successive Sulfidation Cycles of AHI-1 Sorbent
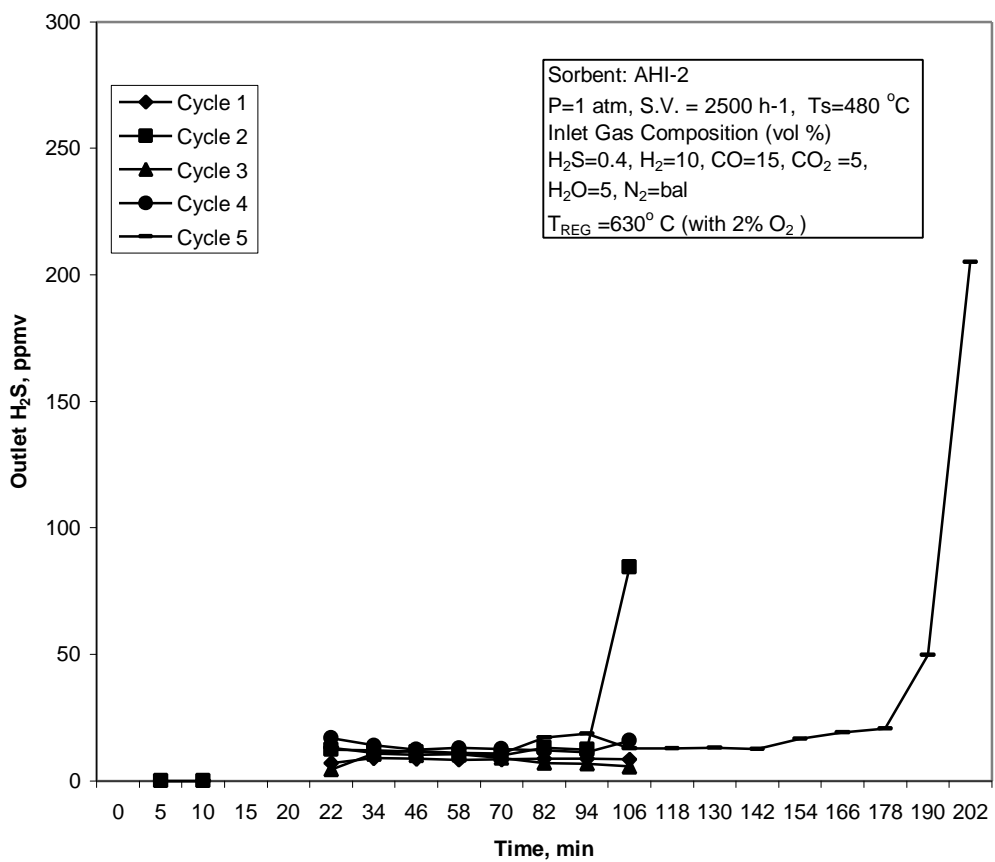
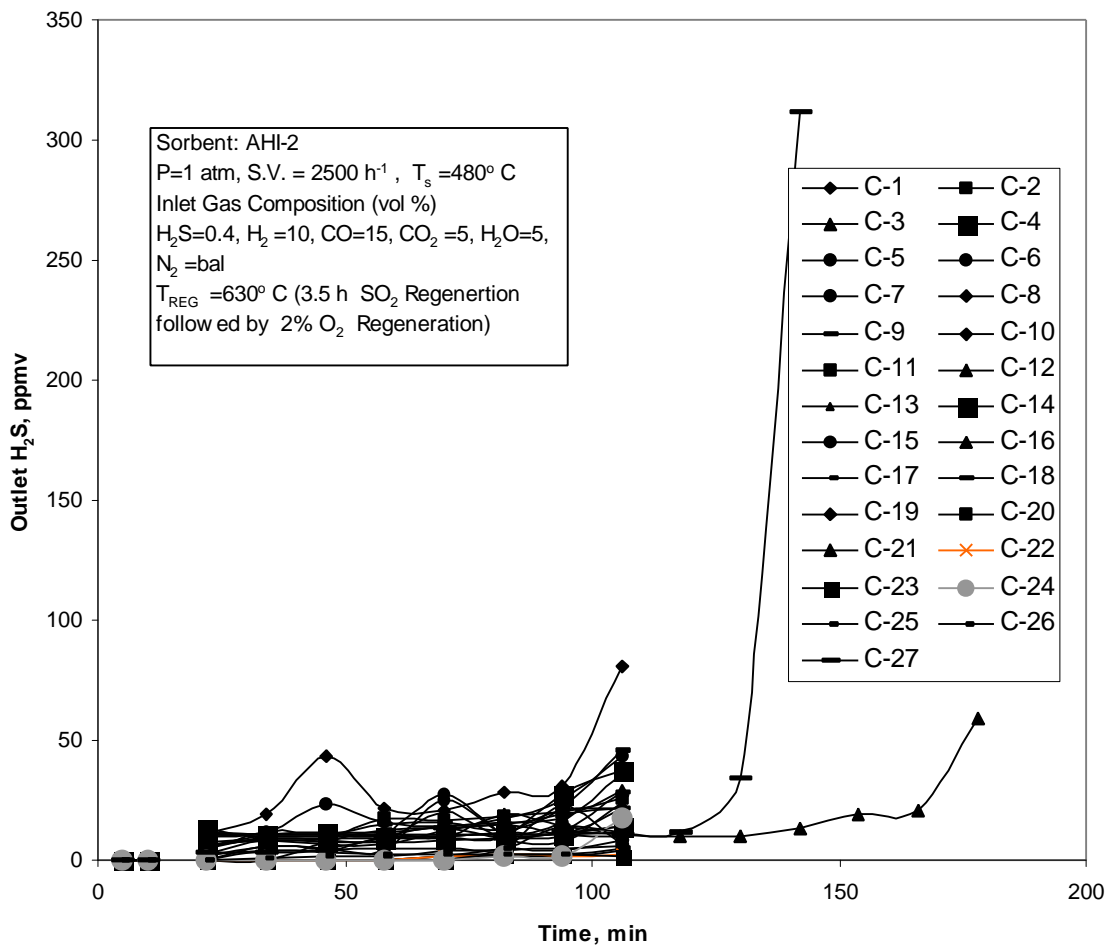Figure 16. H₂S Breakthrough Curves in Successive Sulfidation Cycles of AHI-2 Sorbent

Figure 17. H₂S Breakthrough Curves in Successive Sulfidation Cycles of AHI-2 Sorbent (27 Cycles)

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.

# 5.0 CONCLUSIONS

The techniques employed in this project have successfully demonstrated the feasibility of preparing sorbents that achieve greater than 99% $H_2S$ removal at temperatures $480^oC$ and that retain their activity over 50 cycles. Fundamental understanding of phenomena leading to chemical deactivation and high regeneration light-off temperature has enabled us to successfully prepare and scale up a FHR-32 sorbent that showed no loss in reactivity and capacity over 50 cycles. This sorbent removed $H_2S$ below 80 ppmv and lighted-off nicely at 480oC during regeneration. Overall the test is a success with potential for an optimized FHR-32 to be a candidate for Sierra-Pacific.

An advanced attrition resistant hot-gas desulfurization sorbent that can eliminate the problematic $SO_2$ tail gas and yield elemental sulfur directly has been developed. Attrition resistant Zn-Fe sorbent (AHI-2) formulations have been prepared that can remove $H_2S$ to below 20 ppmv from coal gas and can be regenerated using $SO_2$ to produce elemental sulfur.

## 6.0 RECOMMENDATIONS

Future work should address the following issues:

?? Because the complex nature of coal gas cannot be duplicated completely in the laboratory, additional parametric and long term tests on an optimized FHR-32 sorbent should be performed at high pressure and practical IGCC temperatures as low as 343oC.

?? Further studies should be aimed toward determining the effect of trace contaminants such as chloride, alkali, and particulates on the sorbent kinetics and performance

?? Testing of improved FHR-32 sorbents should be carried out in bench-scale fludized-bed reactors and M.W. Kellogg's transport reactor test unit.

?? Further work should focuses on sorbent improvements using metallic additives to the zinc-iron sorbent to produce advanced attrition-resistant sorbents that can consistently reduce the $H_2S$ during sulfidation to less than 20 ppmv.

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