

TDA Inc./FETC CRADA No. 97-F003, Final Report

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Executive Summary

This report describes the results of a Cooperative Research and Development Agreement (CRADA) between TDA Incorporated and the Federal Energy Technology Center (FETC) in Morgantown, West Virginia. The objective of this CRADA was to evaluate the performance of TDA's hot gas desulfurization (HGD) sorbent for use in fossil fuel gasification processes. This particular sorbent, TNT-MB was developed for use in moving-bed HGD reactors in an integrated gasification combined cycle (IGCC) power plant. Two separate tests were conducted; a 10-cycle test, and a low-temperature scoping test.

The 10-cycle test was part of a testing protocol developed by FETC and General Electric (GE) to simulate operation of GE's moving-bed HGD reactor being used at the DOE-sponsored Tampa Electric Power Company (TECO) Clean Coal Technology Project. The 10-cycle test was conducted according to the protocol guidelines with the exception of some deviation to the regeneration procedures that were identified by TDA to optimize their sorbent performance in the GE reactor at TECO. The general acceptance criteria for the 10-cycle test was as follows:

1. Inlet sulfur loading in the absorber to be greater than or equal to 6.7 lbs of sulfur/ft³ of bed. (This was used to establish 125 minutes of calculated reactant gas flow during sulfidation.)
2. Attainment of sulfur loading without exceeding 200 ppmv H₂S in the absorber outlet. This is defined as "breakthrough" for the Protocol Test. (At TECO, 50 ppmv H₂S is the outlet breakthrough concentration requirement.)

All 10 cycles absorbed H₂S for the prescribed 125 minutes without breakthrough. The H₂S concentration remained below 50 ppmv throughout the 125 minute test period. Cycle 10 was extended until breakthrough which occurred approximately 7.3 hours after the cycle was begun. The sorbent also showed an increase in attrition resistance from 1.8% (fresh) to 0.87% (reactor inlet) and 0.64% (reactor outlet) after 10 cycles.

The other test that was conducted during the course of this effort was a lower temperature scoping test. Inlet absorption gas temperatures of 600 °F and 700 °F were evaluated. Sulfur capture was shown to be very effective at both conditions. Regeneration using 700 °F inlet "air" at 4% oxygen proved to be adequate for oxidizing the sorbent.

The results of an additional attrition test are also contained in this report. As part of the moving-bed test protocol, a 25-cycle test was conducted on the TNT-MB sorbent by the Institute of Gas Technology (IGT). At the request of TDA, FETC performed attrition test ASTM D4058-92 on various sorbent samples from the IGT test. The results can be found at the end of this report.

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1.0 Introduction

This Corporative Research and Development Agreement (CRADA) between TDA Inc. and the Federal Energy Technology Center (FETC) in Morgantown, West Virginia was to evaluate the performance of a hot gas desulfurization (HGD) sorbent being developed by TDA Inc. for use with fossil fuel gasification processes. The sorbent, TNT-MB, was tested under guidelines developed to simulate the Tampa Electric Power Company's (TECO) Clean Coal Technology Project, which is being co-sponsored by FETC DOE. The test protocol guidelines (Appendix A) were developed by FETC with consultation from General Electric, who is the supplier of the moving-bed hot gas desulfurization (HGD) reactor being used at TECO. Specifically, a 10-cycle test as identified by the protocol was conducted with the exception of some regeneration procedure deviations identified by TDA that are particular to the use of their TNT-MB sorbent.

In addition to the 10-cycle test, a lower-temperature scoping test was conducted to assess the sorbents ability to absorb and regenerate utilizing reactant gases at 700 °F inlet temperatures. The need to answer this question necessitated from the possibility that TECO would only be able to supply fuel gas from their gasifier subsystem to the moving-bed HGD reactor at 700 °F as opposed to the planned 900 °F gas delivery temperature.

The results an additional attrition test are also contained in this report. As part of the moving-bed test protocol, a 25-cycle test was conducted on the TNT-MB sorbent by the Institute of Gas Technology (IGT). At the request of TDA, FETC performed attrition test ASTM D4058-92 on various sorbent samples from the IGT test. The results can be found at the end of this report.

2.0 Experimental Facility

2.1 High pressure, high temperature, bench-scale reactor

The experimental facility that was used to conduct this CRADA is located at the Federal Energy Technology Center (FETC) in Morgantown, West Virginia. Among the various process reactors located at the site is a high pressure, hot gas desulfurization unit (HPHGDU). The high pressure HGD unit was designed, constructed, and operated in the late eighties to test and evaluate the performance of various sorbents for hot gas desulfurization in a fixed bed or fluidized bed mode. This unit has been used in the conduct of other CRADAs as well as testing, evaluating, and developing various sorbents in support of the Integrated Gasification Combined Cycle (IGCC) power system, which is one of the coal fired power systems of the Clean Coal Technology Demonstration Program sponsored by the U. S. Department of Energy.

The high pressure HGD unit is a unique facility with high-temperature and high-pressure capability and can be operated either as a fixed bed or a fluidized bed reactor. A simplified process flow diagram of the high pressure unit is shown in Figure 2.1. The reactor is constructed of a 6-inch diameter by 5-feed long Incoloy 800HT alloy steel pressure vessel. Inside the vessel is

a removable, 316 stainless steel sorbent cage for easy loading and unloading of the sorbent. Three different sizes, 2-inch, 3-inch, and 4-inch diameter by 30-inch long sorbent cages, can be suspended from the top flange of the alloy steel reactor shell. A gas distributor is fixed at the bottom of the cage to support the sorbent. The sorbent cage is treated with aluminum oxide to prevent corrosion of stainless steel by sulfur gases in the presence of steam. The entire reactor is housed inside of a three-zone furnace equipped with separate temperature controllers for each zone. The high pressure HGD reactor uses bottled gases, house nitrogen, and distilled water to make up a desired reactant gas composition (usually a simulated coal gas). Oxidizing and reducing gases are controlled with pressure regulators, and metered to the desired flow rate using a set of individual mass flow controllers. Process water is preheated using a small boiler and then fed to the process gas preheater along with the other gases. If hydrogen sulfide and carbon monoxide are used, they are added to the bulk gas stream after the preheater to avoid added corrosion to the preheater. The preheated gas stream enters the bottom of the reactor vessel and flows up and fluidizes the sorbent bed where gases react with the sorbent. The clean gas then exits from the top of the reactor vessel and passes through a thimble filter. Condensate is collected in a two-level knock-out pot system. Following the knock out pots, a filter is located in the line to capture any entrained moisture and particulate prior to exit flow meters and pressure reduction valves. The exit gas (excluding slip-streams for gas analysis) is passed through a final fixed-bed absorber of zinc oxide to remove any hydrogen sulfide remaining in the exit gas before it is vented to the atmosphere. To determine the performance of the sorbent under specific test conditions, small slip-streams of the inlet and exit gas are sampled in a vented sampling chamber. Independent sampling loops for absorption and regeneration are present to avoid misinterpretation of data. Grab samples are taken on a periodic basis and then analyzed by a calibrated battery of gas chromatographs (GC) in the analytical laboratory. Slip-streams are also routed through a Varian Prima 600 Mass Spectrometer (MS) for continuous on-line measurement. A stand-alone on-line Hewlett-Packard Gas Chromatograph (GC) for detection of gas composition such as sulfur dioxide and hydrogen sulfide is provided as a means of a quality check and enhanced control.

The high pressure unit is capable of performing hot gas desulfurization/regeneration under the following operations:

Temperature:	up to 1,400°F (760°C)@ 400 psig
Pressure:	30 to 400 psig (0.21 to 2.80 MPa)
Gas Feed Rate:	up to 600 scfh (16 m ³ /h)

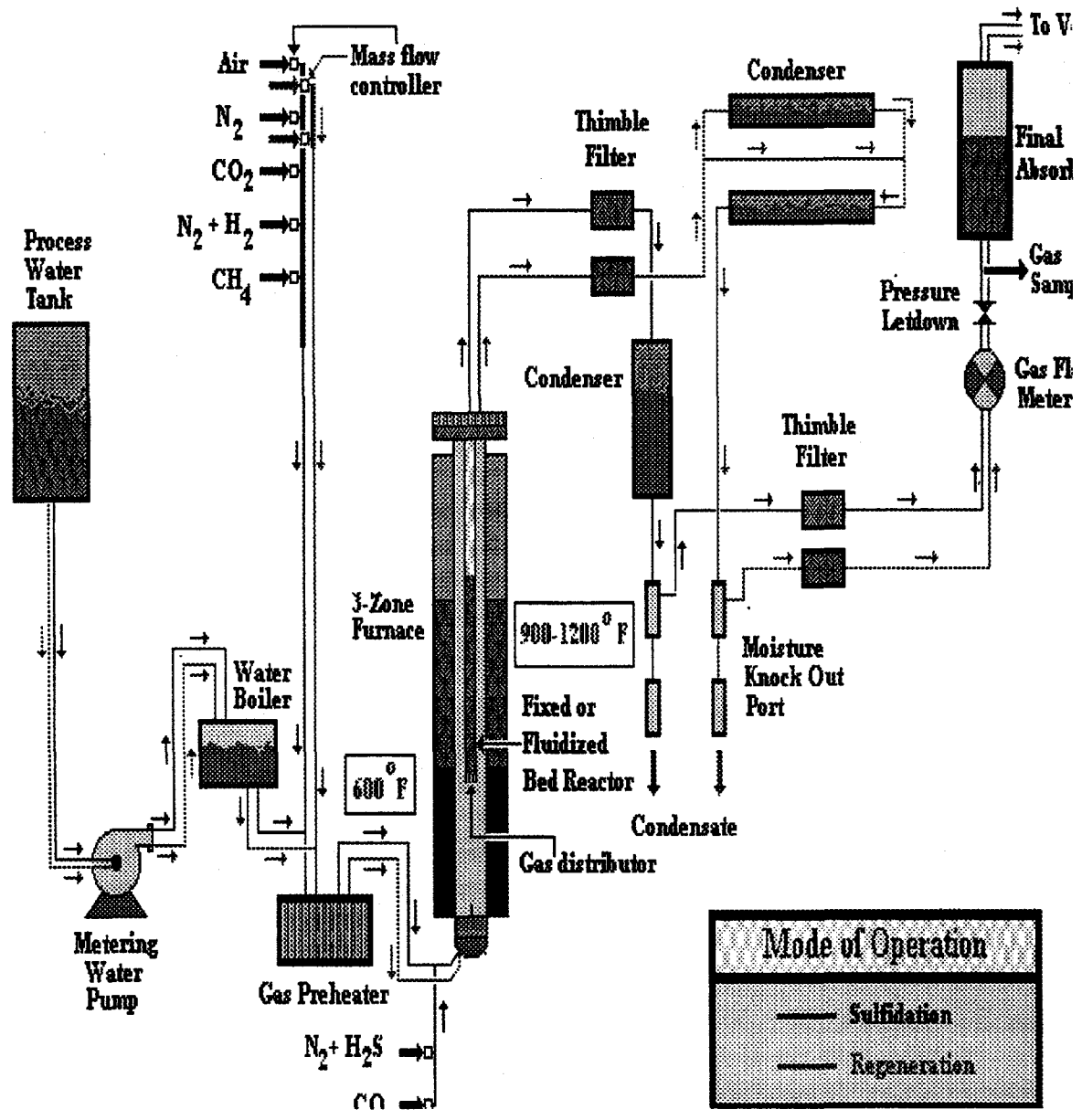


Figure 2.1 - FETC High Pressure HGD Bench-Scale Reactor

2.2 Analytical Equipment

The following equipment shall be used to perform on-line gas analysis for both the inlet and exit gases.

- Varian Prima 600 Mass Spectrometer
- Hewlett-Packard Gas Chromatograph

2.3 ASTM D4058-92 Attrition Test Method

An on-site attrition tester that conforms to ASTM D4058-92, "Standard Test Method for Attrition and Abrasion of Catalysts and Catalyst Carriers" was used to perform attrition testing on both the fresh and spent sorbents.

3.0 10-Cycle Baseline Test

3.1 Objective

The objective of the baseline (10-cycle) tests was to qualify TDA's TNT-MB sorbent for further steady-state desulfurization tests and establish a frame of reference by conducting 10 cycles of absorption and regeneration in the high pressure, high temperature, bench-scale, fixed-bed reactor system at FETC simulating the process conditions at the Tampa Electric Company's Polk Station HGCU system.

3.2 General Test Summary

Test protocol guidelines developed by DOE and GE to simulate the GESEEI moving-bed HGD reactor at TECO (See Appendix A "Test Protocol Testing of Desulfurization Sorbents in a Bench-Scale Facility") was used as a general basis for the test. This test plan for the 10-cycle test of the TNT-MB sorbent (designated HPHGD-060) was modified according to the developer, TDA, to accommodate operational considerations during regeneration that were required for best performance of their sorbent.

The sorbent formulation in the bench-scale reactor should be evaluated primarily by :

- Sulfidation of the sorbent during the absorption step to constant sulfur loading of approximately 6.7 lbs sulfur/ft³ of bed (calculated at the gas inlet location of the bed), as designed for the moving-bed operation of the Tampa Electric Company's Polk Station Hot Gas Cleanup System.
- Measurement of H₂S breakthrough curves as a function of cycle number and time
- Mechanical and physical properties of the fresh and spent sorbents (e. g., attrition

resistance and chemical degradation resistance)

3.3 Test Operations Summary

There were 6 primary steps or stages encountered in conductance of this test:

1. Nitrogen Purge/Heat up
2. Reductive Regeneration
3. Sulfidation
4. Nitrogen Sulfidation Purge
5. Oxidative Regeneration
6. Thermal Decomposition/Regeneration

First, nitrogen was brought on to the desired 900°F and 280 psig operating condition. After temperatures throughout the reactor stabilized, the heater controllers were set at constant flux to simulate adiabatic operation. Next, syngas without the hydrogen sulfide or carbon monoxide was added. This step is usually known as reductive regeneration. This step can also exhibit a slight temperature drop due to the gas-to-water shift reaction which is endothermic (consumes heat). Reductive regeneration was carried out until the hydrogen sulfide concentration was <30 ppm or for 30 minutes, whichever came first. Next, carbon monoxide and hydrogen sulfide were added to start the sulfidation. Temperature rise in the bed was probably due to sulfidation and the exothermic water-gas shift reaction which occurs. Sulfidation was conducted for 125 minutes or until the hydrogen sulfide concentration became greater than 200 ppm. Nitrogen purge was then conducted to ready the reactor for regeneration. At this point, temperature and pressure were reduced to 700°F and 88.2 psig respectively. After temperatures throughout the reactor had stabilized, heater controllers were set at constant flux (manual mode at the displayed percent output). Oxidative regeneration was established by flowing 4% oxygen (balance nitrogen) across the bed. Temperature rise (controlled below 1300°F by reducing oxygen concentration) due to the exothermic oxidation reaction was noted. Oxidative regeneration was conducted until outlet oxygen concentration reached 1%. At this point, thermal decomposition/regeneration was initiated by replacing oxygen with nitrogen and setting the heater controllers on temperature control at 1250°F. This mode was continued for 1 hour after the coolest bed temperature had exceeded 1200°F or sulfur dioxide concentration was <500 ppm, whichever came first. This sequence was conducted for all 10 cycles, with the exception of the 10th sulfidation. The 10th sulfidation was conducted through breakthrough ($H_2S > 500$ ppm at the outlet of the reactor.)

At the end of the 10th sulfidation, the bed was cooled with nitrogen. A sorbent sample for post-test analysis (see sampling section) was removed from the top and bottom of the bed. The bed was replaced and reactor restarted to conduct the 10th regeneration. The bed was then cooled with nitrogen and removed for post-test analysis.

3.4 Tested Material (Sorbent Data)

The sorbents tested was TDA's TNT-MB iron and zinc-based formulation. The sorbent geometry was cylindrical extrudates approximately 3.6 mm in diameter and a length to diameter (L/D) ratio of 1.3. Bulk density was measured at 1.35 g/cc at a calculated particle density of 2.22 g/cc. Approximately one liter of sorbent (400 grams) was used in this test.

3.5 Experimental Conditions :

This section describes specific operating conditions and instructions that were used in conducting the 10-cycle test with the TDA TNT-MB sorbent.

3.5.1 Nitrogen Purge/Preheat

The reactor was purged/preheated to 900°F with nitrogen @ 24.61 scfh to ready the system for sulfidation. Temperature controllers were set to constant flux (percent output in manual mode) after system had come to steady-state.

3.5.2 Reductive Regeneration

Before initiating sulfidation, all reactant gases with the exception of H₂S and CO were turned on for 15 minutes or until H₂S levels were <30 ppm in the outlet. Flow rates for each gas are listed in the sulfidation section below with the exception of CO and H₂S which were replaced with balance nitrogen for a total flow rate of 24.61 scfh

3.5.3 Sulfidation

Flow Direction:	Upflow
Inlet Bed Temperature:	900 °F ± 25 °F
Reactor Pressure:	279.22 psig ± 5 psi
Total Flow Rate:	24.61 scfh
Gas Velocity:	2000 scfh/cf
Gas Composition:	5.9 % Nitrogen
	18.1 % Steam
	12.2 % Carbon Dioxide
	35.8 % Carbon Monoxide
	26.8 % Hydrogen
	1.2 % Hydrogen Sulfide

Flow Rates:

Component	Flow Rate (scfh)
Nitrogen	1.45
Steam	4.45
Carbon Dioxide	3.00
Carbon Monoxide	8.81
Hydrogen	6.60
Hydrogen Sulfide	0.30

End of Stage Criteria: Sulfidation was conducted for 125 minutes after CO and H₂S injection or until the concentration of H₂S was greater than 200 ppm, whichever came first.

*NOTE: Remember that the 10th sulfidation was taken through breakthrough (H₂S > 500 ppm at the outlet of the reactor).

3.5.4 Nitrogen Purge

Nitrogen purge was conducted to ready the reactor for regeneration. System temperature and pressure were reduced to 700°F and 88.2 psig respectively. After temperatures throughout the reactor had stabilized, heater controllers were set at constant flux (manual mode at the displayed percent output).

3.5.5 Oxidative Regeneration Conditions

Flow Direction: Upflow
Bed Temperature: 1225-1275°F
Peak Bed Temperature: 1450°F
Reactor Pressure: 88.17 psig ± 1 psi
Total Flow Rate: 24.61 scfh
Gas Velocity: 2000 scfh/cf

Notes: (1) The "Dry Air" cylinder gas was utilized for the test phase.

- (2) The nitrogen and air flow rates were adjusted to limit the bed temperature between 1225 and 1275 °F.

Inlet Temperature: 700 °F
Gas Composition: 4.0 % Oxygen / balance nitrogen

Flow Rates

Component	Flow Rate for 4% O ₂ (scfh)
Nitrogen	20.27
Air	4.34

End of Stage Criteria: Thermal decomposition was initiated when the oxygen concentration at the outlet of the reactor was greater than 1%.

3.5.6 Thermal Decomposition

After oxidative regeneration, thermal decomposition of sulfates was accomplished by flowing nitrogen across the bed at 1250°F - 1300°F for 1 hour. This is an endothermic reaction, so the reactor heaters needed to be controlled to add heat such that the bed temperature was maintained at that value.

End of Stage Criteria: One hour after lowest temperature in the bed reached 1200°F or outlet SO₂ < 500 ppm for 2 online measurements, whichever comes first, thermal decomposition was completed.

3.6 Sampling and Analysis Procedure

3.6.1 Gas Sampling Equipment and Procedure

Sulfidation and regeneration inlet gases were sampled at the beginning of each half-cycle by gas grab. Outlet gas concentrations were monitored continuously every 30 seconds using a Varian Prima 600 mass spectrometer and every 30 minutes by gas grab samples which were analyzed by gas chromatograph. Additionally, an online Hewlett-Packard gas chromatograph was used to monitor SO₂ during regeneration and H₂S during sulfidation every 7.5 minutes.

Reductive regeneration gases were sampled at the beginning of each run by gas grab. During the reductive regeneration steps the Varian Prima 600 mass spectrometer was used to continuously sample the exit gases every 30 seconds. The online Hewlett-Packard gas chromatograph was used to detect desorbed SO₂. Table 3.1 illustrates the analytical sampling schedule followed for this effort.

3.6.2 Solids Sampling and Analysis Procedure

To establish baseline conditions, fresh sorbent samples were sent to independent laboratories for the following analysis: 1.) ASTM D4058-92 attrition testing; 2.) Chemical analysis of zinc and carbon (atomic absorption); and 3.) Iron carbide content (x-ray photoelectron spectroscopy).

After the completion of the 10th sulfidation (9-1/2 cycles) 50 grams of sorbent was removed from the HPHDG unit and separated as gas inlet (25 grams) and gas outlet (25 grams) samples. Samples were then sent to independent laboratories for sulfur loading analysis, chemical composition, and iron carbide content.

After the 10th regeneration (10 cycles) the remaining sorbent was removed from the HPHGD unit and again separated into gas inlet (175 grams) and gas outlet samples (175 grams). Samples were sent to independent laboratories for ASTM D4058-81 attrition testing, TGA reactivity tests (TDA Inc.), and sulfur/sulfate analysis. Table 3.1. illustrates the solid sampling schedule in tabular form. Table 3.2. gives a breakdown, by mass, of the solids sampled and the analysis procedure that was performed.

3.6.3 Condensate Sampling and Analysis Procedure

Condensate from every sulfidation was collected independently. The ten condensate samples were be sent to an independent analytical laboratory for atomic absorption analysis of zinc, iron, and sulfur which was present. Condensate samples 5 and 6 were

inadvertently combined by the laboratory and are therefore reported together.

Table 3.1. Analytical Sampling Schedule

Step #	Event	Analysis Description	Company
1	Analysis of Fresh Sorbent	Attrition Test - ASTM D4058-92, "Standard Test Method for Attrition and Abrasion of Catalysts and Catalyst Carriers" (110 g of fresh sorbent)	EG&G Washington Analytical Services, Morgantown, WV
2	1st Through 9th Sulfidation	Chemical Composition - Atomic absorption (Zn and Total Carbon) (5 g of fresh sorbent) Gas Analysis - Mass spectrometer (MS, 30 sec.), gas chromatograph (GC, 7.5 min.), gas grab (GG, 1 inlet sample and outlet samples every 30 min)	Galbraith Laboratories, Knoxville, TN FETC and EG&G Washington Analytical Services, Morgantown, WV
3	1st Through 9th Regeneration	Condensate Analysis - Atomic absorption (Zn, Fe, S) Gas Analysis - MS, GC, GG	Galbraith Laboratories, Knoxville, TN FETC and EG&G Washington Analytical Services, Morgantown, WV
4	1st Through 9th Reductive Regeneration	Gas Analysis - MS, GC	"
5	10th Sulfidation	Gas Analysis - MS, GC, GG (Remove 50 g of sorbent for post analysis - separate as 25 g gas inlet and 25 g gas outlet samples)	"
6	Post Sulfidation Analysis of Sorbent After 9-1/2 Cycles	Sulfur Loading Analysis (5 g of sorbent from inlet, 5 g of sorbent from outlet)	CTE Laboratories, Chicago, IL

Step #	Event	Analysis Description	Company
		Chemical Composition - Atomic absorption (Zn, and Total Carbon) (5 g of sorbent)	Galbraith Laboratories, Knoxville, TN
		Iron Carbide Content - XPS, Auger (20 pellets)	Rocky Mountain Laboratories, Golden, CO
		Condensate Analysis - Atomic absorption (Zn, Fe, S)	Galbraith Laboratories, Knoxville, TN
7	10th Regeneration	Gas Analysis - MS, GC, GG (Remove remaining sorbent and separate as gas inlet (175 g) and gas outlet samples (175 g).	FETC and EG&G Washington Analytical Services, Morgantown, WV
8	Post Regeneration Analysis of Sorbent After 10 cycles	Attrition Test - ASTM D4058-92, "Standard Test Method for Attrition and Abrasion of Catalysts and Catalyst Carriers" (110 g of sorbent from gas inlet, 110 g of sorbent from gas outlet)	EG&G Washington Analytical Services, Morgantown, WV
		TGA Reactivity Tests (50 g of sorbent from inlet, 50 g of sorbent from outlet)	TDA Inc.
		Sulfur/Sulfate Analysis (5 g of sorbent from gas inlet, 5 g of sorbent from gas outlet)	CTE Laboratories, Chicago, IL

Table 3.2. Sorbent Post Test Mass Balance

Mass of Sample (g)	Analysis Description
	Post Sulfidation Analysis After 9-1/2 Cycles:
5	-Sulfur Loading analysis from gas inlet sample
5	-Sulfur loading analysis from gas outlet sample
5	-Chemical composition (Zn and Carbon)
10	-Iron carbide content
25	-Residual sample
	Post Regeneration Analysis After 10 Cycles:
110	-Attrition test from gas inlet sample
110	-Attrition test from gas outlet sample
50	-TGA reactivity test from gas inlet sample
50	-TGA reactivity test from gas outlet sample
5	-Sulfur/sulfate analysis of gas inlet sample
5	-Sulfur/sulfate analysis of gas outlet sample
20	-Residual sample
400	Total Sample

3.7 Data Collection and Recording

3.7.1 Quality Assurance of Experimental Data

In an effort to assure quality data, gas flow, temperature, and pressure measurement instruments are calibrated according to schedule. All mass flow controllers, pressure transmitters, thermocouple transmitters, GC's, and mass spectrometers were calibrated prior to the initiation of the subject CRADA. These instruments were calibrated according to the NIST recommended standards. Additionally, the chemical and physical data received on samples collected during the experiments help to verify data. For example, a sulfur balance was performed to evaluate whether or not the sulfur capture of the sorbent was consistent with the gas flow rate and compositions utilized during the experiment.

3.7.2 Data

The following procedures were used to collect and record data during the test:

Pre-Test Data:

- (1) Collect, prepare, and record fresh sorbent samples per schedule as specified in Table 3.1. Send solid samples to independent laboratories for ASTM D4058-92 attrition testing, (atomic absorption) chemical analysis, and (x-ray diffraction) phase determination to establish baseline composition and attrition resistance.

Run Data:

- (1) Record start time, process data (temperatures, pressures, flow rates, and all mass flow controller settings) in data collection forms.
- (2) Record time, temperatures, pressures, flow rates, and all mass flow controller settings every 30 minutes in data collection forms.
- (3) Take inlet gas grab samples at the beginning of each test phase (half cycle). Take gas grab samples to the analytical laboratory immediately for analysis. Record time in data collection forms.
- (4) Take outlet gas grab samples per schedule specified in Table 3.1. Take gas grab samples to the analytical laboratory immediately for analysis. Record time in data collection forms.
- (5) Collect condensate samples per schedule specified in Table 3.1. after each

sulfidation cycle. Record time and amount of condensate. These samples are to be sent to an independent laboratory for Zn, Fe, and S analyses.

- (6) All process data such as temperatures, pressures, flow rates, and mass flow controllers shall be recorded through a PC-based Automatic Data Acquisition System throughout the test.
- (7) Inlet and outlet gas samples shall be analyzed and recorded by an on-line MS and a GC per schedule specified in Table 3.1.

Post-Test Data:

- (1) Per schedule as specified in Table 3.1 collect, prepare, and record inlet and outlet solid samples at the end of the 10th sulfidation (9-1/2 cycles). These samples will be sent to independent laboratories for sulfur loading analysis, chemical composition, phase determination, and iron carbide content as specified in Table 3.2.
- (2) Per schedule as specified in Table 3.1 collect, prepare, and record inlet and outlet solid samples after the completion of the 10th regeneration (10 cycles). Samples will be sent to independent laboratories for ASTM D4058-92 attrition testing, TGA reactivity test, and sulfur/sulfate analysis as specified in Table 3.2.

3.8 Results

In general, TNT-MB sorbent performed well within the requirements of the test protocol for the 10-cycle test. This can best be seen by examining the performance curves in Figure 3.1. All 10 cycles absorbed H₂S for the prescribed 125 minutes without breakthrough. The H₂S concentration remained below 50 ppmv throughout the 125 minute test period. Cycle 10 was extended until breakthrough which occurred approximately 7.3 hours after the cycle was begun. Figure 3.2 is provided to illustrate the temperature distribution throughout the bed as a function of time during a typical sulfidation. The sorbent also showed an increase in attrition resistance from 1.8% (fresh) to 0.87% (reactor inlet) and 0.64% (reactor outlet) after 10 cycles (Table 3.3). One of the concerns with iron-containing sorbents is possible iron carbide formation and carbon deposition. Although the iron carbide information was difficult to obtain (using XPS), the total carbon content of the sorbent was generally < 0.05% and is an indication that no appreciable carbide was formed. The formation of sulfate was evident from examination of the regeneration performance curve in Figure 3.3. After oxygen was removed, the system temperature was increased to approximately 1250 °F in the presence of pure nitrogen. Although no oxygen was present to oxidize the sulfur to sulfur dioxide, evolution of sulfur dioxide was observed in the reactor outlet - an indication of sulfate decomposition. The thermal decomposition appears to be very effective as was evidenced by the low sulfate concentrations noted in the sorbent at the end of the test. The increase in attrition resistance (from beginning to end of test) also gives some indication that sulfate formation was not detrimental to sorbent life/performance for the TNT-MB sorbent. A sulfur balance (Appendix B) was done as a quality check to track sulfur throughout the test. Although cycle-to-cycle variations up to 43% were observed, the overall sulfur balance for all ten cycles was approximately 95%. The cycle-to-cycle variation may be explained by the inability to measure the actual sulfur in the bed during testing. Assumption that all the sulfur absorbed during a cycle is removed during regeneration within the same cycle is invalid as there is no good way to account for accumulation in the bed.

Comparison of Sulfidations for MB-TNT Sorbent Test HP60

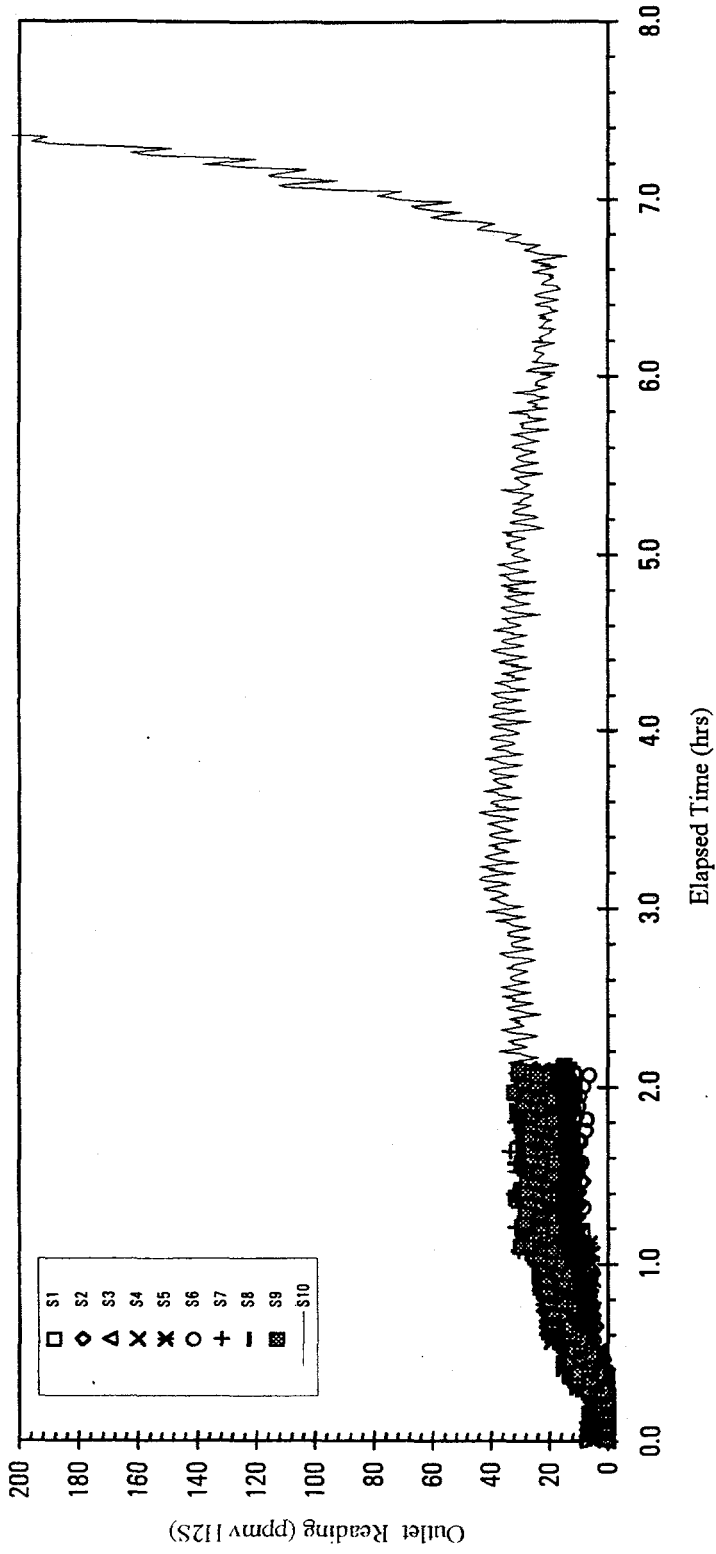
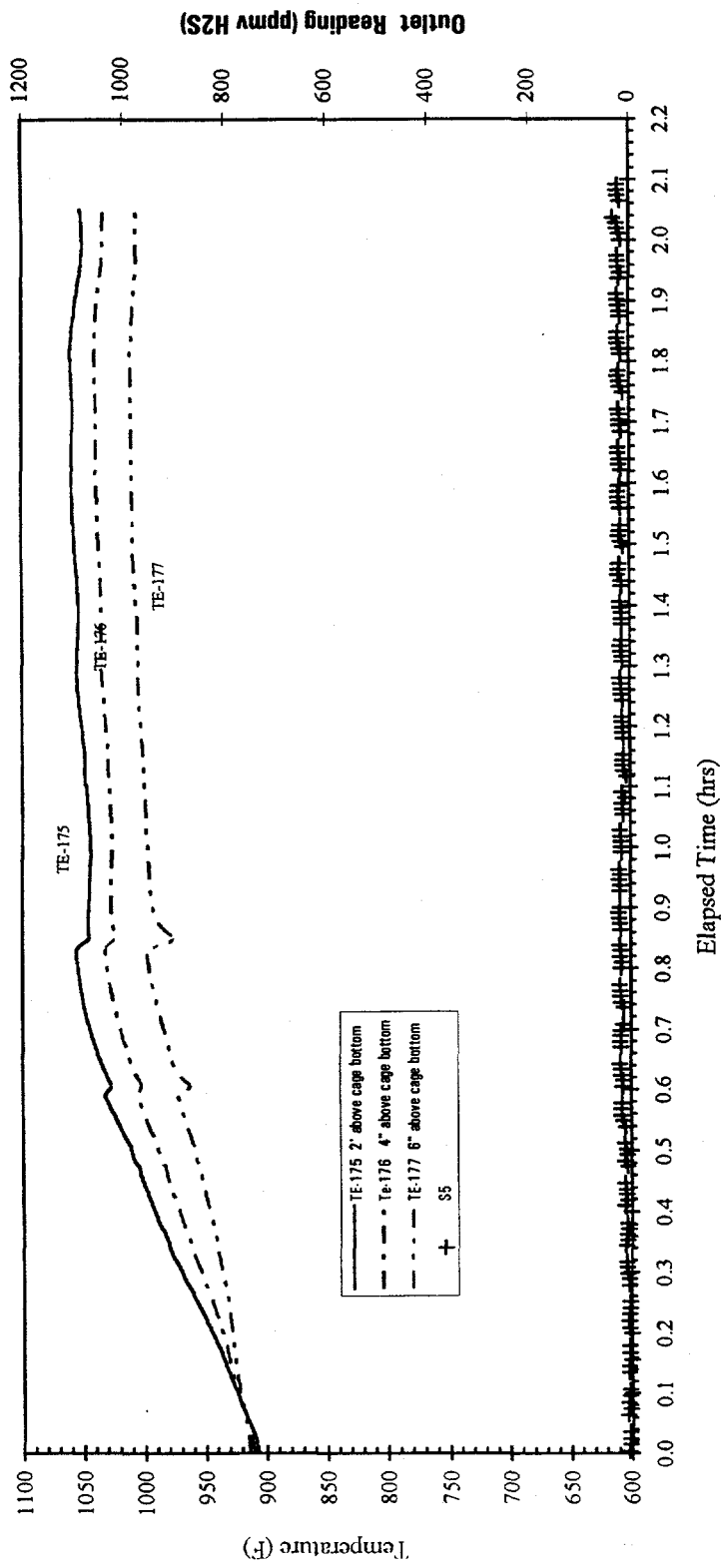


Figure 3.1 "10-Cycle Sulfidation Curves"

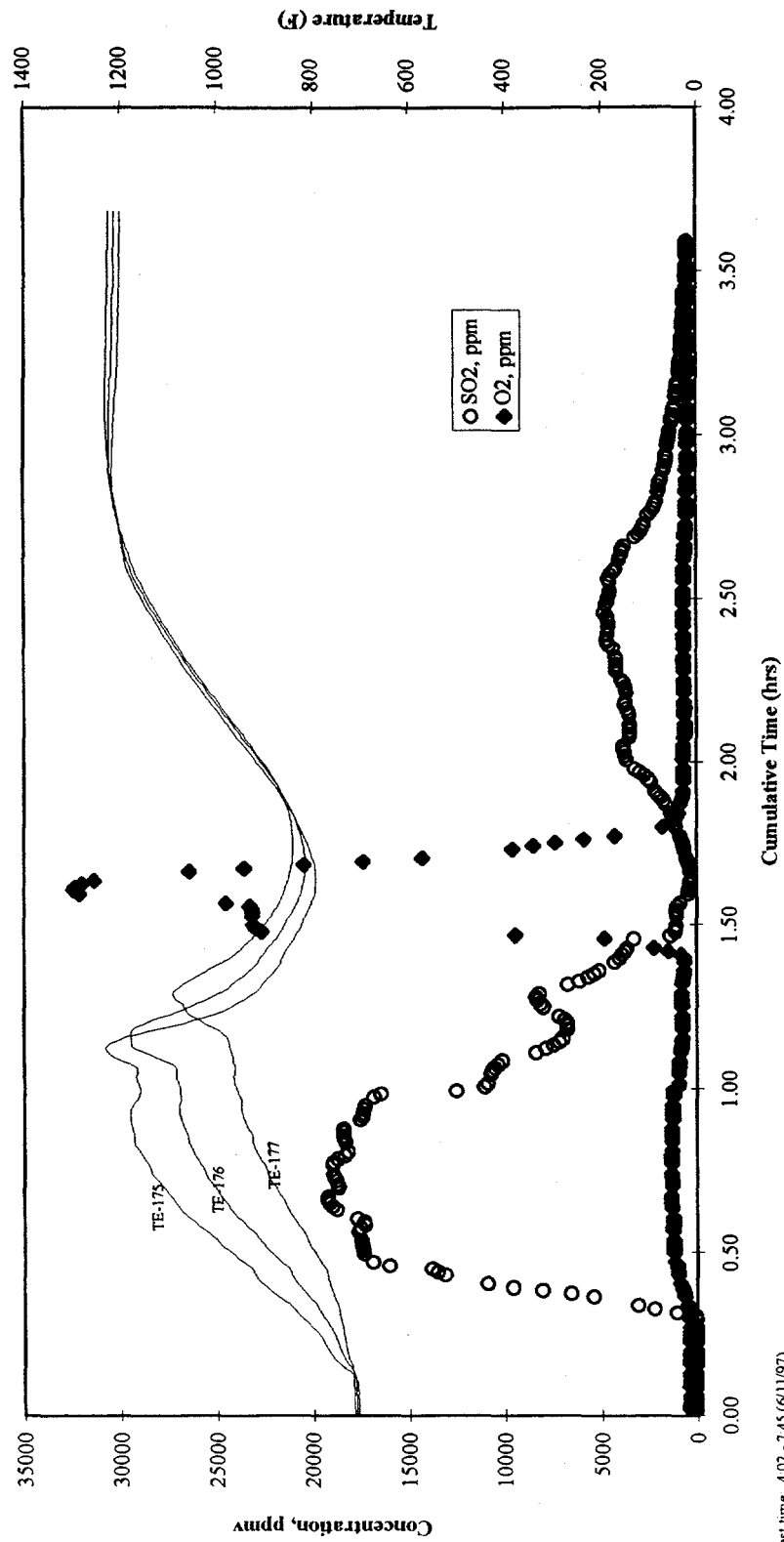
HPGHD-60 Sulfidation 5



Test time: 00:00 - 2:05 (6/11/97)
 Test Duration: 2:05

Figure 3.2 "Sulfidation Curve for 10-Cycle Test"

HPHGCD-60 Regeneration 5



Test time: 4:02 - 7:45 (6/11/97)
 Test Duration: 2:43

Figure 3.3 "Regeneration Curve for 10-cycle Test"

Table 3.3 “Solids Analysis”

	Fresh	Sulfided Inlet (10 th Cycle)	Sulfided Outlet (10 th Cycle)	Regenerated Inlet (10 th Cycle)	Regenerated Outlet (10 th Cycle)
Total Sulfur	0.44%	14.43%	14.41%	2.4%	2.81%
Sulfate	0.42%	0.07%	0.07%	0.31%	0.27%
Zinc	20.3%	18.87%	22.46%	-	-
Carbon	< 0.05%	< 0.05%	< 0.05%	-	-
Iron Carbide	< 0.05%	< 0.05%	< 0.05%	-	-
Attrition	1.8%	-	-	0.87%	0.64%

Table 3.4 “Condensate Analysis”

	Zinc (ppm)	Iron (ppm)	Sulfur (ppm)
Sulfidation 1	170	770	1100
Sulfidation 2	39	250	<500
Sulfidation 3	160	600	600
Sulfidation 4	12	89	<500
Sulfidation 5&6	46	91	540
Sulfidation 7	14	100	<500
Sulfidation 8	10	60	<500
Sulfidation 9	54	110	<500
Sulfidation 10	<5	40	740

Analytical Services

- * Total sulfur/sulfate (solids) analysis: CTE Co.
1919 South Highland Ave. Suite 210-B
Lombard, Illinois 60148
(708) 953-9300

- * Zn/C (solids), Zn/Fe/S (condensate) analysis: Galbraith Laboratories Inc.
P.O. Box 51610
Knoxville, TN 37921-1750
(423) 546-1335

- * Iron Carbide Analysis: Rockey Mountain Laboratories Inc.
Genesee Business Center
602 Park Point Dr. Suite 101
Golden, Colorado 80401
(303) 526-9449

- * ASTM D-4058 Attrition Resistance Analysis: EG&G Technical Services of WV
3610 Collins Ferry Rd.
Morgantown, WV 26507

4.0 Low-Temperature Scoping Test

4.1 Objective

The Objective of this test was to gain operating experience to prepare for the 10-cycle test and evaluate the performance of the TNT-MB sorbent at temperatures lower than identified in the moving-bed test protocol. The need to answer this question arose from the possibility that TECO would only be able to supply fuel gas from their Texaco gasifier subsystem to the GEESI moving-bed HGD reactor at 700 °F as opposed to the planned 900 °F gas delivery temperature.

4.2 General Test Summary

A 3-cycle test of TNT-MB sorbent (designated HPHGD-059) was conducted in the high-pressure, high temperature bench-scale reactor at FETC as described in Section 2.1. Inlet absorption gas temperatures of 600 °F and 700 °F were evaluated. Regeneration using 700 °F inlet 4% oxygen (balance nitrogen) was also conducted.

4.3 Test Operations Summary

There were 6 primary steps or stages encountered in conductance of this test:

1. Nitrogen Purge/Heat up
2. Reductive Regeneration
3. Sulfidation
4. Nitrogen Sulfidation Purge
5. Oxidative Regeneration
6. Thermal Decomposition/Regeneration

First, nitrogen was brought on to the desired 600°F and 280 psig operating condition. After temperatures throughout the reactor stabilized, the heater controllers were set at constant flux to simulate adiabatic operation. Next, syngas without the hydrogen sulfide or carbon monoxide was added. This step is usually know as reductive regeneration. This step can also exhibit a slight temperature drop due to the gas-to-water shift reaction which is endothermic (consumes heat). Reductive regeneration was carried out until the hydrogen sulfide concentration was <30 ppm or for 30 minutes, whichever came first. Next, carbon monoxide and hydrogen sulfide were added to start the sulfidation. Temperature rise in the bed was probably due to sulfidation and the exothermic water-gas shift reaction. Operation at 600 °F was conducted for 30 minutes after which, the system inlet temperature was raised to 700 °F. This condition was maintained for the remainder (95 minutes) of the first sulfidation cycle. The second and third sulfidation cycles were conducted at the 700 °F inlet condition. Sulfidation was conducted for 125 minutes or until the hydrogen sulfide concentration became greater than 200 ppm. Nitrogen purge was then

conducted to ready the reactor for regeneration. At this point, temperature and pressure were reduced to 700°F and 88.2 psig respectively. After temperatures throughout the reactor had stabilized, heater controllers were set at constant flux (manual mode at the displayed percent output). Oxidative regeneration was established by flowing 4% oxygen (balance nitrogen) across bed. Temperature rise (controlled below 1300°F by reducing oxygen concentration) due to the exothermic oxidation reaction was noted. Oxidative regeneration was conducted until outlet oxygen concentration reached 1%. At this point, thermal decomposition/regeneration was initiated by replacing oxygen with nitrogen and setting the heater controllers on temperature control at 1250°F. This mode was continued for 1 hour after the coolest bed temperature had exceeded 1200°F or sulfur dioxide concentration was <500 ppm, whichever came first. This sequence was conducted for all 3 cycles.

4.4 Tested Material (Sorbent Data)

The sorbent tested was TDA's TNT-MB iron and zinc-based formulation. The sorbent geometry was cylindrical extrudates approximately 3.6 mm in diameter and a length to diameter (L/D) ratio of 1.3. Bulk density was measured at 1.35 g/cc at a calculated particle density of 2.22 g/cc. Approximately one liter of sorbent (400 grams) was used in this test.

4.5 Experimental Conditions :

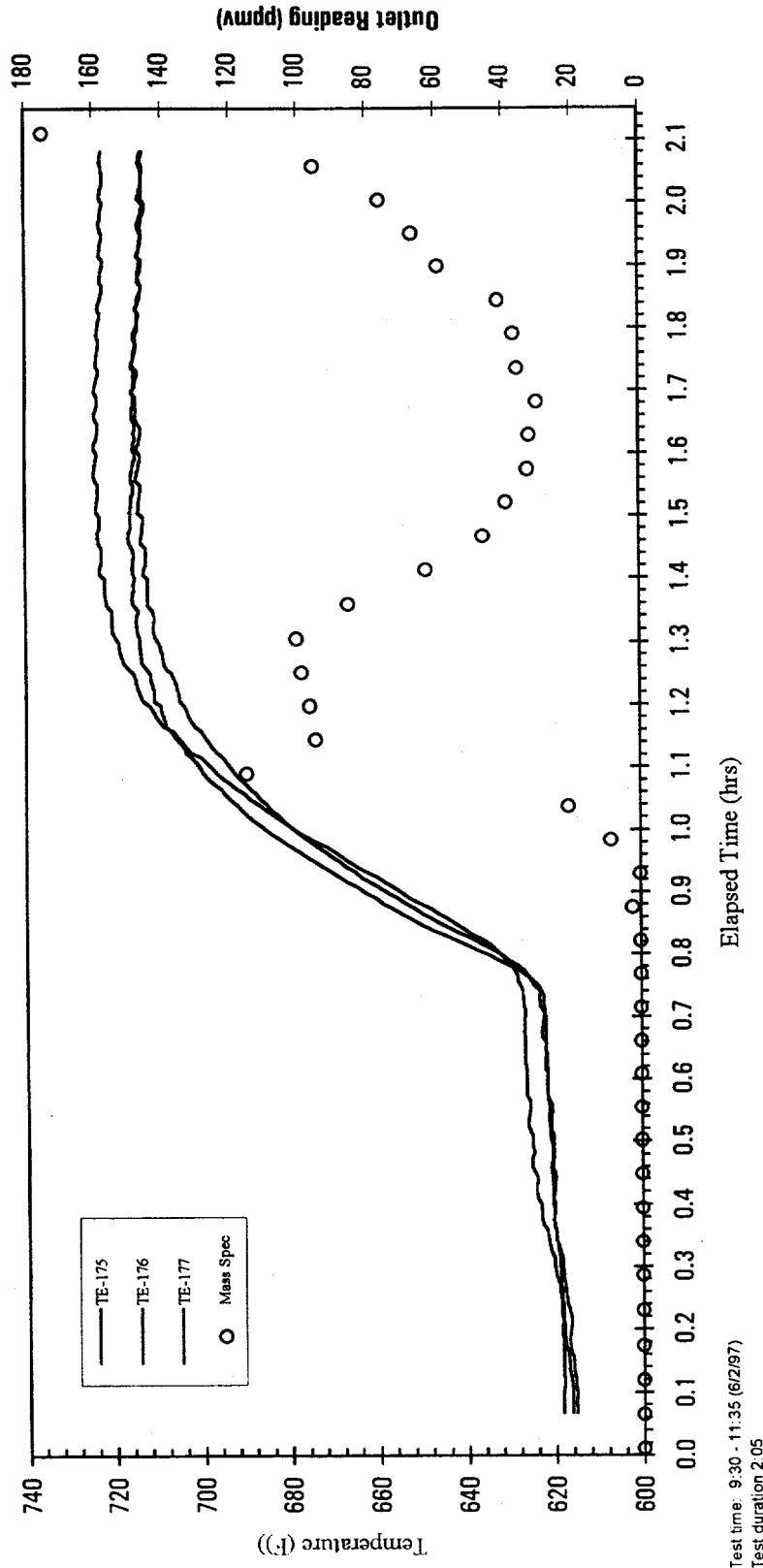
Experimental conditions for the low-temperature test were nearly the same as the 10-cycle test (see section 3.5) with the following exceptions:

- 1.) Cycle 1 absorption was conducted at an inlet temperature of 600 °F for 30 minutes at which point, the inlet temperature was increased to 700 °F for the remaining 95 minutes.
- 2.) Inlet adsorption temperatures for cycles 2 and 3 were conducted at 700 °F.
- 3.) Oxidative regeneration was conducted at 700 °F inlet temperature.

4.6 Results

The sorbent performed very well at the low-temperature conditions. Figure 4.1 illustrates the outlet H₂S concentration as a function of time. For the first 0.75 hours, outlet H₂S concentrations were in the single-digit ppmv level at the 600 °F condition. As the temperature was raised to the 700 °F condition, the H₂S concentration increased to approximately 115 ppmv and then dropped down to approximately 25 ppmv. It is not clearly understood why this occurred. The concentration then rapidly increased at the end of the sulfidation period indicating that breakthrough was occurring. The second sulfidation was conducted at 700 °F (Figure 4.2). Outlet H₂S concentrations generally were below 40 ppmv. The third sulfidation (Figure 4.3) showed very stable H₂S outlet concentrations throughout the test period. Regeneration at the 700 °F inlet temperature appeared reasonable. Figure 4.3 illustrates the first cycle combined oxidative and thermal regeneration. Cycle 2 regeneration in Figure 4.5 includes a trace for outlet oxygen concentration. Although oxygen concentrations were targeted to be below 1% at the outlet, breakthrough was so rapid that it was difficult to maintain. This experience proved useful in the conduct of the 10-cycle test. Between cycles 2 and 3, insulation was added to the exterior of the internal sorbent cage with the pressure vessel. This resulted in a significantly higher exotherm during oxidative regeneration as can be seen in Figure 4.3. The low-temperature scoping test was completed at this point. No solids analysis were conducted.

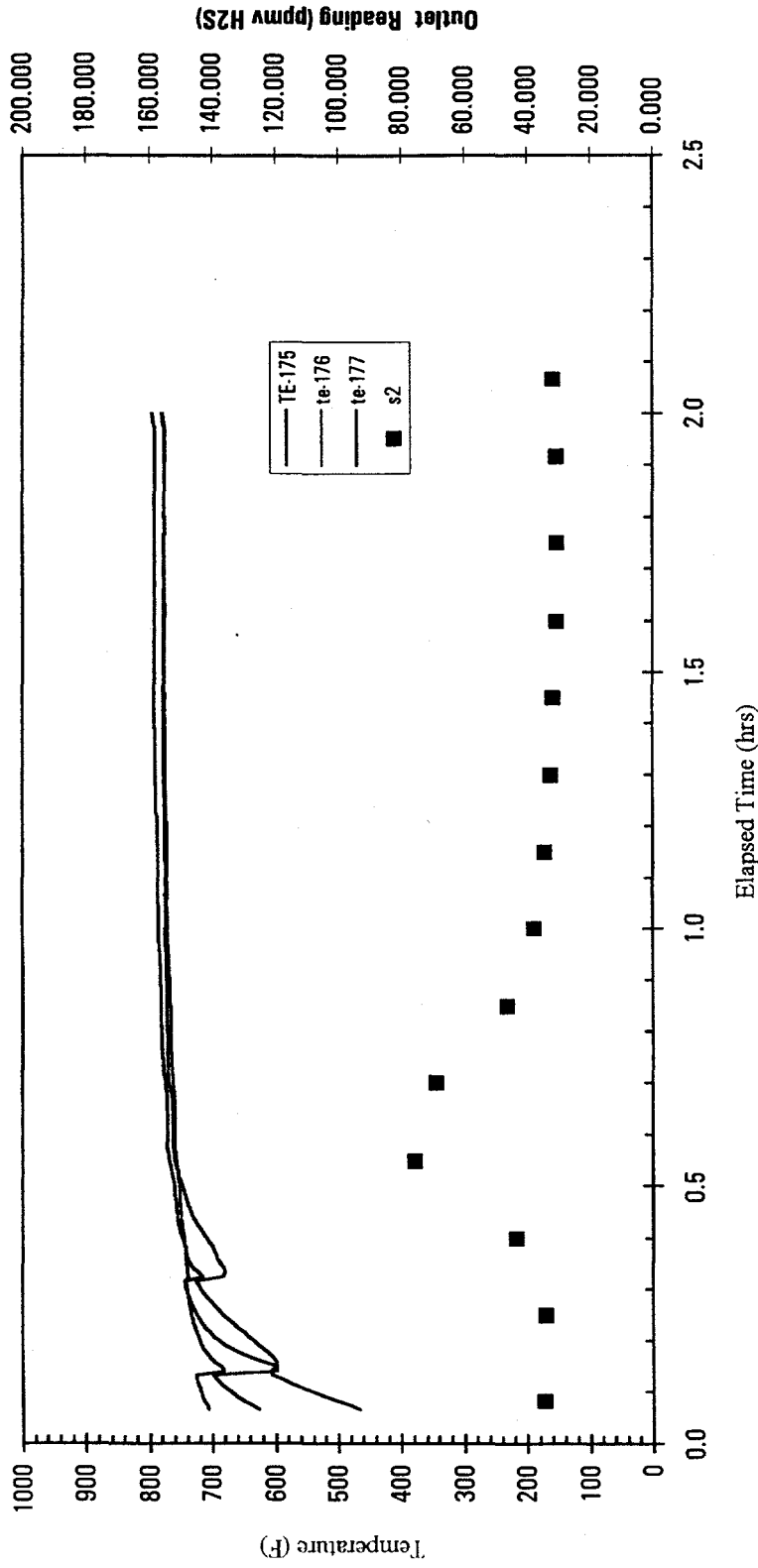
HPHGD-59 Sulfidation 1



Test time: 9:30 - 11:35 (6/2/97)
 Test duration 2:05

Figure 4.1 "Low-Temperature Sulfidation - Cycle 1"

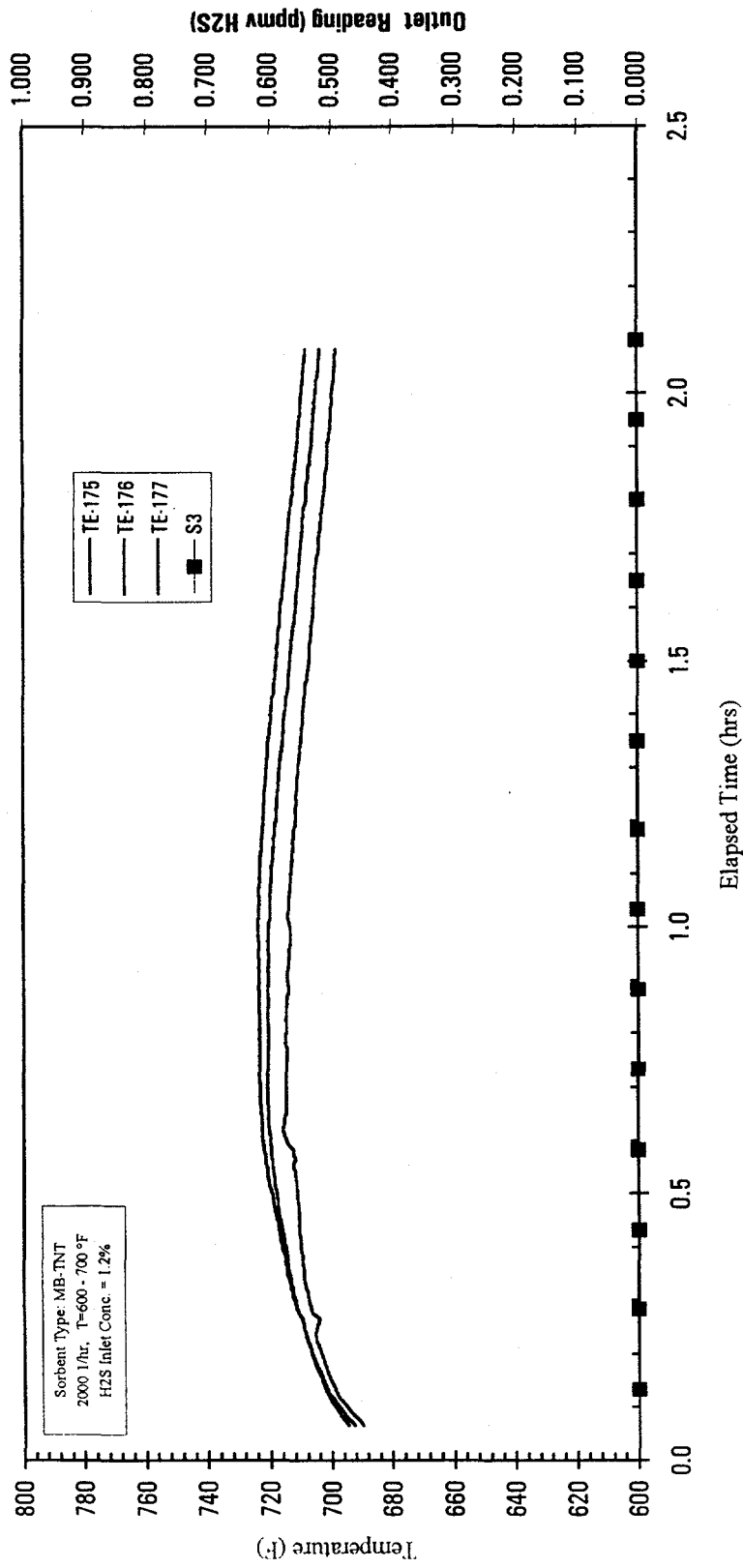
HPHGD-59 Sulfidation 2



Test time: 1300 - 1505 (6/3/97)
 Test duration 2.05

Figure 4.2 "Low-Temperature Sulfidation - Cycle 2"

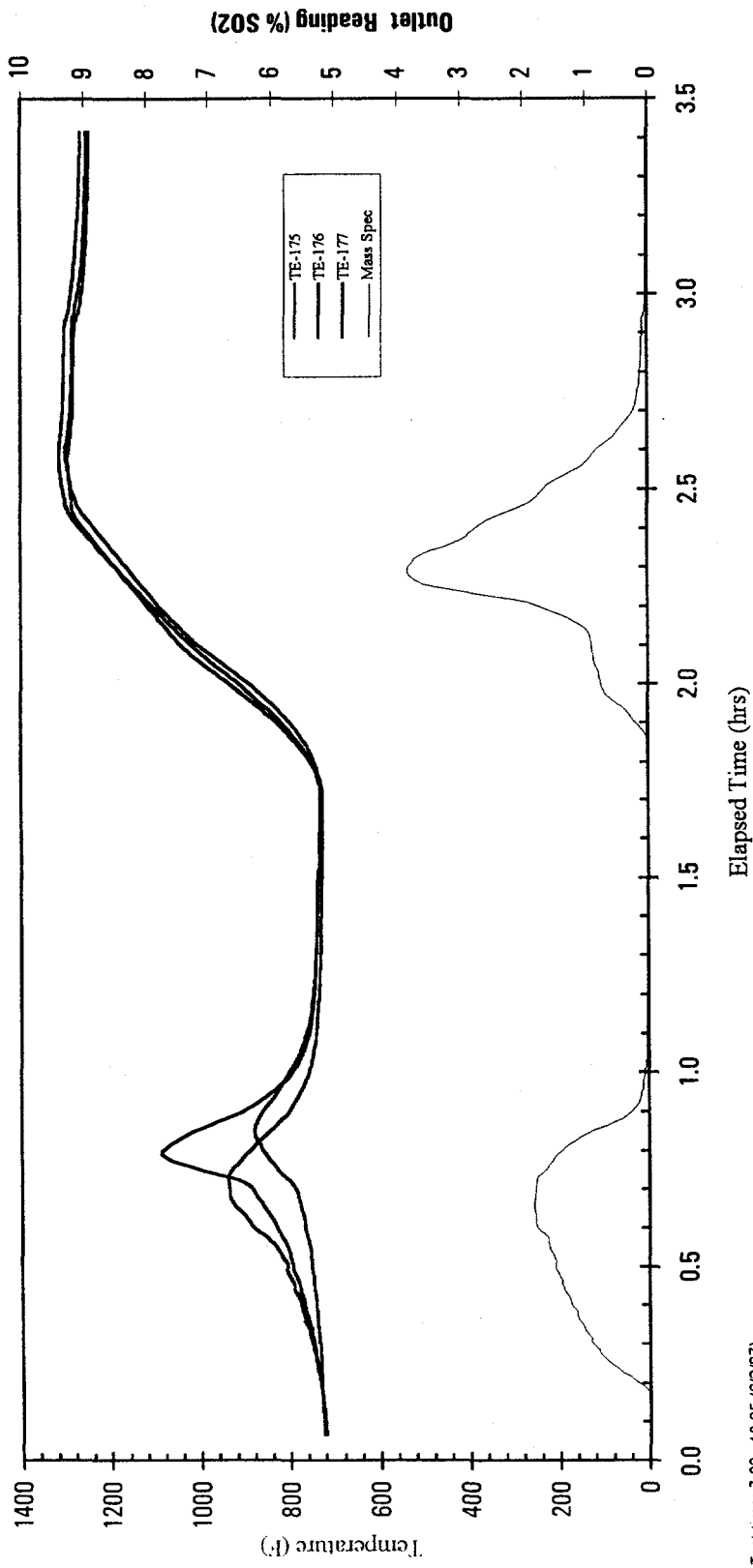
HPHGD-59 Sulfidation 3



Test time: 900 - 1105 (6/5/97)
 Test duration 2:05

Figure 4.3 "Low-Temperature Sulfidation - Cycle 3"

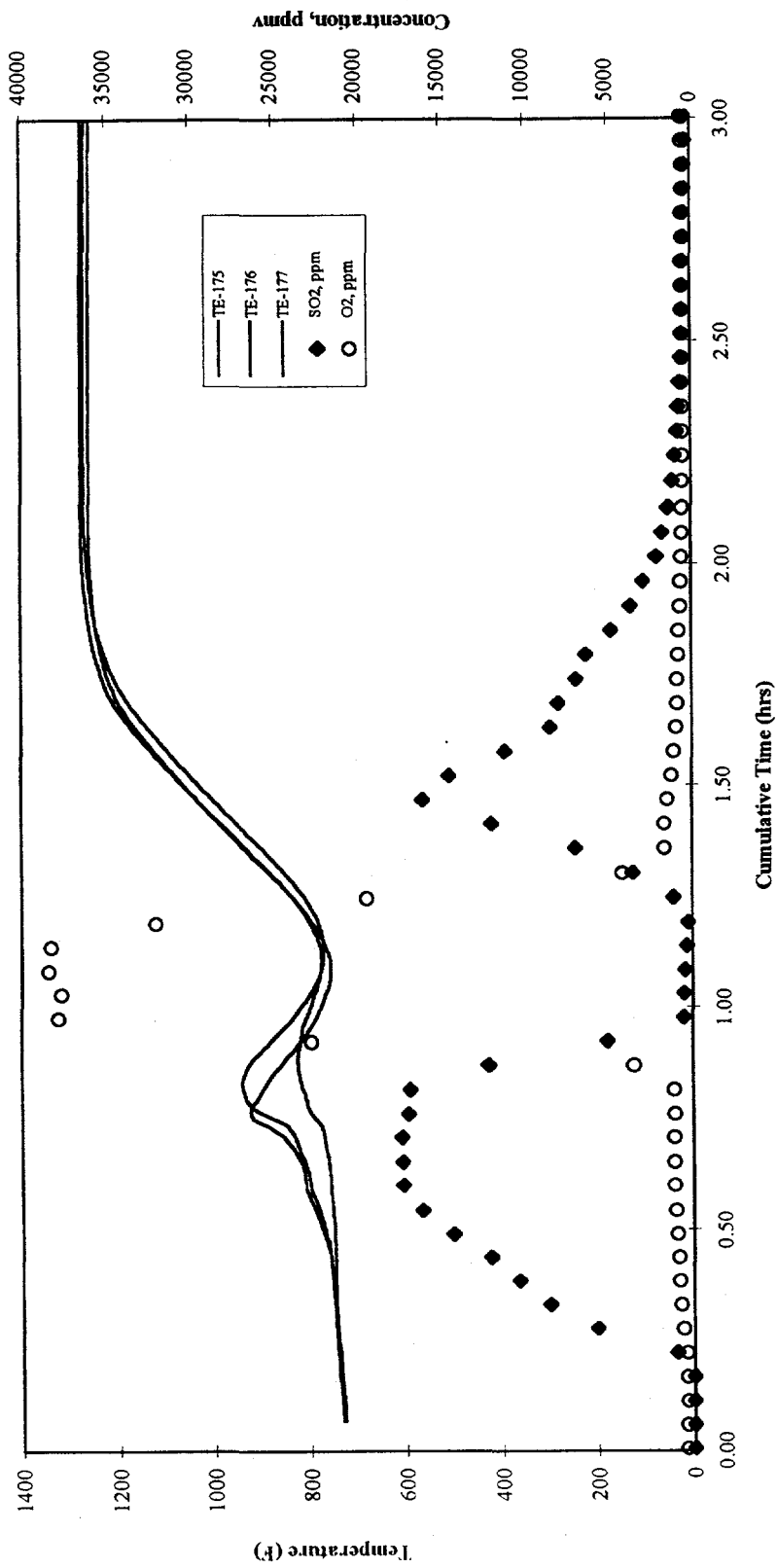
HPHGD-059 Regeneration 1



Test time 7:00 - 10:25 (6/2/97)
Test duration: 3:25

Figure 4.4 "Low-Temperature Regeneration - Cycle 1"

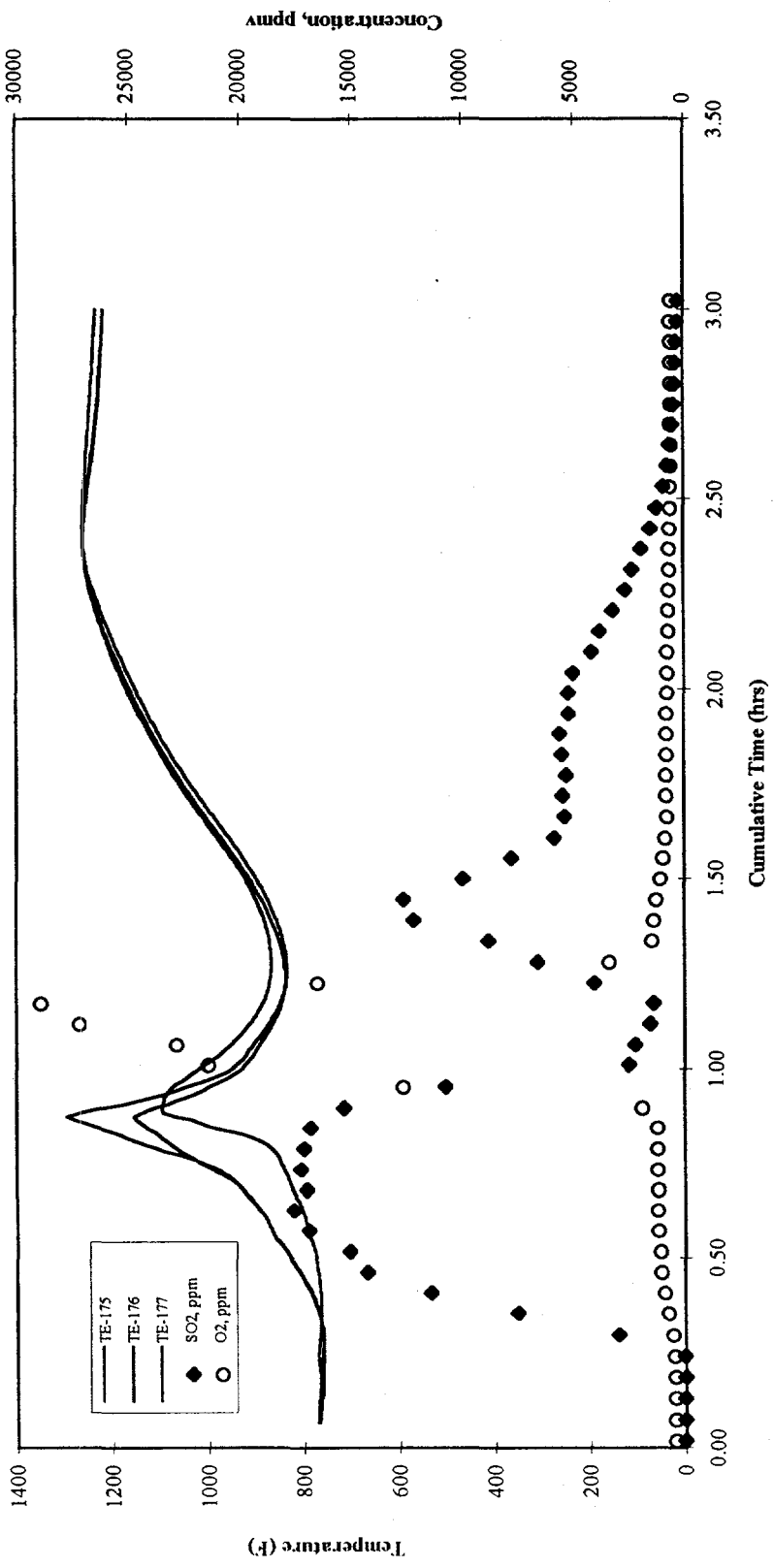
Low-Temperature Regeneration 2



Start Time 0700 6/4/97

Figure 4.5 "Low-Temperature Regeneration - Cycle 2"

Low-Temperature - Regeneration 3



Start Time 1300 6/5/97

Figure 4.6 "Low-Temperature Regeneration - Cycle 3"

5.0 Attrition Analysis for the 25-Cycle Test

The results an additional attrition test are also contained in this report. As part of the moving-bed test protocol, a 25-cycle test was conducted on the TNT-MB sorbent by the Institute of Gas Technology (IGT). At the request of TDA, FETC performed attrition test ASTM D4058-92 on various sorbent samples from the IGT test. The results were as follows:

Sorbent Sample	ASTM D4058-92 Attrition
Fresh	1.67%
24th Cycle	3.30%
24th Cycle	7.14%
25th Cycle	3.06%
25th Cycle	4.78%

APPENDIX A

“Moving-Bed Sorbent Test Protocol”

TEST PROTOCOL

TESTING OF DESULFURIZATION SORBENTS

IN A BENCH-SCALE FACILITY

Objective --

The overall objective of these tests is to determine optimum operating conditions for achieving target performance of desulfurization sorbents for use in the Tampa Electric Company Hot Gas Cleanup Unit employing the GEESI moving-bed desulfurization system process. The objective is also to determine the suitability of each sorbent and to assess the compatibility of each sorbent's optimum operating conditions for use in the Tampa Electric Company's plant hardware as it currently exists.

This test protocol shall provide a description of desulfurization sorbent tests, the prescribed procedures for baseline (10-cycle) tests, scoping experiments, and steady state multi-cycle tests, and the analyses and reporting to be completed. Should any sorbent not perform satisfactorily during the baseline tests, the sorbent shall be considered to be disqualified from further testing.

Sorbent Characteristics --

The sorbents to be tested are zinc-based formulations produced by a commercial manufacturer. The morphology varies from perfect spheres to elongated, edge-rounded cylindrical extrudates. The pellet sizes vary from 1.5-mm to 4.5-mm diameter (o.d.) spheres to extrudates of <9-mm length and diameters of 2 to 3.5-mm. The aspect ratio (length to diameter) of this sorbent is 1 to 1.3 specified from the manufacturer. Approximately one gallon of sorbent will be used in these tests.

Baseline (10-Cycle) Tests

Objective:

The objective of the baseline testing is to qualify the sorbent for further steady-state desulfurization tests and establish a frame of reference by conducting 10 cycles of absorption and regeneration in a bench-scale, fixed-bed reactor system simulating conditions at the Tampa Electric Co.'s Polk Station HGCU system. The sorbent formulation in the bench reactor should be evaluated primarily by:

- Sulfidation of the sorbent during the absorption step to constant sulfur loading of approximately 6.7 lb sulfur/ft³ of bed (calculated at the gas inlet location of the bed), as

designed for the moving-bed operation of the Tampa Electric Polk Station Hot Gas Cleanup System.

- Measurement of H₂S breakthrough curves as a function of cycle number and time.
- Mechanical and physical properties of the fresh and spent sorbents (e.g., attrition resistance and chemical degradation resistance)

Baseline Test Experimental Conditions:

Absorption step:

Simulated coal gas composition is shown in Table 1 and the proposed absorption conditions are shown in Table 2. Components have been taken for a Texaco oxygen blown gasifier and adjusted slightly to accommodate operation of the bench reactor. For instance, H₂O was increased from 14-18% at TECO to 18% to reduce carbon formation in the stainless steel lines upstream of the reactor. The H₂S level was increased from 8,000 ppmv to 12,000 ppmv (1.2 vol%) to obtain the breakthrough in reasonable amount of time (<5 hr) and to match the H₂S partial pressure between TECO and the bench-scale unit

The sequence for initial heating will be:

- Flow N₂ at room temperature for at least 1 hr.
- Increase the temperature to 900°F, still under N₂
- Start the desired flow rates of simulated coal gases except H₂S, and establish a zero-H₂S baseline measurement for reference. This step is usually called "reductive regeneration" and is used to ascertain that the internal components of the reactor are not desorbing H₂S. For subsequent cycles, reductive regeneration ensures that sulfate decomposition (from any previous cycles) has concluded. Carry out reductive regeneration until the SO₂ drops below 30 ppm or the measurement is stable for 30 minutes, whichever comes first.
- Add H₂S to the simulated coal gases and start the measurement of H₂S versus absorption time (i.e., the breakthrough curve).
- When the desired absorption time for target sulfur loading is reached or >200 ppm H₂S in the outlet is measured, whichever comes first, the reaction is stopped.
- Blanket the reactor with N₂ to conclude the absorption step.

Table 1. Test Gas Compositions (vol%)

	<u>Absorption</u>	<u>Regeneration</u>
CO	35.8	
CO ₂	12.2	
H ₂	26.8	
H ₂ O	18.1	
N ₂	5.9	Balance
H ₂ S	1.2	
O ₂	0	0-7

Table 2. - Absorption Conditions

<u>Parameter</u>	<u>Operating Condition</u>
Desired Sorbent Sulfur Loading	6.7 lb S/ft ³ of bed (96.2 g S/liter of bed) at the gas inlet location (bottom third of bed)
H ₂ S Breakthrough point	200 ppm
Gas space velocity	2000 hr ⁻¹ (STP)*
Pressure	20 atm
Temperature	900 - 1050 °F ±25 °F

* STP (standard temperature and pressure is defined at 20 °C and 1 atm).

Bed volume will be adjusted to obtain the desired gas space velocity, meet the requirement of sulfur loading at the gas inlet location, meet the 200 ppmv breakthrough in a reasonable time (<5 hr.).

Test conditions during absorption (Table 2) follow the TECO conditions, except for the reduced pressure (20 atm vs. 30 atm), higher H₂S concentration (12,000 ppmv vs. 8000 ppmv) and definition of breakthrough (200 ppmv vs. less than 50 ppmv). The reduced pressure is a result of limitations in the existing hardware; the definition of breakthrough was selected for ease of measurement and should not affect analysis of results.

Regeneration step:

The gas composition for regeneration is shown in Table 1. An important limitation of the proposed regeneration gas composition is that it will not contain added SO₂, which accelerates sulfate formation.

The regeneration conditions are shown in Table 3. The O₂ concentration to be used at any given time will be determined by the maximum temperature in the bed. A reasonable number (at least 3)

of in-bed thermocouples should be available for monitoring temperatures. The selected pressure is 7 atm. In general, the following approach should be followed:

Each regeneration should be carried out in the same gas flow direction as absorption. O₂ concentration should be the adjustable parameter to keep the bed temperatures below limits.

Regeneration should be performed in the 900 to 1400 °F operating bed temperature range. Gas inlet temperature is 900 °F. Oxygen should be added in the range of 0-7% to maintain temperatures below the maximum allowable reactor temperature of 1400 °F, depending on the sorbent requirements. At the end of regeneration, a purge of the bed with nitrogen at 1 atm should be performed for 15 minutes or less.

Table 3. Regeneration Conditions

<u>Parameter</u>	<u>Operating Condition</u>
Initial Sorbent Bed Temperature	900 - 950 °F (solids temp)
Temperature Control	Normal <1200 °F
Peak	<1350 °F
O ₂ concentration	0-7% O ₂
Pressure	7 atm
Gas space velocity	1000-2000 hr ⁻¹ (STP)

Sampling Considerations:

At the end of the 10th absorption, sulfided samples from the gas inlet and gas outlet locations should be obtained from the bed. These samples will be used for sulfur loading analysis and standard TGA reactivity tests.

The bed should be opened again after the 10th regeneration for the same collection of samples. The bed should be separated, as a minimum, into gas inlet and gas outlet locations and samples labeled accordingly. Standard TGA, sulfur analysis, and ASTM D-4058-81 attrition tests will be performed on the samples from the bed and results compared against fresh samples.

Heating and cooling of the bed to remove sorbent samples should be done under nitrogen to avoid chemical reactions from occurring during the process.

Scoping Experiments

Objective:

The objective is to determine the proper regeneration procedures when high levels of SO₂ are present in the regeneration inlet gas stream resulting in outlet SO₂ levels of 10%. In order to determine the sorbent reactivity, conduct TGA reactivity tests on the pellets in TECo gas composition containing 1.2% H₂S at 900°F, 20 atmospheres pressure monitoring the rate of weight gain and total weight gain to estimate sulfur pickup in 2 hours. Conduct two 3¹/₂ cycle bench-scale tests to study the regeneration behavior when SO₂ is present. Should a sorbent need an activation stage, an additional cycle shall be added to each scoping test where only 0.5% SO₂ in the regeneration inlet gas shall be allowed. Monitor the regeneration temperatures, SO₂ and oxygen concentrations to determine suitable regeneration operating conditions.

Sulfidation Conditions

Flow Direction:	Upflow (regeneration flow is same)
Inlet Bed Temperature:	900°F ± 25°F
Reactor Pressure:	279.22 psig ± 5 psi
Gas Velocity:	2000 scfh/cf (STP= 20°C and 1 atm)

End of Phase Criteria: 125 minutes on-line (time corresponding to sulfur loading ≥ 6.7 lb/ft³ at gas inlet) or to breakthrough (200 ppmv H₂S). Stop at anytime if sulfidation reaches breakthrough. Final sulfidation is conducted to breakthrough.

Gas Composition:	18.1 %	Steam
	12.2 %	Carbon Dioxide
	35.8 %	Carbon Monoxide
	26.8 %	Hydrogen
	1.20 %	Hydrogen Sulfide
	5.90 %	Nitrogen

Oxidative Regeneration Conditions

Initial Sorbent Bed Temperature	900 - 950°F (solids temp)
Flow Direction:	Upflow (same as sulfidation)
Gas Inlet Temperature:	Varied between 900 and 1050°F
Peak Bed Temperature:	1450°F
Reactor Pressure:	Varied at 29.4, 58.8 and 88.2 psig ± 1 psi
Gas Space Velocity:	1000 - 2000 scfh/cf (STP= 20°C and 1 atm)

- Notes: (1) "Dry Air" cylinder gas will be utilized for the test phase.
 (2) The air flow rate may be adjusted to limit the peak bed temperature to 1450°F. **Do Not Allow the Maximum Bed Temperature to rise above 1450°F.**

Gas Composition:

Oxygen	Varied between 0.2 and 7.0 %
SO ₂	Varied to maintain 10%±1% SO ₂ outlet (Start at 8% SO ₂ at inlet) Exception where activation cycle is needed, use 0% SO ₂ inlet during first cycle only.
N ₂	Balance

End of Stage Criteria: Beginning of drop-off from 10% SO₂ in outlet gas; when O₂ concentration at outlet reaches 1%, stop O₂ and SO₂ flow in regeneration feed gas. At least 5 minutes of SO₂ Analyzer readings must be below 1000 ppm SO₂ after the SO₂ in the gas inlet has been turned off to move to the next cycle.

Bench-Scale Testing

Operations Summary:

This test consists of 25 sulfidation-oxidative regeneration cycles. The test will begin with a sulfidation and will end with regeneration. It will be conducted at the RTI (or IGT) High Temperature/Pressure Bench-Scale Hot Gas Desulfurization Unit using a sorbent cage (i.d. = 2.0 inch). A perforated distributor plate will support the sorbent bed.

During sulfidation, the feed gas will be a TECo simulated coal gas containing 1.2% hydrogen sulfide. The reactor pressure will be 20 atmospheres and the bed temperature shall be 900°F. Sulfidation test phases will be run until the desired sulfur loading is achieved. In the event of breakthrough occurring before desired capacity (6.7 #S/ft³) is achieved, sulfidation will be stopped. The 25th sulfidation shall be continued to breakthrough. An on-line gas chromatograph for H₂S monitoring will be utilized during sulfidations. Prior to all sulfidation test phases, a reductive regeneration of 30 minutes will be conducted using clean (H₂S-free) coal gas.

During the regeneration test phases, the system pressure shall be maintained at greater than 3 atmospheres; the goal is to simulate TECo design conditions, thus 7 atm is preferable. The peak bed temperature shall not exceed 1450°F. A dry oxidative regeneration scheme will be used, initiated at a gas inlet temperature of 900-1050°F with 3.0% O₂ feed gas and an appropriate flow of SO₂% to maintain a regenerator SO₂ outlet level of 10% ±1%. Again the goal is to simulate TECo design conditions; thus the regeneration gas inlet temperature should be kept as low as possible, preferably 900°F. The degree of regeneration shall be estimated by continuously monitoring the amount of SO₂ burnt via readings from the SO₂ analyzer. If temperatures appear to be approaching 1450°F, the air flow will be reduced to control the temperature. The oxidative regeneration will be followed by a nitrogen purge, i.e., nitrogen atmosphere with bed temperatures held at 300°F for 30 minutes and a reduced space velocity of 1000 hr⁻¹. Following the nitrogen purge, the pressure in the system will be dropped to 1 atmosphere under nitrogen.

Process Conditions:

Reactor Configuration

Sorbent Bed 6" height of sorbent. Record mass and height of sorbent bed. Bed temperature shall be measured simultaneously at three locations; gas inlet 1-inch from distributor plate, bed middle 3-inches from distributor, and gas outlet 5-inches from distributor. The gas flow direction must always be the same during both sulfidation and regeneration. The duration of the sorbent regeneration half-cycle time shall not be allowed to exceed twice that of the sulfidation half-cycle time.

Reductive Regeneration

Sulfidation to begin as described in this test protocol but before turning on H₂S, allow 30 minutes for reduction regeneration to complete.

Sulfidation Conditions

Flow Direction:	Upflow
Inlet Bed Temperature:	900°F ± 25°F
Reactor Pressure:	279.22 psig ± 5 psi
Gas Velocity:	2000 scfh/cf (STP= 20°C and 1 atm)

End of Phase Criteria: 125 minutes on-line or to breakthrough (200 ppmv H₂S). Stop at anytime if sulfidation reaches breakthrough. Exception is the 25th cycle sulfidation.

Gas Composition:	5.90 %	Nitrogen
	18.1 %	Steam
	12.2 %	Carbon Dioxide

35.8 %	Carbon Monoxide
26.8 %	Hydrogen
1.20 %	Hydrogen Sulfide

Turn on gases in the following order: Nitrogen (N₂), Steam (H₂O), Carbon Dioxide (CO₂), Hydrogen (H₂), Carbon Monoxide (CO), and H₂S containing gas.

- Notes: (1) The heat up of the unit should be performed at no more than 300-400°F per hour.
 (2) During heat up, the total gas flow can be simulated using a nitrogen flow rate. After water flow is initiated, the balance of the gas flow can be simulated using a nitrogen flow rate.
 (3) At the conclusion of the test phase, to prevent a temperature rise in the reactor vessel, the nitrogen should be stepped up an equivalent flow as each other gas is turned off.
 (4) Purge the inlet line for 30 minutes.

Oxidative Regeneration Conditions

Flow Direction:	Upflow
Bed Temperature:	Gas inlet temperature is 900°F. Operating bed temperature to be determined based on scoping tests
Peak Bed Temperature:	1450°F
Reactor Pressure:	To be determined based on scoping tests (7 atm preferred)
Gas Space Velocity:	1000 - 2000 scfh/cf (STP= 20°C and 1 atm)

- Notes: (1) "Dry Air" cylinder gas will be utilized for the test phase.
 (2) The air flow rate may be adjusted to limit the peak bed temperature to 1450°F. **Do Not Allow the Maximum Bed Temperature to rise above 1450°F.**

Oxidative Regeneration:	
Temperature:	Gas inlet temperature is 900°F. Operating bed temperature to be determined based on scoping tests
Gas Composition:	Oxygen -- To be determined based on scoping tests SO ₂ -- As determined best by scoping tests (always first cycle starting at 0% SO ₂ ; second at 0.5% SO ₂ ; third cycle with 3.5% SO ₂ and thereafter 8% SO ₂ inlet) Balance -- N ₂

End of Stage Criteria: Beginning of drop-off from 10% SO₂ in outlet gas; when O₂ concentration

in outlet reaches 1%, stop O₂ and SO₂ flow in regeneration feed gas . At least 5 minutes of SO₂ Analyzer readings must be below 1000 ppm SO₂ to move to the next cycle. Note: the duration of regeneration half-cycle time cannot exceed twice the set time of sulfidation half-cycle time.

The transition from oxidative regeneration to nitrogen purge is as follows:

- (1) Turn the air off and bring the nitrogen flow up; allow the temperature to decrease using 300°F nitrogen. Maintain for 30 minutes.
- (2) Drop the pressure over a duration of 5 - 10 minutes to 10 psig and keep nitrogen flow for 30 minutes.
- (3) Keep the nitrogen at 300°F until end of stage criteria is met.

Nitrogen Purge:

Temperature:	300°F of N ₂ gas inlet
Gas Composition:	0% Oxygen
	100% Nitrogen

End of Stage Criteria: If the On-line GC or SO₂ Analyzer SO₂ concentration is below 500 ppm twice, shut down the test. Maximum on-line time 1 hour.

Hot Hold Conditions: **[Only in the event needed]**

Bed Temperature:	700°F
Reactor Pressure:	0 psig
Nitrogen Flow Setting:	24 scfh

Analyses

Gas Analysis: All outlet gases shall be analyzed via continuous on-line gas chromatograph, O₂ analyzer, and SO₂ analyzer.

Solids Analysis: All sorbent formulations shall be quality checked against specifications from the manufacturer. Fresh as well as sulfided and regenerated sorbent will be tested for its attrition resistance in accordance with the ASTM D4058-81 method. Sample of the regenerated sorbent will be taken after the 24th regeneration. Sample of sulfided sorbent will be taken following the

25th sulfidation after having gone to breakthrough. Physical examination and sieve analyses of the sorbent pellets shall also be done. Total sulfur loading shall be determined on the sorbent pellets by the induction furnace (LECO) method and by TGA analyses on gas inlet samples. The LECO tests shall be done by CTE Labs. Prior to TGA exposure, a 15 minute reductive regeneration will be done. The rate of sulfur loading (reactivity) of the pellets shall be measured using TGA exposed for 2 hours to 12,000 ppm H₂S in simulated TECo coal gas at 900°F and 20 atm.

Reporting

Brief reports of test status and results shall be made to DOE daily during the conduct of the tests. Decision-making discussions will be held as necessary between the test site (RTI or IGT) , DOE, GE, and the sorbent developer. A comprehensive test topical report shall be done at the completion of each test.

APPENDIX B

“Sulfur Balance for the 10-Cycle Test”

Sulfur Balances

Calculations have been performed to prepare an overall sulfur balances for this test. The balance was computed using the results of the laboratory analyses (condensate and sorbent) and calculated inlet flows in conjunction with the outlet gas compositions as found by gas chromatography. A general overall sulfur balance can be written as:

$$M_{S, \text{ sorbent initial}} + \sum_{\text{Sulf/Reg}} M_{S, \text{ inlet}} = \sum_{\text{Sulf/Reg}} M_{S, \text{ outlet}} + \sum_{\text{Sulf/Reg}} M_{S, \text{ condensate}} + \sum_{\text{Sulf/Reg}} M_{S, \text{ sorbent final}}$$

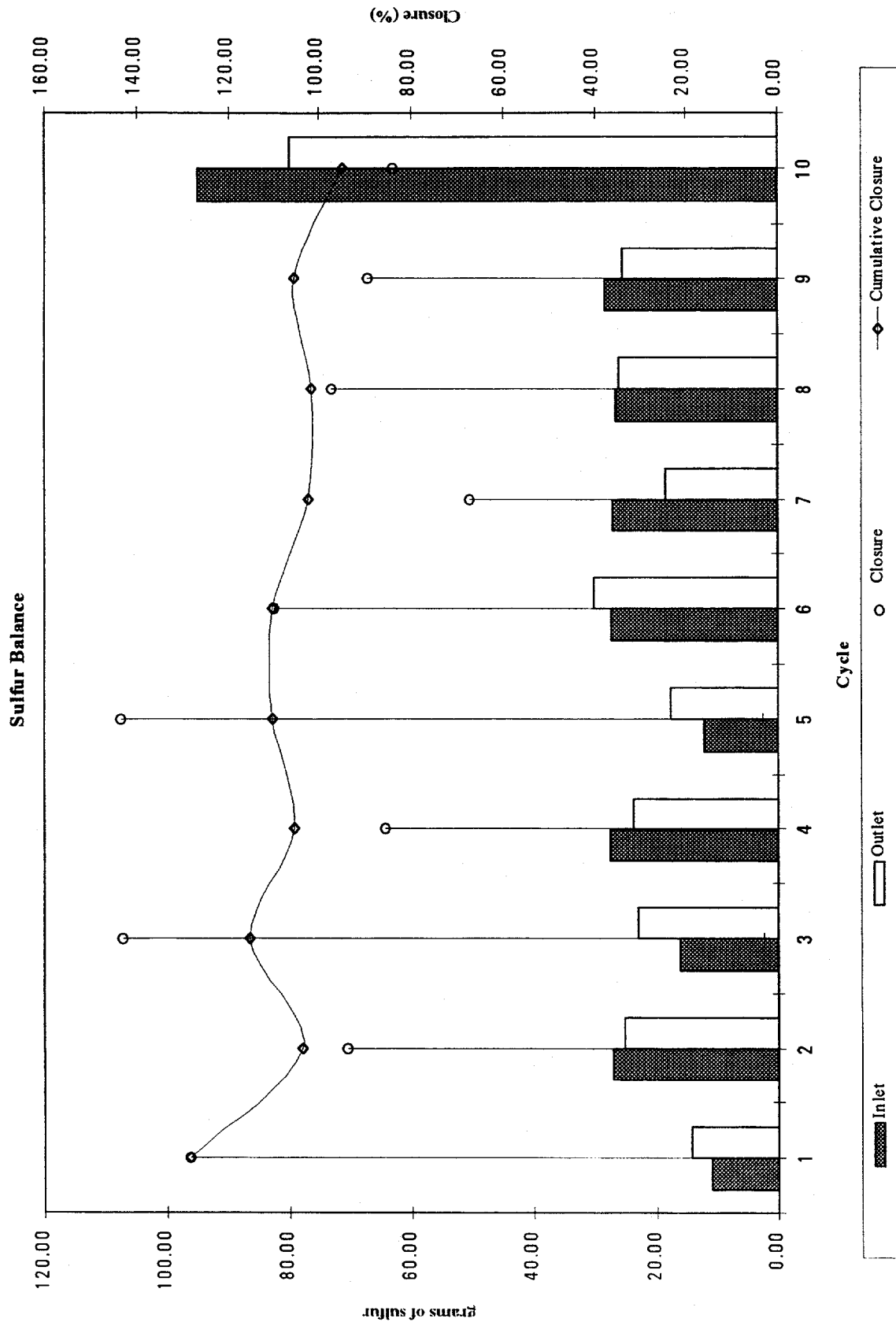
The total amount of sulfur coming into the system with the inlet gas was calculated by a numerical integration (trapezoidal rule) of the inlet sulfur compound flow rates over the time on-line. Using Nitrogen as a tie compound and inlet gas grab data the flow rates could be calculated.

Sulfur leaving the system in the outlet gas was computed using a numerical integration of the exit sulfur concentration over the time on line. The exit sulfur concentration as determined from the gas grab analyses and the calculated exit gas flows were used for this calculation. All sulfur species (SO₂, COS, H₂S) were considered in the calculations involving GC data.

The amount of sulfur in the condensate and the sorbent samples were calculated by multiplying the mass of the sample by the mass fraction of sulfur as determined by laboratory analysis.

The following table summarizes the sulfur balances for test HPHGD-060. Percent closure calculations were also calculated on a per cycle basis.

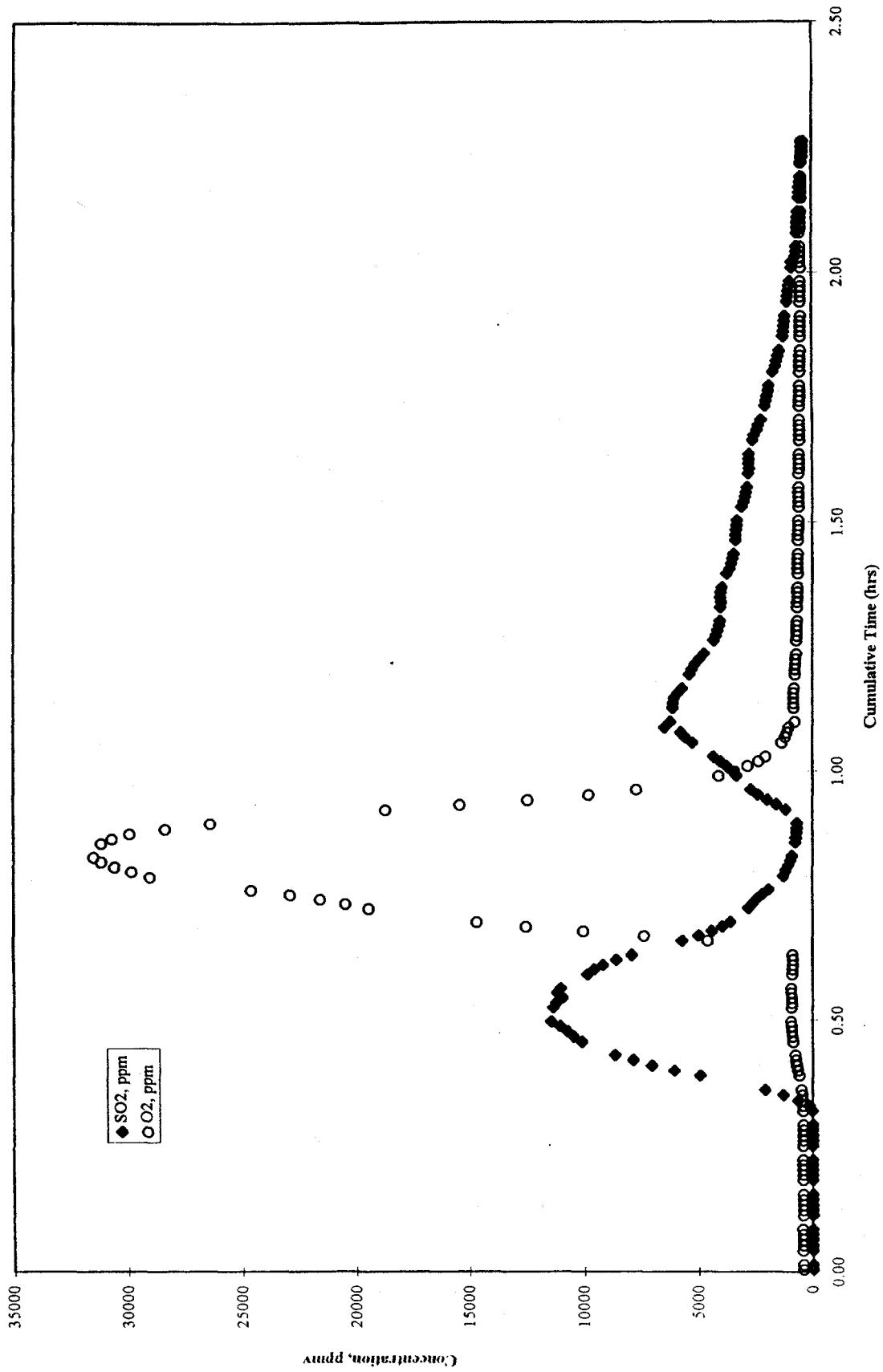
Inlet (grams Sulfur)		Outlet (grams Sulfur)				% Closure (Out/In*100)
	Fresh Sorbent	GC-Based Inlet	GC-Based Outlet	Sorbent Removed	Condensate	
S1	1.95	9.00	0.03	-	0.0110	
R1	-	0.10	14.13	-	0.0000	128.20
S2	-	26.81	0.04	-	0.0000	
R2	-	0.13	25.30	-	0.0000	94.05
S3	-	15.74	0.03	-	0.0042	
R3	-	0.28	22.85	-	0.0000	142.90
S4	-	27.29	0.04	-	0.0000	
R4	-	0.27	23.62	-	0.0000	85.85
S5	-	12.16	0.03	-	0.0043	
R5	-	0.16	17.63	-	0.0000	143.38
S6	-	26.85	0.03	-	0.0000	
R6	-	0.51	30.01	-	0.0000	109.80
S7	-	26.85	0.08	-	0.0000	
R7	-	0.33	18.23	-	0.0000	67.38
S8	-	26.50	0.09	-	0.0000	
R8	-	0.13	25.85	-	0.0000	97.43
S9	-	28.22	0.05	-	0.0000	
R9	-	0.17	25.39	-	0.0000	89.60
S10	-	94.87	0.31	7.21	0.0518	
R10	-	0.17	62.12	10.34	0.0000	84.20
Overall:	1.95	296.53	265.86	17.55	0.07	94.97



APPENDIX C

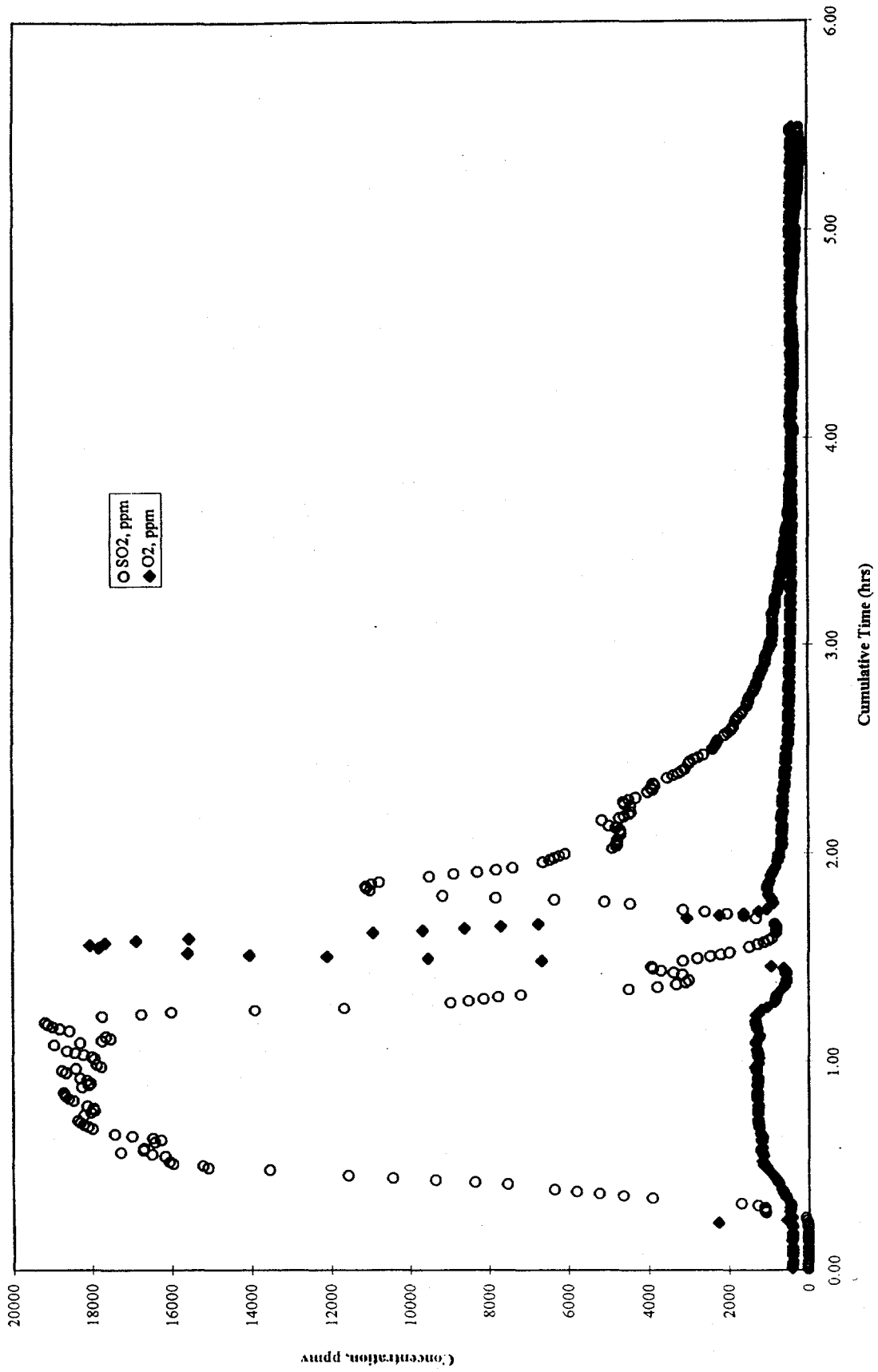
“Regeneration Curves for the 10-Cycle Test”

HPHGD-60 Regeneration 1



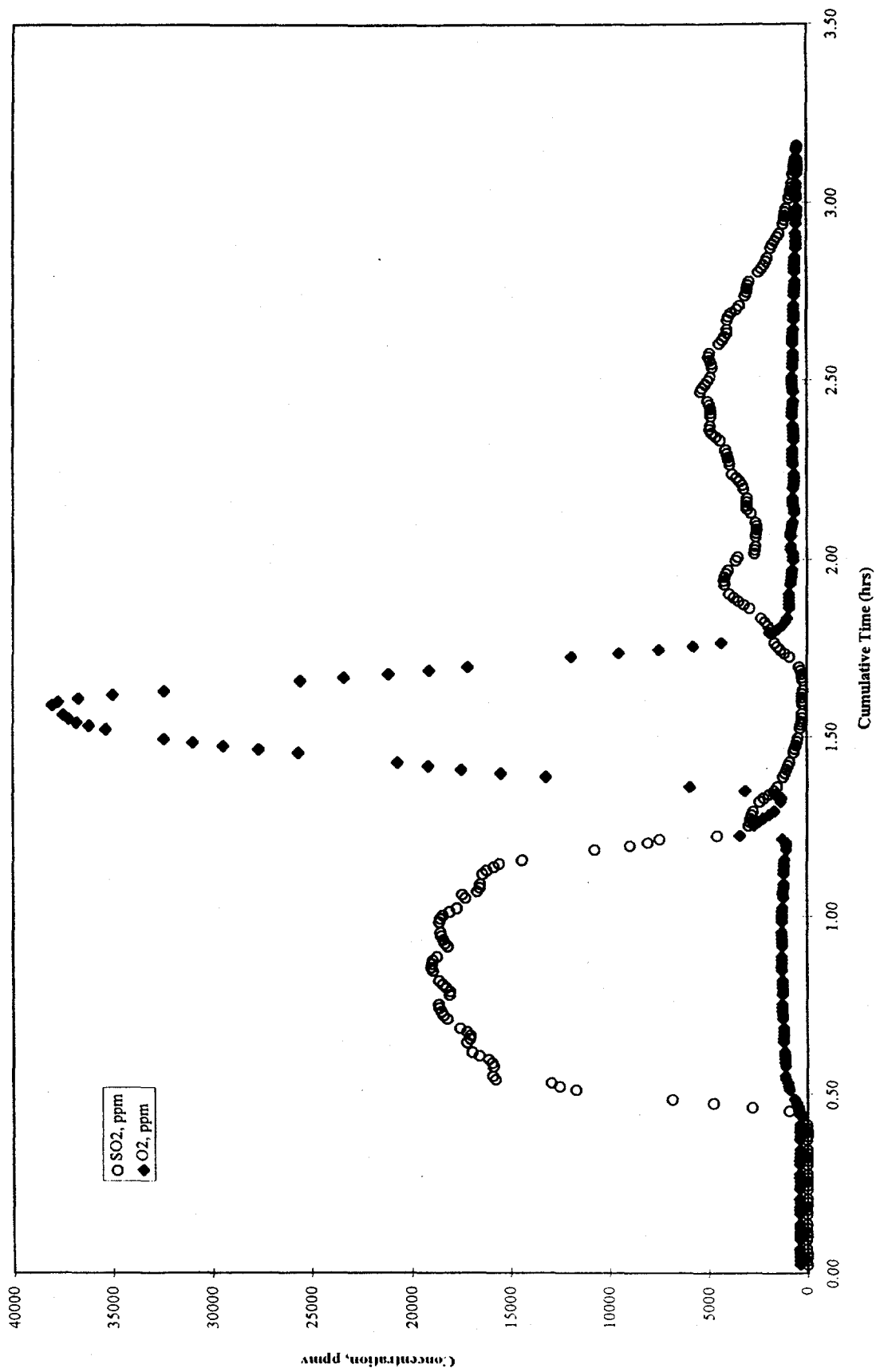
Start Time 10:00 6/9/97

HPHGD-60 Regeneration 2



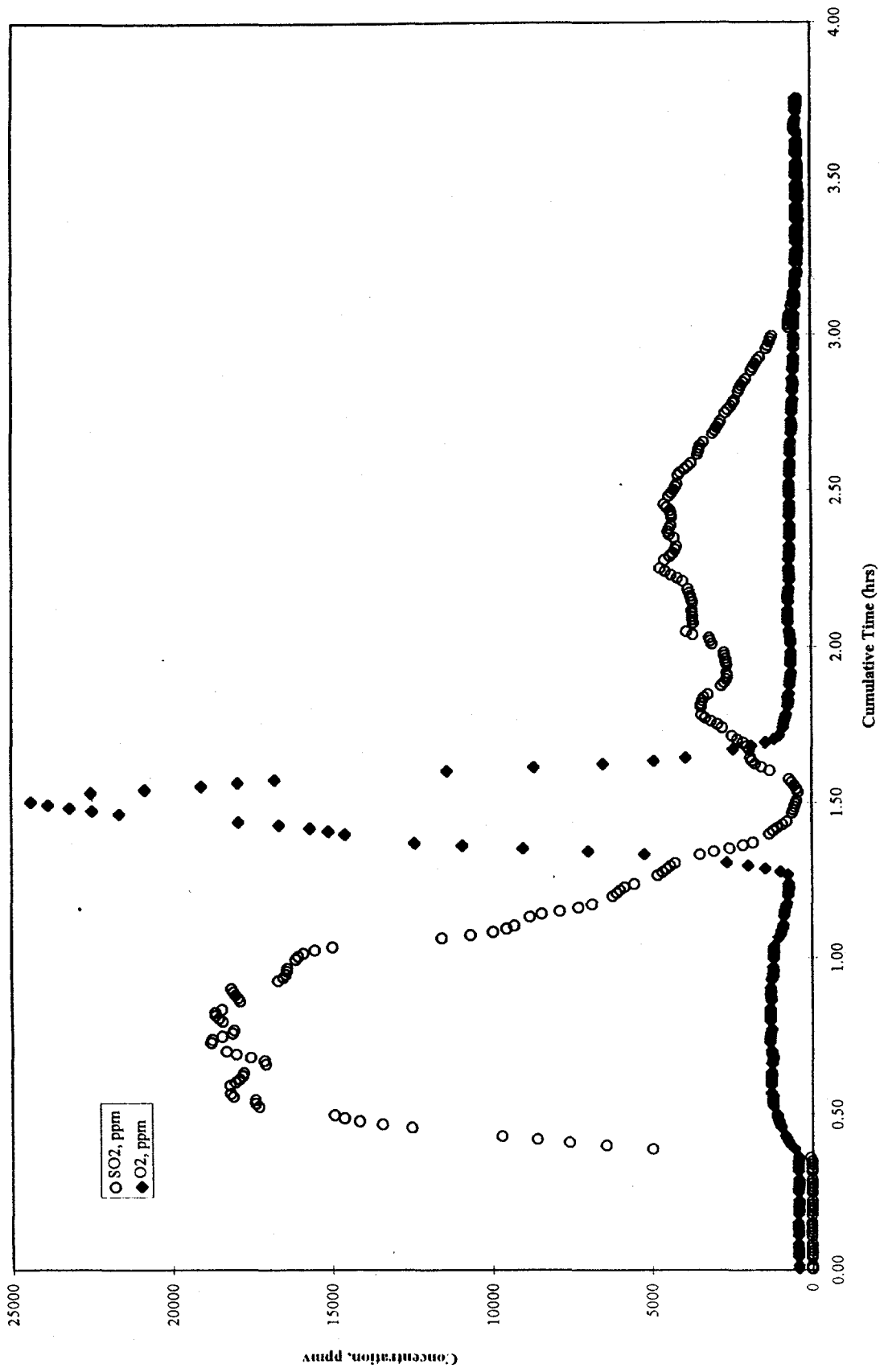
Start Time 19:30 6/9/97

HPHGD-60 Regeneration 3



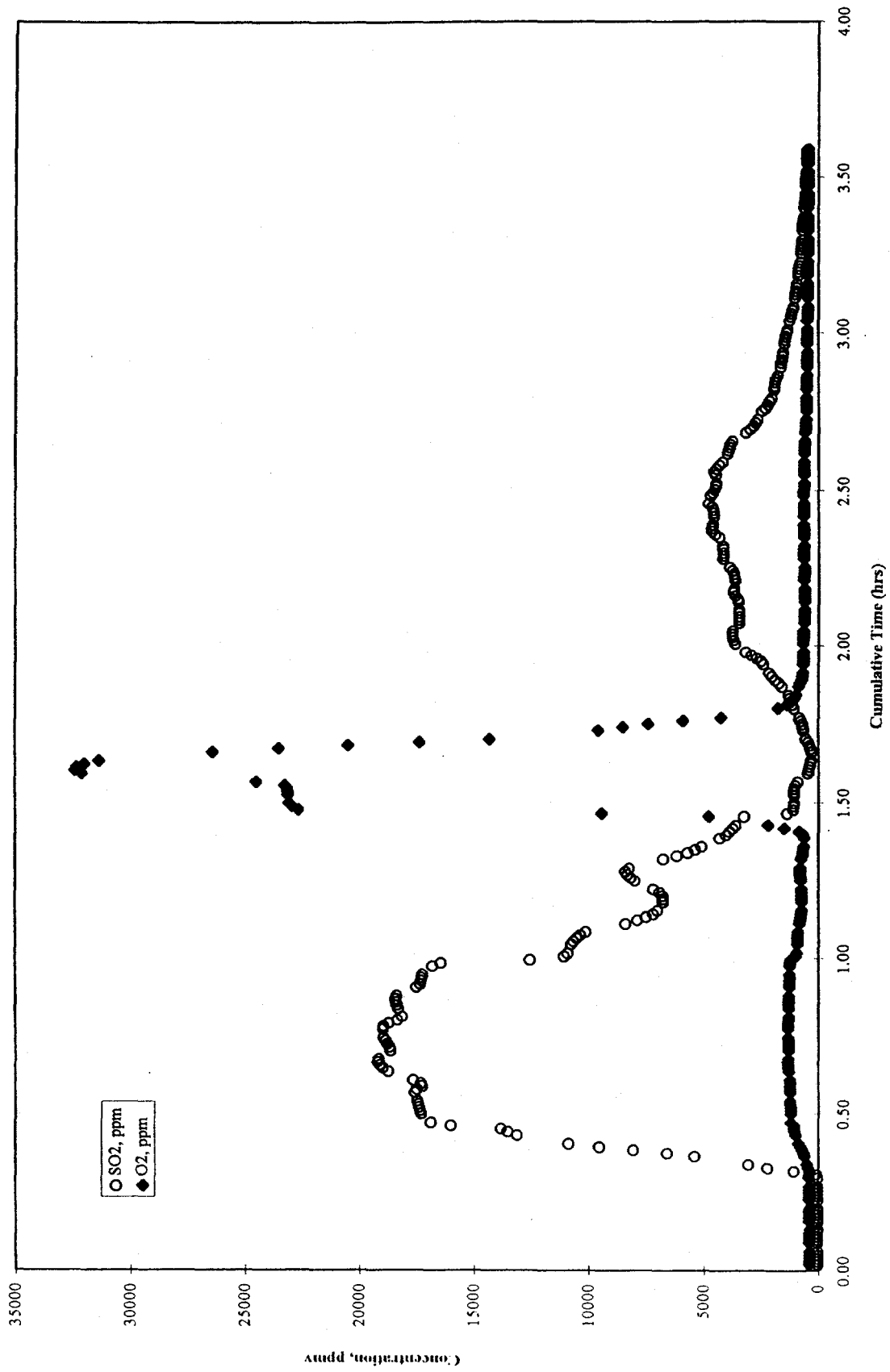
Start Time 8:00 6 10:97

HPHGD-60 Regeneration 4



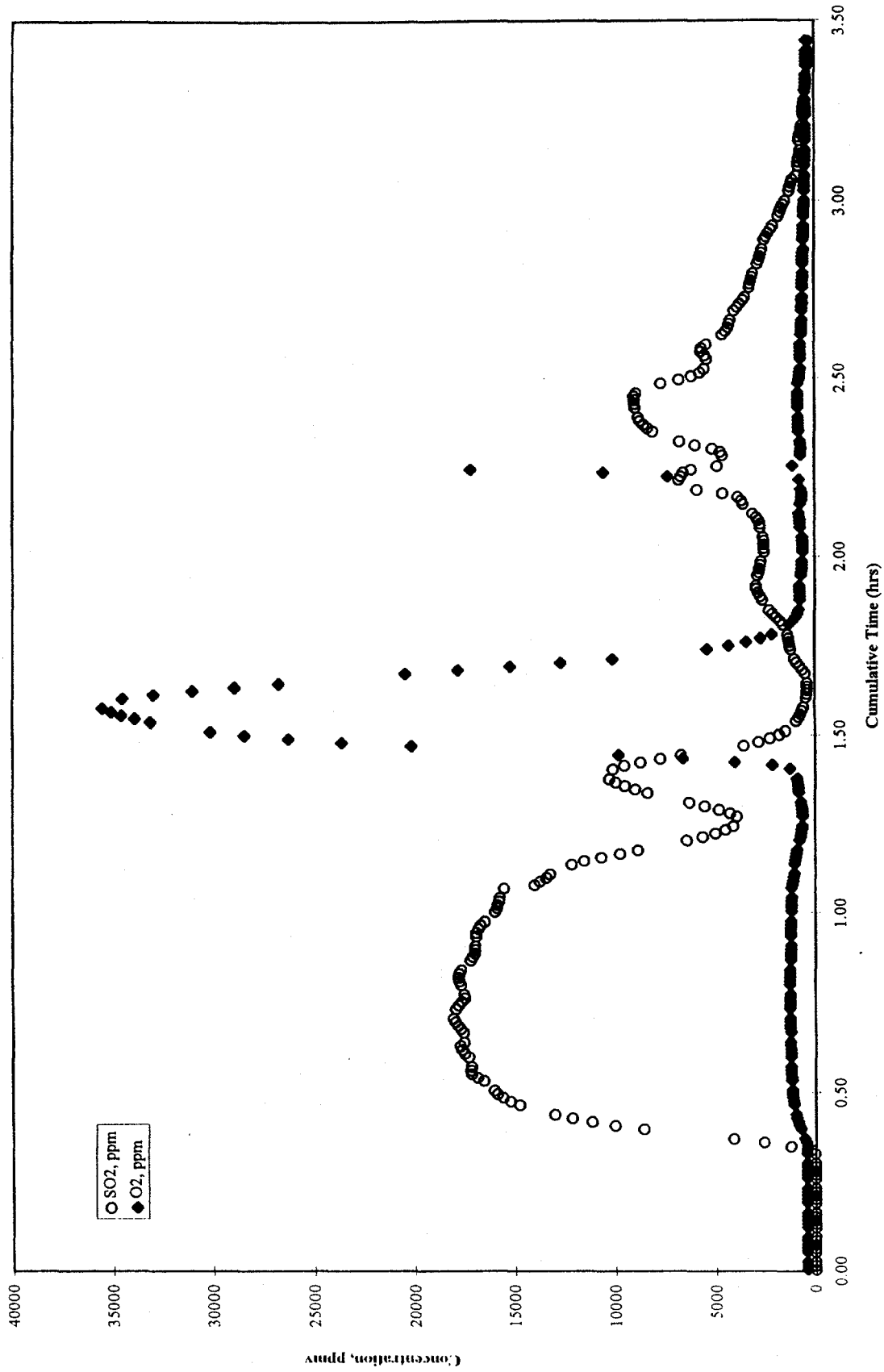
Start Time 18:00 6/10/97

HPHGD-60 Regeneration 5



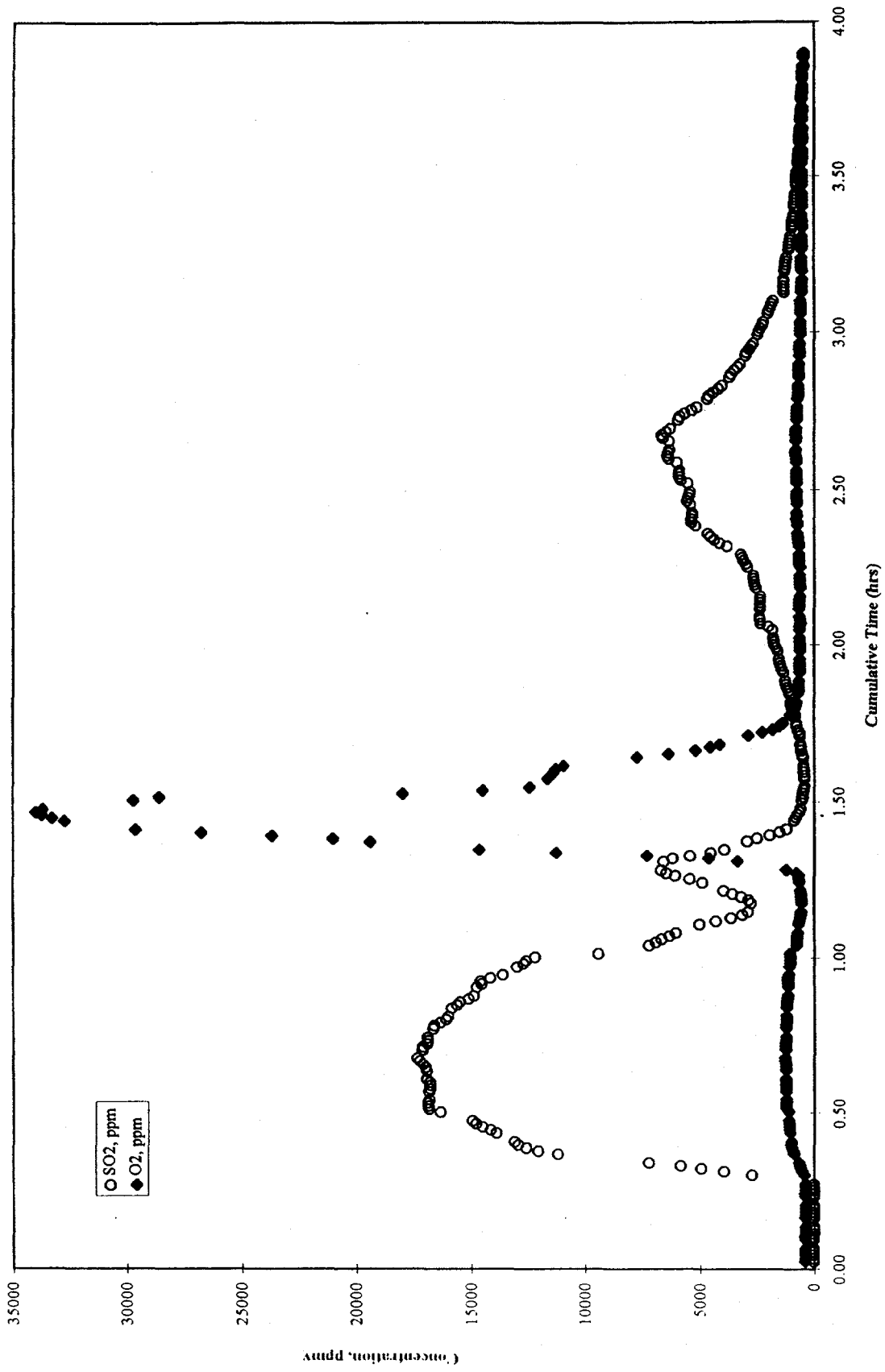
Start Time 4:02:6 11'97

HPHGD-60 Regeneration 6



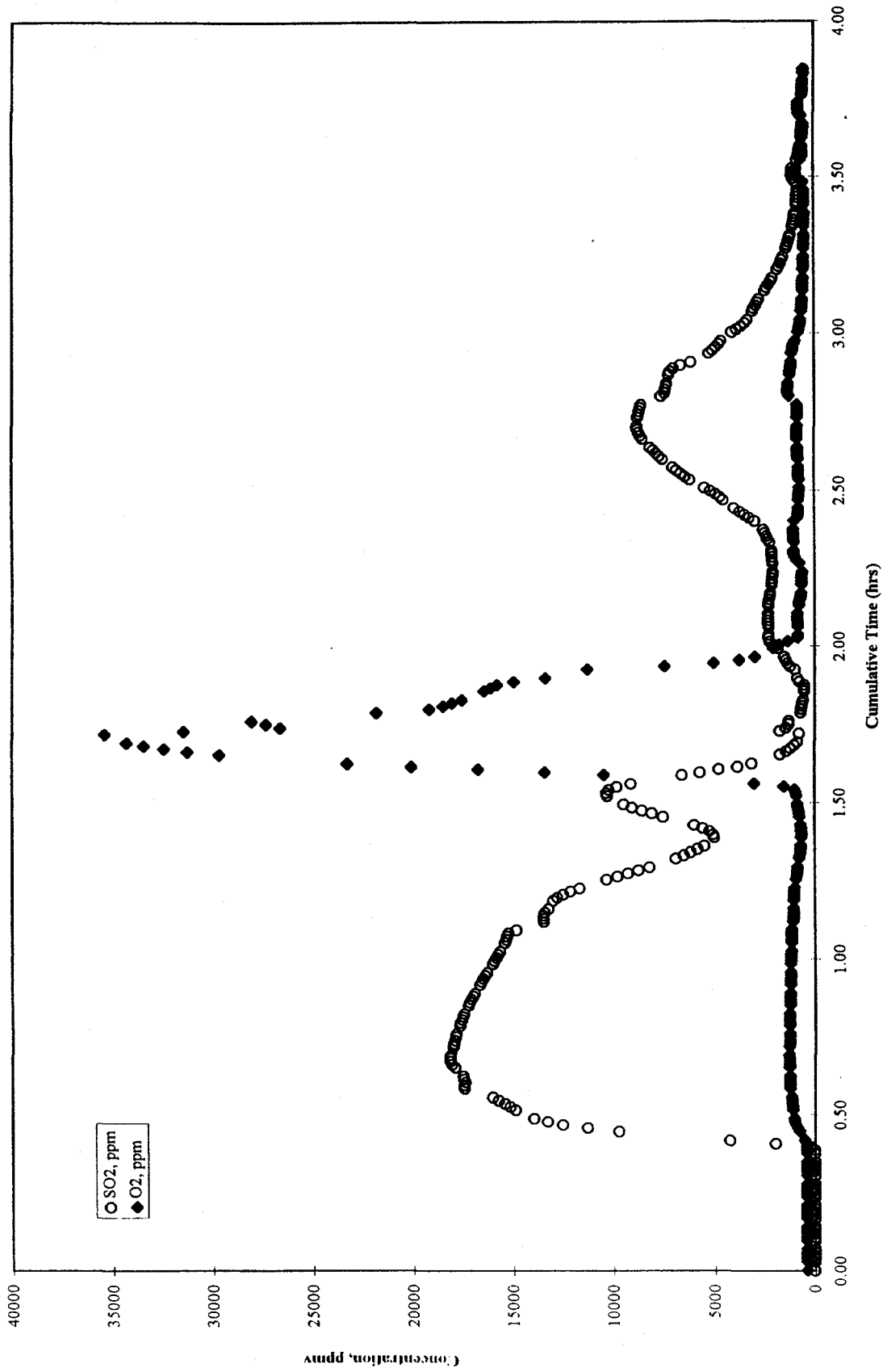
Start Time 13:30 6/11/97

HPHGD-60 Regeneration 7



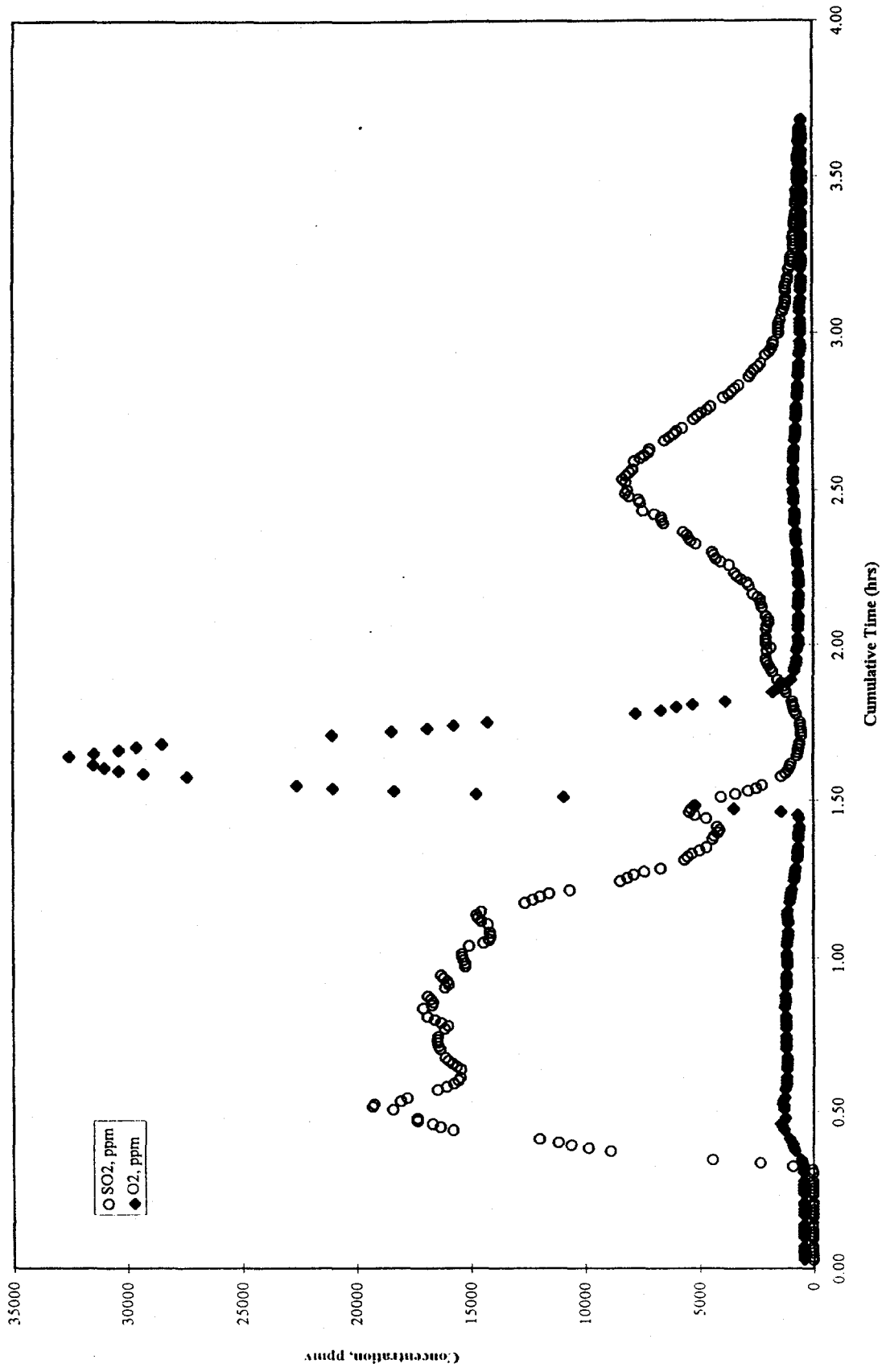
Start Time 1:00 6 12:97

HPHGD-60 Regeneration 8



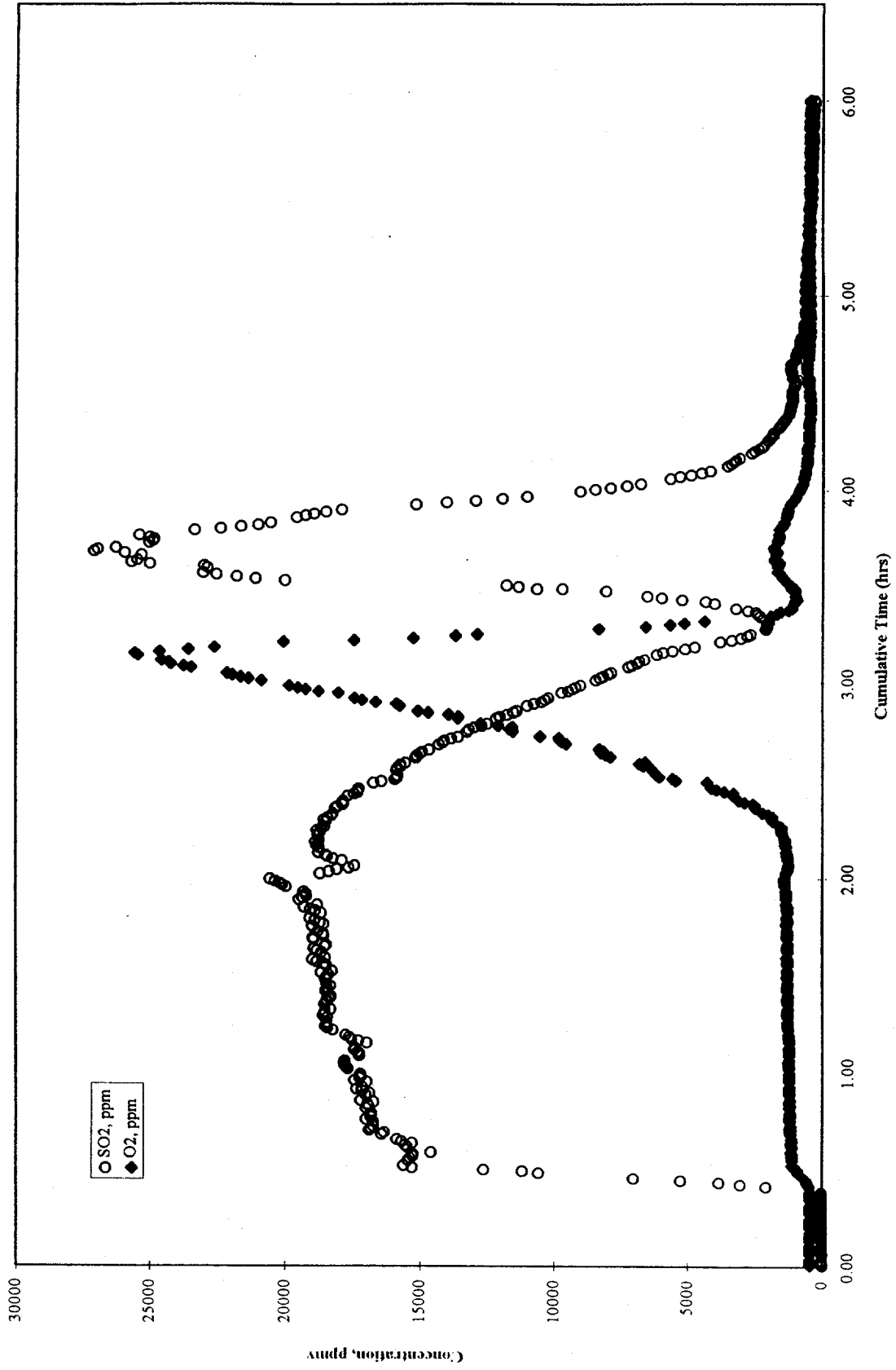
Start Time 11:00 6/12/97

HPHGD-60 Regeneration 9



Start Time 20:30 6:12:97

HPHGD-60 Regeneration 10



Start Time 20:30 6/13/97