

**A Summary of Experiments in Converting
Copper Oxide Process Regenerator Off-Gases to
Elemental Sulfur, CRADA 97-F006, Final Report**

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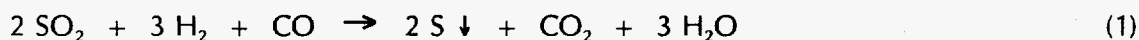
Table of Contents

	<u>Page</u>
I. INTRODUCTION	3
II. PROJECT OBJECTIVES AT FETC	3
III. THE DIRECT SULFUR PROCESS AND SKID-MOUNTED SYSTEM	4
A. The Direct Sulfur Process	4
B. Skid-Mounted Pilot Unit	5
1. Overall Design	5
2. Skid-Mounted System Installation	5
3. Catalyst Reactors	5
4. Computerized Control System	9
5. Sulfur and Water Condensers	9
IV. THE FETC PROJECT TEST PLAN	13
V. EXPERIMENTAL RESULTS	16
A. Simulated Feed Gas	16
B. FETC Off-Gas/Natural Gas Combustion	17
C. FETC Off-Gas/Coal Combustion	18
D. Sulfur-Capture Discussions	18
VI. CONCLUSIONS AND RECOMMENDATIONS	20
A. Conclusions	20
B. Recommendations	20
APPENDIX	21

A SUMMARY OF EXPERIMENTS IN CONVERTING COPPER OXIDE PROCESS REGENERATOR OFF-GASES TO ELEMENTAL SULFUR

INTRODUCTION

Sorbent Technologies Corporation (Sorbtech) of Twinsburg, Ohio has developed a new technology for converting SO₂-rich gas streams directly to elemental sulfur. Key to the technology is a special catalyst that promotes the reaction of SO₂ with reformed natural gas, as follows:



The technology evolved from earlier flue-gas desulfurization (FGD) work that Sorbtech engineers performed in the late 1980's. During the regeneration of Fluesorbents (sorbents employed in Sorbtech's Fluesorbent FGD Process), it was observed that elemental sulfur occurred directly. Applying the same approach to a range of SO₂-containing gases, Sorbtech engineers discovered that elemental sulfur could be produced in all cases. The initial research on the technology was carried out in the laboratory, first in small and large glassware experiments and then in laboratory pilot-test equipment designed for continuous operation. In 1995, with U.S. Department of Energy (DOE) support, Sorbtech designed and constructed a larger, skid-mounted pilot-test unit suitable for demonstrating the new technology in field tests. This unit was eventually moved to DOE's Federal Energy Technology Center (FETC) in Pennsylvania, where it was incorporated into FETC's Copper Oxide FGD Process facilities to convert SO₂-rich regenerator off-gases to elemental sulfur.

This Report summarizes months of preparation work and eight days of testing that were performed at FETC's facilities during late September and early October, 1997.

PROJECT OBJECTIVES AT FETC

- (1) To produce a bright yellow, commercially pure elemental sulfur product.
- (2) To examine the performances of individual components making up the Direct Sulfur system--in particular, the catalyst reactors, the computerized control system, and the sulfur and water condensers.
- (3) To examine the effects of changing important operating parameters, such as the feed-gas composition and feed-gas flow rate, on sulfur yields.
- (4) To demonstrate SO₂-to-elemental-sulfur yields of 95 percent or more.
- (5) To demonstrate sustained, continuous operation of the skid-mounted system.

THE DIRECT SULFUR PROCESS AND SKID-MOUNTED SYSTEM

A. The Direct Sulfur Process

The Direct Sulfur Process was developed to convert sulfur dioxide (SO₂) continuously as a once-through system to liquid or solid elemental sulfur. It was designed to process waste-gas streams with relatively high SO₂ concentrations (5 percent or more by weight). Six simple steps are involved in the Process; they include:

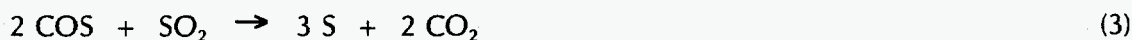
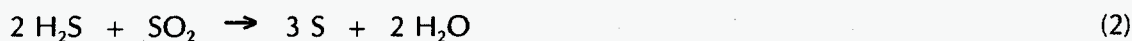
- Passing the waste gas with a reducing gas addition through a bed of Sorbtech catalyst.
- Condensing and removing the elemental sulfur produced.
- Condensing and removing entrained moisture.
- Continuing the gas flow through a bed of alumina (Claus catalyst).
- Condensing and removing any additional elemental sulfur that is produced.
- Releasing the gas to an incinerator and/or the atmosphere.

The amount of reducing gas that is added to and mixed with the entering feed gas is important in controlling the process. If the feed gas is of constant composition, control is easy. The amount of reducing gas addition is maintained at a constant rate. However, the composition of the entering feed gas is rarely constant, so adjustments in the rate of reducing-gas addition must be made. This is accomplished in the Direct Sulfur Process by employing an on-line gas chromatograph and a computer that continually monitors the composition of the incoming feed gas and makes programmed adjustments to supplied reducing gases. The adjustments that are made depend on the reducing gases that are employed. In the past, methane, carbon monoxide, hydrogen and combinations therefore were used successfully as reducing gases. Of these gases, methane or a combination of hydrogen and carbon monoxide (at a reformed natural gas ratio of 3 to 1) is preferred.

Condensation of gaseous sulfur and water vapor is achieved by simply lowering the temperature of the gas stream. Theoretically, sulfur condenses at about 440°C and water at 100°C. Unfortunately, sulfur can occur in several different molecular forms, such as S, S₂ and S₆, so condensation can occur over a temperature range. The sulfur form found to be most prevalent in direct-sulfur processing in the past has been S₂.

The gas exiting the Sorbtech catalyst bed typically consists of gaseous elemental sulfur, water vapor, carbon dioxide, nitrogen, and small amounts of SO₂, H₂S and COS. The purpose of the second bed is to promote the reactions between these residual sulfur species, SO₂, H₂S, and COS, resulting in additional elemental sulfur production. The second bed, consisting of small alumina beads, performs this function well.

Important reactions that occur in the second bed are:



B. Skid-Mounted Pilot Unit

One of Sorbtech's goals for 1997 was to scale up the Direct Sulfur Process to a meaningful size and to demonstrate it on a real waste-gas stream. The sorbent regenerator at FETC's Copper Oxide FGD Process pilot plant produces a suitable waste-gas stream. DOE-FETC offered its facilities as a demonstration site, as part of a CRADA agreement. A plan was subsequently developed and carried out that included designing and constructing a skid-mounted system, pretesting the system at Sorbtech's Twinsburg laboratories, and then moving the skid to FETC where it was incorporated into FETC's Copper Oxide Process facilities.

Overall Design. The scale-up in equipment size in going from the laboratory pilot system to the skid-mounted system was about 10. The earlier pilot system could process a feed gas at a rate of 1 to 2 liters per minute; the newer pilot system was designed for a flow rate of 15 liters per minute at standard conditions. The design and construction of the catalyst reactors, the computerized data-acquisition sub-system, the water condenser, and the sulfur collection sub-system were performed by Sorbtech engineers. The design and construction of the sulfur condensers, on the other hand, was sub-contracted to Heat Exchanger Design, Inc., a firm with reported experience in designing sulfur-condensing systems.

The skid-mounted pilot unit, along with auxiliary equipment at FETC, occupied a space approximately 12 feet by 8 feet. The tallest component in the system was the skid frame supporting the catalyst heaters at about 7 feet.

A photograph of the skid-mounted unit appears in Figure 1. A table holding process-control and data-acquisition equipment is shown in the foreground. In the background on the floor, but mostly shielded from view, is the sulfur condenser. The catalyst reactors can be seen on the far left.

Skid-Mounted System Installation. With the exception of the process-control and data-acquisition equipment, all major components of the system were mounted on the skid frame. The entire system was delivered to the FETC Pittsburgh site by truck and was off-loaded with a forklift tractor. Parsons and FETC personnel then lifted the assembly by crane three stories to the top of the Copper Oxide FGD Process facility. It was then set down and secured in an open area not far away from the regenerator-gas exhaust line.

Prior to the installation of the skid-mounted unit, Parsons personnel placed a surge tank, shown in Figure 2, at the end of the regenerator exhaust-gas line. The surge tank was installed to accumulate exhaust gas and to reduce the wide variations in gas flows and composition that often occur as a result of the manner in which the regenerator is normally operated. Also installed was a cabinet to house the calibration gases used in process control and data collection (See Figure 3).

Once the unit was in place, the gas supply lines carrying reducing gases from a remote storage location to the pilot plant site were plumbed into the skid-mounted unit (See the center of the photograph in Figure 4) and necessary instrumentation and data-acquisition connections were made (See Figure 5). Also, the unit's exhaust gas line was tied into FETC's existing incinerator.

Catalyst Reactors. Two catalyst reactors were employed in the system. Each was comprised of a straight length of 3-inch D quartz tubing supporting an approximately 10-inch

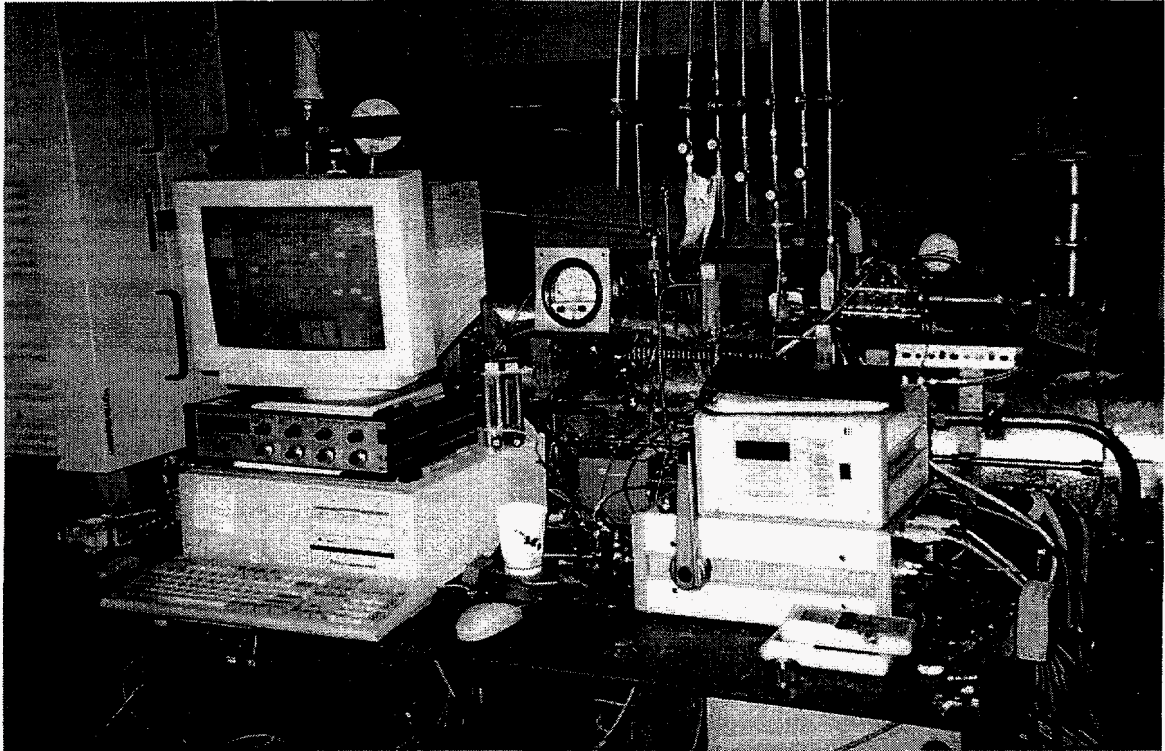


Figure 1. Skid-Mounted Direct Sulfur System

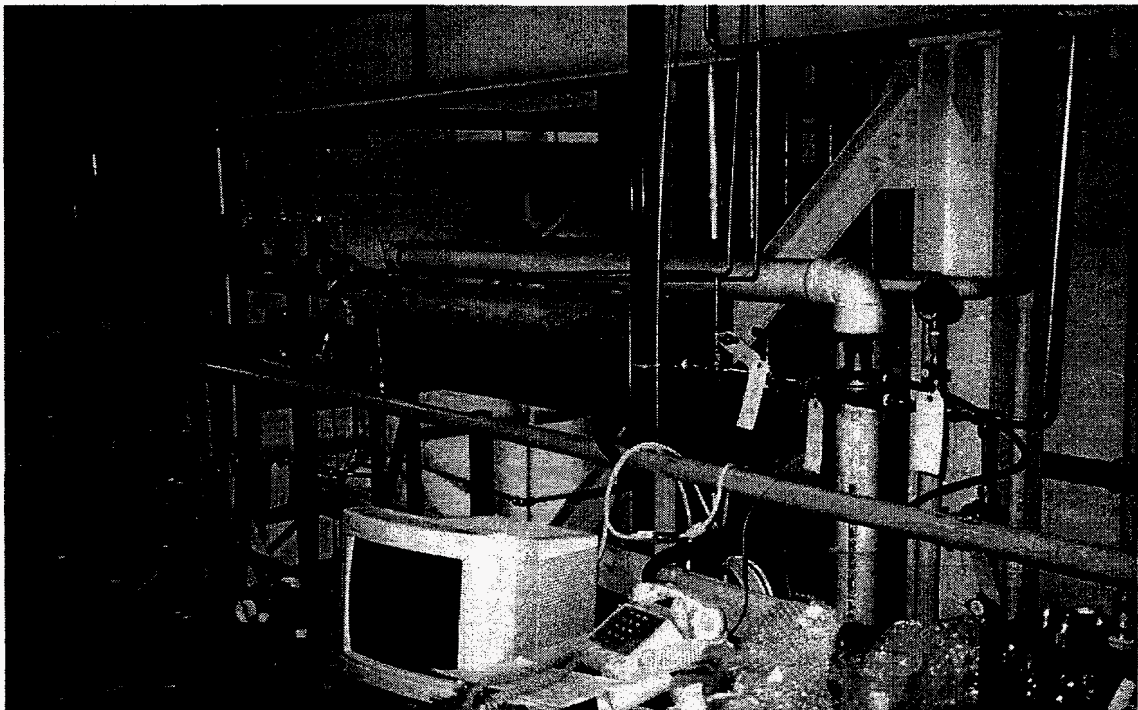


Figure 2. Regenerator Waste-Gas Surge Tank (Center of the Photograph Above the Computer Screen)



Figure 3. Cabinet Holding Calibration Gases

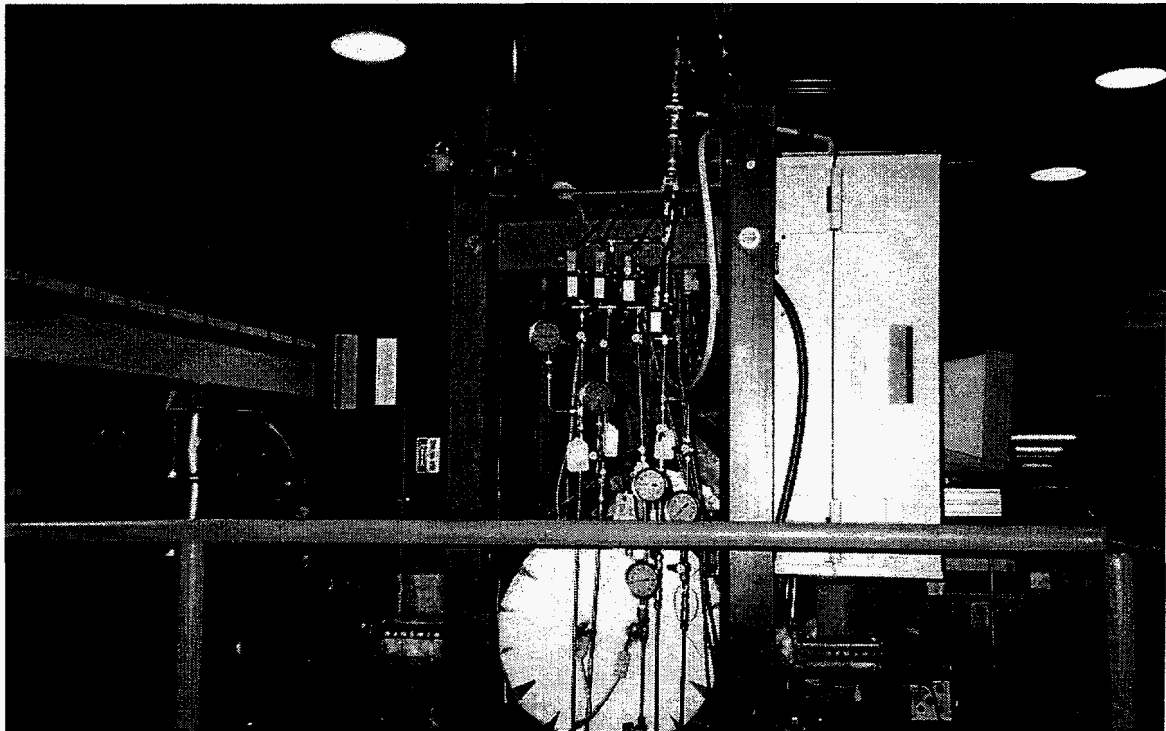


Figure 4. A View of the Left End of the Skid-Mounted Direct Sulfur System Showing Gas Lines, Furnaces, the Sulfur Condenser and the Skid Structure

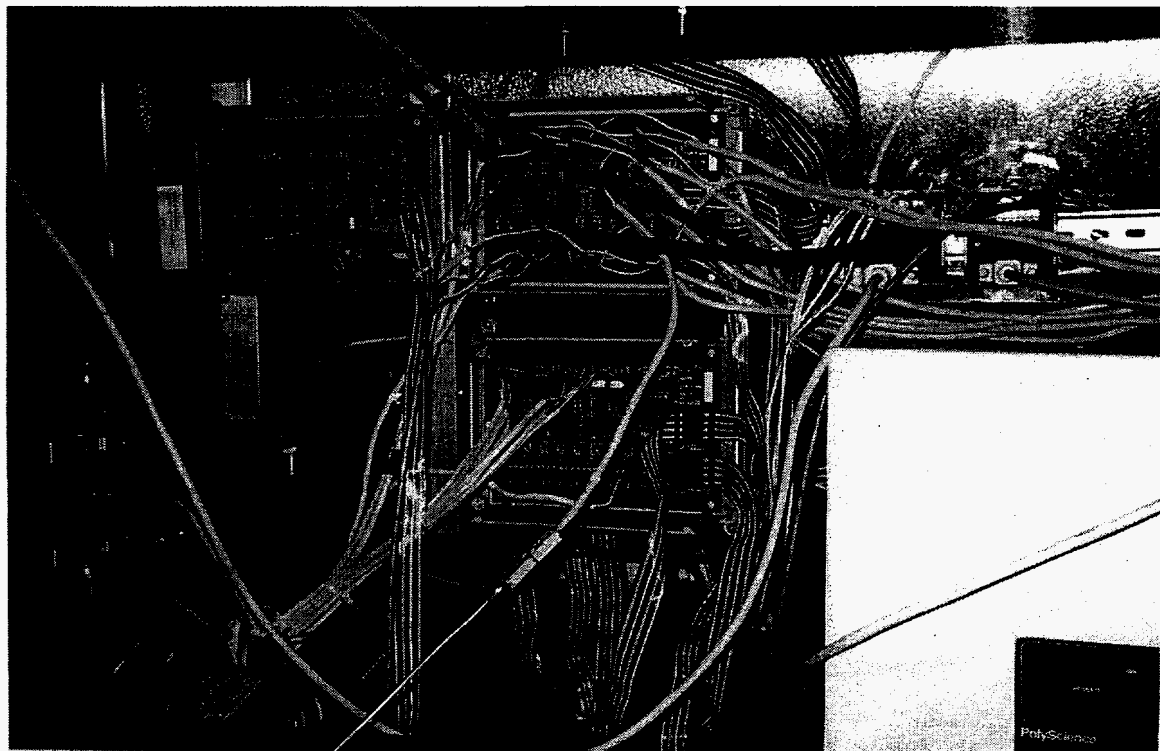


Figure 5. Electrical and Instrument Connections

bed of catalyst. Sorbtech's proprietary vermiculite-MgO catalyst was employed in Reactor 1; an alumina catalyst was used in Reactor 2. The reactors were oriented vertically in two separate split-hinge Lindberg/Blue M tube furnaces supplied by Thomas Scientific. The furnaces can be seen in Figure 4. An open furnace exhibiting a reactor containing catalyst is shown in Figure 6.

Computerized Control System. A personal computer (PC)-based data-acquisition (DAQ) system was designed, assembled and integrated with an on-line gas chromatograph (GC), supplied by MTI Analytical Instruments, to provide real-time gas analyses data. Samples were taken periodically of gases entering the system. Gas samples were also taken downstream from the sulfur and water condensers. The latter approach was carried out to ensure that reasonably dry, particulate-free samples were collected. Samples were taken every three minutes while alternating between sampling locations after the two process stages. A time of about 45 seconds was necessary to ensure that a representative gas sample was introduced satisfactorily to the GC, via an internal sampling pump, and 130 seconds were required for analysis. A computer was utilized to coordinate the positions of the sample-line switching valve and the onset of the GC sampling pump. The line-switching valve was supplied by Valco Instruments.

The DAQ system recorded temperatures, pressures, inlet gas flows, and gas composition data as a function of time. Temperatures were sensed by type-K thermocouples at 12 different locations. In the reactors, multi-point thermocouples with four sensing locations spaced at one-half inch intervals were used to detect temperature variations or hot spots inside the catalyst beds. Three pressure transducers allowed continuous monitoring of pressure drop for each stage of the process. These indicators also aided in troubleshooting and pinpointing problem areas as a result of unwanted sulfur deposition. In all cases, either a simulated regenerator off-gas or actual regenerator off-gas was introduced to the Direct Sulfur system. Nitrogen, SO₂, CO₂, the regenerator off-gases, and a reducing gas were regulated and introduced to the system, as needed, through Brooks Instruments mass-flow controllers after which they were mixed. Based upon the GC analyses, the amount of reducing gas delivered to the skid was operator-controlled.

Sulfur and Water Condensers. Separate sub-systems were employed to condense sulfur and water in the system. A single vessel, partitioned into two separate vertical sections, was designed and constructed to condense sulfur after treatments in the two catalyst reactors. The vessel was 116 inches long and contained bundles of condensing tubes. See Figure 7 for drawings of the sulfur condenser. The section nearest Reactor 1 was employed to condense sulfur from gases exiting Reactor 1; the section nearest Reactor 2 was employed to condense sulfur from gases exiting Reactor 2. The end of the sulfur condenser can be seen in the photograph in Figure 4. The condenser is between the two catalyst-reactor furnaces near the floor.

The sulfur-condensing unit was designed with straight 1-inch D condensing tubes at a slight angle with the horizontal so condensed liquid sulfur would flow toward the exit end of the unit. At the end of the unit was heat-traced metal tubing to transport the liquid sulfur to the heated and insulated metal collection pots.

Gases exiting the Reactor 1 side of the sulfur condenser were directed to a water condenser. The water condenser was a crude device consisting of a 15-foot long, 1-inch diameter coil of Teflon submerged in an ethylene glycol bath maintained at a temperature of 0.5°C. Gases after passing through the condenser were directed back to Reactor 2.

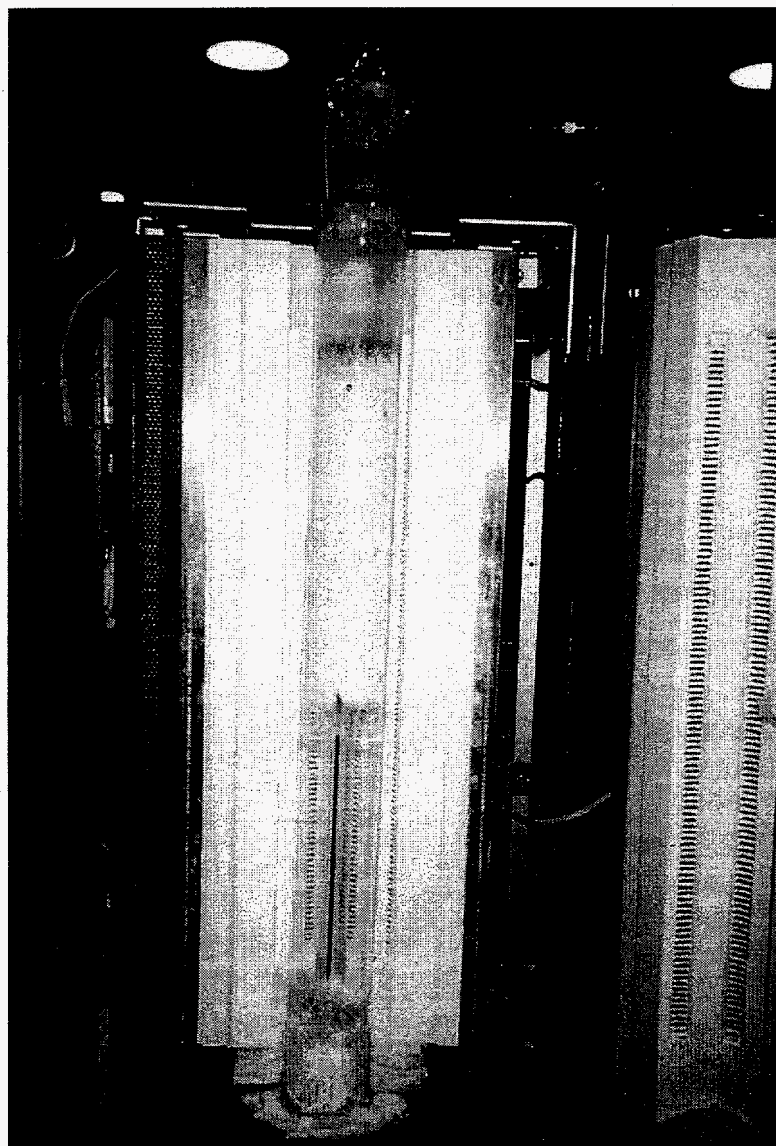


Figure 6. Furnace Opened to Display Reactor Containing Process Catalyst

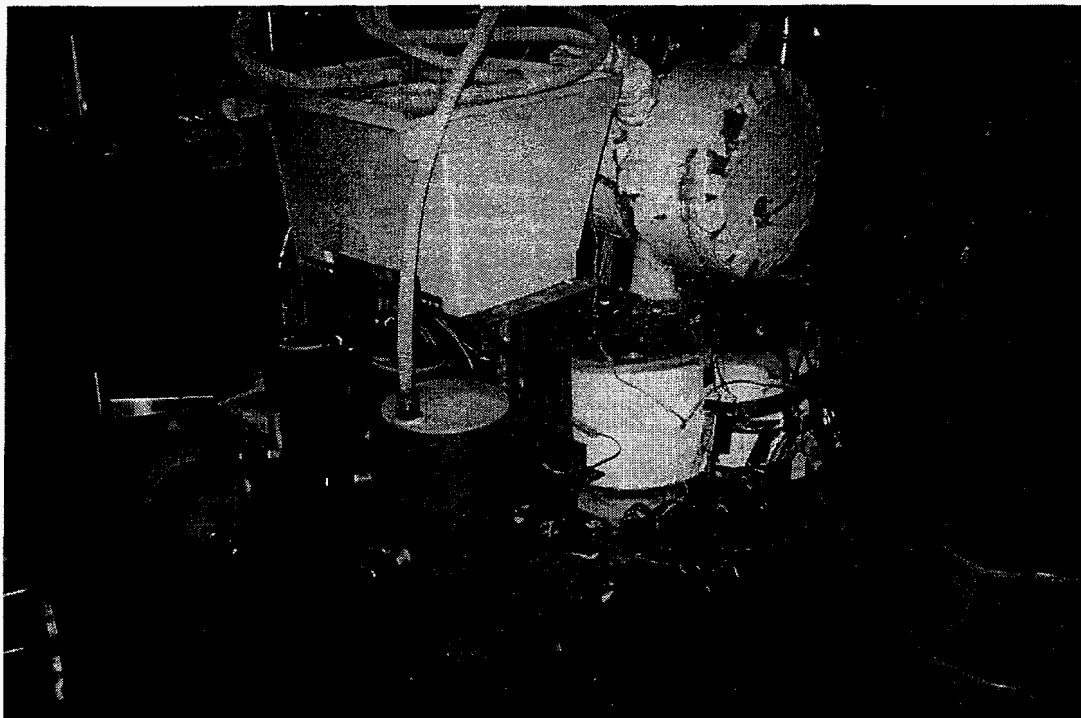


Figure 8. A View of the Right End of the Skid-Mounted Direct Sulfur System, Showing the Water and Sulfur Condensers and Water and Sulfur Collection Pots

Figure 8 shows the exit end of the sulfur condenser, the liquid sulfur collection pots, and the water condenser. The collection unit on the floor in the center of the photograph was employed to collect condensed water.

THE FETC PROJECT TEST PLAN

The program planned FETC's Copper Oxide Process Life Cycle Test System (LCTS) at Pittsburgh consisted of a baseline operating test and a series of parametric tests made to collect baseline data when operating under three major feed conditions:

- A) A simulated feed gas utilizing bottled industrial gases;
- B) FETC regenerator off-gas, utilizing natural gas spiked with SO₂ as feed to the LCTS unit; and
- C) FETC regenerator off-gas, utilizing an Illinois coal feed for combustion to the LCTS unit.

- Objectives:
- 1) To maximize elemental sulfur yield and/or minimize SO₂ emissions to the LCTS incinerator.
 - 2) To operate the Direct Sulfur unit for a continuous run of at least eight (8) hours, achieving 95% or higher conversion of SO₂ to elemental sulfur.

The test-plan baseline operating conditions for Sorbtech's Direct Sulfur Process skid-mounted system were as follows:

Baseline Feed-Gas Composition:

<u>Component</u>	<u>Volume %, Dry</u>
SO ₂	43.0
CO ₂	21.0
N ₂	36.0

Bed Temperatures:

Reactor 1	850°C
Reactor 2	300°C

Reducing Gas Composition:

<u>Component</u>	<u>Volume %, Dry</u>
H ₂	75.0%
CO	25.0%
Total	100.0%

Space Velocity:

Reactor 1	2000/hr ⁻¹
Reactor 2	800/hr ⁻¹

The plan was to operate the Direct Sulfur unit at normal baseline conditions with bottled industrial gas until the LCTS was running and achieving steady-state conditions. In the initial work with the LCTS System, natural gas, spiked with SO₂ was to be employed as the fuel to the LCTS unit. Later, coal was to be used as the fuel.

The LCTS incinerator was to be used in all test work. The purpose of the incinerator was to convert any non-SO₂ species to SO₂ and to combust any residual fuel species that might be present before releasing the exhaust gases to the atmosphere.

The initial one or two runs with bottled gas was to be the baseline operating test. The purpose of this test was to determine and confirm that operating conditions and results observed in Sorbtech's laboratories could be repeated at FETC. The results then would serve as standards with which all other test results could be compared.

After the initial work with simulated regenerator off-gases, the plan was to proceed with actual regenerator off-gases. FETC contractor Parsons and FETC personnel would decide when the change from simulated gas to actual gas would occur and when the fuel changes would be made.

After the baseline tests, the plan was to carry out a series of runs examining how changes in different process variables affect sulfur dioxide-to-elemental sulfur yields. Parameters believed important included:

- 1) Exhaust gas composition, including the presence of methane.
- 2) Reactor temperatures.
- 3) Reducing gas composition.
- 4) Residence time in the reactors.

The test plan that was originally developed for parametric runs in the project is summarized in Table 1. As will be noted in the next section of this Report, it was necessary to deviate significantly from this plan owing to problems that arose during the program.

TABLE 1
TEST PLAN FOR PARAMETRIC
RUNS ON LCTS REGENERATOR EXHAUST GASES

<u>Run No.</u>	<u>Temperatures °C</u>		<u>Space Velocity</u>		<u>Reducing Gas</u>
	<u>Reactor #1</u>	<u>Reactor #2</u>	<u>Reactor #1</u>	<u>Reactor #2</u>	<u>To SO₂</u> <u>Mol Ratio</u>
<u>Variable: Temperature Effect</u>					H ₂ + CO
I-1	850	275	2000	800	2
I-2	850	300	2000	800	2
I-3	900	300	2000	800	2
I-4	900	275	2000	800	2
<u>Variable: Reducing Gas</u>					H ₂
II-1	850	300	2000	800	2
II-2	900	300	2000	800	2
<u>Variable: Space Velocity</u>					H ₂ + CO
III-1	850	300	2000	800	2
III-2	850	300	1500	600	2
<u>Variable: Catalyst Bed Depth</u>					H ₂ + CO
IV-1	850	300	2500	1000	2
IV-2	850	300	2000	800	2
IV-3	850	300	1500	600	2

EXPERIMENTAL RESULTS

The test program at FETC was plagued with problems due primarily to plugging of the equipment with elemental sulfur condensing in inappropriate areas of the system. Yields of elemental sulfur, however, throughout the program were exceptionally high, 93 to 98 percent, and selectivities of the catalyst and system for sulfur, in preference to other sulfur species from SO_2 , were even higher, ranging typically from about 95 to 100 percent.

Because of the propensity of the system to plug with sulfur, the data collected in each individual run were analyzed with the idea in mind of selecting the best steady-state operating conditions available in any given run and utilizing that data to develop a mass balance for the system. This would of necessity consider both reactors, the sulfur yields, and the exit-gas conditions, such that sulfur, both entering and leaving the two-reactor system, could be verified. Because of the short overall duration of some runs, steady-state conditions were selected as the basis of analyses, and not the times that necessarily demonstrated the highest apparent sulfur yields.

A. Simulated Feed Gas

Three runs were made with simulated exhaust gases from gas cylinders to the Direct Sulfur unit prior to introducing regenerator off-gases from the Copper Oxide Process.

The first two simulated feed-gas runs were adversely affected by the improper installation of an excess-flow (SO_2) safety check valve located in the FETC cylinder room. The improper installation caused a severe restriction in gas flow and variations in the rate of gas flow to the Direct Sulfur unit. The rate was well below capacity and very unsteady. During the second run, Reactor 1, which was made of glass, was found to be cracked at the outlet to the sulfur condenser and required replacement with a standby unit.

A third run was begun on simulated gas after the improper valve installation was corrected by FETC. During the third run, it was decided to couple into the FETC-LCTS Unit, which was then on-line—that is, to switch operation from the simulated (bottled) gas mixture to the Copper Oxide Process regenerator gas from the LCTS Unit. At this time, the Copper Oxide Process was producing an actual flue gas; the flue gas was the result of combustion of natural gas that was spiked with SO_2 . This Run No. 3 had a total elapsed time of 2.1 hours, of which 1.29 hours were operated on actual Copper Oxide Process regenerator gas.

The run data were carefully reviewed to select a sequence of sampling which had steady-state data, insofar as throughput rates were concerned. Data were analyzed to determine a materials balance, yields of sulfur from SO_2 , and selectivity in the conversion of SO_2 . The results for Run Nos. 2 and 3 were as follows:

	<u>Yield ⁽¹⁾</u>	<u>Selectivity to S ⁽²⁾</u>
Run No. 2	97.6%	98.7%
Run No. 3	96.9%	97.9%

⁽¹⁾ Yield of elemental sulfur from SO_2 .

⁽²⁾ Selectivity of S from SO_2 , the remaining sulfur being H_2S or trace amounts of COS.

It should be noted that these yields and selectivity values were not the highest numbers observed in the data that were collected, but rather those which best indicated steady-state operation.

B. FETC Off-Gas/Natural Gas Combustion

During the Run Nos. 4 through 18, the Direct Sulfur unit processed LCTS regenerator off-gas, where the LCTS combustion source was natural gas, spiked with SO₂.

Run No. 4 was aborted and the unit was bypassed due to a fire alarm at FETC (unrelated to the project).

Run No. 5 through Run No. 10 were a series of runs with frequent plugging problems with elemental sulfur. Plugging occurred in a number of specific spots in the system. Runs No. 5 through No. 10 totaled 12.28 hours; the longest run without a plug that required bypassing the gas to the incinerator was 3.44 hours.

During the Run Nos. 5 through 10, steady-state data were taken and sulfur yields and conversions were as follows:

<u>Run No.</u>	<u>Yield of Elemental Sulfur</u>	<u>Selectivity to Sulfur from SO₂</u>
5	97.2%	99.4%
6	No Steady State	No Steady State
7	96.8%	99.1%
8*	85.3%	—
9	95.4%	98.8%
10	No Steady State	No Steady State

*No Reactor 2 data. Based on previous run data, yields of 95.0% to 97.0% would be predicted had No. 2 gas chromatograph data been available.

Toward and at the end of Run No. 10, severe plugging of the sulfur traps and the chiller coil (stage one) occurred. This required a complete clean-out of these pieces of equipment prior to resuming the test runs. Also, beginning in Run No. 9 and continuing through Run No. 10, the system experienced low feed-gas flow rates. Run No. 10 was halted owing to Copper Oxide Process instability; FETC requested a shutdown.

Prior to Run No. 11, all lines and auxiliary components in the system were fully cleaned of sulfur. The unit was then brought on-line. Run Nos. 11 and 12 were carried out with a feed-gas rate of 14 slpm, and the unit was kept on stream despite continued plugging in various sulfur traps, etc. Sulfur yields and selectivities in Runs No. 11 and No. 12 were as follows:

<u>Run No.</u>	<u>Yield of Elemental Sulfur</u>	<u>Selectivity to Sulfur from SO₂</u>
11	95.9%	95.9%
12	96.6%	98.3%

The total on-stream time for the two runs was 2.75 hours.

Run No. 13, which had a total elapsed time of less than 1 hour, did not achieve a sufficiently steady-state condition to provide data for a mass balance. The second reactor inlet plugged relatively quickly and reduced flow, and ultimately the plug shut off flow to Reactor 2.

Run Nos. 14 through 18 were punctuated with continual plugging problems primarily in the sulfur traps and the chiller stages (following each pass through the sulfur condenser). In each of these five runs, steady-state conditions were reached sufficiently to develop a material balance for each run. The results were as follows:

<u>Run No.</u>	<u>Yield of Elemental Sulfur</u>	<u>Selectivity to Sulfur from SO₂</u>
14	92.4%	96.5%
15	93.3%	99.1%
16	98.1%	99.3%
17	92.6%	94.7%
18	96.3%	97.1%

The total operating time on Copper Oxide regenerator gas in these runs was 8.32 hours. Run No. 18 was terminated early due to a substantive drop in feed-gas flow (from 14 slpm to 10 slpm) and to fluctuations in gas-flow rate from the LCTS system.

C. FETC Off-Gas/Coal Combustion

Run Nos. 19 and 20 were completed with a feed-gas flow ratio of 10 slpm to the Direct Sulfur unit. The Copper Oxide FGD System was being fired with an Illinois coal. The Copper Oxide Process regenerator off-gas contained SO₂ from the combustion of this coal. The SO₂ content of the regenerator gas was in the range of 23 to 25 percent by volume. Steady-state data indicated sulfur yields as follows:

<u>Run No.</u>	<u>Yield of Elemental Sulfur</u>	<u>Selectivity to Sulfur from SO₂</u>
19	95.1%	96.0%
20	96.8%	97.4%

A complete summary of all runs is provided in the Appendix of this report.

D. Sulfur-Capture Discussions

The most severe problem encountered in the Direct Sulfur runs that were conducted at FETC was the unwanted condensation and solidification of sulfur in the process-gas lines. Undesirable deposits that built up in the lines and fixtures connected to the lines eventually choked off gas flow in the system. This, in turn, necessitated prematurely terminating most runs.

Following the tests at FETC, a visit was made to the Claus Plant at BP Oil Company's Toledo refinery to observe BP Oil's handling of sulfur. Extensive discussions were held with Todd Becker, the Chemical Engineer in charge of the Claus Plant facilities. Mr. Becker discussed

at length his experiences in handling sulfur and sulfur-containing gases at the refinery and sulfur freezing and clogging problems encountered at BP Oil Company in the past. Mr. Becker made the following recommendations with regard to the Sorbtech system.

- (1) Never allow the sulfur to solidify until it is completely outside the system. This can be accomplished by maintaining the temperature of the sulfur-containing gas well above the freezing point of sulfur (118°C) at all times.
- (2) Allow the water in the process gas to remain with the gas until final cooling at the end of the system.
- (3) Operate the sulfur condenser at 148°C, and never allow the temperature to fall below 140°C.
- (4) If liquid sulfur is collected in a reservoir at the end of the sulfur condenser, consider installing a heated demister at the exit of the condenser.

The temperature of the process gas in Sorbtech's system at FETC was lowered to below 1°C to condense out water between the two process stages. The sulfur condenser was generally operated at 120°C or lower, although, at times, the exit end of the condenser was heated to slightly higher temperatures.

In Sorbtech's early Direct Sulfur Process development work, two essentially identical Magsorbent catalyst beds were employed in series to produce elemental sulfur, with sulfur and water condensation and removal steps carried out between the beds. Water condensation and removal was found necessary because high water levels in the process gas were observed to affect elemental sulfur production adversely in the second bed. Later in Sorbtech's development work, it was found that substituting a Claus catalyst for Magsorbent in the second bed markedly improved overall sulfur yields.

According to Becker, the presence of water in the process gas does not affect the performance of a Claus catalyst significantly. If this is true, the water condensation and removal step in the Direct Sulfur Process is not now necessary. Elimination of the water-condensing step, in turn, should eliminate most of the sulfur-clogging problems that occurred in the system.

CONCLUSIONS AND RECOMMENDATIONS

A. Conclusions

On the basis of the results of this phase of the project, the following conclusions were made:

- (1) The chemistry of the new technology was well proven and demonstrated at FETC. The overall SO₂-to-elemental sulfur yields were typically in the range of 93 to 98 percent. (The project goal was 95 percent, so the goal was exceeded).
- (2) Sulfur selectivity values, indicating the tendency of SO₂ to be converted to elemental sulfur in preference to H₂S or COS, were typically in the range of 98 to 100 percent.
- (3) Bright yellow sulfur of high quality was produced at FETC.
- (4) The FETC regenerator exhaust gas presented no processing difficulties. Swings in the level of methane in the exhaust gas were handled with relative ease.
- (5) With the exception of the water condenser, all system components performed well.
- (6) Condensing of the sulfur after its production was a serious problem at FETC. Solid sulfur deposits built up in the process-gas lines at several locations in the system. Clogging of the lines necessitated terminating runs typically after 2 to 4 hours of operation. Clogging problems were most severe in the water condenser. Many planned parametric tests were not run because of the sulfur plugging problems.
- (7) Several suggestions were made by BP Oil Company for solving the sulfur plugging problems. Among the suggestions were to never allow the temperature of the process gas to fall below 118°C, to increase the temperature of the sulfur condenser to 148°C, and to eliminate the water condenser from the system entirely.

B. Recommendations

On the basis of the above conclusions, Sorbtech recommends that work on the Direct Sulfur Process be continued. More specifically, it recommends that the suggestions made by BP Oil Company be implemented and that additional test runs with FETC's Copper Oxide FGD system be performed. One objective of the FETC work, the demonstration of long-term continuous operations of the Direct Sulfur Process skid, was not attained. With the changes suggested by BP Oil, there is a high probability that this objective can be achieved. Other actions that are recommended include the following:

- (1) installing the skid-mounted unit in other systems that have troublesome concentrated SO₂ streams, such as with the H₂S sorber/regenerator in FETC-developed Coal Gas Treatment Process or in a petroleum refinery application, to demonstrate the new technology; and
- (2) scaling up the system to treat larger gas volumes, preferably at a full, commercial size.

APPENDIX

DOE-4, Direct Sulfur
Testing at FETC 9-23-97 to 10-1-97

Test #	Date	Time of Day	DAQ Time		Runtime			MBCuO gas (hrs)	Reason for stopping test	Max. Flow (slpm)	Notes
			start	end	(sec)	(hours)	Simulated (hrs)				
Simulated Gas											
1	9/24/97		7650	13500	5850	1.63	1.63		Unsteady SO2 line pressure	2.2 slpm SO2	
			13900	14750	850	0.24	0.24		Unsteady SO2 line pressure	2 slpm SO2	
			16800	20900	4100	1.14	1.14		Unsteady SO2 line pressure		
			21100	21200	100	0.03	0.03		Unsteady SO2 line pressure	3.5 slpm SO2	Improper installation of SO2 excess flow safety
			21650	22250	600	0.17	0.17		Unsteady SO2 line pressure	2.5 slpm SO2	check valve located in FETC cylinder room
			22550	23600	1050	0.29	0.29		Plug in cooling coils		
				Total	12550	3.49					
2	9/25/97	2:30 AM	1500	6500	5000	1.39	1.39		Oxygen increasing in GC analyses		Cracked RX1 out socket
Start with simulated and switch to MBCuO Process gas (Natural gas fired flue gas w/ SO2 spiking)											
3	9/26/97	1:00 AM	800	3700	2900	0.81	0.81			3 slpm SO2	Install old reactor 1, N2 in @center ~0.5slpm
			3700	4400	700	0.19	0.19	0.19			Begin simulated gas feed
			0	1150	1150	0.32	0.32	0.32		12.5	Begin FETC gas feed, restart DAQ
			1150	3950	2800	0.78	0.78	0.78	Plug in S2 trap stage I inlet	12	End simulated feed
				Total	7550	2.10					
MBCuO regenerator gas											
4	9/26/97	9:30 AM	8000	13700	5700	1.58	1.58	1.58	FETC fire alarm	9	
			14600	16450	1850	0.51	0.51	0.51	Plug in chiller coil stage II	4	Restart then sulfur plugging, 4 slpm max
				Total	7550	2.10					
5	9/26/97	1:20 PM	21850	28100	6250	1.74	1.74	1.74	Plug in both chiller coils stage I	12	
6	9/26/97	6:30 PM	40250	46750	6500	1.81	1.81	1.81	Plug in S2 trap stage I	10	
7	9/27/97	12:00 AM	2500	7000	4500	1.25	1.25	1.25	Plug inlet to RX2	14	Increased pitch in chiller coils
8	9/27/97	3:20 AM	800	5850	5050	1.40	1.40	1.40	Inline filter stage II, chiller coil stage I-1	14	
9	9/27/97	6:30 AM	1250	10750	9500	2.64	2.64	2.64	Plug in S2 trap stage I, chiller coil stage I-2	10	
10	9/27/97	12:40 PM	21900	29050	7150	1.99	1.99	1.99	Plug in chiller coil stage I-2 bottom	8.1	
			34500	39750	5250	1.46	1.46	1.46	MBCuO Process shutdown	9	Clean sulfur traps
				Total	12400	3.44					
11	9/27/97	9:40 PM	1700	7150	5450	1.51	1.51	1.51	Severe plug in sulfur trap stage I inlet, plug in stage I-1 water trap outlet	14	Frequent online changing of inline filter stage II
12	9/28/97	2:30 AM	650	3950	3300	0.92	0.92	0.92	Plug in chiller coil stage I-1 (above glycol bath)	14	Frequent online changing of inline filter stage II
			4250	5400	1150	0.32	0.32	0.32	Plug in chiller coil stage I-1 (above glycol bath)	14	Try to recover from sulfur plug
				Total	4450	1.24					
13	9/28/97	8:50 AM	5600	9050	3450	0.96	0.96	0.96	Plug inlet to RX2	10.1	Frequent online changing of inline filter stage II
14	9/28/97	11:55 AM	17450	22450	5000	1.39	1.39	1.39	Plug in S2 trap stage I outlet, chiller coil stage I-1	14.1	Frequent online changing of inline filter stage II
15	9/28/97	4:05 PM	31600	36100	4500	1.25	1.25	1.25	Plug in chiller coil stage I-2, line to RX2	10.2	Frequent online changing of inline filter stage II
16A	9/29/97	7:00 AM	1100	2550	1450	0.40	0.40	0.40	Plug in chiller coil stage I-2	12	Frequent online changing of inline filter stage II

Testing at FETC 9-23-97 to 10-1-97

Test #	Date	Time of Day	DAQ Time		(sec)	Runtime (hrs)	MBCuO gas (hrs)	Reason for stopping test	Max. Flow (slpm)	Notes	
			start	end							
16	9/29/97	10:45 AM	15250	20650	5400	1.50		Decreased MBCuO supply flow, plug line from RX2 to S2 condenser (heat tape off)	14		
17	9/29/97	6:30 PM	42800	47050	4250	1.18		Fluctuating MBCuO supply gas	14	Frequent online changing of inline filter stage II Reduce flow to 10 slpm	
18	9/30/97	11:40 AM	1450	10800	9350	2.60		Plug in chiller coil stage I-2, plug in S2 trap inlet and outlet	10	Thoroughly clean entire system before run Frequent online changing of inline filter stage II Why only 10 slpm max flow? Problem with FETC or Sorbtech? Recalibrate inlet mass flowmeters, (cal. Ok)	
Switch to coal fired flue gas											
19	10/1/97	9:08 AM	500	5550	5050	1.40		Plug in S2 trap stage I	10	FETC found leak in permeation dryer tube, flow problem solved Thoroughly clean entire system before run Frequent online changing of inline filter stage II	
20	10/1/97	7:00 PM	800	2600	1800	0.50				Before run: lower S2 condenser temperature ~115 C, remove S2 trap stage I and use trap to replace water trap stage I-2, Restart DAQ, communications error	
			0	7850	7850	2.18		DP1 > 40"	10	Thoroughly clean entire system before run, inline filter stage II DP1 fluctuating, sulfur condenser plugging?	
Total						6.19					31.78 hrs.