Advanced Sulfur Control Concepts for Hot Gas Desulfurization Technology

Quarterly Report
October 1 - December 31, 1997

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For
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TABLE OF CONTENTS

LIST OF FIGURES

1. CONTRACT OBJECTIVE:

The objective of this project is to develop a hot-gas desulfurization process scheme for control of H_2S in HTHP coal gas that can be more simply and economically integrated with known regenerable sorbents in DOE/METC-sponsored work than current leading hot-gas desulfurization technologies. In addition to being more economical, the process scheme to be developed must yield an elemental sulfur byproduct.

2. TECHNICAL APPROACH:

The Direct Sulfur Recovery Process (DSRP), a leading process for producing an elemental sulfur byproduct in hot-gas desulfurization systems, incurs a coal gas use penalty, because coal gas is required to reduce the SO_2 in regeneration off-gas to elemental sulfur. Alternative regeneration schemes, which avoid coal gas use and produce elemental sulfur, will be evaluated. These include (I) regeneration of sulfided sorbent using SO_2; (ii) partial oxidation of sulfided sorbent in an O_2 starved environment; and (iii) regeneration of sulfided sorbent using steam to produce H_2S followed by direct oxidation of H_2S to elemental sulfur. Known regenerable sorbents will be modified to improve the feasibility of the above alternative regeneration approaches. Performance characteristics of the modified sorbents and processes will be obtained through lab- and bench-scale testing. Technical and economic evaluation of the most promising processes concept(s) will be carried out.

3. CONTRACT TASKS:

Phase I - Concept Assessment:

Completed.

Phase II:

Economic Analysis and Process Simulation

The process simulations were essentially completed this quarter for both the Advanced Hot Gas Desulfurization Process (AHGP) and the DSRP-based processes. The flow rates of all the streams and the ratio of active ingredients to inert ingredients in the sorbents were adjusted so that adiabatic reactor blocks would predict acceptable outlet temperatures. This approach resulted in simpler reactor designs, at the cost of higher flow rates in some instances, and thus larger reactors.

The current revision of the AHGP ASPEN PLUS simulation is attached as Appendix A. The target reactor outlet temperatures were achieved by adjusting the sorbent composition and flow rate. This change resulted in a very large required sulfur dioxide (SO_2) recycle

loop flow to satisfy the fluidization velocity and residence time requirements of the SO_2 regenerator reactor design, as originally conceived. That design was reexamined, and a deeper bed concept was used to reduce the SO_2 recirculation rate to a more reasonable level, although the reactor still ended up being larger in diameter than the initial rough calculations suggested. The attached simulation flow sheet includes these changes. The group of blocks that represent the SO_2 and O_2 regeneration are labeled as a "Three Stage Regenerator" on this flow sheet. The top stage, designated HX-STAGE, represents the heat transfer between the cooler sorbent coming from the desulfurization reactor, and the hotter regeneration gas rising from the SO_2 regenerator. The middle stage is designated REGEN2 and models the SO_2 regeneration. The bottom stage, designated REGEN1, represents the O_2 regeneration. The SO_2 recirculation rate was fine-tuned using "manual iteration" to achieve the required volumetric flow at the predicted reactor conditions (based on adiabatic reactor operation). The sorbent fluidization velocity for the bubbling bed regenerator was what determined the required volumetric SO_2 flow.

For the DSRP-based process, the finalized process design uses a transport reactor for the desulfurizer, a transport reactor for the air regenerator, and a fast fluid-bed reactor for the DSRP reactor. The DSRP reactor design is a change from the earlier concept in which a bubbling fluid bed was being considered. The change means that the main vessel of the reactor will be adiabatic, and that the heat of reaction will be removed from the recirculating DSRP catalyst in a standpipe.

The steam generation portions of the two processes were modeled using separate flow sheets. Some interations in equipment arrangement and stream conditions were required to make them consistent with the major process equipment flow sheets. Some fine tuning was necessary after a meeting to discuss the details of modeling the steam and cooling water loops.

The reactor costing methodology was devised and reactor cost calculations were performed. The costing is based on the bulk weight of metal required to fabricate the required pressure vessels using wall thicknesses determined by the ASME code. Factors for the cost of stainless steel, and for the installation cost based on the fabrication cost, are applied to the base carbon steel fabricated cost to estimate the total installed cost of a stainless steel vessel.

Some additional costing bases were established for the economic analysis:

C   The incremental oxygen required for the AHGP regeneration was valued at $20 per ton. The existence of an air separation plant was assumed, so no capital cost estimate is needed for the analysis.

C   Rather than attempting to calculate the incremental additional electrical power that could be produced from the steam raised from the reactor waste heat, an operating cost credit of $3.90 per thousand pounds of steam was assigned.

C   Both hot gas desulfurization processes consume a quantity of the coal gas that is being desulfurized, and thus reduce the amount of electricity that could be generated from a given quantity of coal charged to the gasifier. No information on gasifier economics was readily available with which to calculate a coal gas value. Therefore, the value of the consumed coal gas was assumed to be equal to the value of electricity that could have been produced from it, based on an electricity cost of $0.04 per kilowatt-hour.

The calculation of the amount of electricity equivalent to a quantity of coal gas requires a number of assumptions for energy transformation efficiency . To simplify this calculation, the design of the Sierra Pacific IGCC plant was taken as the basis to relate coal gas flow and net power output. A close review of the final process simulations showed that the plant capacity assumptions that had been used up to this time did not quite match this design basis, and some calculations were refined slightly.

The ASPEN software does not automatically calculate pressure drop through the equipment blocks, and after several revisions of flow rates and clarification of the reactor design being simulated, the original assumptions used in both processes seemed too low. Some additional effort was expended to arrive at reasonable pressure drops for both process simulations. This information was needed to estimate the cost and duty of the SO_2 recycle compressor in the AHGP, and the cost and duties of the air compressor and the tail gas compressor in the DSRP-based process. This work will be concluded during the preparation of the revised final report, when it is expected that revised process simulations will be generated.

Capital cost estimates for the reactors were prepared using the methodology described last month. The internal ASPEN cost estimating algorithms were used for the heat exchangers. Operating costs were estimated utilizing the factors discussed above, plus additional assumptions. This information was included in the draft final report that was received from NCSU. Review of the draft report suggested that the lower operating cost of the AHGP, corresponding to lower coal gas consumption, may offset the AHGP's higher capital cost to yield a lower levelized cost contribution to electricity. However, this result is currently preliminary and under review. A revised final report was due to RTI on December 18, 1997, with a draft topical report to be prepared by the end of January, 1998. However, during review of the draft report from NCSU some areas of incompleteness were noted in the process simulations that could have a bearing on the overall conclusions. Additional simulation work needed to be done before the final report could be prepared.

Because the estimates of the equipment and system pressure drops in the AHGP simulations that were used to prepare the draft final report were quite low, it seemed likely that the power requirement of the sulfur dioxide (SO_2) recycle compressor was understated. Similarly, low pressure drop estimates in the DSRP simulation resulted in an understatement of the required discharge pressure of the regeneration air compressor. The AHGP reactor sizing estimates also needed to be revised so that the proposed

vessels would fit realistic shipping size limitations. Although this constraint resulted in the need for multiple reactors, the total capital cost may be reduced.

The revisions to the process simulations, and the resulting revisions to the cost estimates resulted in more work to be done than could be accomplished by the end of December. Therefore, the schedule for a final revised report from NCSU will not be met, as noted below in Open Items.

Bench-Scale Sorbent Testing

Bench-scale testing was conducted with the first candidate sorbent. Eight cycles were completed with mixed results. Designated FHR-4, the sorbent is ?-alumina impregnated with iron and molybdenum, intended to replicate the type of sorbent described by ECN researchers[1] as being able to reduce the H_2S concentration below 20 ppm. A fixed-bed microreactor test achieved this level of performance, as Figure 1 shows. Based on the composition described in the reference, small batches were prepared following three different preparation methods. Of the three techniques, the one designated FHR-3 gave the longest time to breakthrough. That method was used for preparation of the larger batch, FHR-4, that was tested in the bench unit.

The initial bench-scale testing did not appear to achieve either the activity or the capacity exhibited in the microreactor tests.   Close observation of the apparent sorbent behavior as indicated by the gas analyses suggested that the disappointing results may not have been representative of the sorbent, but may have been artifacts caused by contamination from the process equipment. After completion of four cycles, the decision was made to replace all of the preheater coils with new tubing, and to route the hydrogen sulfide-containing gas mixture to the reactor separately from the other components of the synthetic coal gas mixture. Furthermore, a separate air line was installed so that the regeneration air would be introduced directly into the reactor without passing through any tubing that might have coking present. Figure 2 is a process flow diagram showing the revised configuration of the bench unit.

Following the the equipment modifications, the testing was completed with somewhat disappointing results. Figure 3 summarizes the results of the sulfidation testing by plotting the H_2S breakthrough curves in a dimensionless format. The ratio of the observed sorbent capacity to the theoretical capacity (C/C_0 on the y-axis) is plotted as a function of the ratio of the elapsed time that H_2S was flowing compared to the theoretical elapsed time (t/t_0 on the x-axis). The pre-breakthrough concentration of H_2S during the 8 cycles of testing was acceptable, at 30 ppm or less. However, Figure 3 shows that there was a significant loss

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[1]deWild, P.J., J.H.A. Kiel, and E. Schenk. "Iron Oxide/Molybdenum Oxide Sorbents for High Temperature Fuel Gas Desulfurization." In *Procedings of the Thirteenth Annual International Pittsburgh Coal Conference (1996)*.

Figure 1. Results of Microreactor Sulfidation Tests.
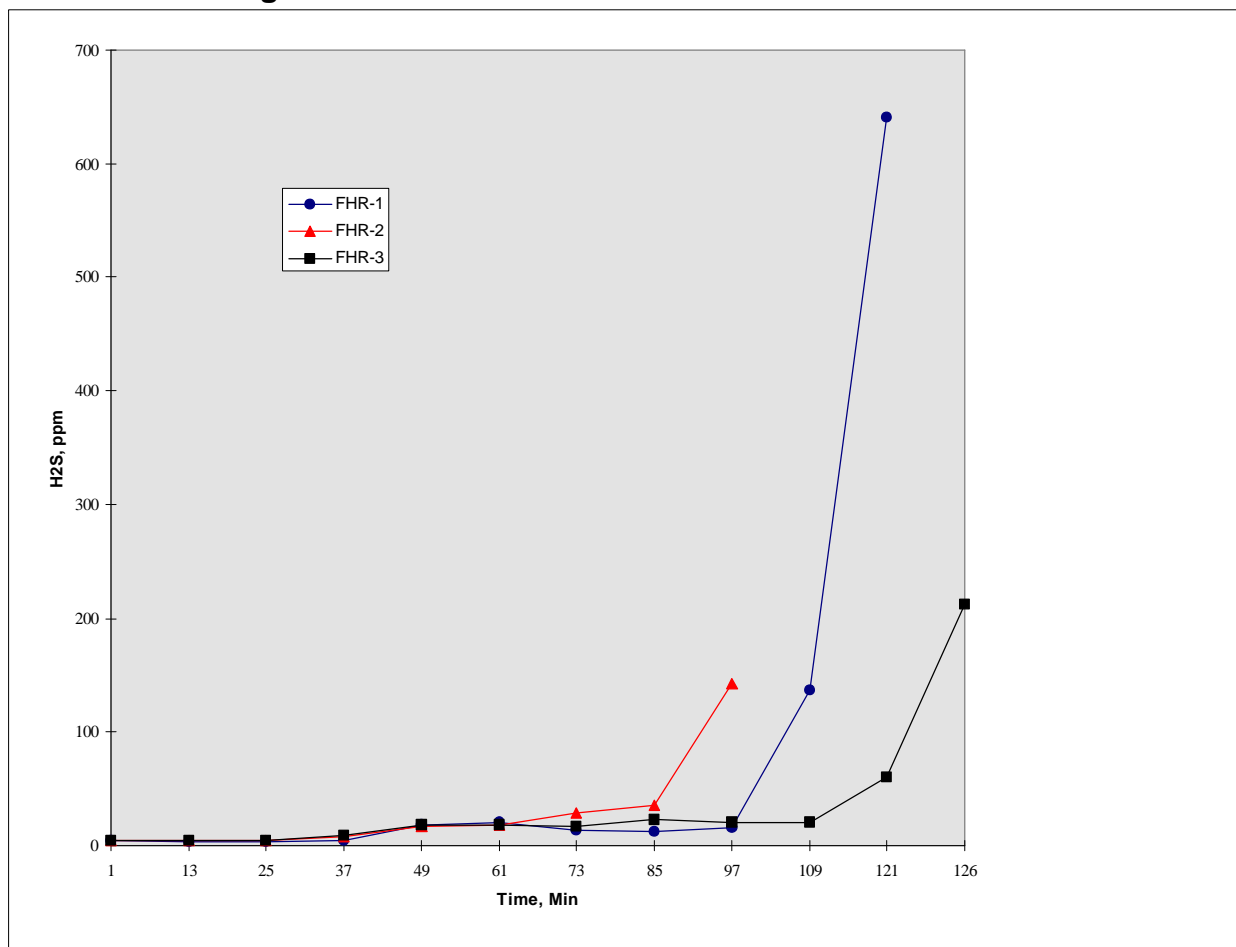
of capacity. Ideally, on a graph of this type, the data from all the cycles would be coincident.

The SO_2 evolved during the air regeneration half cycles was monitored closely, and a sulfur material balance was attempted. It appeared that a significant portion of the absorbed sulfur was not released during regeneration, and the formation of sulfate was suspected. This idea was at least partially confirmed when reductive regeneration conditions at the start of the subsequent sulfidation half cycle resulted in H_2S evolution. The capacity of the sorbent could not be fully restored, however.

The FHR-4 sorbent was removed from the reactor and additional physical tests of the sorbent are underway to try to determine the reason for the loss of capacity.

Potential sorbents are currently being tested with the micro-scale reactor to determine the conditions that result in sulfate formation (sulfation), and to determine the effect of multiple cycles of sulfidation and regeneration. The sorbent calcination temperature, additives (Ni, Co, Mo) and additive content are systematically being evaluated. This small scale work is being conducted prior to selecting the next candidate for bench-scale tests.

5

Figure 2. Revised Configuration of Bench-Scale Sorbent Test Unit for AHGP Sorbent Testing.
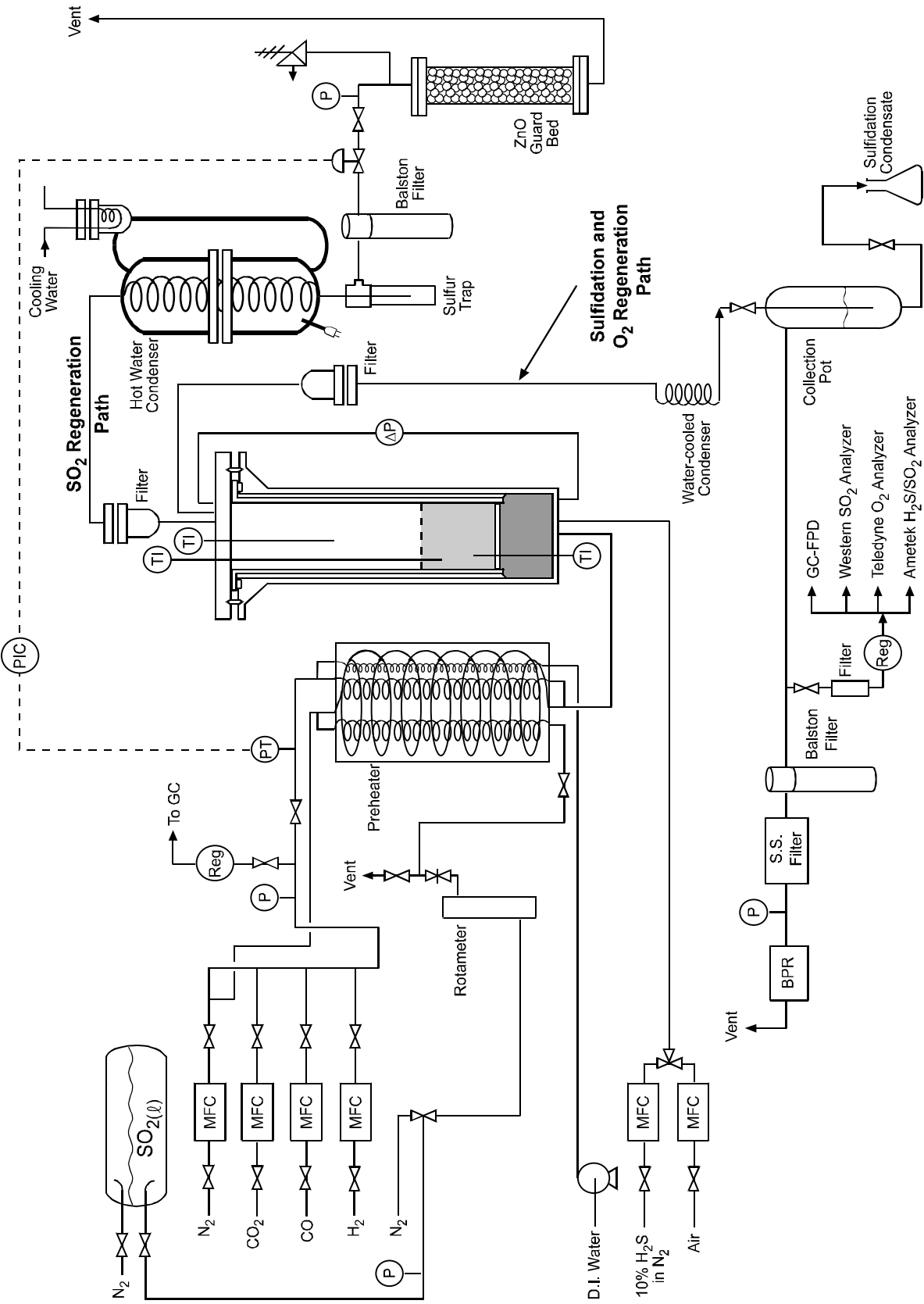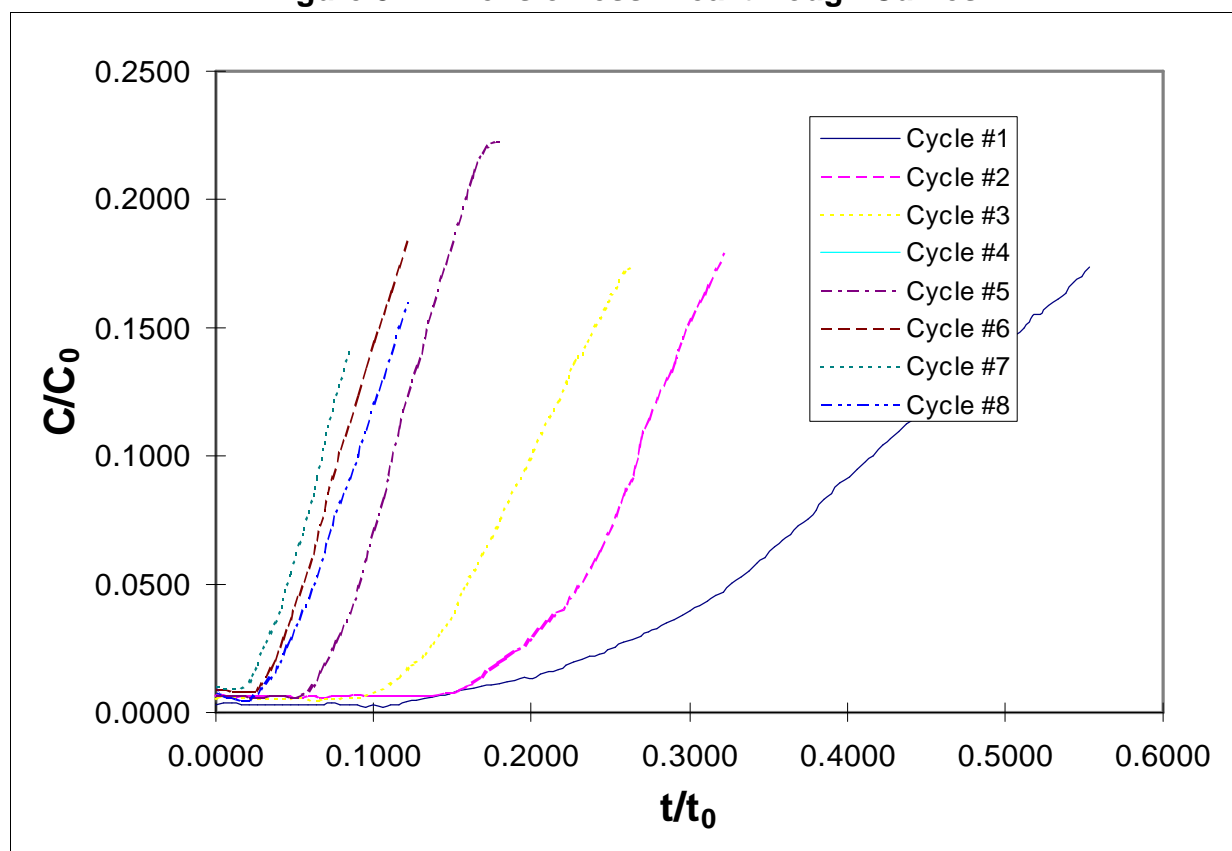
6

Figure 3. Dimensionless Breakthrough Curves.

Some preliminary results are available from the additional mircoreactor testing. Runs with sorbents FHR-6 and FHR-8 showed that using a higher calcination temperature resulted in stable capacity from cycle to cycle after the third cycle. However, sulfation continued to occur on the sorbent as evidenced by the evolution of SO_2 during sulfidation.

Figure 4, the sulfidation performance of sorbent FHR-6, shows equivalent performance in cycles 3 and 4. Figure 5, regeneration with 4.8% oxygen in nitrogen, shows that the amount of SO_2 produced in cycles 3 and 4 (area under the curve) was approximately the same — further evidence of stable sorbent capacity. However, as Figure 6 shows, there is some evolution of SO_2 at the start of each subsequent sulfidation cycle, presumbably arising from the decomposition of sulfate formed during the previous sulfidation half-cycle.

Figures 7-9 present similar information for sorbent FHR-8. Figure 7, the sulfidation results, shows superior performance in terms of reduced H_2S outlet concentration (less than 10 ppm). Figure 8, regeneration, shows relatively consistent capacity from cycle to cycle for this material. But, as Figure 9 shows, there is still sulfate being decomposed at the start of each subsequent sulfidation half-cycle.

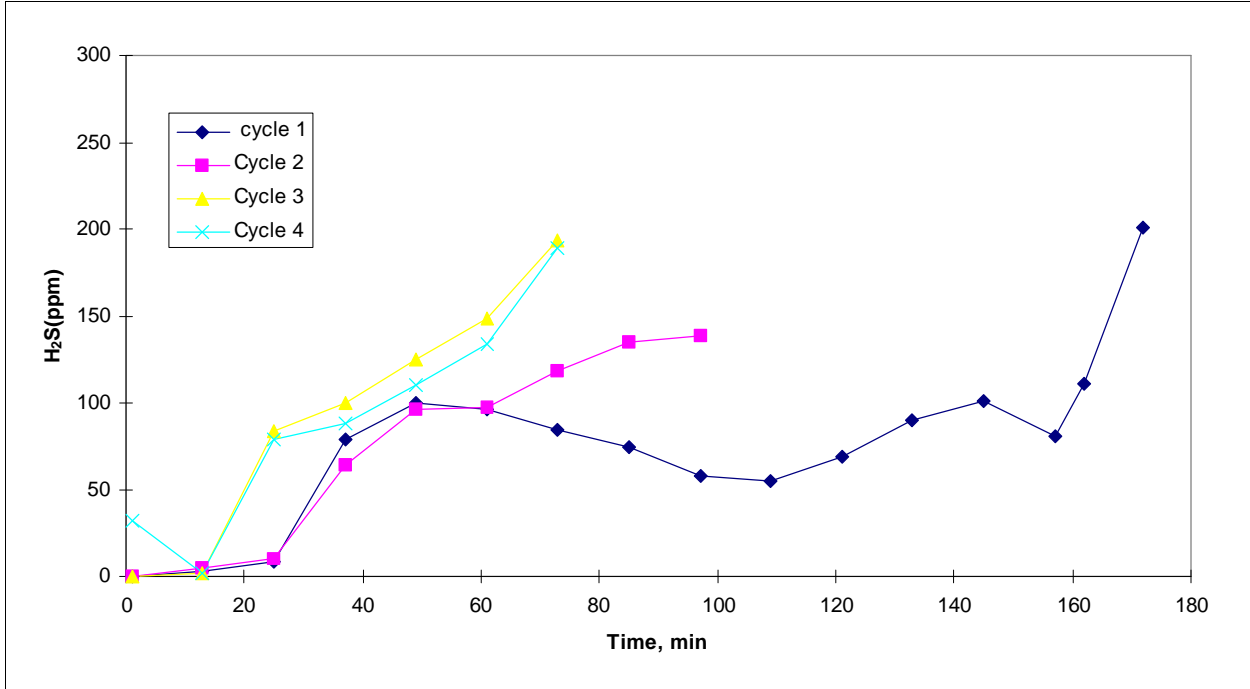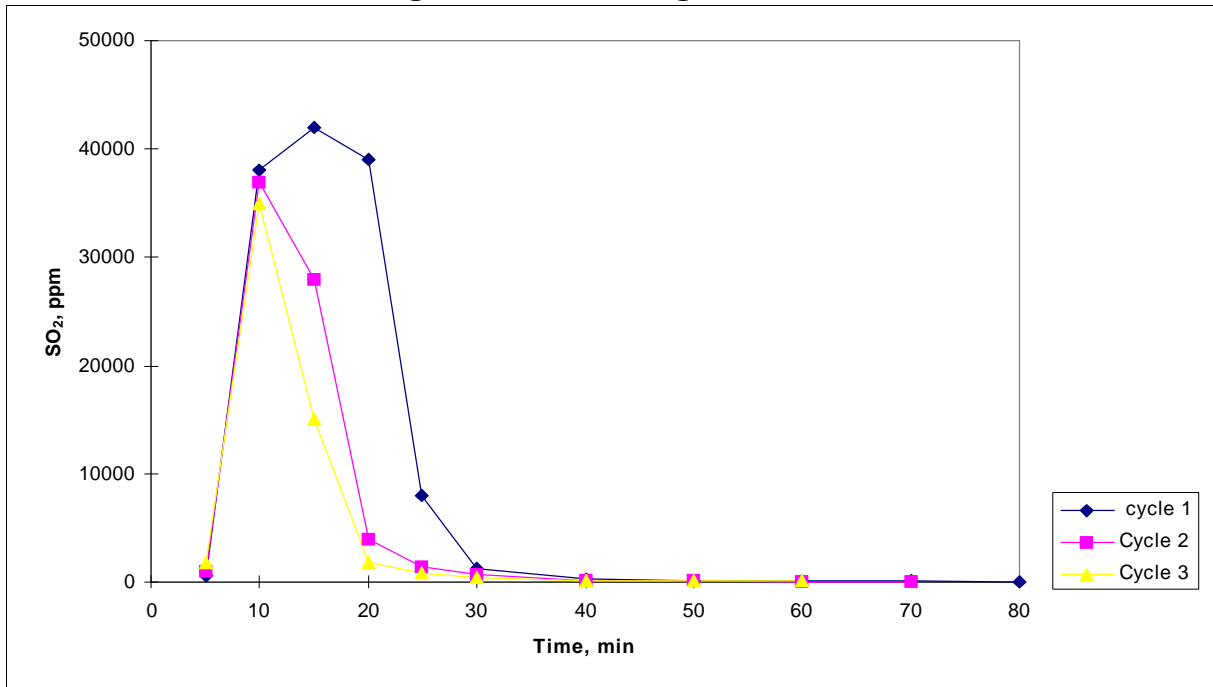**Figure 4. FHR-6 Sulfidation.**

Figure 5. FHR-6 Regeneration.
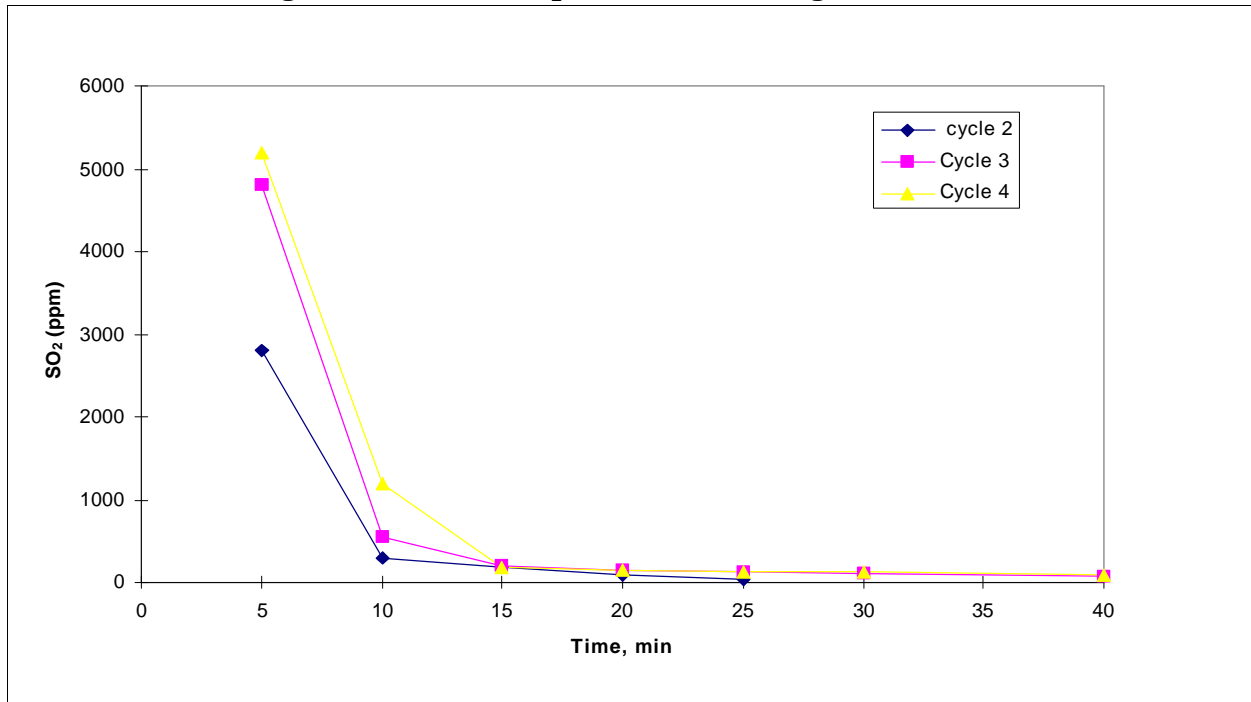

8

Figure 6. FHR-6 SO$_2$ Evolution During Sulfidation.
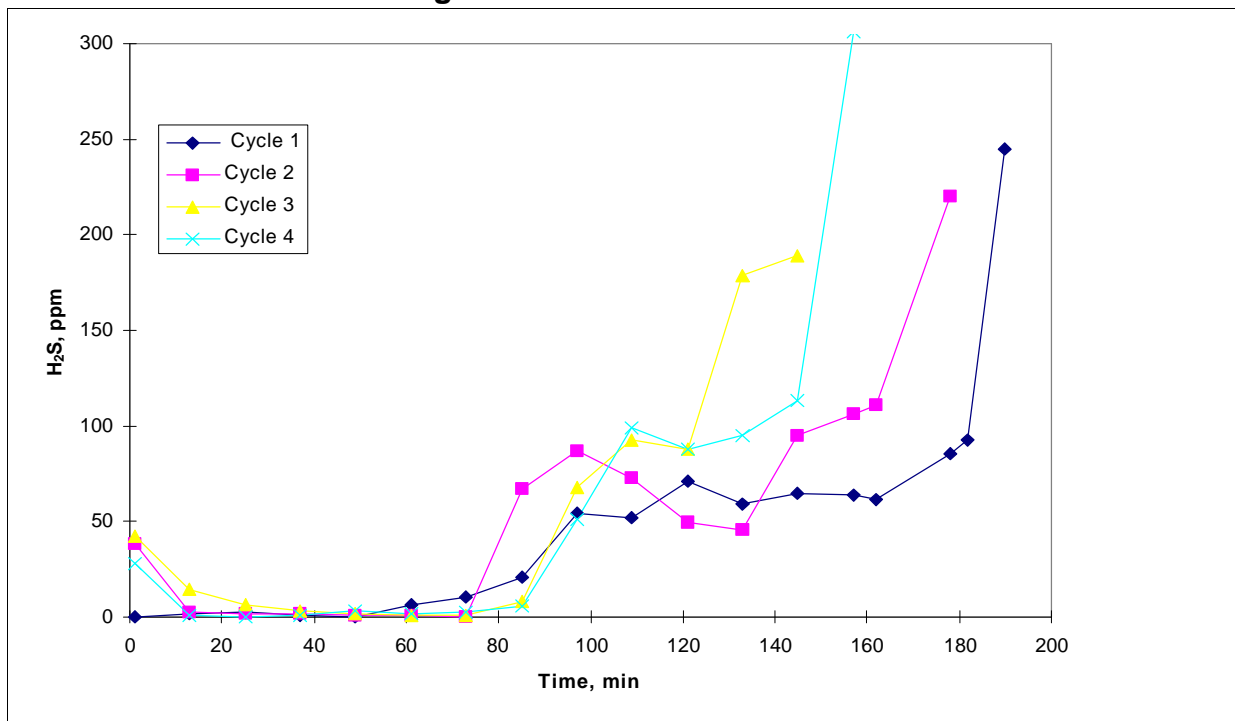

Figure 7. FHR-8 Sulfidation.
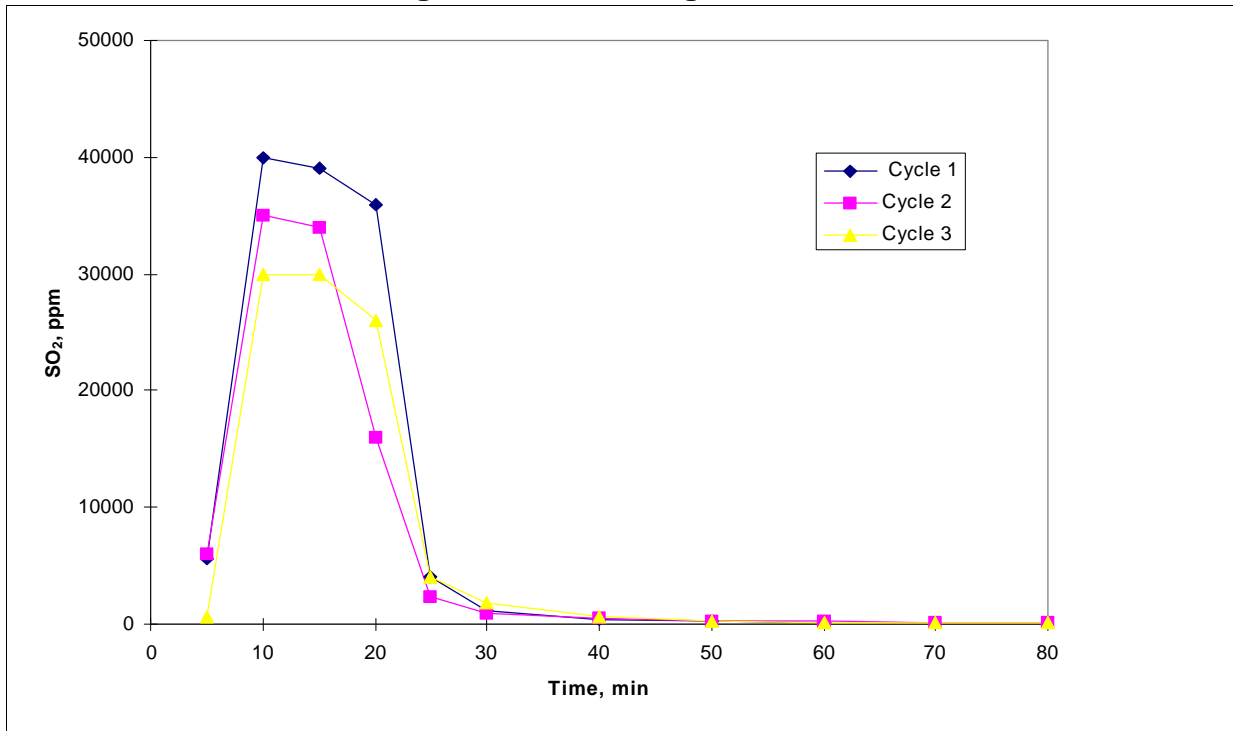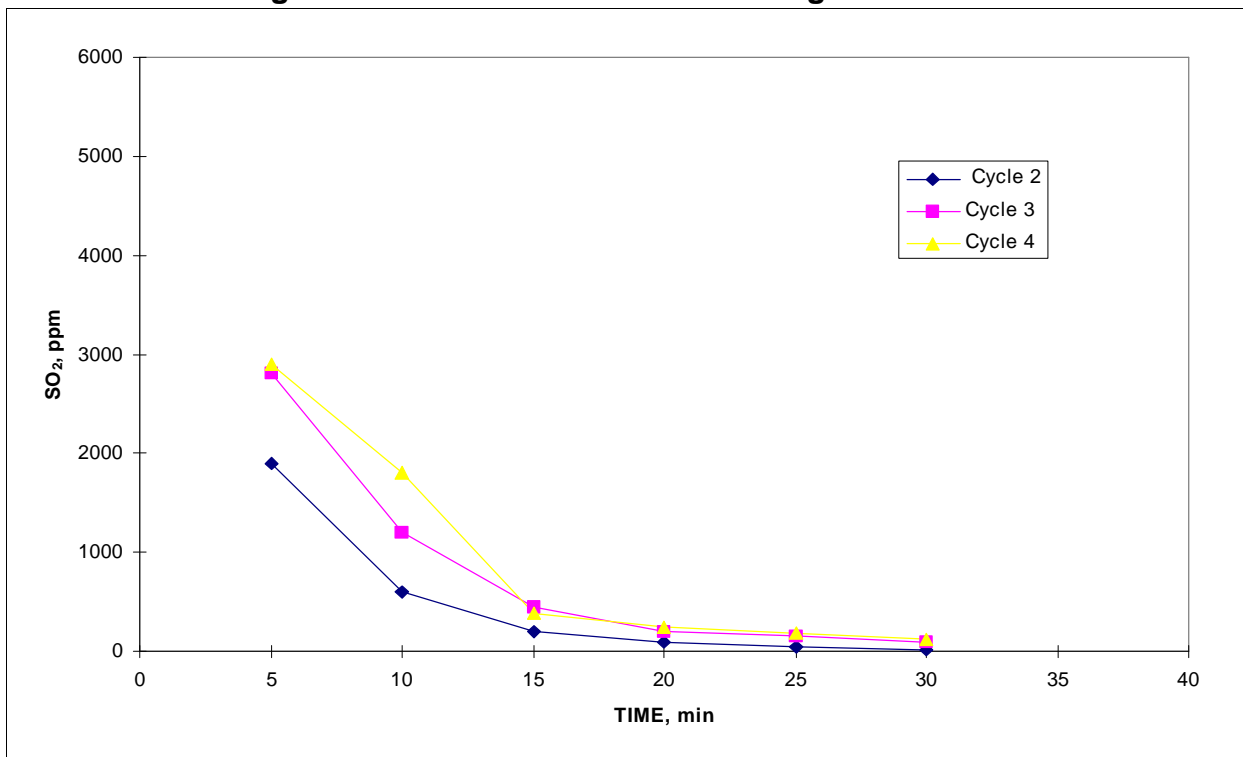
Figure 8. FHR-8 Regeneration.

Figure 9. FHR-8 SO2 Evolution During Sulfidation.

<u>PSDF Field Test</u>

The Mobile Laboratory has been temporarily installed at RTI and electrical service has been provided so that interior construction and renovation work can begin. Work has started on the preliminary design and engineering of the renovations to the Mobile Laboratory bench-scale sorbent test rig. A meeting was held at the Power Systems Development Facility (PSDF) on December 19, 1997, with key personnel from Southern Company Services, the on-site contractor, to discuss the implementation of the planned slipstream field test. The sorbent test program is going to be easily integrated with the concurrent Direct Sulfur Recovery Process slipstream test, also discussed at the PSDF meeting.

4.   OPEN ITEMS

The milestone date for submission of the topical report covering the economic analysis and process simulation was originally set for January 31, 1998. However, as of the writing of this report, the revised final report had not been received from N.C. State University. The expectation is that this information will be available by mid-February, 1998, so that a draft topical report can be submitted March 15, 1998.

5.   PLANS FOR NEXT QUARTER:

!   Complete the ASPEN PLUS simulations by incorporating revised pressure drop estimates into the SO_2 recycle loop of the AHGP process, and complete the sizing and cost estimating of the SO_2 recycle loop compressor.

!   Review the final report from NCSU and incorporate it into a topical report covering the economic analysis and process simulation.

!   Continue to conduct microreactor tests with selected sorbents.

!   Prepare draft and final trip report covering the December 19, 1997, meeting at PSDF.

!   Continue the engineering design effort for refurbishing the Mobile Laboratory.

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AHGP Advanced Hot Gas Process

AHGP 10/16/97

Legend:
- Temperature (C)
- Pressure (PSI)
- Flow rate (LB/HR)
- Q   Heat duty (BTU/HR)
- W   Power (HP)

CLEAN-CG
482 / 275 / 448832

H2S-CG
482 / 275 / 450484

DESULF
RSTOIC
Q =0

INDESULF

DSULSTND
SEP
482 / 275 / 780851
Q =0

450 / 275 / 164358
COLDSORB

RGENSTND

STNDPIPE
482 / 275 / 166009
Q =0

FES-ZNS
482 / 275 / 166009

Q =-14850
631 / 275 / 164358

LIFTDFEO

631 / 275 / 35000
N2EXIT

LIFTPIPE
SEP
Q =0

N2-COOLR

Q =-715149
200 / 260 / 35000

N2-COOL

LIFTCOMP

W =-66

210 / 275 / 35000
N2SOURCE

FEO-ZNO

UNP-RSO2
140 / 270 / 68674

SO2-COMP
W =-14

142 / 275 / 68674
RECYCLE

Three Stage Regenerator

HX-STAGE
REQUIL
Q =0

512 / 275 / 74586
COOLS2

580 / 275 / 74586
MADE-S2

512 / 275 / 166009
COOLFES

REGEN2
RSTOIC
Q =0

556 / 275 / 239767
INREGEN2

S-REGEN2
REQUIL
Q =0

714 / 275 / 73758
MADESO2

580 / 275 / 165181
FEO-ZNS

714 / 275 / 164358
FEO-ZNO

S-REGEN1
SEP
Q =0

714 / 275 / 238116
INREGEN1

REGEN1
RSTOIC
Q =0

441 / 275 / 72935
FEEDRG1

FEEDRG1

COND-EQ
RSTOIC
Q =-5380022

IN-COND
140 / 270 / 74586

DEMISTR
FLASH2

140 / 270 / 5912
PS2
Q =0

127 / 15 / 181
UP-SO2

CON-COMP
W =8

499 / 275 / 181
P-SO2

SO2MIX

143 / 275 / 68855
RECYCLES

315 / 74586
S2V+L

LP-COND
FLASH2
Q =0

127 / 15 / 5731
SULFUR

HEATX
Q =5096530

240 / 72935
WARMRCY

RCYHEATR
Q =2593862

143 / 68806
MOD-RECY

X-FLOW

134 / 275 / 72935
COLDFEED

MIXFEED

30 / 275 / 4129
O2