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Quality Assurance of FBC H_2SO_4 Measurements

Interagency Energy/Environment R&D Program Report

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Quality Assurance of FBC H_2SO_4 Measurements

by

T. R. Acciani and R. F. Maddalone

TRW Defense and Space Systems Group
One Space Park
Redondo Beach, California 90278

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EPA Project Officer: Frank E. Briden

Industrial Environmental Research Laboratory
Office of Energy, Minerals, and Industry
Research Triangle Park, NC 27711

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Office of Research and Development
Washington, DC 20460

ABSTRACT

The objectives of this report are to evaluate the existing data on H_2SO_4 measurements from FBC processes, determine the true value of the sulfuric acid concentration which might have been obtained had the control condensation procedure been used, and run a material compatibility study to find possible alloys which could be used in the fabrication of a controlled condensation sampling system.

The current sampling system at the Exxon FBC facility was reviewed and it has been estimated that H_2SO_4 values are 12% low with another reduction of 10-25% because of low sampling temperatures and Balstron filters. The Controlled Condensation System with an acid/base titration using Bromophenol Blue as the indicator is the recommended sampling/analysis method for sulfuric acid sampling at the Exxon FBC facility. The material of construction for the Controlled Condensation System can be 316L Stainless Steel. 316L Stainless Steel had the best performance when subjected to various tests used to simulate an FBC environment and will easily withstand the pressures found at the Exxon FBC facility.

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1. INTRODUCTION

This report has been prepared for the Process Measurement Branch of the Industrial Environmental Research Laboratory of the Environmental Protection Agency, Research Triangle Park, North Carolina, as Task 3, Contract No. 68-02-2613. Task 3 is devoted to quality assurance of FBC H_2SO_4 measurements and is under the direction of EPA Project Officer, Frank Briden.

The objectives of this report are to evaluate the existing data on H_2SO_4 measurements from FBC processes, determine the true value of the sulfuric acid concentration which might have been expected had the control condensation procedure been used, and run a material compatibility study to find possible alloys which could be used in the fabrication of a Controlled Condensation System.

The pressurized fluidized bed combustion (FBC) of coal is a new combustion technique which can reduce the emissions of SO_2 and NO_x from the burning of sulfur-containing coals. At Exxon, the FBC unit is pressurized at 10 atm which contains a mixture of limestone or dolomite and coal in the bed. To measure the effect of sorbent to coal ratios, extractive sampling for SO_2 and SO_3 is performed on the outlet gas streams. When the controlled condensation system was used at Exxon the results were erratic. This report reviews the current sampling methods, points out the problems which currently exist in the method and recommends the necessary changes.

In order to have a SO_2/SO_3 sampling system which could function at higher than atmospheric pressure, a material compatibility study was conducted to find an alloy to replace the all glass/quartz fabrication of the current CCS. The compatibility study centered around three experiments to determine the resistance of the alloy to corrosive vapors (HCl, SO_2, H_2SO_4), catalytic activity ($SO_2 \rightarrow SO_3$), and the reactivity of the alloys toward both dilute and concentrated sulfuric acid. This report will describe the results of these tests and make recommendations on the materials usable for the high pressure train.

2. REVIEW OF FBC DATA

Under this phase of the task existing reports and procedures for SO_2/SO_3 testing at the Exxon FBC facility were reviewed to determine the error associated with data obtained. This review also provided a basis for the critique of the sampling and analysis methods.

2.1 CONDITIONS AT FBC

The FBC unit at Exxon is pressurized at 10 atm and uses a mixture of limestone or dolomite and coal in the bed. The dolomite or limestone controls the SO_2 levels in the flue gas by trapping the SO_2 as $CaSO_4$. Steam is produced by circulating water through tubes immersed in the bed. The major components in the gas phase are shown in Table 1.

TABLE 1. TYPICAL FBC GAS PHASE CONCENTRATIONS

Species	Concentration
SO_2	30-600 ppm
SO_3	5-12 ppm
NO_x	100-140 ppm
Cl^-	30-50 ppm
F^-	7-15 ppm
O_2	6-8%
CO_2	10-14%
H_2O	5-7%

Figure 1 is taken from Battelle's preliminary report on the comprehensive sampling and analysis at the Exxon mini-plant. As the diagram shows, particulate material is removed by the Balstron filters in a heated hot box at 177°C (350.7°F). The cleaned gas is distributed to the gas sampling trains through a heated [177°C (350.6°F)] stainless steel manifold. Connection between the trains and the manifold is made with a short length of Teflon tubing.

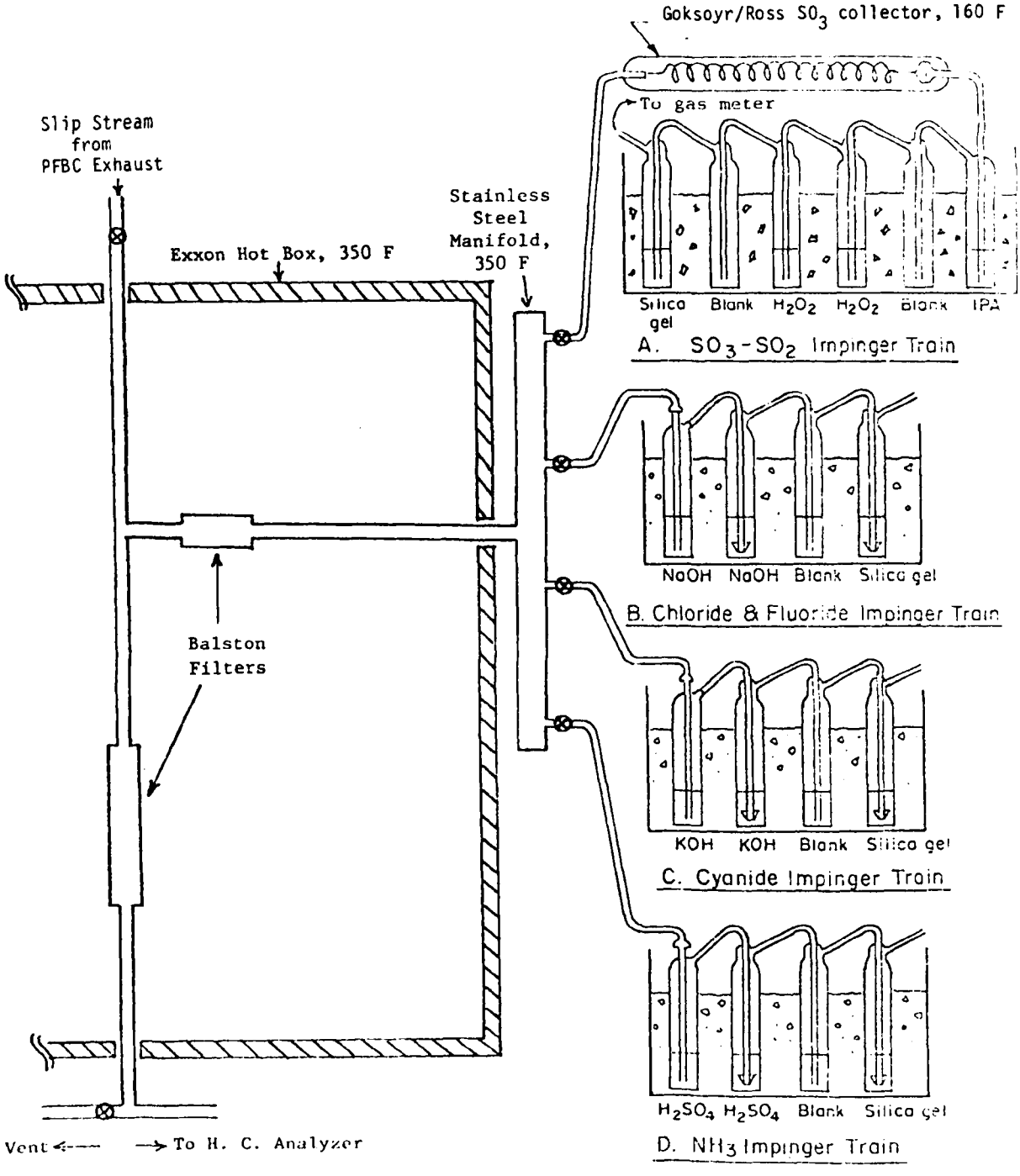


Figure 1. Midget Impinger Sampling Arrangement for Stream 1p

Collection of the SO_3 (H_2SO_4) was accomplished by using a Goksoyr-Ross coil (Controlled Condensation Coil — CCC). Sulfur dioxide was trapped using a NaOH impinger system as a separate train.

Since the FBC was at 10 atm, flow through the sampling systems was maintained by individual needle valves. During each run, the trains were operated for approximately 100 minutes at flow rates between 7 to 12 lpm.

2.2 SO_3 SAMPLING SYSTEMS

The systems used to quantify H_2SO_4 are based on selective absorption or controlled condensation. A series of workers[1, 2, 3] have refined the selective IPA absorption method. This approach uses an impinger with 80% isopropyl alcohol to collect the SO_3 and to pass the SO_2. The SO_2 is collected in a back-up impinger of 3% H_2O_2. This method is currently the basis of the EPA compliance test[4] for sulfuric acid mist at acid plants. The major problem with this procedure for combustion processes is the lack of a pre-filter to effectively prevent particulate matter from reaching the IPA impinger. The particulate matter in the impinger can act either as a direct interferent by contributing $SO_4^=$ from sulfate salts, or as an indirect interferent by catalyzing the $SO_3^=$ to $SO_4^=$ oxidation in the liquid phase through action of trace elements like Fe or V.

The controlled condensation (Figure 2) approach was first proposed by Knol[5] and has been further developed by Goksoyr and Ross.[6] The Goksoyr-Ross system is the basis of an ASTM procedure for SO_x.[7] In the controlled condensation approach, H_2SO_4 is separated from the gas stream by cooling the temperature of the flue gas below the dew point for SO_3 but above the dew point of H_2O. The resulting aerosol is either collected on the walls of the cooling coil or on a back-up frit. Investigators [8, 9] studying controlled condensation in the laboratory have found the precision and accuracy to be $\pm 6\%$ in synthetic gas streams. Hillenbrand, et al,[10] have also suggested that SO_2 can be oxidized by fly ash.

Work[11] by this laboratory has defined the operating parameters necessary to optimize a sampling system for H_2SO_4. It was found that:

- The quartz filter system should be heated above 288°C (550.4°F) to avoid acid fallout.

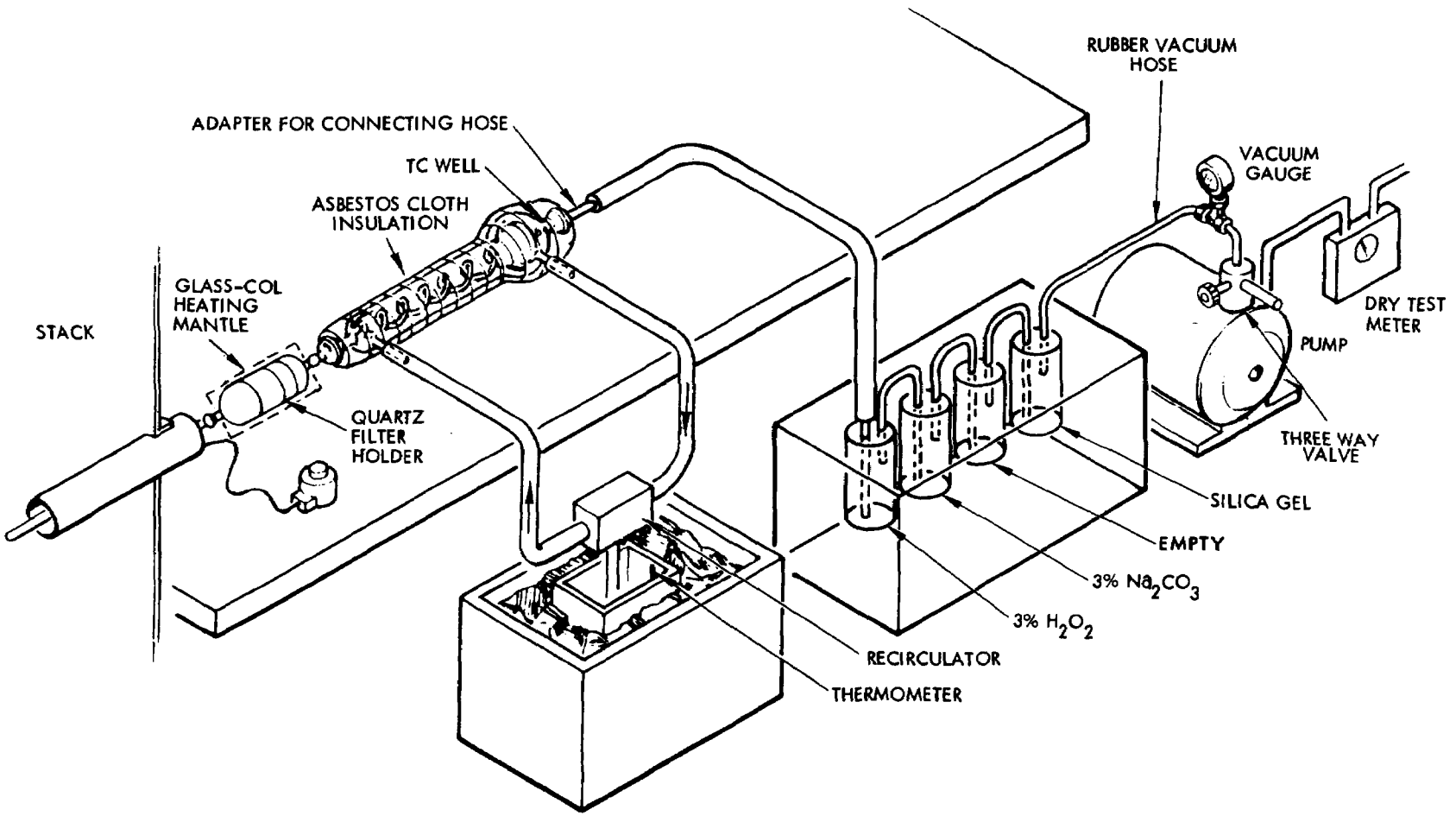


Figure 2. Controlled Condensation System Set-up

- Fly ash at the level of 0.3 g on the surface of the filter can reduce the amount of H_2SO_4 recovered by 12% when a 10 ppm gas stream of H_2SO_4 was passed through the system.

- Extensive field evaluation under high (11 g/m^3) mass loading and high SO_2 (4000 ppm) concentrations showed that as little as 0.1 ppm of H_2SO_4 can be detected.

- The coefficient of variance for the percentage removal of H_2SO_4 by wet scrubbers at a coal-fire utility was found to be ±18%. This value compares well with the ± 16% for the estimated field accuracy.

- Oxidation of SO_2 at the recommended filter holder temperatures, 4000 ppm SO_2 and 8% O_2 did not occur. When fly ash from a coal-fired utility was placed on the filter, it did not have a catalytic effect under those conditions.

On the basis of this work it was possible to evaluate the quality of samples taken at the Exxon plant.

2.3 CRITIQUE OF SO_3 SAMPLING AT EXXON

Using the Controlled Condensation System (CCS) to sample $SO_3(H_2SO_4)$ requires precise control of filter and condensation coil temperatures. The Exxon hot box in Figure 1 has several potential problems that could lead to low SO_3 values since the hot box and manifold temperature is ~176°C. Experiments with quartz liners and filters showed combined retention values of -25% of the H_2SO_4 input at 200°C (392°F). At 176°C (348.8°F) the retention of H_2SO_4 would be higher, but experiments have shown that quantitative H_2SO_4 recovery is only attainable above 288°C.

The inertness of the Balstron filters toward H_2SO_4 is unknown, since TRW's experience to date has been with quartz filters. It can be stated that with the higher capacity by these types of filters, the highly alkaline nature of the particulate matter (CaO + fly ash), and the lower sampling temperature would all lead to H_2SO_4 recovery values than the 88% normally expected.

The use of a short piece of unheated Teflon line to connect the trains to the manifold can lead to serious errors. It has been found that even unheated ball/socket joints in the CCS can lead to premature condensation of water. Normally this will lead to a positive error due to SO_2 being scrubbed out of the gas and measured as H_2SO_4. If a connecting line must be used, then it should be heated above 250°C. In

this case a 316 SS line with a Teflon ball or socket could be used to connect the train to the manifold.

Figure 3 shows plots of dew point vs SO_3 concentration at two pressures. The dew point data at 10 atm and 1 atm were calculated[12] and a second set at 1 atm was obtained experimentally[13]. The normal operating temperature for the controlled condensation coil is 60°C (140°F), Exxon had sampled with the CCC at 73°C (163.4°F). The high operating temperature should not affect the results because Figure 3 shows that 73°C (163.4°F) is low enough to remove most of the SO_3 from the gas phase. It is recommended that the temperature be reduced further, to ensure that the gas is completely cooled below the SO_3 dewpoint in the confines of the Controlled Condensation Coil (CCC).

Use of an 80% IPA impinger to collect sulfuric acid in the presence of SO_2 can cause large positive errors due to pick-up of SO_2 by the IPA solution. It has been found that the IPA lots contain small quantities of peroxides. The IPA can be checked colorimetrically by adding a KI solution to an aliquot of the IPA. Formation of a straw brown color indicates the IPA cannot be used. Furthermore, the CCC has been shown to be ~100% efficient in removing H_2SO_4, so a back-up impinger is not required. It is recommended that the impinger system consist of two H_2O_2 impingers, a sodium carbonate impinger, a blank and a silica gel impinger. This system, together with the CCC, will quantitatively collect H_2SO_4(CCC), SO_2(H_2O_2) and HCl or HF (Na_2CO_3).

The recommended analysis method for the sulfuric acid collected in the CCC is an acid/base titration using Bromophenol Blue as the indicator. An alternate method is to perform a sulfate titration with Sulfonazo III as the indicator. This approach is less sensitive, but still accurate, and it also can be used to measure the sulfate collected in the H_2O_2 impingers. Current EPA methodology (Methods 6 and 8) uses Thorin as the indicator, however, Thorin has an indistinct end point and suffers from interferences by Cl^-, F^- and $PO_4^{=}$. Sulfonzao III exhibits little or no effect from those anions.

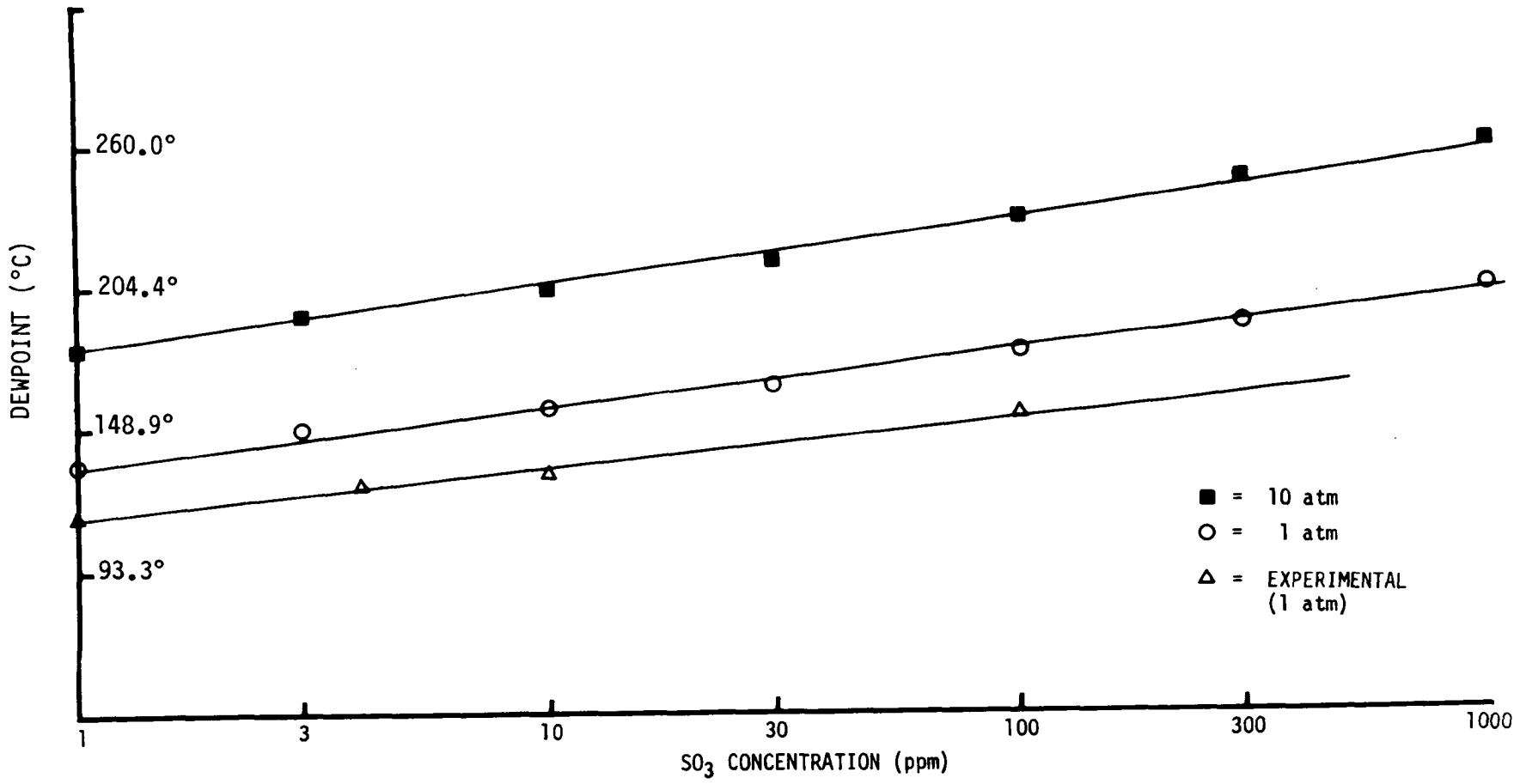


Figure 3. Dewpoint in °C for Various SO_3 Concentrations and Pressures

2.4 SUMMARY

Using the current sampling system at Exxon, it is estimated that the H_2SO_4 values are a minimum of 12% low compared to the best attainable recoveries of the standard CCS. Due to the combination of the low sampling temperatures and Balstron filters, the H_2SO_4 recovery was reduced by another 10-25%. The exact amount of H_2SO_4 fallout is impossible to estimate accurately, since the above estimates are based on laboratory studies of a fly ash/quartz filtration system.[12] In order to improve the SO_3 sampling at the Exxon mini-plant it is recommended that:

- The hot box temperature be increased to provide a gas-out temperature >250°C (482°F) with 288°C (550.4°F) as an optimum average.
- Heat the connecting line from the manifold to the gas trains.
- Reduce the CCC temperature to within 4°C (39.2°F) of the maximum water dew point.
- Eliminate the 80% IPA impinger and use a system of H_2O_2 and NaOH impingers to trap SO_2, HCl and HF.
- Quantitate the H_2SO_4 in the coil using an acid/base titration on the coil rinse with Bromophenol Blue indicator.
- Use Sulfonazo III indicator for the sulfate titration of the H_2O_2 impingers.

3. MATERIAL COMPATIBILITY STUDIES

The investigation of material compatibility with the FBC gas streams was initiated to find a suitable metal to be used in the probe and coil sections of a Controlled Condensation System (CCS) designed for high pressure sampling at a FBC facility. The most important properties the probe and coil material must have are: resistance to HCl, SO_2, and H_2SO_4 fumes; low reactivity with condensed H_2SO_4; lack of catalysis of SO_2 to SO_3.

3.1 PRELIMINARY SCREENING OF METALS

In order to ascertain the most appropriate metal for use in fabrication of a probe and coil, a preliminary evaluation of various materials was made. Several materials were selected based on general compatibility and suspected reactivity (or lack thereof) with an FBC environment. Tables 2 and 3 list the composition of various alloys and compatibility of these alloys with chemicals which are found in an FBC environment. The final selection of material was based upon probable chemical resistance, strength, availability, and ductability. The initial materials selected were: 316L Stainless Steel, Hastelloy C-276, Durimet 20, Chlorimet 2, Tantalum, and Inconel 671.

3.2 CHEMICAL RESISTANCE

A preliminary screening was initiated to examine the chemical resistance of the various materials. Since the environment of an outlet flue gas stream at a FBC facility consists of HCl, H_2SO_4, SO_2 and H_2O vapors at 300°C (572°F) and 150 psi, these experiments consisted of exposing various metal coupons to HCl, SO_2 and H_2SO_4 vapors individually and to all three vapors collectively.

3.2.1 Experimental

Table 4 gives a complete listing of the chemicals and conditions employed for each environment. The initial pressure in the reaction vessel was 75 psi which increased to 150 psi when heated to 300°C (572°F). Hydrochloric acid and H_2SO_4 were initially introduced into the reaction vessel as solutions and later vaporized during the experiment.

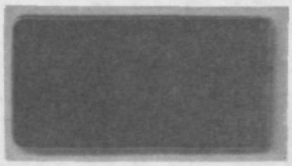
TABLE 2. METAL COMPOSITION*

	SS316	SS446	Monel	Hastaloy B	Durimet T	Durimet 20	Chlorimet 2	Nichrome	Tantalum
Fe	Base	Base	1.4	3-7	Base	Base	3 max	-	-
Cr	16-18	23-27	-	-	19	20	-	20	
Ni	10-14	-	67	Base	22	29	63	78.5	-
C	0.1 max	0.35 max	0.15	0.02-0.12	0.07 max	0.07 max	0.15 max	-	-
Mo	1.75-2.75	-	-	24.32	2	2	32	-	-
N	-	0.25 max	-	-	-	-	-	-	-
Cu	-	-	30	-	1	4	-	-	-
Si	-	-	0.1	-	1	1	1	1.5	-
Mn	-	-	-	-	-	-	1	-	-
Ta	-	-	-	-	-	-	-	-	99.9+

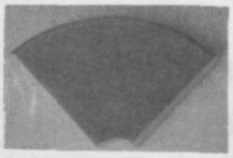
TABLE 3. COMPATIBILITY*

Vapor	SS316	SS446	Monel	Hastaloy B	Durimet T	Druimet 20	Chlorimet 2	Nich-rome	Tantalum
Hydrochloric Acid	NG	NG	<0.5% OK	OK	OK	OK	OK	?	OK 662° max
Sulfur Dioxide	OK	OK	dry-OK wet-NG	wet-NG	OK	OK	OK except with high temp	?	OK 392° max
Sulfuric Acid	NG	OK	OK <19% boil	OK <60%	OK <10%	OK <25% NG >78% hot	OK except >80% hot	?	OK 347° max at 98%

*Referenced from "Chemical Engineers Handbook"



316L STAINLESS STEEL



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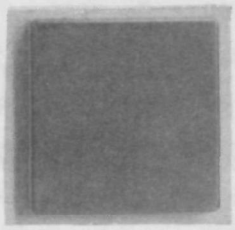
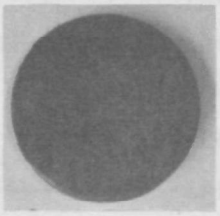
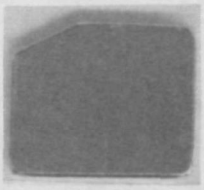


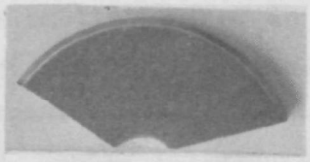
INCONEL 671



TANTALUM



HASTELLOY C-276



CHLORMET 2

Figure 4. Metal Coupons Before Chemical Resistance Tests

TABLE 4. CHEMICAL ENVIRONMENTS

Test Series	H_2O 10%	O_2 8%	SO_2 2000 ppm	H_2SO_4 500 ppm	HCl 500 ppm	Remainder N_2
1. Control	X	X				X
2. SO_2	X	X	X			X
3. HCl	X	X			X	X
4. H_2SO_4	X	X		X		X
5. Total	X	X	X	X	X	X

*Total pressure in system was 75 psi at 25°C (77°F).

The metal coupons shown in Figure 4 were cut, ground, and vapor honed to help assure a uniform surface and eliminate any large physical differences in textures. The mass of each sample was determined and photographs (100X and 400X magnification) of the grain structure were taken initially to give a reference point for the starting material. Figures 5 and 6 show the grain structure of 316L Stainless Steel at 100X and 400X magnification. The metal coupons were then placed into the reaction vessels where they were pressurized, sealed, and heated. After 72 hours of heating, the specimens were immediately vented to atmosphere and removed from the reaction vessel to prevent any condensation of gases on the metal coupons. The exposed metal coupons were weighed, photographed at 100X and 400X magnification, and critically examined for degradation.

In order to carry out the above evaluation, the reaction vessels which had to maintain a corrosive environment, and a gas manifold which was needed to fill the vessels, had to be constructed. The reaction vessels

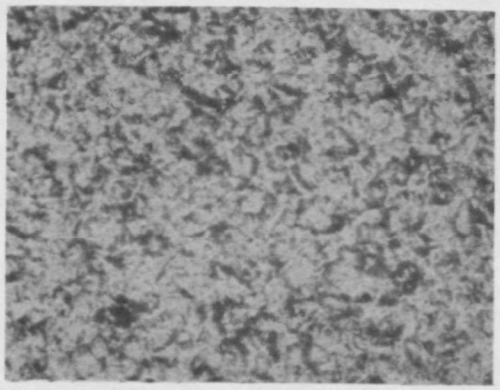


Figure 5. Stainless Steel 316L at 100X Magnification

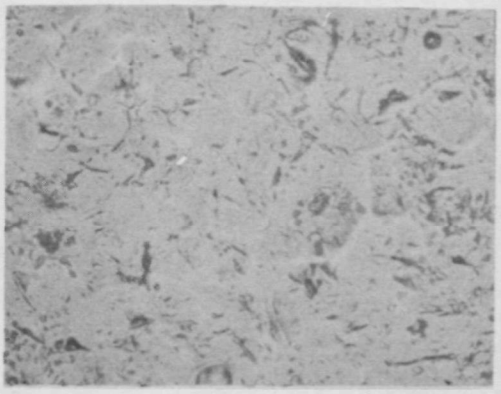


Figure 6. Stainless Steel 316L at 400X Magnification

were constructed from 1" I.D. standard wall pyrex tubing. Figure 7 shows a pyrex reaction vessel which held six metal coupons. To prevent dissimilar metal contact with the resultant galvanic corrosion, metal coupons were first placed into quartz boats, which were then placed into the reaction vessel. Additional quartz boats were placed into the reaction vessel to hold the HCl and H_2SO_4 solutions.

Figure 8 shows the complete laboratory set-up for the chemical resistance experiments. The gas manifold along with the various valves and gauges were all stainless steel. Since very specific quantities of SO_2 were required for the FBC environments, a (zero to 1600 Torr) Wallace and Tierman pressure gauge, which accurately measures pressure to one Torr, was incorporated into the manifold system. Two zero-to-100 lbs. pressure gauges which accurately measure pressure to one lb. were used to monitor the filling of O_2 and N_2 gases into the reaction vessel.

3.2.2 Results

The results of the initial investigation indicated that only tantalum could not withstand the FBC environment. The high temperature [300°C (572°F)] along with the chemical environment caused the tantalum to oxidize. Durimet 20, Inconel 671 and Chorimet 2 were fairly resistant to the FBC environment but some slight staining and pitting of the metals' surface was observed. Hastelloy C-276 and 316L Stainless Steel had the best overall performance with some slight discoloration of the metals but no apparent chemical attack. The results are summarized in Table 5.

3.3 CATALYTIC ACTIVITY STUDY (Acid/Base Titration Method)

A second evaluation was designed to examine the lack of catalytic activity of the metal to participate in the SO_2 to SO_3 oxidation. Both Hastelloy C-276 and 316L Stainless Steel would have been tested for their catalytic property but a problem arose. The manufacturer of Hastelloy C-276 would not sell the necessary material needed for the experiment because their stock of material was defective. This problem did not seriously impair the results of the study, since 316L Stainless Steel was shown to be a suitable material for the train fabrication and was readily available.

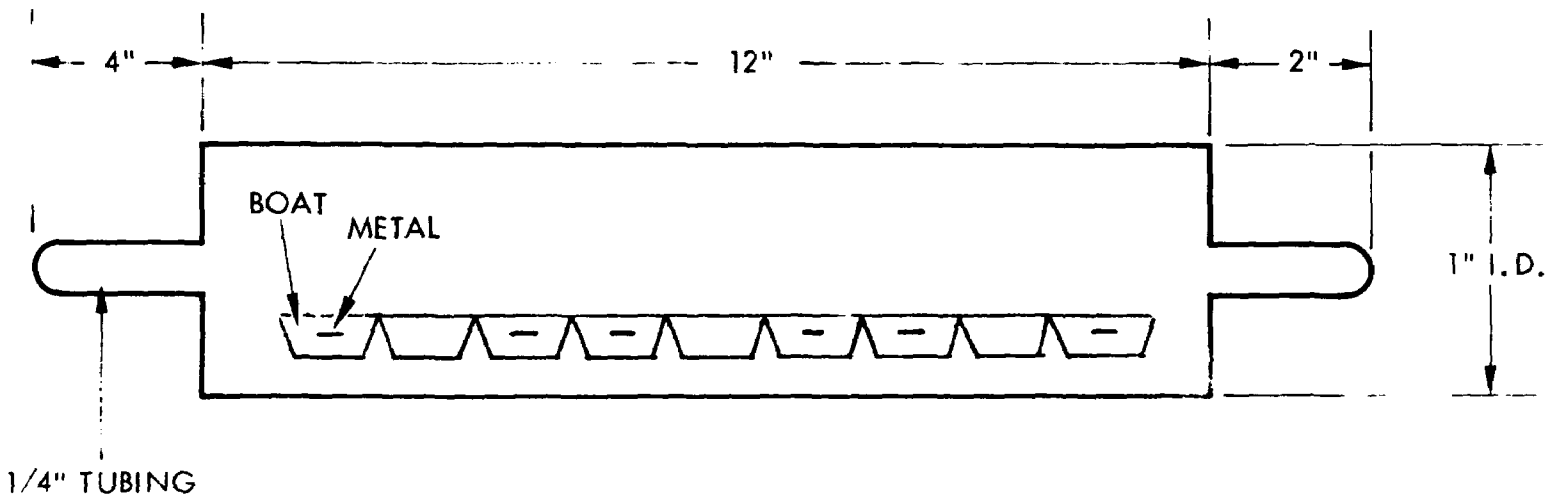


Figure 7. A Pyrex Reaction Vessel

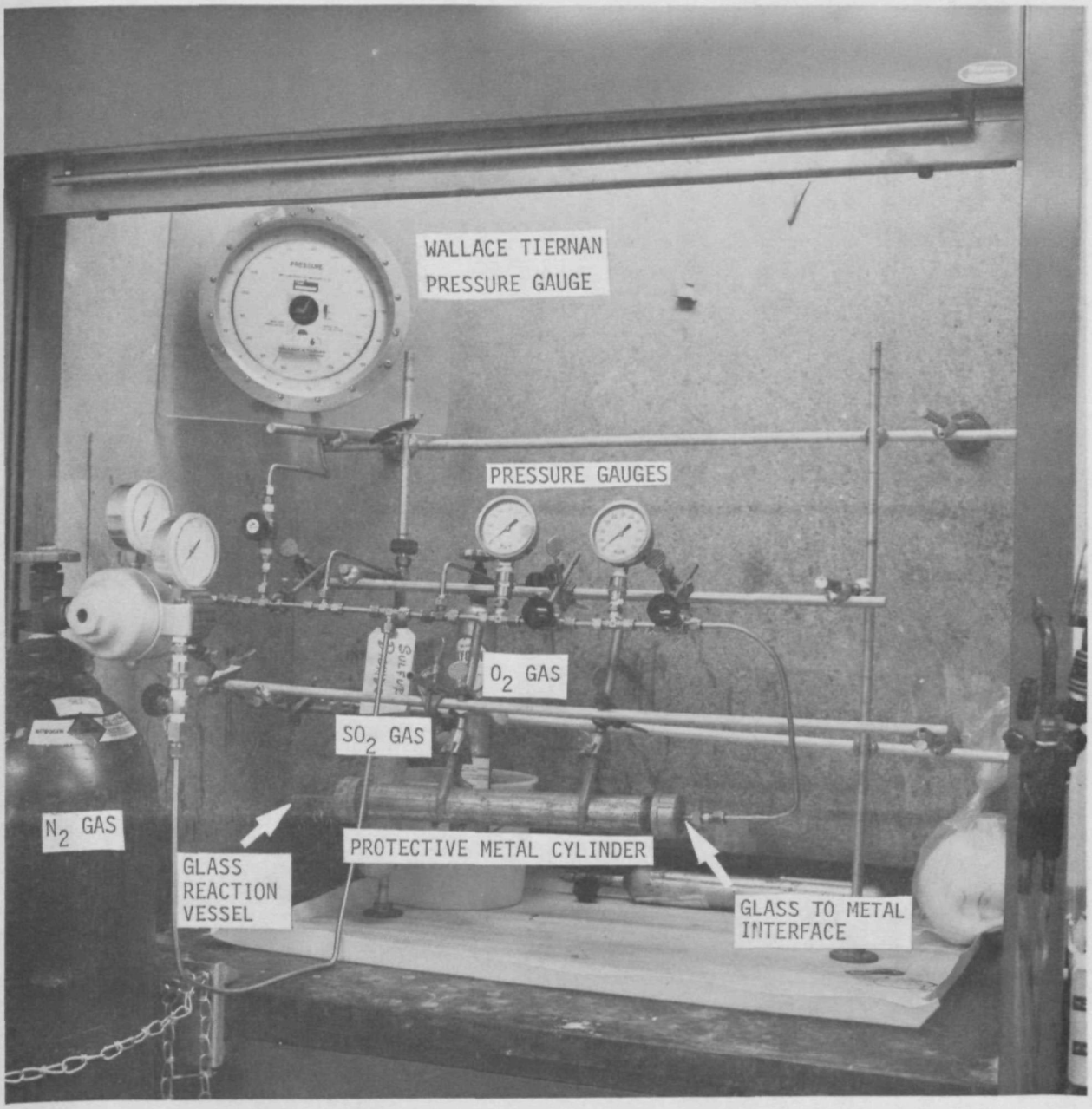


Figure 8. The Complete Laboratory Set-up for the Chemical Resistance Experiments

TABLE 5. PRE-TEST AND POST-TEST ANALYSIS RESULTS

MATERIAL	TEST ATMOSPHERE	WEIGHT IN GRAMS PRE-TEST	POST-TEST	Δg	POST-TEST OBSERVATIONS
HASTELLOY C-276	SO_2	7.6555	7.6551	-.0004	NO APPARENT ATTACK
	HCl	8.9545	8.9545	.0000	NO APPARENT ATTACK
	H_2SO_4	7.9626	7.9619	-.0007	OVERALL STAINING, NO APPARENT ATTACK
	SO_2, HCl, H_2SO_4	8.5847	8.5844	-.0003	NO APPARENT ATTACK
	Control	7.8274	7.8274	.0000	NO APPARENT ATTACK
316 L	SO_2	3.5107	3.5103	-.0004	AMBER COLOR, NO APPARENT ATTACK
	HCl	4.1576	4.1572	-.0002	DARK AMBER, CONTINUOUS COLOR, NO APPARENT ATTACK
	H_2SO_4	3.8447	3.8443	-.0004	BLUE-PURPLE COLOR, NO APPARENT ATTACK
	SO_2, HCl, H_2SO_4	3.7728	3.7728	.0000	LIGHT AMBER COLOR, NO APPARENT ATTACK
	Control	3.8574	3.8576	+.0002	LIGHT BLUE COLORATION, NO APPARENT ATTACK
DURIMET 20	SO_2	5.7834	5.7832	-.0002	AMBER COLORATION, NO APPARENT ATTACK
	HCl	5.7016	5.7017	+.0001	CRYSTALLINE FORMS, SLIGHT SURFACE ATTACK
	H_2SO_4	6.1724	6.1717	-.0007	SOME STAINING & CRYSTAL FORM
	SO_2, HCl, H_2SO_4	6.1544	6.1541	-.0003	AMBER COLORATION, NO APPARENT ATTACK
	Control	5.8666	5.8667	+.0001	SOME CRYSTAL FORMATIONS, AND SLIGHT ATTACK

- Continued -

TABLE 5. PRE-TEST AND POST-TEST ANALYSIS RESULTS (Continued)

MATERIAL	TEST ATMOSPHERE	WEIGHT IN GRAMS PRE-TEST	POST-TEST	Δg	POST-TEST OBSERVATIONS
CHLORIMET 2	SO_2	12.0106	12.0103	-.0003	SLIGHT ATTACK ON ONE SIDE
	HCl	10.1746	10.1741	-.0005	LOCALIZED CRYSTAL FORMATIONS, SLIGHT ATTACK
	H_2SO_4	11.7105	11.7100	-.0005	LOCAL STAINS AND CRYSTAL
	SO_2, HCl, H_2SO_4	11.2442	11.2438	-.0004	NO APPARENT ATTACK
	Control	10.6229	10.6227	-.0002	DISCOLORATION, NO APPARENT ATTACK
TANTALUM	SO_2	18.2257	18.2256	-.0001	METAL TURNED BLUE (OXIDATION)
	HCl	14.5883	14.5884	+.0001	METAL TURNED BLUE (OXIDATION)
	H_2SO_4	20.7296	20.7299	+.0003	METAL TURNED BLUE (OXIDATION)
	SO_2, HCl, H_2SO_4	18.9315	18.9320	+.0005	METAL TURNED BLUE (OXIDATION)
	Control	14.0782	14.0786	+.0004	METAL TURNED BLUE (OXIDATION)
INCONEL 671	SO_2	9.9561	9.9554	-.0004	LOCAL STAINS
	HCl	9.7145	9.7141	-.0004	LOCAL STAINS
	H_2SO_4	9.4317	9.4311	-.0006	LIGHT AMBER COLOR, LOCAL CRYSTALS AND STAINS
	SO_2, HCl, H_2SO_4	10.0606	10.0605	-.0001	LOCAL STAINS
	Control	9.5944	9.5940	-.0004	DISCOLORATION

3.3.1 Experimental (acid/base titration method)

The experiment consisted of passing a gas stream of N_2 (90%), O_2 (10%), and SO_2 (8000 ppm) through a 1.5M (0.635 cm I.D.) 316L Stainless Steel pipe at 300°C for one hour at a flow rate of 8 l/min. The N_2 and O_2 gases were saturated with H_2O before mixing with SO_2. After the gases passed through the metal pipe, they entered a controlled condensation coil which would condense any H_2SO_4 generated during the experiment. The remaining gases were then passed through two 3% H_2O_2 impingers which converted SO_2 to H_2SO_4. The actual amount of SO_2 in the gas stream was determined by titrating the acid in the impingers after the test run. Figure 9 shows the complete laboratory set-up for the catalytic effect experiment.

3.3.2 Results (acid/base titration)

After running the gases through the experimental system for one hour, the controlled condensation coil and the 316L Stainless Steel pipe were rinsed with D.I. water and each solution was titrated with NaOH (Bromophenol Blue indicator) to determine the amount of H_2SO_4 present. The impinger solutions were also titrated with NaOH (Bromophenol Blue indicator) to determine the amount of SO_2 passing through the system. The rinse solution from the controlled condensation coil had 0.27 $\pm$ 0.02 ppm of H_2SO_4 and no H_2SO_4 was found in the 316L Stainless Steel pipe.

3.4 CATALYTIC ACTIVITY STUDY (Sulfate Titration)

The results of the SO_2 catalysis by 316L Stainless Steel were based on an acid/base titration. There was a possibility that any H_2SO_4 formed in the 316L Stainless Steel pipe might have reacted with the pipe and never have reached the Controlled Condensation Coil (CCC). Consequently, an acid/base titration of the pipe would not show any H_2SO_4 formed. In order to eliminate this possibility, a sulfate titration was performed on the rinse solution after the catalytic effect experiment was repeated.

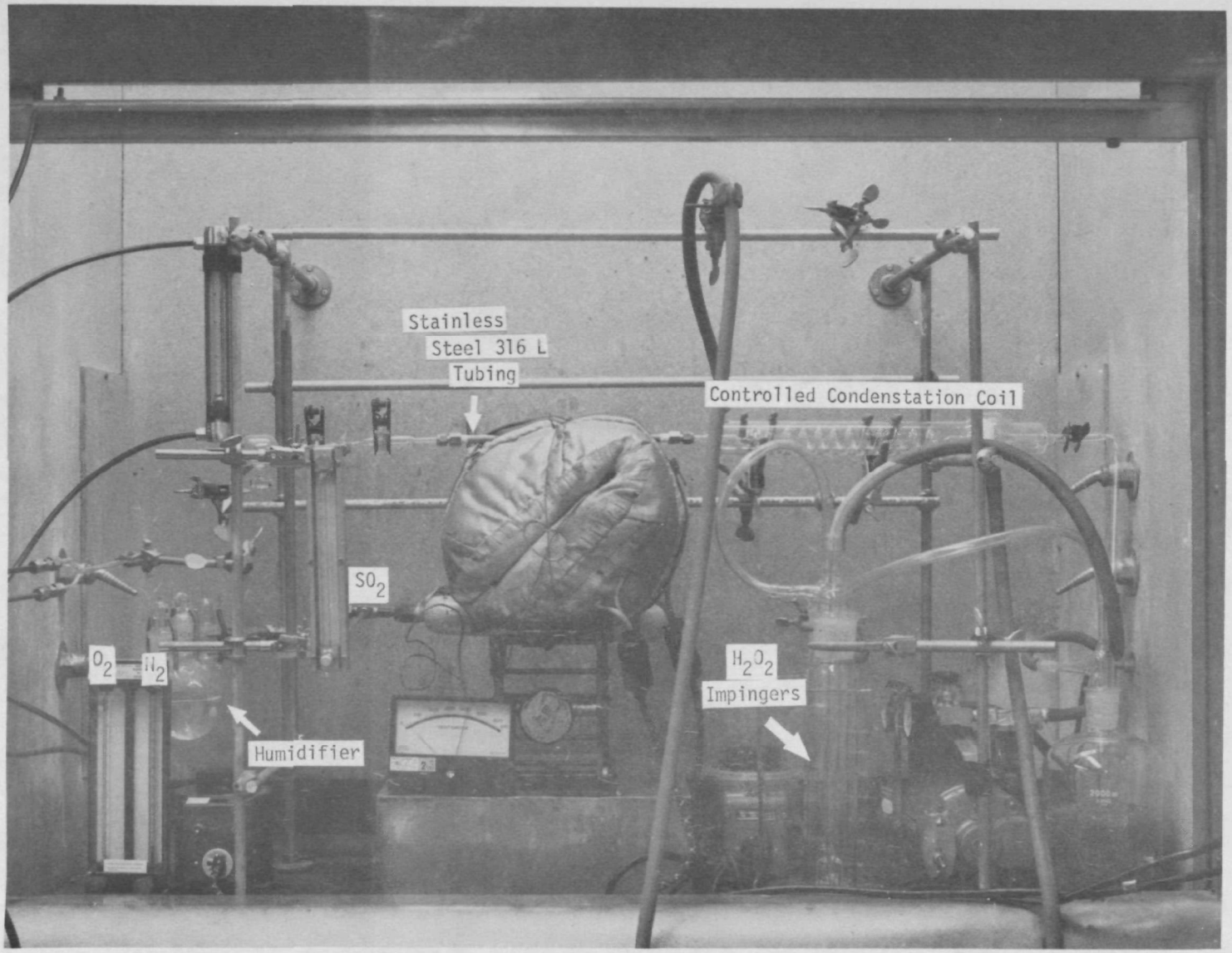


Figure 9. The Complete Laboratory Set-up for the Catalytic Effect Experiment

3.4.1 Experimental (sulfate titration)

The same experimental conditions were employed as in Section 2.3.1.

3.4.2 Results (sulfate titration)

At the end of one hour, the Controlled Condensation Coil and the 316L Stainless Steel pipe were rinsed with D.I. water and each solution was titrated with $Ba(ClO_4)_2$ and Sulfonazo III indicator to determine the amount of $SO_4^=$ ion present. These titrations showed that the pipe and the Controlled Condensation Coil did not contain any $SO_4^=$ ion. The minimum detectable quantity of $SO_4^=$ for the $Ba(ClO_4)$ titration was 0.01 millimoles, which corresponds to a minimum detection gas concentration of 0.02 ppm under the conditions of the test. These results confirm that 316L Stainless Steel does not catalyze SO_2 to SO_3 at the conditions tested.

3.5 REACTIVITY OF ALLOYS WITH CONDENSED SULFURIC ACID

The third evaluation was designed to examine the reactivity of the metal with condensed H_2SO_4. Both Hastelloy C-276 and 316L Stainless Steel were tested for reactivity in two different sets of experiments.

3.5.1 Experimental

The first experiment was to depost 100μl of concentrated sulfuric acid on the metal surface, place the metal in a closed environment of air saturated with 50°C D.I. H_2O for one hour. At the end of the time period, the acid was rinsed off with 50 ml of D.I. H_2O and the rinse was titrated with NaOH (Bromophenol Blue indicator) to determine the acidity of the solution. The same procedure was performed on a piece of Teflon which was used as control. By comparing the acidity of the rinse solution of the metals to the rinse of the control, the amount of reactivity was determined. Also, the acidity of a solution made up of 100μl of concentrated H_2SO_4 and 50 ml of D.I. H_2O was determined and compared to the rinse from the metals and control.

The second experiment for reactivity was to place the metal into a 1N H_2SO_4 solution at 50°C for one hour. The degree of reactivity of the metal toward the acid was determined by a change in the acidity of the solution and the weight of the metal sample. If a reaction occurred between the acid and metal, the acidity of the solution would drop and the sample would be reduced. The acidity of the 1N H_2SO_4 solution was determined by titration with NaOH (Bromophenol Blue indicator).

3.5.2 Results

The results of the first experiment with concentrated sulfuric acid are listed in Table 6 and indicate that both 316L Stainless Steel and Hastelloy C-276 are inert toward H_2SO_4.

The results of the second experiment with dilute sulfuric acid showed that the weight of the Hastelloy C-276 and 316L Stainless Steel samples did not change and the normality of the H_2SO_4 solution remained constant. The results indicate that both metals are inert toward the H_2SO_4 solution.

TABLE 6. RESULTS OF H_2SO_4 DROPLETS ON METAL SURFACE

Type of Surface	Amount of H_2SO_4 Placed on Surface	Average titration volume
Blank	100 μl	3.65
Teflon	100 μl	3.66
Hastelloy C-276	100 μl	3.68
Stainless Steel 316L	100 μl	3.70

3.6 SUMMARY OF MATERIAL COMPATIBILITY STUDIES

The initial materials selected, based upon a literature survey were: 316L Stainless Steel, Hastelloy C-276, Durimet 20, Chlorimet 2, Tantalum, and Inconel 671. This preliminary screening indicated that 316L Stainless Steel had two advantages over the other alloys, cost and availability.

The chemical resistance experiments have shown that both Hastelloy C-276 and 316L Stainless Steel are resistant to the FBC flue gas environment. Tantalum had oxidized in the FBC environment. Durimet 20, Chlorimet 2, and Inconel 671 had shown signs of chemical reactions which would indicate that these alloys would break down under constant exposure to the FBC environment.

The catalytic activity experiments have shown that 316L Stainless Steel does not act as a catalyst for SO_2 to SO_3 oxidation.

The chemical reactivity experiments have shown that both 316L Stainless Steel and Hastelloy C-276 were inert toward both dilute and concentrated sulfuric acid.

The results of the material compatibility studies have shown that 316L Stainless Steel can be employed as the probe and coil material for the Controlled Condensation System. 316L Stainless Steel had the best overall performance for the three chemical tests. Hastelloy C-276 is another possible alloy to be employed as probe and coil material but further experimentation must be done on its ability not to catalyze SO_2 to SO_3.

4. CONCLUSIONS

The current sampling systems employed at the Exxon FBC facility was reviewed and it is estimated that the H_2SO_4 values are 12 to 37% low compared to the actual amount of output.

The H_2SO_4 sampling at the Exxon FBC can be improved by:

- Increasing the hot box temperature so a gas-out temperature of at least 250°C is obtained with 288°C as an optimum average
- Maintaining a uniform heat throughout the entire CCS
- Employing a H_2O_2 and NaOH impinger system to trap SO_2, HCl, and HF
- Using an acid/base titration method with Bromophenol Blue indicator to quantitate H_2SO_4 in the coil
- Using Sulfonazo III indicator for the sulfate titration of the H_2O_2 impingers.

316L Stainless Steel can be employed as the material of construction for the probe and coil sections of the CCS. Hastelloy C-276 could be a second possible alloy.

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16. ABSTRACT The report gives results of a study to: evaluate existing data on H2SO4 measurements from fluidized-bed combustion (FBC) processes; determine the true value of the H2SO4 concentration which might have been obtained had the control condensation (Goksoyr/Ross) procedure been used; and run a material compatibility study to find alloys that can be used to fabricate a controlled condensation sampling system. The sampling system at Exxon's FBC facility was reviewed: H2SO4 values are about 12% low with another reduction of 10-25% because of low sampling temperatures and Balstron filters. The control condensation system with an acid/base titration using bromophenol blue as the indicator is the recommended sampling/analysis method for H2SO4 sampling at the Exxon facility. Construction material for the controlled condensation system can be 316L stainless steel, which had the best performance when subjected to various tests used to simulate an FBC environment and will easily withstand the pressures found at the Exxon facility.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS		b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group	
Pollution	Condensing	Pollution Control	13B	07D
Sulfuric Acid	Quality Assurance	Stationary Sources	07B	
Sulfur Trioxide	Alloys	Goksoyr/Ross Method		11F
Measurement			14B	
Combustion			21B	
Fluidized Bed Processing			13H, 07A	

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