

**Project S66 Benchscale Testing of  
Gas Absorption in Wet Scrubbers**

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# Project S66 Benchscale Testing of Gas Absorption in Wet Scrubbers

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**Abstract:** This interim report presents detailed information on the experimental system and results of the benchscale experiments on packed-bed wet scrubbers. The benchscale testing was performed to examine fundamental absorption behavior of selected individual chemical compounds and gas mixtures typical of semiconductor fabs. All gases were measured by Fourier transform infrared spectroscopy (FTIR), except fluorine and chlorine. These were measured by the standard Environmental Protection Agency (EPA) wet chemical method for halogen gases. Mass transfer behavior at low concentrations and in mixtures in an air stream were examined. The report discusses project objectives and technical approach; the experimental system and procedures; results; summary and conclusions; and recommendations. The appendices provide additional technical information.

**Keywords:** Absorption, Corrosive Exhaust, Chemical Compounds, Hydrogen Compounds, Halogen Compounds, Fourier Transform Infrared Spectroscopy, Wet Scrubbers

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## **1 EXECUTIVE SUMMARY**

This report documents the results of the benchscale testing portion of SEMATECH's S66a project.

As a prelude to pilot-scale testing, the benchscale experiments were conducted in a scrubber using commercial scale packings on an actual fab stream. The purpose of the tests was to obtain fundamental data on selected corrosive gases, not in current scientific or engineering literature, to ultimately improve the design and operation of wet scrubbers.

The benchscale testing provided data on mass transfer rates under different conditions of gas and liquid flow rates with a weak (pH of 9) sodium hydroxide solution and, in some cases, with deionized water. Since these tests sought basic data, they were conducted with a once-through scrubbing liquid. Therefore, while the data provide valuable information on chemical compound behavior that can be applied to estimating behavior for future pilot-scale scrubbing tests, they should not be used directly for larger-scale scrubbers or those operating with a recirculating liquid. Pilot tests will be used to develop final design data for wet scrubbers and for investigating aerosol phenomena.

In addition to the mass transfer data, the benchscale tests provided information on other chemical and physical effects in these systems and forecasted potential problems in larger-scale systems. Also, the benchscale work was used to verify and adjust various sampling and analytical methods to overcome industry problems in the chemical analysis of the inlet and outlet streams to wet scrubbers.

**Test System:** The benchscale test system consisted of a small-scale, vertical, countercurrent, packed-bed scrubber with a one-inch circular cross section and a two-foot packed-bed. A special benchscale packing was used for which correlations to commercial-scale packing previously had been established. All gases were measured by Fourier transform infrared spectroscopy (FTIR), except fluorine and chlorine. These were measured by the standard Environmental Protection Agency (EPA) wet chemical method for halogen gases (EPA Method 26a).

**Test Gases:** The gases tested during the benchscale experiments represent those that are absorbed in wet scrubbers in semiconductor fabs. They included hydrogen chloride, hydrogen fluoride, hydrogen bromide, nitric acid, sulfuric acid, acetic acid, chlorine, fluorine, boron trichloride, boron trifluoride, tungsten hexafluoride, ammonia, and hydrogen peroxide. Because sulfur hexafluoride and nitrogen trifluoride are neither soluble nor reactive in aqueous, acidic, or alkaline wet scrubber streams, they were not studied.

### **1.1 Findings**

Most of the gases behaved as previous experience and theoretical analysis predicted. Some exceptions might merit further investigation beyond this project.

The goals of the benchscale test program were attained. The benchscale tests provided a screening study for mass transfer behavior of various gases of interest, a verification of sampling and analytical methods, and insights into absorption behavior of dilute mixtures of the targeted gases. A relative ranking of removal rates was obtained.

In most cases, good removal rates were achieved using a dilute sodium hydroxide in water solution at a pH of 9. Tests with deionized water with an acidic pH of 4.7 yielded lower removals for acid gases and higher removals for ammonia. No mixture effects on removal could be established with certainty. Absorption rate did not appear to depend on gas or liquid flow rate, except with chlorine, which showed a substantial dependence on the liquid flow rate. This is consistent with literature reports that the absorption rate of chlorine in water is liquid phase controlled. The behavior in the benchscale tests shows that a pH of 9 sodium hydroxide solution might be too dilute to alter this dependency. Therefore, chlorine removal will require more concentrated sodium hydroxide solutions with a pH of 10 or higher as suggested by various suppliers. The low removal rates of chlorine relative to the other compounds show that it is probably the most difficult to remove compound on the list.

## **1.2 Recommendations**

1. The uncertain behavior of boron trifluoride in the benchscale testing suggests that special attention needs to be given to this compound.
2. Since benchscale testing showed that chlorine is not as easy to remove as the other absorbable compounds, to remove at least 90% of all absorbable compounds will require that scrubbers be designed and operated to efficiently remove chlorine rather than hydrogen chloride or hydrogen fluoride.
3. Since scrubber design will be based on chlorine removal results in a larger (and more costly) scrubber, a clear definition of design objectives and removal priorities should be developed for each scrubber design. If 90% chlorine removal is a paramount concern, then the system should be designed on that basis. However, if chlorine removal is not a priority, then the scrubber should be designed on a less costly basis, with the understanding that high removal efficiency for chlorine might not be attained.

## **2 INTRODUCTION**

### **2.1 Project S66a Program Overview**

Information obtained from each phase of project S66 provides is necessary to design and implementation of the succeeding phase. The benchscale experiments were needed to fill in data gaps on chemical behavior in a scrubber environment before testing a pilot-scale scrubber. The pilot system will provide data demonstrating the performance capabilities of a well designed and operated full-scale system. Information from the pilot study and some computer modeling will finally be incorporated into a scrubber design and operation guidelines for SEMATECH's member companies. The phases of Project S66a are summarized as follows:

1. Phase One—Information Gathering: Data was gathered from scientific and engineering literature and member companies on existing wet scrubber systems. It identified data gaps to be closed by benchscale and pilot-scale testing. The information gathering effort was completed in Q3 1994.

2. Phase Two—Benchscale Testing: This phase has just been completed. The benchscale testing was performed to examine fundamental absorption behavior of some selected individual chemical compounds and chemical compound mixtures. Mass transfer behavior at low concentrations and in mixtures in an air stream were examined.
3. Phase Three—Pilot-scale Testing: Pilot-scale testing will be performed at two sites during April, May, and June. Pilot testing will provide data to confidently design high efficiency (90% or greater removal) wet scrubbers and will validate computer model output for scrubber systems based upon the data obtained from the initial literature search and the benchscale testing.
4. Phase Four—Guidelines Document: This document will provide the necessary information and models to confidently design, operate, and maintain efficient corrosive gas scrubbers and to use analytical methods to measure performance.

## **2.2 Benchscale Testing Program Overview**

This report describes benchscale testing that provides data on mass transfer rates for removal under different conditions of gas and liquid flow with a weak (pH of 9) sodium hydroxide solution and in some cases deionized water. All work was done with once-through in contrast with recirculating scrubbing liquid. Pilot tests will be used to develop final design data for wet scrubbing. In addition to the mass transfer data, the benchscale tests provide information on other chemical and physical effects that one would expect to encounter in these systems and forewarn of potential problems to be encountered in larger-scale systems. Also, the benchscale work was used to verify and adjust various sampling and analytical methods to overcome industry problems in the chemical analysis of the inlet and outlet streams to wet scrubbers. Findings of this study will be used to plan specific experiments for, predict performance of, and focus on problem areas needing resolution during pilot testing.

## **3 PROJECT OBJECTIVES AND TECHNICAL APPROACH**

### **3.1 Objectives of Benchscale Testing**

The overall objective of benchscale testing was to fill certain data gaps on absorption phenomena of selected target chemical compounds and to provide background data needed to facilitate effective pilot-scale testing.

A fundamental purpose of the benchscale tests was to determine mass transfer data of the target chemical compounds as gases to predict pilot-scale performance. Questions that were to be answered included the following:

1. What do the benchscale tests predict about relative absorption rates for the various compounds?
2. What are the mass transfer rates for boron trichloride, boron trifluoride, and tungsten hexafluoride for which there are no known mass transfer data?
3. Do mixtures affect individual gas mass transfer rates?

The work was to be done for the low concentrations typically found in fab exhaust streams. Some compounds were tested individually; some, in mixtures. The benchscale effort reflected how

much information required for this project could not be obtained from the technical literature, from SEMATECH member companies, and from further tests on the pilot-scale scrubber units.

The gases tested in the program were taken from the list of chemicals shown in Table 1. Not all the compounds on the list are found as gases at the conditions typical to a fab exhaust stream. These include phosphoric acid, ammonium fluoride, sodium hydroxide, and ammonium hydroxide. The first three are solids, and the other compounds can exist only in an aqueous solution. They may exist as a mist or aerosol, but not as a gas. Consequently, they were excluded from the benchscale testing.

**Table 1      Chemical Compounds for Fab Exhaust Stream Wet Scrubbers**

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<b><u>Halogen Acid Gases</u></b>
Hydrogen chloride
Hydrogen fluoride
Hydrogen bromide
<b><u>Other Acid Gases and Mists</u></b>
Nitric acid (gas and mist)
Sulfuric acid (gas and mist)
Phosphoric acid
Acetic acid (gas)
<b><u>Halogens</u></b>
Chlorine
Fluorine
<b><u>Other Halogen Compounds</u></b>
Tungsten hexafluoride
Boron trifluoride
Boron trichloride
Nitrogen trifluoride
Sulfur hexafluoride
<b><u>Alkaline Gases</u></b>
Ammonia
<b><u>Other Compounds</u></b>
Ammonium fluoride
Ammonium hydroxide
Sodium hydroxide
Hydrogen peroxide

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Another chemical, sulfuric acid, is unlikely to be found as a gas at any significant concentrations. Its origin in the fab, as well as its vapor pressure and affinity for moisture, suggests that it will be found primarily as an aerosol. Nonetheless, a benchscale test was made to generate and absorb it as a gas. (Measurable vapor concentrations were not achieved.)

The final two compounds, sulfur hexafluoride and nitrogen trifluoride, are not soluble in water or sodium hydroxide solution at fab exhaust stream conditions and cannot be removed in a wet scrubber. Therefore, they too were not tested.

### **3.2 Test Strategy**

Experiments were designed to measure mass transfer rates for an air stream containing one compound at a time or a mixture of compounds (see Table 2). The actual experiments required

changes in these proposed combinations (see Section 5). Since fundamental data were sought, all tests were done with a once-through or single-pass of scrubbing liquid rather than recirculating liquid.

**Table 2 Single Components and Mixtures Originally Selected for Benchscale Testing**

<u>Single Components</u>		
	Hydrogen chloride	
	Hydrogen bromide	
	Boron trichloride	
	Boron trifluoride	
	Tungsten hexafluoride	
	Tungsten hexafluoride	
	Ammonia	
	Hydrogen peroxide	
<u>Mixture 1</u>		<u>Mixture 2</u>
Hydrogen chloride		Hydrogen chloride
Chlorine		Chlorine
Hydrogen fluoride		Tungsten hexafluoride
Boron trifluoride		Boron trifluoride
		Acetic acid
<u>Mixture 3</u>		<u>Mixture 4</u>
Hydrogen chloride		Nitric acid
Hydrogen bromide		Sulfuric acid
Hydrogen peroxide		
Boron trifluoride		
Fluorine		

\*Not tested, as explained in report.

Finally, the tests were to provide information on other phenomena involving chemical or physical effects (such as reactions/destruction of the chemicals before reaching the scrubber) as well as practical information on sampling and analysis techniques that would later be applied to the pilot unit.

## 4 EXPERIMENTAL SYSTEM AND PROCEDURE

### 4.1 General Approach

Experimental work was conducted in a benchscale absorber at the University of Texas Separations Research Program facilities in the J. J. Pickle Research Center. Target gases in an air mixture were contacted with a dilute solution of sodium hydroxide in a water stream (pH 9) in a small countercurrent packed-bed scrubber. The gas flow rate, temperature, inlet and outlet concentrations of the gas stream; and the scrubber liquid flow rate, inlet temperature, and pH were all measured. Outlet pH was measured in some of the initial runs.

Online FTIR was used to measure all gases except chlorine and fluorine. For these gases, EPA Method 26a, impinger train sample collection method, was used followed by a laboratory analysis of the impinger solutions. (See Appendix C.)

Data were tabulated for the target gases in the benchscale apparatus.

## **4.2 Experimental Apparatus**

The process flow diagram of the experimental apparatus is shown in Figure 1. The system consists of the scrubber and all peripheral equipment to supply the test gases and scrubber liquid to the scrubber. (See Appendix A for a full listing of equipment and description of the system.)

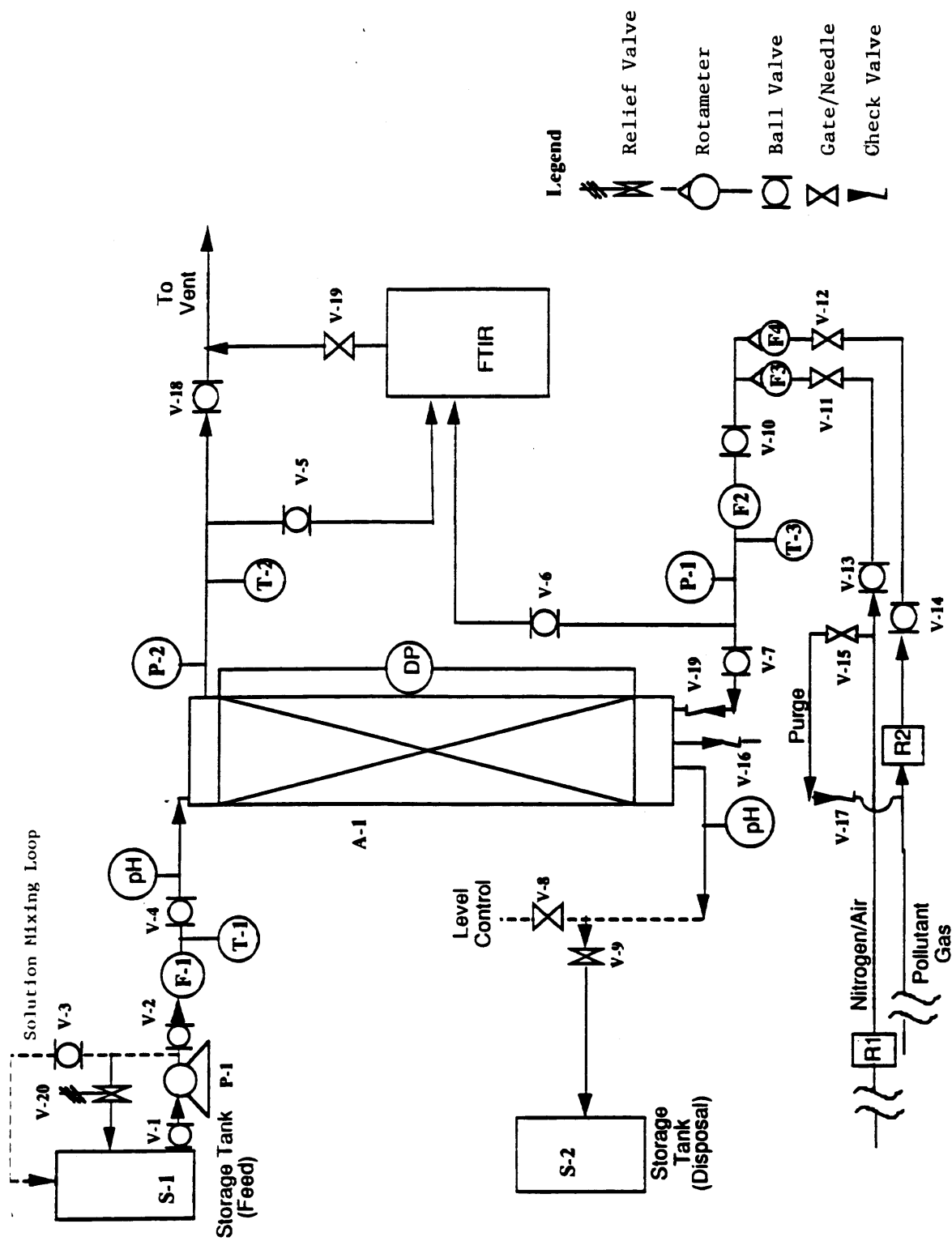


Figure 1 Schematic of Benchscale Test System

### **4.3 Test Procedure**

#### **4.3.1 Experimental Procedure**

Test gases were purchased in prediluted mixtures in air in standard pressurized gas cylinders. The test gases were supplied from the cylinders through pressure regulators to the inlet feed line of the scrubber. Inlet concentrations of all the gases ranged from 1 to 10 parts per million by volume (ppmv) according to availability from the test gas suppliers. An aqueous sodium hydroxide (NaOH) solution (pH 9) or deionized water was supplied to the scrubber from a liquid feed tank. The pH was measured with a manual pH meter. Temperature for both the inlet gas and liquid was measured using thermocouples. Experiments were conducted at 22°C. (See Appendix B for details of the test procedure.)

The inlet gas sample for each run was routed to the FTIR from a tee-in to the scrubber feed line. The outlet sample was similarly taken. FTIR was chosen as the primary test method because it could simultaneously analyze most of the gases with a single instrument system at low detection limits. Since FTIR cannot be used for chlorine and fluorine, the EPA Method 26a impinger method was used. The impinger samples were analyzed for chloride and fluoride ions by ion chromatography using EPA Method 300.

More details on analytical methods are provided in Appendix C.

#### **4.3.2 Test Runs**

The test series consisted of runs with gas flow rates ranging from 0.012 and 0.064 lb/min and liquid rates from 0.011 to 0.042 lb/min. Standard combinations of gas and liquid rates were used. Most runs used a sodium hydroxide solution with a pH of 9. Some runs also used deionized water with a recorded pH of 4.7.

Runs were made with individual chemical compounds and with mixed compounds in air. Attempts to run boron trichloride, boron trifluoride, and tungsten hexafluoride in pure form in air were impossible with the gas mixtures available. As analyzed from the feed cylinder, the boron trichloride contained some hydrogen chloride and the boron trifluoride and tungsten hexafluoride contained some hydrogen fluoride. Since these gases in fact decompose rapidly on contact with moisture, their presence in the feed was not considered a problem.

## **5 RESULTS AND DISCUSSION**

Results of the experiments are summarized in Table 3 through Table 7. Additional details are provided in the tables of Appendix D.

Tests consisted of runs with single compounds in air and mixed gases in air. Single component tests include runs for hydrogen chloride, boron trichloride, boron trifluoride, tungsten hexafluoride, ammonia, hydrogen bromide, and hydrogen peroxide. These results are summarized in Table 3.

**Table 3 Summary Single Component Mass Transfer Test Data**

<b>HYDROGEN CHLORIDE</b>						
Run No.	1-1	1-2	1-3	1-4	1-5	
Gas Rate (lb/min)	0.064	0.064	0.021	0.021	0.12	
Liquid Rate (lb/min)	0.042	0.032	0.042	0.012	0.021	
Inlet concentration (ppmv)	9.83	9.83	9.83	9.83	10.93	
Outlet concentration (ppmv)	0.33	0.21	0.21	0.19	0.33	
<b>BORON TRICHLORIDE*</b>						
Run No.	2-1	2-2	2-3			
Gas Rate (lb/min)	0.064	0.042	0.021			
Liquid Rate (lb/min)	0.042	0.042	0.042			
Inlet concentration (ppmv)	1.7	1.7	4.3			
Outlet concentration (ppmv)	FLOOD	<0.10*	<0.10*			
<b>BORON TRIFLUORIDE**</b>						
Run No.	3-1	3-2	3-3	3-4		
Gas Rate (lb/min)	0.064	0.64	0.021	0.021		
Liquid Rate (lb/min)	0.042	0.032	0.042	0.042		
Inlet concentration (ppmv)	13.14	13.14	13.14	13.14		
Outlet concentration (ppmv)	<3.09	<2.77	-	<1.78		
<b>TUNGSTEN HEXAFLUORIDE**</b>						
Run No.	4-1	4-2	4-3	4-4	4-5	4-6
Gas Rate (lb/min)	0.064	0.042	0.064	0.042	0.042	0.012
Liquid Rate (lb/min)	0.042	0.042	0.032	0.021	0.042	0.024
Inlet concentration (ppmv)	13	16	16	15	15	15
Outlet concentration (ppmv)	<0.16	<0.16	<0.16	<0.21	<0.21	<0.21
<b>AMMONIA</b>						
Run No.	5-1	5-2	5-3	5-4	5-5	
Gas Rate (lb/min)	0.021	0.042	0.021	0.021	0.021	
Liquid Rate (lb/min)	0.042	0.042	0.012	0.042	0.012	
Inlet concentration (ppmv)	8.91	8.91	9.40	9.12	9.12	
Outlet concentration (ppmv)	<0.26	<0.39	<0.17	<0.26	<0.25	

Table 3 Summary Single Component Mass Transfer Test Data continued

<b>HYDROGEN BROMIDE***</b>			
Run No.	10-1	10-2	10-3
Gas Rate (lb/min)	0.021	0.021	0.042
Liquid Rate (lb/min)	0.042	0.012	0.042
Inlet concentration (ppmv)	11.4	11.4	35.0
Outlet concentration (ppmv)	<0.28	<0.28	<0.32

\*Contaminated with hydrogen chloride. See table in Appendix D.

\*\*Contaminated with hydrogen fluoride. See table in Appendix D.

\*\*\*Vapor generated by bubbling nitrogen through concentrated hydrobromic acid and diluting saturated stream with more nitrogen.

Hydrogen chloride behaved as expected. Absorption in the scrubbing solution was rapid as indicated by the high removal rate. Liquid-to-gas ratios in the study range of 4 to 17 gallons per minute per thousand cubic feet (gal/kcf) appeared to have little effect on removal efficiency. This is consistent with the expectation that hydrogen chloride absorption has a gas phase-controlled absorption rate based on high solubility.

Boron trichloride appeared to decompose, as predicted from the technical literature. At inlet concentrations of 1.7 and 4.3 ppmv, the decomposition was so rapid that boron trichloride in the outlet gas was below the detection limit of 0.1 ppmv. The exact rate of reaction could not be determined because of analytical limitations. The decomposition of boron trichloride yields hydrogen chloride, which absorbs in the same manner as the hydrogen chloride originally in the feed gas. For runs conducted at low liquid-to-gas ratios, the test column became plugged. This suggests the formation of solids, which could be undissolved boric acid, sodium borate, or boron oxide. The solids could not be characterized at this time. Commercial scrubber design and operating improvements will need to account for solids formation under some operating conditions.

No published data were found on the aqueous solubility of boron trichloride at the concentrations studied. Similarly, the rate of reaction between boron trichloride and water in the liquid or vapor phases is not known.

The boron trichloride feed stream contained some hydrogen chloride. However, only the data for boron trichloride are shown in Table 3. (See Table D-1 in Appendix D for the hydrogen chloride data.)

The hydrogen chloride in the boron trichloride feed provided the opportunity to compare the hydrogen chloride absorption in these runs with the pure hydrogen chloride runs. No significant differences were found. Under the conditions tested, neither gas seems to interfere with the absorption of the other.

Boron trifluoride runs took place at an inlet concentration of 13 ppmv. Boron trifluoride did not behave as expected. Decomposition in a manner analogous to boron trichloride was anticipated. However, it appears that rather than a straight decomposition and easy removal, a hydrate or other complex might have formed, which was not easily removed by the scrubber. This possibility is suggested by the FTIR absorbance spectra.

The boron trifluoride experiments showed an effluent boron trifluoride concentration below the detection limit of the FTIR. Because of the strong interaction between the absorbance spectra of boron trifluoride and water, it was difficult to quantitate the concentration of boron trifluoride. Additional investigation on the scrubbing of the boron trifluoride would be useful. Further work will be required on analytical methods for boron trifluoride. Removing at least 90% of boron trifluoride might sometimes be more difficult removing other compounds in wet scrubbers. This will be a key issue in the pilot-scale testing.

Tungsten hexafluoride decomposed rapidly. Evidence for its decomposition was seen in Runs 4-4, 4-5, and 4-6, where the outlet concentration of the tungsten hexafluoride was below the FTIR detection limit, while the concentration of hydrogen fluoride increased. Tungsten hexafluoride decomposes to hydrogen fluoride and either tungsten acid or tungsten oxide. The test gas feed mixture contained some hydrogen fluoride, presumably from premature decomposition of the tungsten trifluoride. In the test series of six runs, a hydrogen fluoride analysis was available for only three of the runs.

No published data were found on the solubility of tungsten hexafluoride in water. Similarly, the reaction rate between tungsten hexafluoride and water vapor or liquid is not known. The exact rate of reaction could not be monitored.

The exit concentration of hydrogen fluoride was greater than the inlet concentration of hydrogen fluoride in Runs 4-4, 4-5, and 4-6 shown in Table D-4, Appendix D. Tungsten hexafluoride data were interpreted in terms of hydrogen fluoride. The analysis presented in Table D-4 assumes a complete breakdown of tungsten hexafluoride before reaching the packed section of the column to give a total inlet concentration of 99 ppmv of hydrogen fluoride at the inlet. The absorption of the hydrogen fluoride improves as the liquid-to-gas ratio increases from 4 to 17 gal/kcf. This increase suggests some liquid phase resistance to absorption.

Ammonia tests were run to see how well the ammonia would absorb in an alkaline medium. The result was that efficiencies of over 90% could be obtained, suggesting that in a fully acidic scrubbing solution, the absorption of ammonia should be even better. However in a recirculating system, ammonia, which is volatile, could be subsequently stripped from the scrubber liquid in an ammonia-lean gas stream following a period of scrubber operation with an ammonia-rich gas stream.

The experiments shown in Table 3 suggest that the absorption of ammonia, with the once-through scrubbing liquid, is gas phase-controlled over the range of liquid-to-gas ratios examined since there is no significant change in absorption efficiency with liquid flow rate. Additional tests run with deionized water did not differ significantly, although the pH of inlet deionized water was 4.7 instead of 9.0.

Hydrogen bromide was generated from an aqueous solution of hydrobromic acid (48% wt). Hydrogen bromide was studied as a single component after gaseous concentrations of hydrogen bromide were found to be extremely low in a gas mixture supplied from the test gas cylinder intended for mixture tests. The concentration of hydrogen bromide was maintained at 11 ppmv for Runs 10-1 and 10-2 by dilution with nitrogen. These runs were conducted at liquid-to-gas ratios of 5 and 7 gal/kcf, respectively. The concentration of hydrogen bromide was increased to 35 ppmv for Run 10-3. The liquid-to-gas ratio was maintained at an intermediate value of

8 gal/kcf. At the higher inlet concentration of 35 ppmv, no detectable levels of hydrogen bromide were observed in the effluent gas with a detection limit of 0.32 ppmv.

Hydrogen peroxide was not detected in the sample stream; it is believed to be too unstable to exist as a gaseous species under the conditions tested. None was detected in a bubbler air stream designed to provide a saturated vapor of hydrogen peroxide for analysis by FTIR, although its vapor was sufficiently high to generate measurable amounts of it (100 ppmv). An aqueous solution containing hydrogen peroxide (40% wt) was used to generate hydrogen peroxide vapor. The runs shown in Table D-13 (Appendix D) represent experiments conducted with hydrogen peroxide. For these experiments, the cell temperature (FTIR) was reduced to 50°C. However, examination of spectra associated with the feed and effluent gas streams did not reveal any hydrogen peroxide. A similar set of experiments used a cell temperature of 105°C, again detecting no hydrogen peroxide.

Mixtures of compounds were selected to look for possible absorption interferences or beneficial synergism among compounds. Results of mixtures are shown in Table 4 through Table 7. The following mixtures of gases in air were tested:

- Hydrogen chloride with chlorine
- Hydrogen chloride, chlorine, acetic acid, tungsten hexafluoride, and hydrogen fluoride
- Hydrogen chloride, fluorine, boron trifluoride, and hydrogen fluoride
- Nitric acid and sulfuric acid

Mixture No. 1 results are shown in Table 4. The absorption efficiency of hydrogen chloride is comparable to its removal efficiency in the single component tests. No chlorine measurements were available for Run 6-1. Measurements for both hydrogen chloride and chlorine are available in Runs 6-2 and 6-3. When the liquid-to-gas ratio increased from 8 gal/kcf to 17 gal/kcf, the absorption of hydrogen chloride as well as chlorine improved. Removing chlorine is more difficult than hydrogen chloride, as expected from the literature and other industrial experience. This indicates the presence of a notable liquid phase resistance for chlorine absorption and perhaps a slight liquid phase resistance for hydrogen chloride absorption in the presence of chlorine, although it might be due to greater total acidity. The rate of absorption of chlorine itself is consistent with expectations based on technical literature and supplier information.

**Table 4 Summary Mixed Component Mass Transfer Test Data for Mixture No. 1\***

Run No.	6-1	6-2	6-3
Gas Rate (lb/min)	0.042	0.042	0.021
Liquid Rate (lb/min)	0.042	0.042	0.042
<b>HYDROGEN CHLORIDE</b>			
Inlet concentration (ppmv)	14.0	6.13	6.13
Outlet concentration (ppmv)	0.26	0.28	0.20
<b>CHLORINE</b>			
Inlet concentration (ppmv)	-	15.7	15.7
Outlet concentration (ppmv)	-	10.2	8.1

\*While this test mixture was supposed to include boron trifluoride and hydrogen fluoride, no boron trifluoride was found in the supply cylinder and no hydrogen fluoride was measured because of analytical problems.

Additional runs shown in Table D-11 (Appendix D) provide replicate experiments for hydrogen chloride using a mixture of hydrogen chloride and chlorine. The concentration of chlorine was not recorded during the experiments. The hydrogen chloride concentration in the outlet gas is below the FTIR detection limit for all three runs. Experiments shown in Table D-12 show the possible effect of sodium hydroxide on hydrogen chloride absorption. The removal in Run 12-1 when sodium hydroxide was used is greater in Run 12-2 when sodium hydroxide was not used.

Mixture No. 2 contained hydrogen chloride, chlorine, acetic acid, tungsten hexafluoride, and hydrogen fluoride. Experimental results are shown in Table 5. The first two runs used a mixture of hydrogen chloride, chlorine, and acetic acid. The presence of chlorine or acetic acid appears to reduce the absorption efficiency of hydrogen chloride.

**Table 5 Summary Mixed Component Mass Transfer Test Data for Mixture No. 2**

Run No.	7-1	7-2	7-3	7-4
Gas Rate (lb/min)	0.042	0.042	0.021	0.021
Liquid Rate (lb/min)	0.042	0.021	0.012	0.012
<b>HYDROGEN CHLORIDE</b>				
Inlet concentration (ppmv)	4.0	4.0	6.8	-
Outlet concentration (ppmv)	0.43	0.35	0.11	-
<b>CHLORINE</b>				
Inlet concentration (ppmv)	15.2	15.2	14.0	-
Outlet concentration (ppmv)	7.9	7.8	1.4	-
<b>HYDROGEN FLUORIDE</b>				
Inlet concentration (ppmv)	-	-	19.3	22.3
Outlet concentration (ppmv)	-	-	<1.0	<1.0
<b>TUNGSTEN HEXAFLUORIDE</b>				
Inlet concentration (ppmv)	-	-	4.26	7.70
Outlet concentration (ppmv)	-	-	<0.16	<0.16
<b>ACETIC ACID</b>				
Inlet concentration (ppmv)	10.3	10.3	6.2	12.6
Outlet concentration (ppmv)	1.13	1.52	<0.19	<0.28

In Run 7-4, no hydrogen chloride or chlorine was present in the feed gas. The concentrations of tungsten hexafluoride and acetic acid were higher than for Run 7-3. Both reached concentration levels below the detection limit.

A comparison of the absorption efficiency of acetic acid in Runs 7-1 and 7-2 with Run 7-4 shows that in the presence of hydrogen chloride and chlorine the absorption of acetic acid decreases even though the liquid-to-gas ratio is higher. A comparison between Runs 7-1 and 7-2 shows that at higher liquid-to-gas ratios the absorption for acetic acid is higher.

Run 7-3 contained tungsten hexafluoride. A high absorption was observed with both chlorine and hydrogen chloride. This behavior was unexpected and cannot be explained. The absorption of acetic acid was also higher in Run 7-3 than in Runs 7-1 and 7-2 even though the liquid-to-gas ratio was less. This could be due to the lower inlet concentration of acetic acid as compared to Runs 7-1 and 7-2 (6 ppmv compared to 10 ppmv) and lower total acidity.

Mixture No. 3 contained hydrogen chloride, hydrogen bromide, fluorine, boron trifluoride, and hydrogen fluoride. Results are shown in Table 6. The first three runs used a mixture of boron trifluoride and nitrogen. Only 2.8 ppmv of boron trifluoride were detected in the gas cylinder although the cylinder was expected to contain 40 ppmv. The quantity of the hydrogen bromide in the supply gas was also below the expected concentration.

**Table 6 Summary Mixed Component Mass Transfer Test Data for Mixture No. 3\***

Run No.	8-4	8-5	8-6	8-7	8-8
Gas Rate (lb/min)	0.042	0.042	0.021	0.021	0.064
Liquid Rate (lb/min)	0.042	0.042	0.042	0.012	0.032
<b>HYDROGEN CHLORIDE</b>					
Inlet concentration (ppmv)	-	8.9	8.9	8.9	8.6
Outlet concentration (ppmv)	-	<0.13	<0.18	<0.12	<0.15
<b>HYDROGEN BROMIDE</b>					
Inlet concentration (ppmv)	-	0.25	0.32	0.32	0.41
Outlet concentration (ppmv)	-	<0.20	<0.18	<0.17	<0.24
<b>FLUORINE</b>					
Inlet concentration (ppmv)	2.8	2.2	0.30	0.30	0.10
Outlet concentration (ppmv)	1.0	0.60	0.20	0.10	0.10
<b>HYDROGEN FLUORIDE</b>					
Inlet concentration (ppmv)	8.9	11.1	12.6	12.6	15.3
Outlet concentration (ppmv)	<1.0	<1.0	<1.0	<1.0	-

\*While this test mixture was supposed to include boron trifluoride, no boron trifluoride was found in the supply cylinder.

Runs 8-4 through 8-8 provided data for fluorine. High removal efficiencies were observed for hydrogen chloride and hydrogen fluoride.

Mixture No. 4 results are presented in Table 7. These runs were designed to test the absorption of nitric and sulfuric acid vapors. Nitric acid vapor was generated using an aqueous solution of nitric acid (40% wt). The nitric acid concentration was maintained at 14 ppmv for Runs 9-1 and 9-2 by dilution with nitrogen. These runs were conducted at liquid-to-gas ratios of 17 gal/kcf and 5 gal/kcf. The nitric acid concentration in the outlet gas stream was below detection limits of 0.55 ppmv for both these runs. The nitric acid concentration was increased to 52 ppmv for Run 9-3. This run was also conducted at an intermediate liquid-to-gas ratio (8 gal/kcf). With the high inlet concentration of 52 ppmv, no detectable levels (0.57 ppmv) of nitric acid were observed in the outlet.

**Table 7 Summary Mixed Component Mass Transfer Test Data for Mixture No. 4\***

Run No.	9-1	9-2	9-3
Gas Rate (lb/min)	0.021	0.021	0.042
Liquid Rate (lb/min)	0.042	0.012	0.042
<b>NITRIC ACID</b>			
Inlet concentration (ppmv)	13.8	13.8	52.1
Outlet concentration (ppmv)	<0.57	<0.57	<0.57

\*Although sulfuric acid was used with a bubbler system to introduce sulfuric acid vapor with the nitric acid vapor, no sulfuric acid vapor was detected in the inlet or outlet.

No sulfuric acid vapor was detected in either the inlet or outlet gas stream. The vapor pressure of sulfuric acid is extremely low at conditions of ambient temperature and pressure (2 ppbv) at 20°C and a pressure of 1 atmosphere. Although a concentrated solution of sulfuric acid (98% wt) was used to generate a vapor, the concentration of sulfuric acid in the feed gas was below the detection limit of the analytical method (50 ppbv).

From the benchscale tests, the relative rate of absorption of the various gases, with a once-through scrubbing liquid, can be expressed by three groupings as follows:

- Relatively rapid rate: hydrogen chloride, hydrogen bromide, boron trichloride, tungsten hexafluoride, and ammonia
- Moderately rapid rate: nitric acid, boron trifluoride, hydrogen fluoride
- Relatively slow rate: chlorine and fluorine

If hydrogen chloride removal is used as the basis for scrubber design, then the other halogen-containing gases in its grouping should be removed to comparable levels; ammonia absorption would proceed rapidly in an acidic scrubbing liquid; and the gases in the other two groups would be less rapid. To ensure fluorine and chlorine are sufficiently removed, the scrubber would have to be designed using one of these gases as the design basis. A sodium hydroxide solution with a relatively high pH would also be required. The behavior of boron trifluoride will be examined further during the pilot-scale testing program. Pilot-scale experiments will further extend these benchscale study findings to provide a firmer foundation for the design and operation of packed-bed wet scrubbers for fab exhaust streams.

The benchscale work should be considered only as a general guide to phenomena that might be encountered in a larger-scale system. The results of the pilot study will provide the number of transfer units (NTU) and heights of transfer units (HTU) applicable to commercial scrubber design.

## 6 SUMMARY AND CONCLUSIONS

The goals of the benchscale tests were attained. They provided a screening study for mass transfer behavior of various gases of interest, a verification of sampling and analytical methods, and insight into the absorption behavior of dilute mixtures. The mass transfer behavior of various

acid gas compounds, boron trichloride, boron trifluoride, tungsten hexafluoride, and ammonia were determined in a benchscale test column.

In most cases, a 90% or better removal rates of acid gases in the bench tests was achieved using dilute sodium hydroxide in water at a pH of 9. These results may not apply on full-scale units. No mixture effects on absorption mass transfer could be conclusively established. There was little dependence of absorption rate on gas or liquid flow rate except for chlorine, which showed a substantial dependence on the liquid flow rate. This is consistent with literature reports that the absorption of chlorine in water is liquid phase controlled. This behavior shows that sodium hydroxide solution at a pH of 9 might be too dilute to alter this dependency. Therefore, chlorine removal may require more concentrated sodium hydroxide solutions with a pH of 10 or higher. The low removal efficiencies of chlorine compared to the other compounds show that it is probably the most difficult to remove of the absorbable target chemicals.

Absorption rates for most of the gases appear to be gas phase limited, with the once-through scrubbing liquid, which means that as long as the liquid concentration of the gas is not too high, the liquid rate does not significantly affect absorption rates. An exception is chlorine; other possible exceptions are hydrogen fluoride, fluorine, and acetic acid, which may show more liquid phase controlled absorption.

To optimize scrubbers under the high loading conditions found in some fab exhaust streams, a moderate to strong alkaline solution with a pH of 10 or higher may ensure consistent performance. Scrubber design based on hydrogen chloride absorption alone may not be sufficient to achieve a 90% removal of all the gases. This conclusion will be further evaluated during pilot-scale testing.

High removal efficiencies (greater than 90%) were observed for hydrogen chloride, hydrogen bromide, hydrogen fluoride, nitric acid, ammonia, acetic acid, tungsten hexafluoride, and boron trichloride. The apparent breakdown of boron trichloride to hydrogen chloride and tungsten hexafluoride to hydrogen fluoride in the presence of moisture was observed. The absorption of ammonia, with the once-through scrubbing liquid, was found to be gas phase controlled over a range of pH from 4.5 to 9.

Solids appear to form with boron trichloride, boron trifluoride, and tungsten hexafluoride. Flooding was observed in some instances where solids formed at the packed-bed inlet. In choosing scrubber internals as well as in system operation, the possibility of solids formation must be kept in mind.

The experimental study has been helpful in understanding the capabilities and limitations of FTIR. This will save time and resources for the pilot-scale study.

## **7 RECOMMENDATIONS**

Because the intent of the benchscale tests was to fill data gaps and serve as a screening study before pilot-scale testing, recommendations are primarily directed toward the pilot-scale program rather than full-scale operations. Recommendations for full-scale operations will be made after pilot testing; however, some of the following recommendations can also be applied, with caution, to full-scale operations:

1. Based on the information from the benchscale tests, the next phase of the project should proceed as planned. As a result of the low removal efficiency of chlorine and fluorine, chlorine should be tested with pH and alkalinity as a variable in the pilot study.
2. Since benchscale testing showed that chlorine is not as easy to remove as the other absorbable compounds, assurance of removing at least 90% of all absorbable compounds will require scrubbers to be designed and operated on the basis of chlorine removal rather than hydrogen chloride or hydrogen fluoride removal. Since scrubber design based upon chlorine removal results in larger (and more costly) scrubbers, member companies should have a clear definition of design objectives and removal priorities for each scrubber design. If 90% chlorine removal is a paramount concern, then the system should be designed on that basis. However, if acid gas removal is the priority, then the scrubber should be designed on a less costly basis. Project S66a will provide the data for either contingency.
3. Insoluble solids create a persistent and costly problem in fab scrubbers. Further work should be done to characterize and to limit the impact of the decomposition products of boron trichloride, boron trifluoride, and tungsten hexafluoride. This is not within the scope of this study.
4. The behavior of boron trifluoride in possibly forming complexes in the benchscale testing suggests that special attention will have to be given to this compound during pilot testing.

## APPENDIX A      LISTING OF EXPERIMENTAL EQUIPMENT

The instrumentation and process equipment have been named according to ISO standards. The first letter in the name of the instrument is designated based on function (e.g., F indicates flow measurement). Because about 20 valves were used, their nomenclature is based on function as well as stream. The valves associated with the inlet liquid stream are designated by A at the end of their names. Similarly B, C, D are used to designate exit liquid, inlet gas, and exit gas streams respectively.

Table A-1

Major Equipment List

A-1	Scrubber
DP	Differential Pressure Cell
FTIR	Fourier Transform Infra Red Spectrometer
P-1	Liquid Feed Pump
R1	Pressure Regulator (Nitrogen)
R2	Pressure Regulator (Pollutant)
S-1	Storage Tank for Feed Solution (5 gal.)
S-2	Storage Tank for Exit Solution (5 gal.)

Table A-2

Valves and Instrumentation

Name	Stream <sup>⊠</sup>	Function
F4	Inlet Gas	Flow Indicator (Micromotion)
P-1	Inlet Gas	Pressure Indicator (Micromotion)
R1	Inlet Gas	Pressure Regulator on Nitrogen Supply
R2	Inlet Gas ‡	Pressure Regulator on the Pollutant Gas Supply
S.V.	Inlet Gas †	Safety Valve Used to Isolate the Pollutant Gas Supply
T-3	Inlet Gas	Temperature Indicator (Micromotion)
V-10C	Inlet Gas	Check Valve Preventing the Back Flow of Liquid into Gas Sparger
V-11C	Inlet Gas	Valve Isolating FTIR from Inlet Gas
V-1C	Inlet Gas †	Supply Valve on Pollutant Gas Cylinder
V-2C	Inlet Gas ‡	Valve on Purge Assembly
V-3C	Inlet Gas ‡	Valve Used to Isolate Purge Lines, and Maintain N <sub>2</sub> Flow Through Process
V-4C	Inlet Gas ‡	Check Valve Used to Prevent Pollutant Gas from Going into Nitrogen Lines
V-5C	Inlet Gas †	Valve for Adjustment of Gas Flow Through Rotameter
V-6C	Inlet Gas ‡	Valve Associated With Regulator For Pollutant Gas.

Name	Stream <sup>⊠</sup>	Function
V-7C	Inlet Gas <sup>‡</sup>	Valve on Gas Supply of Nitrogen
V-8C	Inlet Gas	Valve used to isolate Absorber A-1, allowing gas flow to FTIR
V-9C	Inlet Gas	Pressure Regulator For Reducing The Pressure Of Gas Into The Absorber A-1
P-2	Exit Gas	Pressure Indicator
T-2	Exit Gas	Temperature Indicator
V-1D	Exit Gas	Valve for Switching On (/Off) The Supply Of Gas into the FTIR.
V-2D	Exit Gas	Valve for Isolating The Gas Vent from the Equipment, Allowing Flow of Gas into FTIR.
V-3D	Exit Gas	Valve for Turning On/Off Gas Flow from the FTIR.
T-4	Exit Gas	Temperature Indicator
F-1	Inlet Liquid	Flow Indicator (Micromotion)
pH-1	Inlet Liquid	pH Indicator
T-1	Inlet Liquid	Temperature Indicator
V-1A	Inlet Liquid	Valve for Opening the Liquid Supply from the Storage Tank (S-1)
V-2A	Inlet Liquid	Valve Allowing Flow of Liquid into Process or Isolating the Equipment and Recirculating Liquid into Storage Tank
V-3A	Inlet Liquid	Valve on Recycle loop
V-4A	Inlet Liquid	Valve Used to Isolate Liquid Flow from Absorber, A-1
V-5A	Inlet Liquid	Relief Valve to Prevent Over Pressurizing Liquid Flow Lines
pH-2	Exit Liquid	pH Indicator
V-1B	Exit Liquid	Shut-off Valve
V-2B	Exit Liquid	Level Control Valve

<sup>⊠</sup>Inlet/Outlet Streams denote inlet and outlet stream with respect to Absorber A-1

<sup>‡</sup>Test gas

<sup>‡</sup>N<sub>2</sub>/Air

### Equipment Information

The system consists of the scrubber itself and all the peripheral equipment to supply the test gases and scrubber liquid.

The experimental apparatus was mounted on two skids. One of skids held the scrubber liquid feed solution (NaOH or water) and the liquid feed metering pump. The other skid held the absorber column, Micromotion mass flow detector, and most of the valves and tubing. The FTIR spectrometer sat on a table behind the two skids. The FTIR sample cell was a long cylindrical tube projecting from the FTIR in the space between the two skids. All of the equipment was contained within a ventilation hood for safety reasons. The ventilation rate of the hood was two volumes per minute.

**Feed Tank**—A feed tank of five gallons volume was used to store NaOH solution (pH of 9). The solution was supplied from the feed tank to the scrubber column using a reciprocating pump. The

pump was operated to maintain a steady liquid flow rate. A by-pass valve was used to adjust the liquid flow rate into the column; the remaining liquid was recycled back to the feed tank. All the tubing to transport of liquid was 0.25" in diameter.

**Pump**—A Milroyal C-type reciprocating positive-displacement controlled volume or metering pump was used to pump liquid to the top of the absorption column. The delivered volume was controllable within 1% of the chosen setting. The flow rate of liquid was noted using a Micromotion mass flow detector. The readings from the Micromotion flow detector were verified using a bucket stopwatch method.

**Scrubber Column**—The absorber column was a vertical countercurrent, stainless steel column containing two feet of 0.24" nominal Pro-Pak stainless steel packing. Solution from the feed tank was sprayed into the top of the column and flowed downward through the packing countercurrent to the upward moving gas introduced at the bottom of the column.

The scrubber had an internal diameter of 2.58 cm, a height of 121.9 cm, fabricated from 7.62 cm by 7.62 cm bar stock. Twelve pairs of 1.75 cm diameter borosilicate windows, spaced 5.08 cm apart (center to center), were located on opposite sides of the column: five pairs at the top of the vessel, four in the middle, and three at the bottom. The effective diameter of the column, which accounted for the dead volume of between the inner face of each window and the inner wall of the column, was 2.58 cm, larger than the 2.54 cm bore diameter.

**Column Internals**—In addition to the packing, internals consisted of the liquid distributor, gas distributor and packing support. The liquid distributor was a 0.64 cm diameter stainless steel tube with 1.91 cm diameter, hollow circular ring brazed onto the end. Twelve 0.16 cm diameter holes were tapped into the ring to allow adequate dispersion of the liquid over the diameter of the packed bed. A similar distributor was used for introducing gas into the column. The distributors had a length of 22.23 cm and 44.13 cm at the top and the bottom of the column, respectively. A packing height of 6" was measured in a measuring cylinder of 2.54 cm internal diameter. Two feet of packing was added to the column using four such sets of 6" each. The height of packed bed was confirmed using a tape measure.

**Effluent Liquid Storage Tank**—The effluent liquid from the scrubber was discharged to a waste storage tank. The liquid from this tank was transferred periodically to 5 gallon storage tanks. The solution pH in these tanks was recorded. If necessary the solutions were neutralized to a pH of 7, before direct disposal into the drainage system. Samples of solution were placed in 100 ml bottles.

**Level Control**—A transparent Tygon tube was mounted outside the column. The ends of the tube were connected to the bottom of the column and the downstream pressure tap of the differential pressure cell (third window from the bottom). The level of liquid in the tube matched the liquid level inside the column. The flow of liquid from the column was adjusted so that the liquid level remained at half the height of the tube (~ 6" from the bottom of the column). If the liquid level was above that of the tube then the differential pressure cell could get flooded. If the liquid level fell below that of the tube, the liquid seal from the column would be lost. Both of these conditions were avoided during the experimental runs. The liquid level was controlled using a combination of a needle valve and a ball valve for adjustment of the flow rate of solution inside the column.

**Sampling and Analytical Equipment**—A Nicolet FTIR spectrometer was used to detect all targeted chemical concentrations in the feed gas as well as the effluent gas leaving the scrubber column except chlorine and fluorine. Two valves located near the FTIR cell was used to switch the flow of gas between inlet and exhaust streams. The FTIR was maintained at 185°C to prevent condensation of moisture on the internal parts of the FTIR. Concentrations measured by the FTIR were displayed on a Macintosh IIC-I placed outside the hood area. This computer is also used to specify operating parameters to the FTIR using Nicolet Nic-IR software. See Appendix C for more details.

**Impinger Sampler and Ion Chromatography Analysis**—Chlorine and fluorine samples were collected by modified EPA Method 26a and analyzed by EPA Method 300.0. In Method 26a, a test gas is bubbled through an aqueous solution of sodium hydroxide. To ensure fluorine absorption, we added a reducing agent, sodium thiosulfate, to the solution. Fluorine and chlorine are captured as fluoride and chloride salts respectively. The 26a solution is then analyzed by ion chromatography (EPA Method 300.0).

## APPENDIX B OPERATING PROCEDURES

### Summary of General Operating Procedures

Operating procedures consisted primarily of preparing feed solution for a run, adjusting gas and liquid flow rates during a run, and operating the sampling and analytical equipment to record data.

Aqueous sodium hydroxide solution with a pH of 9 was prepared in the liquid feed tank. Reagent grade sodium hydroxide was mixed with deionized water to make up the feed solution to the prescribed pH. The pH was measured with a pH meter.

Liquid was fed to the scrubber by pumping and adjusting the flow with a metering valve until the desired flow rate was reached, as measured by the flowmeter readout. Gas flow was started by opening the cylinder valves and adjusting the flows according to calibrated rotameter settings.

Temperature for both the inlet gas and liquid was measured using thermocouples. Experiments were conducted at 22°C.

The general sequence of procedures was as follows:

**Liquid Flow Rate and Level Control** (liquid seal)—The liquid flow rate was set at the desired value by reading the Micromotion flowmeter and adjusting the pump discharge and recirculation loop valves. Before changing the flow rate of liquid during the experiments, the flow rate of the test gas was reduced to avoid the chance of liquid entrainment from flooding.

**Gas Flow Rate and Level Control** (liquid seal)—The desired gas flow rate was set by slowly increasing the gas flow rate (~0.01 lb/min increments) using a needle valve at the bottom of the scrubber column. The liquid level in the bottom of the column was closely regulated by observing the level indicator and adjusting the scrubber bottom valve. If the liquid level began to fall rapidly, a quick shut-off valve between the column bottom and liquid discharge collection tank could be closed to prevent gas from escaping to the tank from bottom of the column. With each incremental change in gas flow rate, the pressure recorded by the differential pressure (DP) cell (inches of water) was recorded. Excessive pressure drop was an indication of flooding.

**Data Acquisition**—Before data were recorded, the liquid and gas flow rates were allowed to reach a steady state. Thereafter, the liquid seal was checked to confirm that it was intact and steady. The pressure drop across the column and pressure at the bottom of the column were also checked to confirm a steady state condition. When all conditions reached steady state, the exit gas flow was sampled by FTIR and/or the impinger sample train. A VARIAC controller was used to control a heat wrap on equipment to maintain the desired gas temperature (185°C) of the gas going into the FTIR. The steady state concentration was recorded when the change between three successive readings was less than the error bar and the difference between successive readings did not show a trend.

## Detailed Operating Procedures

### Start-up Procedures

Before start-up, ensure all valves are closed. Turn on the power supply outside the hood for the liquid pump and instruments.

#### 1. Preparing Sodium Hydroxide Solution

Before starting an experiment, make sure that at least 3-4 gallons of NaOH solution is available in S-1. If more solution is required, a measured amount of sodium hydroxide is mixed with a measured amount of liquid in S-1. Then open valves V-1A and V-3A and start pump P-1 to recirculate the solution and dissolve NaOH. This procedure will require 15 minutes.

#### 2. Maintaining Liquid Seal in Absorber A-1

To start the flow of liquid into absorber A-1, open valve V-2A and reduce the opening of valve V-3A until the desired flow rate is reached. After a few minutes, a level can be observed in the external level indicator tube at the bottom of the absorber. Open valve V-1B and use the level control valve V-2B to maintain a desired liquid level (near the mark on the level indicator tab). The level of the liquid seal must be monitored closely. If it exceeds the top of the level indicator, it can cause error in the readings of the differential pressure cell (DP). If the level falls below the bottom of the level indicator, then the liquid seal may be lost leading to release of the test gas.

#### 3. Opening Valves Associated With Gas Flow

Before starting the flow of test gas, make sure that the Valves V-11C, V-1D (to the FTIR) and V-3C (purge) are shut. Valves V-6C, V-5C, V-8C, and V-2D need to be opened to ensure a continuous flow of gas through the column to the vent. The pressure regulator V-9C should be kept completely open to prevent loss of liquid seal from sudden entry of high volume (pressure) flow of gas. Gas flow can be controlled using regulator V-9C.

### Process Operation

These process operating procedures are followed for the data runs.

#### 1. Liquid Flow Rate and Level Control (liquid seal)

Adjust Valve V-2A and Valve V-3A to reach the desired liquid flow rate. Ensure that the liquid flow rate is at the desired level by reading of the Micromotion flowmeter. Thereafter, adjust V-2B to maintain a desired liquid level at the bottom of the column.

#### 2. Gas Flow Rate and Level Control (liquid seal)

To reach the desired gas flow rate, slowly increase the gas flow (~0.01 lb/min increments) using the regulator Valve V-9C. Closely monitor the liquid level at the bottom of the column by observing the level indicator. If the liquid level begins to fall rapidly, shut-off valve V-1B to prevent gas from directly leaving the bottom of the column. Also adjust valve V-2B to maintain the desired level. With each gas flow rate, note the pressure recorded by the DP cell (inches water) to ensure that the reading is a few inches W.G. and that no flooding is indicated.

#### 3. Recording Data

Before recording data, note that the liquid and gas flow rates are steady. Then, double-check that the liquid seal is intact and steady. Note that the pressure drop across the column and pressure at the bottom of the column (PI) are steady. Note the solution pH at the bottom of the scrubber. Verify that the solution pH is steady. Then, open V-1D and to send a sample flow of exit gas to the FTIR cell. The setting on the VARIAC controller should be increased or decreased to obtain desired gas temperature of 185°C for the exit gas going into the FTIR. The temperature of this stream is noted on T-4. Note that at least three readings of the FTIR indicate a steady exit gas concentration.

After noting satisfactory conditions, record another gas concentration after a period of five minutes, and close Valve V-1D to isolate the FTIR from the exit gas stream. Once the above readings have been noted, open V-11C and V-3D to divert the inlet gas into the FTIR. Note that the FTIR reading confirms that the inlet gas concentration is as expected. During the process of diverting inlet gas, the level of liquid seal can rise. Ensure that a steady value is maintained. After the readings have been noted close V-11C and V-3D.

In summary, each experiment must include the following readings: liquid and gas flow rates, pressure drop across the absorber, pressure at the bottom of the absorber, inlet and exit liquid pH, and inlet and exit gas concentrations.

#### 4. Purge Before Recording Exit Concentrations

The FTIR cell and the tubing leading to it are susceptible to adsorption of test gases. This could seriously affect the accuracy of the recorded concentrations, especially for the exit gas stream. Therefore a nitrogen purge is necessary between analyses.

To initiate a purge, V-11C and V-3D are opened and V-8C is closed. Thereafter, safety valve (S.V.) is closed to isolate the supply of the test gas and V-3C and V-2C are opened. V-7C is opened to start the supply of nitrogen into the lines. This procedure continues until the reading in the FTIR indicates that the FTIR cell is free of test gas. Then, V-11C and V-3D are shut-off to isolate the FTIR. At this time, either a new gas or liquid rate can be used or the exit gas concentration can be sampled again. The procedures for changing the gas and liquid flow rates are described below. If the exit gas needs to be sampled at the same operating conditions, the procedures outlined in Step 3 need to be followed.

#### 5. Changing the Flow Rate of Gas

To record readings at a new gas flow rate, follow the procedures outlined in Step 2. Upon reaching a steady-state, follow all the procedures described in Step 3.

#### 6. Changing the Flow Rate of Liquid

Before changing the flow rate of liquid, reduce the flow rate of gas (this is a precaution to avoid liquid entrainment and flooding). Thereafter, follow the instructions from Step 1 on.

### **Shut-Down Procedure (Daily) and Change of Test Gas Cylinder**

The purpose of these procedure is to ensure that the lines do not contain any contaminating gas and that most of the liquid is drained out of the column. Both of these procedures are similar in many respects. The major difference involves the process of purging the line between the safety valve (S.V) and V-1C (in the case of changing a cylinder).

#### 1. Closing the Supply Valve of the Test Gas

To prevent any mishaps during operation of Valve V-1C, the safety valve (S.V) is shut-off using the pneumatic switch. This isolates the test gas supply from the rest of the system. Then, turn off valve V-1C.

## 2. Purging the Tubing and Equipment

During purging, the liquid seal must be maintained. This is done by turning off the liquid flow and closing valve V-1B (when the liquid has reached the appropriate level). Then, turn off pump P-1 and close valves V-1A, V-4A and V-2A.

Open valves V-3, V-2C, and V-7C to start the purge. This directs the flow of gases into the scrubber through the gas inlet lines. The test gas lines are now being purged up to S.V. Open S.V. allowing the rest of the line between S.V. and V-1C to be purged. Valve V-11C and V-3D are opened to the sample inlet stream of gas, ensuring that the gas lines up to that point are clean. Then, close V-11C and open V-1D. The process of purging is continued until the FTIR indicates that the lines are free of test gas.

If the purpose of the purge is to discontinue experimentation for the rest of the day, the flow of nitrogen is continued overnight. If, however, the purpose is to change the gas cylinder, then the procedure for changing the gas cylinder must be followed.

For a complete shut-down, close the exit gas valves beginning with V-2D, V-3D, V-1D, V-11C, V-9C, V-5C, V-3C and V-7C. Open valve V-1B and drain liquid from the system as much as possible. Introduce nitrogen, if necessary, to force the liquid seal out of the column.

After all the shut-down procedures have been completed, turn off the main power supply switch (outside the hood).

## APPENDIX C SAMPLING AND ANALYTICAL EQUIPMENT AND METHODS

### FTIR Analysis

FTIR spectroscopy, like other spectroscopy, uses known absorptivity constants of the test chemical compounds at specified wavelengths to determine the concentration of the sample. By applying the absorptivity and path length through Beer's Law, the primary equation in spectroscopy, the concentration of the test gas can be measured. Beer's law states:

$$\text{Concentration} = \text{Absorbance}/(\text{absorptivity} \times \text{optical path length})$$

The absorbance is the value measured on the FTIR and then automatically converted to concentration units by calculation through preprogrammed system software. To increase instrument sensitivity and limit instrument (electrical) noise, the FTIR collected a sample spectrum about every two seconds and then integrated the 60 or more spectra into a single two minute average. The average was then compared to the reference spectra to determine chemical concentrations.

Major components and operating principles of the FTIR system are as follows:

**The Michelson Interferometer:** This optical system generates and receives the infrared (IR) signal. The interferometer contains two mirrors, a beam splitter, and a detector. The interferometer is configured as a cross, with the infrared source and one mirror, which moves, opposing each other. The second mirror and the IR detector are situated perpendicular to the source and moving mirror, lying opposite each other. In the center of the cross is the beam splitter, which reflects 50% of the IR light to the stationary mirror and 50% of the IR light to the moving mirror. Light reflected from the two perpendicular mirrors passes through the test gas in the sample cell and then to the IR detector.

**Multiple Path Measurements:** In passing through the FTIR sample cell, IR light is reflected back through the cell 16 times by a set of three mirrors. Based on Beer's Law, by increasing the cell path length by a factor of 16, the FTIR dramatically increases the sensitivity of the concentration measurement. The effective optical path length of the cell increases 16 times, from 0.75 meters to 12 meters.

**Generation of the Interference Pattern:** In the Michelson Interferometer, by moving slowly and precisely, the moving mirror alters the effective path length of one of the two paths of IR light. The second mirror, which is stationary, transmits light of a fixed path length.

Infrared light, like all electromagnetic radiation, consists of waves. Before the mirror moves, the light from the two IR sources converge on the detector and superimpose on one another. As the mirror moves, the path difference modulates the light intensity at each wavelength, which is seen by the system's IR detector. The modulated signal correlated to the position of the moving mirror is called the interferogram.

**The Infrared Detector:** After passing through the FTIR sample cell, the modulated IR light reaches an mercury-cadmium-telluride (MCT) photovoltaic detector, cooled below ambient temperature with liquid nitrogen. The MCT converts the IR light beam into a weak electrical current in a manner similar to a solar cell converting sunlight into electrical current. The MCT detector has a spectral response of from 500 to 5,000 wave numbers, covering all but the

outermost regions of the infrared spectrum. The current generated by the MCT detector is amplified and then digitized for computer analysis.

**Computer Analysis:** The digitized interferogram is stored in an Apple computer for analysis. The computer extracts the infrared spectrum from the interferogram using Fourier Transform. A complex series of waves can be mathematically described by a series function sum of sine and cosine waves known as a Fourier Series. By extracting the nonperiodic functions as an integral over the range of frequencies scanned, the spectrum can be isolated from the signal generated by the light source. The background spectrum (air sample with no chemicals) is then subtracted from the sample spectrum leaving the absorbance spectrum. For all analyses the total noise and uncertainty in the spectrum should be less than 5% of the range of the absorbance value.

### **FTIR Data Reduction**

The first step in the preparing the FTIR for the benchscale tests was creating a complete digital library of the test gases. Since digitized IR spectra of many of the gases of interest were not readily available, we had to generate a spectral reference for these gases ( $\text{BCl}_3$ ,  $\text{BF}_3$ ,  $\text{WF}_6$ , etc.) by recording the spectrum of their respective gas standards.

The absorbance spectrum is compared to a library of digitally stored chemical reference spectra for identification and quantification of the infrared absorbing species in the gas sample. An appropriate absorbance peak, which had a high absorption coefficient and no interferences from other chemicals present in the sample, was determined for each chemical.

The FTIR system automatically corrects for deviations of the spectra and gas density resulting from changes in temperature and pressure. It also automatically accommodates Beer's Law deviations in very dilute samples. The resultant data are then tabulated, reported, and stored in the computer. The interferogram is also stored on the computer for future reference.

### **FTIR Sampling Description**

For the FTIR measurements, the exact sample flow rate into the sample cell is not critical since these samples are collected into a fixed-volume reservoir. What is required is an exact knowledge of the sample path length, which is a precisely measured constant in the FTIR system. The sample path length is the primary determinant of sensitivity according to Beer's Law. The mirror to mirror path length inside the sample cell was measured precisely by the manufacturer (Nicolet) and was provided with the instrument documentation.

Flow through the scrubber system and into the FTIR sample cell was produced at a setting of 8 psig on the cylinder. Gaseous samples were extracted from ports installed in the inlet and outlet of the benchscale scrubber. For the inlet samples, gas was transported four meters by an unheated one-quarter inch stainless steel sample line and through stainless steel flow controller at a nominal flow of between 10 and 30 liters/min to the heated FTIR white cell (sample cell) heated to 185°C. Since the FTIR technology does not measure liquids, it was important to avoid condensation within the FTIR sample cell. The cell was therefore heated to 185°C.

The sample line from the scrubber outlet was one and a half meters long, one-quarter inch stainless steel sample line. The outlet sample line, which contained the moisture saturated air stream, was heated to 185°C to convert acid mists, primarily nitric or sulfuric acid, to their vapor state and to preclude condensation in the sample line. The outlet sample line operated at one liter/minute with the remaining (9 to 27 liters/minute) outlet gas flow being vented to a chemical

scrubber. The 1:27 split of outlet gas was done to prevent sample flow through the FTIR from creating back pressure, in the scrubber, that would alter the critical liquid-to-gas flow ratio during a scrubber experiment.

Both the inlet and outlet lines were connected to a three-way valve at the inlet to the FTIR to allow for rapid and safe switching between inlet and outlet gases during an experiment. The pressure drop in the sample cell during measurement was maintained at 5 mm Hg over ambient and data corrected to standard temperature and pressure (STP) based upon the cell pressure. The FTIR's three volume exchange time (the time to reliably purge one sample and begin to measure a second sample) for the 8 liter sample cell was 24 minutes for the 1 liter/min outlet sample and one minute for the 28 liter/minute inlet flow.

The analysis started by recording the infrared interferogram (once every two seconds). To reduce the impact of instrument noise and physical vibration, the interferograms were integrated electronically into a two-minute signal.

During the benchscale testing, two events caused some downtime. Both events were caused by condensation on the FTIR's potassium bromide (KBr) detector window. The first failure occurred when liquid nitrogen (used to cool the FTIR detector) was spilled on the detector assembly during filling. This caused the polymer seals to leak, allowing water to condense on the detector cell. The window had to be replaced and the assembly dried. In a similar event, liquid water entered the FTIR cell during a "flooding" simulation of the benchscale scrubber. Again the detector window had to be replaced and the cell dried. Preventive measures were instituted to avoid similar episodes during remaining bench tests.

### **EPA Method 26a Sampling Overview**

Method 26a is designed for collecting samples of acid gases such as hydrogen chloride, hydrogen fluoride, and hydrogen bromide, and the halogen gas, chlorine. For the benchscale tests, the method was modified slightly to capture the strong oxidizing gas, fluorine, as well. Method 26a uses a variant of the EPA Method 5 sample train, with four impingers, for absorbing the gases. For this project, the first two impingers contained a 0.1 normal aqueous solution of sulfuric acid to absorb the halogen acids from the sample stream. Where FTIR was used to measure hydrogen chloride and the other halogen acids, the first set of impingers, containing sulfuric acid, was used as "knock-outs" to remove the acids so that they would not interfere with the chlorine and fluorine captured in the back two impingers. The sulfuric acid impingers reduced interfering dissolution of the acid gases by preventing their migration to the back impingers where they would distort the chlorine and fluorine analyses by showing up as chloride and fluoride ions.

Chlorine and fluorine, which were not absorbed in the acid solutions in the first two impingers, were trapped in the rear set of impingers containing an aqueous solution of 0.1 Normal sodium hydroxide. Radian elected to add the mild reducing agent sodium thiosulfate at .05 normal to the sodium hydroxide solution to convert residual hypochlorous (HClO) acid from chlorine absorption to the chloride ion and to convert fluorine gas to fluoride. Ten percent of the first and second impingers were tested to make certain that no acid gas breakthrough occurred. In all cases, the halide concentration in the fourth impinger was less than 3% of the concentration in the third impinger. In all cases, both impingers containing sodium hydroxide solution were analyzed for chloride and fluoride residuals.

For Method 26a sample collection, the exact sample flow rate into the sample system must be known so that the ions extracted from the gas sample can be related back to the volume of air sampled (micrograms of chemical to liters of gas sampled). Sample volumes were measured using a calibrated gas meter attached to the exhaust of the impinger train. The test gases used were generated from pressurized gas stored in aluminum cylinders (AL150). The meter was calibrated by a National Bureau of Standards (NBS) traceable bubble meter. Flow through the scrubber system and into the Method 26a sample train was by positive gas pressure from the cylinders with the cylinders' pressure regulators set at 8 psig and controlled by electronic flow controllers.

Two Method 26a sample trains were used during each experiment with chlorine or fluorine, one on the inlet stream and one on the outlet stream. For the inlet samples, gas was transported 4 meters by an unheated one-quarter inch stainless steel sample line and through stainless steel flow controller at a nominal flow of between 10 and 30 liters/min. A tee was attached to the inlet line and gas was diverted to the Method 26a sample stream at approximately 1 liter/minute. The sample line from the scrubber outlet was one-and-a-half meter, one-quarter inch stainless steel sample line. The outlet sample line for Method 26a was connected to the scrubber outlet prior to the FTIR's heated line. Again, flow through the sample train was adjusted to a nominal flow of 1 liter/minute with the remaining sample flowing into the heated sample line.

#### **Analysis of Method 26a Samples Using EPA Method 300.0**

Samples collected by Method 26a were analyzed in Radian's chromatographic laboratory by EPA Method 300.0, which employs ion chromatography for analysis. Ion chromatography physically separates the chloride and fluoride ions in solution in a manner in which the ions can be quantitated.

One milliliter aliquots of the Method 26a samples are introduced into a tube containing a gel that selectively adsorbs the ions as the sample solution flows through the column. The 1 ml sample is forced through the column by an inert carrier liquid. As the sample passes through the column, the ions separate by adsorption on the gel. An eluent fluid then is passed through the column to desorb the ions as it passes. The column retains some chemicals longer than others so that as the carrier fluid now containing the desorbed ions reaches the detector, the ions reach the detector in inverse order of retention.

As each ionic component passes through the detector, the electrical conductivity of the solution increases in a normal Gaussian distribution (a symmetrical peak). The time from injection of the sample to the peak maximum is called the retention time. The retention time is characteristic of each ion and identifies it. The area under the peak is a measure of the ion's concentration. In conductivity detectors used in this study, peak area is linearly related to ion concentration. Before sample analysis, the analyst injects a series of calibration standards to establish the conductivity-concentration relationship, which is subsequently related to sample area to determine sample concentration.

For this study, samples collected from the impingers were decanted and sample volumes measured in a 25-milliliter graduated cylinder and the sample volume recorded. The total volume of test gas passing through the impingers was measured by the gas meter and the sample temperature was also recorded.

The samples were analyzed on a completely inert, metal-free Dionex DX-300 gradient ion chromatography system. For chloride and fluoride determination, an AG4A guard column and an

AS4A-SC anion separator column were used. The ions were eluted using a 17 Molar sodium carbonate and 18 Molar sodium bicarbonate buffer solution. The detector was the DX-300's conductivity detector.

Before the start of each analysis series, four reference standards of chloride and fluoride salts dissolved in the Method 26a absorbing solution were prepared and injected onto the DX-300 system to develop a calibration curve. To establish the baseline or zero response of the system, unadulterated Method 26a absorbing solution was injected onto the system. Duplicates, replicates, and field blank samples were analyzed according to EPA Method 300.0 and the Radian plan for Method 300.0 quality assurance. Laboratory calibration standards and quality control check samples were prepared from NBS-traceable chemical stock at Radian's laboratory. Volumetric standards employed both for field preparation of absorbants and in the laboratory were specified to be accurate to within 2% by the manufacturer.

The laboratory adhered to Method 300.0 specifications for calibration and quality control. Before sample analysis, the instrument was calibrated using five standards over the expected sample concentration range. A least squares fit applied to the ion's calibration curve had to have a correlation of 0.995 or better. In addition, a laboratory blank was used to confirm the calibration intercept. The intercept and blank value had to agree with 1 ug/ml. The calibration curve was validated at the beginning the and end of the day by a certified standard from an independent source. The concentration of the "second source" standard was set at the mid-range of the calibration curve. The drift allowable from the calibration curve was not allowed to exceed 5%. Matrix spiked samples were analyzed at a frequency of 10%. The window for spiked samples was 90% recovery or better.

For Method 300.0 (impinger sample analysis), the peak identification and concentration were performed by an experienced chemist. Fluoride and chloride were identified by comparing the retention time (time from sample injection to appearance of the maxima of a chemical) of the unknown to that of the calibration standard. Retention times had to be within 5% of the standard to be identified as the compound of interest. Concentrations were determined by dividing the chromatographic peak area by the chemical response curve and multiplying it by the total volume of the impinger solution. The resultant value is reported in micrograms (ug). The gas concentration is then determined by dividing the resultant (ug) by the total gas flow through the impinger as measured in liters (l). The concentration is then reported as ug/l or converted to parts per million on a volume/volume basis (ppmv).

## APPENDIX D      DETAILS OF EXPERIMENTAL DATA

The following tables (Tables D-1 through D-13) contain a summary of the operating conditions for the experiments conducted between 1/9/95 and 03/03/95 at the Pickle Research Campus at the University of Texas at Austin.

The nomenclature used in these tables is explained below.

G = Gas flow rate (lb/min)

L = Liquid flow rate (lb/min)

L/G = Ratio of liquid to gas flow rate (gal/Mcf or gal/1000 ft<sup>3</sup>)

DP = Pressure drop across the column (inches of water)

K<sub>og</sub> = Overall gas phase mass transfer coefficient (cm/s)

a = Specific area of mass transfer (cm<sup>2</sup>/cc)

The concentrations of each compound in streams entering and leaving the scrubber are denoted by "in" and "out" respectively. These concentrations have been reported in parts per million by volume (ppmv).

The term "no detect" is used to indicate that the concentration detected by the FTIR was below the confidence interval calculated by it. In many of these cases, this confidence interval is used as a conservative estimate of concentration.

The temperature of the gaseous and liquid streams entering and leaving the column was as follows:

Liquid: T<sub>in</sub> = 22(+/-2), T<sub>out</sub> = 22(+/-2)

Gas: T<sub>in</sub> = 22(+/-2), T<sub>out</sub> = 21(+/-2)

The temperature was measured in degrees C.

TABLE D-1							
Components:		Run 1-1	Run 1-2	Run 1-3	Run 1-4	Run 1-5	Run 1-6
	HC1	1/9/95	1/9/95	1/9/95	1/9/95	1/23/95	1/23/95
G	lb/min	0.064	0.064	0.021	0.021	0.012	0.064
L	lb/min	0.042	0.032	0.042	0.012	0.021	0.128
L/G	gal/kcf(22°C)	5.49	4.19	16.74	4.78	14.65	16.74
_P	in. water	1.93	1.88	0.44	0.42	0.28	
HC1(in)	ppmv	9.83	9.83	9.83	9.83	10.93	
HC1(out)	ppmv	0.33	0.21	0.21	0.19	0.33	
K <sub>og</sub> a(HCl)	1/s	4.61	5.20	1.71	1.76	0.89	
Footnotes: *Flooding occurred. No concentration data were obtained.							

TABLE D-2				
Components:		Run 2-1	Run 2-2	Run 2-3
	BCl <sub>3</sub> (HCl)			
		1/16/95	1/16/95	1/26/95
G	lb/min	0.064	0.042	0.021
L	lb/min	0.042	0.042	0.042
L/G	gal/kcf (22°C)	5.49	8.37	16.74
_P	in. water	**	1.04	0.71
BCl <sub>3</sub> (in)	ppmv	1.71	1.71	4.32
BCl <sub>3</sub> (out)	ppmv		0.6*	0.6*
HCl(in)	ppmv	12.40**	12.40	11.05
HCl(out)	ppmv		0.45	1.03***
K <sub>og</sub> a(HCl)	1/s		3.04	1.30
Footnotes:				
*No detect				
**Flooded within 2 minutes				
***Flooded after 2.5 hours				

TABLE D-3					
Components:		Run 3-1	Run 3-2	Run 3-3	Run 3-4
	BF <sub>3</sub>	1/17/95	1/17/95	1/17/95	1/31/95
G	lb/min	0.064	0.042	0.064	0.021
L	lb/min	0.042	0.042	0.032	0.042
L/G	gal/kcf(22°C)	5.49	8.37	4.19	16.74
_P	in. water	1.53	0.80	1.40	0.37
BF <sub>3</sub> (in)	ppmv	13.14	13.14	13.14	13.14
BF <sub>3</sub> (out)	ppmv	3.09*	2.77*	-	1.78*
K <sub>og</sub> a(BF <sub>3</sub> )	1/s	>1.96	>1.38		>0.8
Footnotes:					
*No detect					
Analysis of spectra revealed that there was no BF <sub>3</sub> present in the feed gas.					
Data taken during Run 3-4 showed that there was no HF present in the feed or effluent either. Closer inspection of spectra revealed the presence of a compound other than BF <sub>3</sub> .					

TABLE D-4							
Components:		Run 4-1	Run 4-2	Run 4-3	Run 4-4	Run 4-5	Run 4-6
	WF <sub>6</sub>	1/18/95	1/18/95	1/18/95	2/1/95	2/1/95	2/1/95
G	lb/min	0.064	0.042	0.064	0.042	0.42	0.12
L	lb/min	0.042	0.042	0.032	0.021	0.042	0.024
L/G	gal/kcf(22°C)	5.49	8.37	4.19	4.19	8.37	16.74
_P	in. water	1.36	0.77	1.33	0.40	0.90	0.20
WF <sub>6</sub> (in)	ppmv	16.01	16.02	16.02	14.96	14.96	14.96
WF <sub>6</sub> (out)	ppmv	0.16*	0.16*	0.16	0.21*	0.21*	0.21*
HF(in)	ppmv	**	**	**	8.95	8.95	8.95
HF(out)	ppmv	**	**	**	<21.23	<16.51	<13.00
K <sub>og</sub> a(HF)	1/s				>1.36	>1.59	>0.51
Footnotes:							
*No detect							
**Not Analyzed. The method for analyzing HF had not been established for Runs 4-1, 4-2, and 4-3.							
Note: WF <sub>6</sub> is analyzed as equivalent HF, i.e., 6 HF=WF <sub>6</sub> .							
Because of the rapidity of decomposition of WF <sub>6</sub> at the scrubber inlet to HF, K <sub>og</sub> (WF <sub>6</sub> ) was not calculated, rather the K <sub>og</sub> a(HF) will prevail.							

TABLE D-5						
Components:		Run 5-1	Run 5-2	Run 5-3	Run 5-4	Run 5-5
	NH <sub>3</sub>					
		2/13/95	2/13/95	3/2/95	3/2/95	3/2/95
G	lb/min	0.021	0.042	0.021	0.021	0.021
L	lb/min	0.042	0.042	0.012	0.042	0.012
		Caustic (pH=9)	Caustic (pH=9)	Caustic (pH=9)	Water (pH=4.7)	Water (pH=4.7)
L/G	gal/kcf(22°C)	16.74	8.37	4.78	16.74	4.78
_P	in. water	0.35	0.72	0.51	0.45	0.45
NH <sub>3</sub> (in)	ppmv	8.91	8.91	9.40	9.12	9.12
NH <sub>3</sub> (out)	ppmv	0.26*	0.39*	0.17*	0.26*	0.25*
K <sub>oga</sub> (NH <sub>3</sub> )	1/s	>1.61	>2.86	>1.80	>1.61	>1.63
Footnotes:						
*No detect						
Runs 5-4 and 5-5 made with deionized water, pH=4.7.						

TABLE D-6				
Components:		Run 6-1	Run 6-2	Run 6-3
	Mixture 1:			
	HCl/Cl <sub>2</sub> ; BF <sub>3</sub> /HF	2/8/95	2/13/95	2/13/95
G	lb/min	0.042	0.042	0.021
L	lb/min	0.042	0.042	0.042
L/G	gal/kcf(22°C)	8.37	8.37	16.74
_P	in. water	1.05	0.66	0.70
HCl(in)	ppmv	14.03	6.13	6.13
HCl(out)	ppmv	0.26	0.28	0.20
K <sub>OGa</sub> (HCl)	1/s	3.55	2.74	1.52
Cl <sub>2</sub> (in)	ppmv	**	15.7	15.7
Cl <sub>2</sub> (out)	ppmv	**	10.2	8.10
K <sub>OGa</sub> (Cl <sub>2</sub> )	1/s		0.38	0.29
BF <sub>3</sub> (in)	ppmv	*	*	*
BF <sub>3</sub> (out)	ppmv	*	*	*
HF(in)	ppmv	*	*	*
HF(out)	ppmv	*	*	*
Footnotes: *No detect.				
**No analysis for Cl <sub>2</sub> in Run 6-1.				
Analysis of gas from cylinder containing BF <sub>3</sub> /HF did not reveal the presence of either of these components. The readings for Cl <sub>2</sub> (out and in) were obtained using samples from the impinger.				

TABLE D-7					
Components:		Run 7-1	Run 7-2	Run 7-3	Run 7-4
	Mixture 2: HCl/Cl <sub>2</sub> , CH <sub>3</sub> COOH, WF <sub>6</sub> , HF				
		2/14/95	2/16/95	2/14/95	
G	lb/min	0.042	0.042	0.021	0.021
L	lb/min	0.042	0.021	0.012	0.012
L/G	gal/kcf(22°C)	8.37	4.19	4.78	4.78
_P	in. water	0.70	0.32	0.31	0.31
HCl(in)	ppmv	4.00	4.00	6.77	
HCl(out)	ppmv	0.43	0.35	0.11*	
K <sub>oga</sub> (HCl)	1/s	1.99	2.15	1.83	
Cl <sub>2</sub> (in)	ppmv	15.20	15.20	14.00	
Cl <sub>2</sub> (out)	ppmv	7.90	7.80	1.40	
K <sub>oga</sub> (Cl <sub>2</sub> )	1/s	0.58	0.59	1.02	
CH <sub>3</sub> COOH (in)	ppmv	10.27	10.27	6.20	12.58
CH <sub>3</sub> COOH (out)	ppmv	1.13	1.52	0.19*	0.28*
K <sub>oga</sub> (CH <sub>3</sub> COOH)	1/s	1.96	1.70	1.55	1.69
WF <sub>6</sub> (in)	ppmv			4.26	7.70
WF <sub>6</sub> (out)	ppmv			<0.16*	<0.16*
K <sub>oga</sub> (HF <sub>6</sub> )	1/s			>1.39**	>1.58**
HF(in)	ppmv			19.30	22.25
HF(out)	ppmv			1.00*	1.00*
Footnotes: *No detect,**WF <sub>6</sub> as HF					
NOTE: For Runs 7-1 and 7-2, WF <sub>6</sub> was not used as the FTIR showed no detectable WF <sub>6</sub> in the cylinder. On the next day (Runs 7-3 and 7-4), a second cylinder was used, which showed detectable levels of WF <sub>6</sub> . In order to maintain higher levels of WF <sub>6</sub> and CH <sub>3</sub> COOH, HCl was not used in Run 4.					

TABLE D-8									
Components:		Run 8-1	Run 8-2	Run 8-3	Run 8-4	Run 8-5	Run 8-6	Run 8-7	Run 8-8
	Mixture 3: HCl/HBr, F <sub>2</sub> , BF <sub>3</sub> , HF	2/20/95	2/20/95	2/20/95	2/21/95	2/21/95	2/21/95	2/21/95	2/21/95
G	lb/min	0.042	0.021	0.021	0.042	0.042	0.021	0.021	0.064
L	lb/min	0.042	0.042	0.012	0.042	0.042	0.042	0.012	0.032
L/G	gal/kcf(22°C)	8.37	16.74	4.78	8.37	8.37	16.74	4.78	4.19
_P	in. water	1.08	0.53	0.51	0.85	0.87	0.41	0.46	1.20
HCl(in)	ppmv					8.89	8.88	8.88	
HCl(out)	ppmv					0.13*	0.18*	0.12*	0.15*
K <sub>oga</sub> (HCl)	1/s					3.75	1.88	1.91	
HBr (in)	ppmv					0.25	0.32	0.32	0.41
HBr (out)	ppmv					0.20*	0.18*	0.17*	0.24*
F <sub>2</sub> (in)	ppmv				2.80	2.20	0.30	0.30	0.10
F <sub>2</sub> (out)	ppmv				1.00	0.60	0.20	0.10	0.10
K <sub>oga</sub> (F <sub>2</sub> )	1/s				0.91	1.15	0.18	0.49	
BF <sub>3</sub> (in)	ppmv	2.84	2.84	2.84					
BF <sub>3</sub> (out)	ppmv	3.51*	3.51*	3.51*					
HF(in)	ppmv				8.92	11.05	12.65	12.65	15.29
HF(out)	ppmv				<1.00*	<1.00*	<1.00*	<1.00*	**
K <sub>oga</sub> (HF)	1/s				>1.94	<2.13	>1.13	>1.13	
Footnotes:									
NOTE: Runs 1-3 were made using a cylinder supposed to contain BF <sub>3</sub> in Nitrogen.									
Upon further analysis of the available spectrum (from Runs 1-3) it was found that there was no BF <sub>3</sub> (or HF) present in this cylinder.									
F2=0.1 ppmv is very close to the detection limit of the impinger.									

TABLE D-9				
Components:		Run 9-1	Run 9-2	Run 9-3
	HNO <sub>3</sub>			
		2/23/95	2/23/95	2/23/95
G	lb/min	0.021	0.021	0.042
L	lb/min	0.042	0.012	0.042
L/G	gal/kcf(22°C)	16.74	4.78	8.37
_P	in. water	0.98	1.17	1.09
HNO <sub>3</sub> (in)	ppmv	13.77	13.77	52.09
HNO <sub>3</sub> (out)	ppmv	<0.57*	<0.57*	<0.57*
K <sub>oga</sub> (HNO <sub>3</sub> )	1/s	>1.41	>1.41	>4.01
Footnotes:				
*No detect.				
NOTE: HNO <sub>3</sub> vapor was generated using a solution of nitric acid (40% wt.)				
These experiments were conducted to study the absorption efficiency of HNO <sub>3</sub> and H <sub>2</sub> SO <sub>4</sub> .				
Due to the low vapor pressure of sulfuric acid (even in 98% solution) none was detected in the vapor phase.				

TABLE D-10				
Components:		Run 10-1	Run 10-2	Run 10-3
	HBr			
		2/27/95	2/27/95	2/27/95
G	lb/min	0.021	0.021	0.042
L	lb/min	0.042	0.012	0.042
L/G	gal/kcf(22°C)	16.74	4.78	8.37
_P	in. water	0.36	0.34	0.95
HBr (in)	ppmv	11.42	11.42	35.03
HBr (out)	ppmv	<0.28*	<0.28*	<0.32*
K <sub>oga</sub> (HBr)	1/s	>1.58	>1.58	>3.04
Footnotes:				
*No detect.				
NOTE: HBr vapor was generated using a solution of hydrobromic acid (48% wt.).				

TABLE D-11				
Components:		Run 11-1	Run 11-2	Run 11-3
	HCl			
		2/28/95	2/28/95	3/1/95
G	lb/min	0.021	0.021	0.21
L	lb/min	0.042	0.042	0.042
L/G	gal/kcf(22°C)	16.74	16.74	16.74
_P	in. water	0.43	0.30	0.32
HCl(in)	ppmv	14.01	14.01	12.91
HCl(out)	ppmv	<0.18*	<0.18*	<0.18*
K <sub>oga</sub> (HCl)	1/s	>1.93	>1.93	>1.90
Footnotes:				
*No detect.				
NOTE: The above experiments were replicate runs. The cylinder consisting of HCl/HBr was used, since the delay in obtaining new HCl cylinders could not be accommodated in the experimental schedule.				

TABLE D-12			
Components:		Run 1	Run 2
	HCl		
		3/1/95	3/1/95
Scrubbing Liquid		caustic(pH = 9)	water(pH = 4.7)
G	lb/min	0.021	0.021
L	lb/min	0.042	0.042
L/G	gal/kcf(22°C)	16.74	16.74
_P	in. water	0.27	0.48
HCl(in)	ppmv	7.02	7.02
HCl(out)	ppmv	0.19	0.68
K <sub>oga</sub> (HCl)	1/s	1.60	1.04
Footnotes:			
NOTE: Distilled Water at pH=4.7 was used for Run 2.			
The above experiments were conducted using a feed cylinder of HCl/Cl <sub>2</sub> . These experiments were conducted to study the absorption of HCl in the presence and absence of NaOH. The time delay in obtaining new cylinders of HCl caused us to use the HCl/Cl <sub>2</sub> cylinder available.			

TABLE D-13				
Components:		Run 13-1	Run 13-2	Run 13-3
	H <sub>2</sub> O <sub>2</sub>			
		3/3/95	3/3/95	3/3/95
G	lb/min	0.021	0.021	0.042
L	lb/min	0.042	0.012	0.042
L/G	gal/kcf(22°C)	16.74	4.78	89.37
_P	in. water	0.34	0.34	0.75
H <sub>2</sub> O <sub>2</sub> (in)	ppmv	*	*	*
H <sub>2</sub> O <sub>2</sub> (out)	ppmv	*	*	*
Footnotes:				
* No detect				
NOTE: Hydrogen peroxide vapor was generated using a 40% solution of hydrogen peroxide.				
No hydrogen peroxide was detected in the vapor phase.				





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