

**Appendix AMP – Alternative Monitoring Plan:**

EPA Approval dated April 21, 2005

CF Industries' Additional Information dated February 25, 2005

CF Industries' Application for Approval of Alternative Monitoring Plan dated May 3, 2004



UNITED STATES ENVIRONMENTAL PROTECTION AGENCY

REGION 4  
ATLANTA FEDERAL CENTER  
61 FORSYTH STREET  
ATLANTA, GEORGIA 30303-8960

APR 21 2005

RECEIVED

APR 25 2005

4APT-ATMB

Herschel E. Morris  
General Manager  
CF Industries, Inc.  
Plant City Phosphate Complex  
P. O. Drawer L  
Plant City, Florida 33564-9007

BUREAU OF AIR REGULATION

Dear Mr. Morris:

This is in response to your letter dated May 3, 2004, regarding an application for approval of alternative monitoring for the CF Industries, Inc. Plant City Phosphate Complex (CFI), and also your letter dated February 25, 2005, regarding additional information to support the alternative monitoring request. CFI is subject to the Phosphate Acid Manufacturing MACT, 40 CFR Part 63, Subpart AA, and the Phosphate Fertilizers Production MACT, 40 CFR Part 63, Subpart BB. Alternative monitoring is being requested, pursuant to Subpart BB, for the Granulation Plants A, X, Y, and Z.

Granulation Plants X, Y, and Z are identical plants producing granulated ammonium phosphate fertilizer products. The gas streams from each of the three plants pass through systems of 10 individual scrubbers, consisting of primary (phosphoric acid scrubbing medium) scrubbers, secondary (process water scrubbing medium) scrubbers, and a final pH-controlled fresh water spray, fluoride abatement scrubber. Scrubber segments (groups of scrubbers treating gases from the respective Fume, Dryer, Cooler, or Dust sources) are connected in series with the flow of gases through the entire segment to be monitored by the combined pressure drop across the segment. The liquid delivery pressure in the pond water cyclonic scrubbers will be measured and recorded manually. The water flow and pH of the abatement scrubber water will be monitored and recorded continuously. The flow of the phosphoric acid scrubbing medium to the primary scrubbers will not be monitored, as these scrubbers do not function to remove fluorides from the gas stream.

Granulation Plant A also produces granulated ammonium phosphate fertilizer products. Although the equipment and process in Plant A is very similar to the equipment and process in Plants X, Y, and Z, Plant A is older, smaller, and serves as a back-up unit for the other three plants. CFI is proposing to continuously monitor the gas pressure drop across each of the scrubber segments, and to continuously monitor the water flow in the header line to the freshwater downcomer scrubber nozzles, the water flow to the fluoride abatement scrubber, and the pH of the abatement scrubber water.

The proposed alternative monitoring consists of the following:

1. In each of the four granulation plants, continuous monitoring and recording of the fluoride abatement scrubber liquid pH is proposed in lieu of the pressure drop across the abatement scrubber. A minimum pH of 4.5 has been demonstrated to the Florida Department of Environmental Protection to be a viable limitation and is a condition of CFI's current Title V permit. The pressure drop across the abatement scrubber is not proposed for measurement because it is an extremely low value and meaningful variations would not be detectable.
2. In each of the four granulation plants, the pressure drop for each of the parallel scrubber segments upstream of the fan and fluorine abatement scrubber is proposed to be continuously monitored and recorded, in lieu of the pressure drop across each scrubber.
3. In Granulation Plant A, continuous monitoring and recording of the water flow through the header feeding the three downcomer scrubbers is proposed.
4. In Granulation Plants X, Y, and Z, the secondary scrubber liquid flow condition is proposed to be monitored by pressure gauges with the readings manually recorded at 2-hour intervals.
5. In each of the four granulation plants, CFI proposes not to monitor the liquid flows to the primary scrubbers on the basis that they are inherent process equipment which serves the purpose of recovering and returning product (i.e., nitrogen and phosphate) to the production process.

Justification for the proposed alternative monitoring is based on CFI's determination that the Subpart BB scrubber monitoring requirements will not result in an appreciable environmental benefit through a reduction in hydrogen fluoride emissions, requires a substantial expenditure of funds for the purchase and installation of monitoring equipment due to the unusually large number of scrubbers in the CFI Granulation plants, and due to the large number of scrubbers there is an unreasonably high cost-to-benefit ratio in comparison with the acceptable ratio stated by the Environmental Protection Agency (EPA) in the Subpart BB preamble.

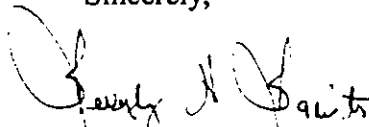
We have completed our review of the CFI proposed alternative monitoring plan and have one outstanding issue regarding the test plans to establish scrubber segment pressure ranges in each of the four granulation plants. In section 3 of the HF MACT Initial Performance Test Plan for CF Industries, dated February 2005, the test plans for establishing the allowable scrubber segment pressure range describe the process as a minimum of two test runs, with a minimum of one test run performed at the lower end of the scrubber pressure drop and liquid flow rate range, and a minimum of one test run performed at the upper end of the scrubber pressure drop range and liquid flow rate range. It is our position that a minimum of three test runs should be conducted at both the lower and upper end of the pressure drop to improve the odds of obtaining representative results. In addition to concerns about the representativeness of results from a

single test run, CFI could have difficulty complying with the scrubber flow limits set using the test results if there are any process or testing anomalies during a single test run. Therefore, as a final action on CFI's alternative monitoring request and based on information contained in the original May 3, 2004, request and the additional information dated February 25, 2005, EPA approves CFI's alternative monitoring request for Granulation Plants A, X, Y, and Z with the following condition:

- \* For establishing the scrubber segments pressure drop range during the required performance test, CFI shall perform a minimum of three test runs for the lower end of the pressure drop range and a minimum of three test runs for the upper end of the pressure drop.

Please note that the review and approval of CFI's alternative monitoring request was coordinated with the Hillsborough County, Florida, Environmental Protection Commission. If you have questions regarding this alternative monitoring request, please contact Lee Page of the EPA Region 4 staff at (404) 562-9131.

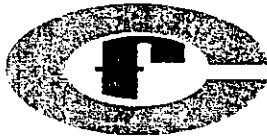
Sincerely,



Beverly H. Banister  
Director  
Air, Pesticides & Toxics  
Management Division

cc: Ron Dennis, Hillsborough County EPC  
✓ Cindy Phillips, FLDEP

P.O. Drawer L.  
Plant City, Florida 33564-9007  
Telephone: 813/782-1591



**CF Industries** Inc.  
Plant City Phosphate Complex

February 25, 2005

RECEIVED  
FEB 28 2005  
Bureau of Air Monitoring  
& Mobile Sources

R. Douglas Neeley  
Chief  
Air Toxics and Monitoring Branch  
Air, Pesticides, and Toxics Management Division  
United States Environmental Protection Agency  
Region IV  
Atlanta Federal Center  
61 Forsyth Street  
Atlanta, Georgia 30303-8960

Dear Mr. Neeley:

Enclosed is the CF Industries, Inc., response to your October 12, 2004, letter requesting addition information regarding the CF proposed alternative monitoring plan. This response, as requested, includes specific answers for the requests posed by the Environmental Protection Commission of Hillsborough County; a consolidated presentation of the proposed plan, and an Initial Performance Test Plan.

As stated in CF's May 3, 2004, submittal, CF remains available and would welcome a meeting with EPA to discuss this proposal.

Please call Tom Edwards at 813-364-5608 with any questions on this submittal, or to arrange such a meeting.

Sincerely,

Herschel E. Morris  
Vice President Phosphate Operations and  
General Manager

cc: Errin Pichard, FDEP  
Ronald Dennis, EPCHC  
Tom Edwards, CFI  
Jim Alves, HGS

**Responses to Environmental Protection Commission of Hillsborough County**  
**Requests Dated July 6, 2004**

**EPCHC Request 1:**

1. We assumed that the proposed alternative monitoring plan is the one summarized in Attachment 7 and dated May 3, 2004. If this is so, we need more details on this plan like those that were provided in the earlier one given in Appendix E. In particular, we would like to see Figure 1 – XYZ Granulation Scrubber Schematic – Single Granulation Train updated to reflect the table in Attachment 7. We also would like to see a similar schematic for the A Granulation Plant. While the appendices and attachments given in the application were informative from an historical perspective, they were confusing as to what was the final alternative monitoring plan being requested. Therefore, we would like to see a more detailed and coherent alternate monitoring plan application presented for approval that meets the requirements of 40 CFR Part 63.8(f)(4)(ii).

**CF Industries Response:**

The final proposed alternative monitoring plan is enclosed, and includes the summary monitoring table, the schematic diagrams, and the other necessary information.

**EPCHC Request 2:**

2. For Fume Pondwater Cyclonic Scrubbers, Dryer Pondwater Scrubbers, and Cooler Pondwater Scrubbers, the alternative monitoring plan presented in Attachment 7 shows that liquid monitoring will be conducted by 2-hour interval delivery pressure. Even though CF Industries has shown in Figure 4 of Appendix E a relationship between the TDH of the pump and flow rate, this relationship is curvilinear and will not correspond one-to-one to the plus or minus twenty percent of the baseline average value for liquid flow specified by 40 CFR 63 Subpart BB.

**CF Industries Response:**

The original CF proposal dated June 5, 2003, was to monitor total dynamic head (TDH) on the liquid feed pumps to the freshwater abatement scrubbers. The proposal was changed in later submittals to delete the TDH measurement and substitute flow measurement, which is the same indicator parameter specified by the Subpart BB rule.

For the secondary pond water cyclonic scrubbers, CF proposes the 2-hour interval monitoring of the spray header pressure. The third EPCHC comment concurs that this proposal is acceptable.

### EPCHC Request 3:

3. CFI has three sets of scrubbers considered to be part of separate scrubbing systems and a final abatement scrubber. Pressure drops are measured and recorded per scrubbing system and not per scrubber. In addition, liquid flow rate is currently not monitored in the system and is not proposed to be monitored as required in the above mentioned monitoring requirements. EPC staff does not have reasonable assurance that this monitoring approach will be adequate in showing problems in the system.

For example, CFI conducted a test on the "Z" granulation unit on March 11, 2003. This test had to be postponed after the first run showed fluoride emissions above the permit limit. Indicators such as the pressure drop across the scrubber system and scrubber pump delivery pressure showed normal values. Further investigation showed that the sprayer in the fume cyclonic acid scrubber fell off, thus affecting the efficiency of the entire scrubber system. Even though according to CFI this was a one time event, problems like this are a possibility and CFI does not appear have the proper measures in place to identify these types of problems.

On the other hand, we have no objection to the 2-hour interval for monitoring the water delivery pressure on the spray headers for the primary and secondary scrubbers. Even though 40 CFR 63 Subpart BB specifies 15-minute block averages for the liquid monitoring system, this is not a significant change since most spray header failures will be gradual rather than catastrophic.

In this application, CFI submitted a summary table (see Attachment 7) that shows the proposed liquid and gas monitoring that will be conducted as part of their alternative monitoring plan to comply with 40 CFR Part 63.625. However, even though this plan does not appear to meet the scrubbing control system monitoring requirements specified in 40 CFR Part 63.250 (c) (1) and (2), EPC staff believes that the plan can be acceptable with some changes described below.

CFI should measure the water delivery pressure on the spray headers for the primary and secondary scrubbers and measure the pressure drop on the venturi scrubbers. The primary and secondary scrubbers are cyclonic spray scrubbers. Typically, these scrubbers have a relatively small pressure drop across them (i.e., 1 to 2 inches of water). It is very unlikely that any loss of water to such a scrubber would be detected in the segment pressure drop. Therefore, a measure of liquid flow is needed. Since delivery pressure is a surrogate for liquid flow, we can accept it for liquid monitoring provided it is measured at the spray header and not at the scrubber pump. On the other hand, pressure drop across a venturi scrubber, which is much higher than that across a cyclonic spray scrubber, is affected by both the gas velocity and the scrubbing liquid flow rate. Therefore, we can accept the segment pressure drop for both liquid and gas monitoring of the venturi scrubbers.

**CF Industries Response:**

Regarding the EPCHC reservations about the CF proposal not to monitor liquid flows, the comment does not recognize the flow monitoring proposed for the freshwater fluorine abatement scrubber. CF maintains that this approach is justified due to the lower-than-expected concentrations of hydrogen fluoride shown to be present in the stack gases, the cost of the flow monitoring instrumentation for the number of scrubbers present, and the fact that the fluorine abatement scrubber is a unique and significant extra layer of scrubbing not used commonly in the phosphate industry. By providing these fresh water scrubbers, CF has placed significant financial resources into extra pollution control equipment to reduce fluoride emissions, and therefore the monitoring of upstream scrubbers does not carry as much importance as it does for other systems with fewer scrubbers.

The 2003 incident cited by the EPCHC, in which an acid spray nozzle was missing in the fume cyclonic scrubber, has been determined by CF not to be the cause of elevated fluoride emissions. The comments by the design engineers included in Appendix B of the enclosed Alternative Monitoring Plan support this conclusion. The phosphoric acid used in these scrubbers does not remove fluorides from the gas stream. Consequently, CF proposes not to monitor the acid flow or pressure to these scrubbers, as they are not fluoride emission control equipment. This rationale is presented in Section 5.0 of the enclosed Alternative Monitoring Plan.

The EPCHC comment concludes that the measurement of water delivery pressure to the secondary cyclonic scrubbers and segment pressure drop are acceptable.

**EPCHC Request 4:**

4. If further evaluation of this proposed monitoring plan is take place, CFI should identify the different types of contingencies that could take place in their granulation processes and the monitoring measures that will identify each problem properly and in a timely manner.

**CF Industries Response:**

This analysis is provided in the enclosed Alternative Monitoring Plan, Section 5.0.



**ALTERNATIVE MONITORING PLAN**

**CF Industries, Inc.  
Plant City Phosphate Complex  
10608 Paul Buchman Highway  
Plant City, Florida 33565**

**February 25, 2005**

## ALTERNATIVE MONITORING PLAN

### TABLE OF CONTENTS

0.0	Proposed Alternative Monitoring Plan Summary	1
1.0	Phosphoric Acid Plants	1
1.1	Performance Indicators	1
1.2	Measurement Techniques	1
1.3	Monitoring Frequency	1
1.4	Averaging Time	1
2.0	“X, Y, and Z” Granulation Plants	1
2.1	Performance Indicators	2
2.2	Measurement Techniques	2
2.3	Monitoring Frequency	3
2.4	Averaging Time	3
3.0	“A” Granulation Plant	3
3.1	Performance Indicators	4
3.2	Measurement Techniques	4
3.3	Monitoring Frequency	4
3.4	Averaging Time	4
4.0	Economic Justification for Alternative Monitoring	4
5.0	Technical Justification for Alternative Monitoring	5

### TABLES

Table 1 – Alternative Monitoring Plan Summary	6
Table 2 – Emission Estimates for HF	7
Table 3 – Equipment List for Rule – specified Monitoring	8
Table 4 – Cost Estimate for Rule-specified Monitoring	9

## **FIGURES**

Figure 1 – XYZ DAP/MAP Granulation Block Flow Diagram	10
Figure 2 – XYZ DAP/MAP Granulation Scrubber Schematic	11
Figure 3 – A DAP/MAP Granulation Block Flow Diagram	12
Figure 4 – A DAP/MAP Granulation Scrubber Schematic	13

## **APPENDICES**

Appendix A -	Extractive FTIR Testing for Hydrogen Fluoride in the X-DAP, Y-MAP, B-PAP, and ACU Stack Emissions, May, 2002.
Appendix B -	Design Engineer's Comments
Appendix C -	HF MACT Initial Performance Test Plan

## **0.0 Proposed Alternative Monitoring Plan Summary**

The proposed monitoring in the phosphoric acid plants will meet the requirements of the Hydrogen Fluoride Maximum Achievable Control Technology (HF MACT) Rule, 40 CFR 63, Subpart AA. However, in the granulation plants (A, X, Y, and Z) substantial changes to the Subpart BB Rule monitoring are being proposed in the Alternative Monitoring Plan. Table 1 provides a summary of the proposed scrubber monitoring. Sections 1.0 through 3.0 of the Plan describe the pollution control systems and the proposed monitoring of those systems in the phosphoric acid plants and granulation plants which are subject to the rule. Sections 4.0 and 5.0 discuss the economic and technical justification for the proposed alternative monitoring plan. The emissions from the affected plants currently meet the NESHAP emission standards established in the rule and additional pollution control equipment is therefore not required for HF MACT compliance.

### **1.0 Phosphoric Acid Plants**

In the phosphoric acid plants (EU 004, EU 009) there are no planned deviations from the monitoring required in the HF MACT Rule, Subpart AA. These plants operate horizontal cross flow packed bed scrubbers and utilize process water for the scrubbing medium. The "A" Phosphoric Acid Plant (EU 004) has the existing installed equipment required to monitor scrubber water flow and pressure drop across the scrubber. In the "B" Phosphoric Acid Plant (EU 009), a scrubber water flow meter and differential pressure transmitter will be installed on the scrubber in order to meet the requirements.

#### **1.1 Performance Indicators**

The monitoring indicators specified by Subpart AA will be used. The scrubber water flow rate provides an indication that the water flow to the scrubber is sufficient, and the gas pressure drop is an indicator of scrubber packing integrity.

#### **1.2 Measurement Techniques**

The scrubber water flows and pressure drops will be monitored continuously using a magnetic flowmeter and differential pressure transmitters.

#### **1.3 Monitoring Frequency**

An Aspen Data Historian will record the values every 30 seconds.

#### **1.4 Averaging time**

The Data Historian will convert the measured values to fifteen-minute block averages. The Historian will average the fifteen-minute values over three-hour periods for the determination of compliance.

## **2.0 "X, Y, and Z" Granulation Plants**

Granulation Plants "X", "Y", and "Z" (EU011, EU012, EU013), are identical plants producing granulated ammonium phosphate fertilizer products (MAP and DAP). Alternatives to the monitoring required in the HF MACT Rule, Subpart BB, are being proposed for these plants, for the reasons explained in Sections 4.0 and 5.0. The gas streams from each of the three plants pass through systems of 10 individual scrubbers.

The scrubber system for each plant consists of primary (phosphoric acid scrubbing medium) venturi and cyclonic scrubbers on the fume, dryer, and dust systems for ammonia and product recovery; secondary (process water scrubbing medium) cyclonic scrubbers on the fume, dryer, and cooler systems; and a final pH-controlled, fresh water spray, fluoride abatement scrubber. The fluoride abatement scrubber collects the gas streams from the fume, dryer, cooler, and dust scrubber segments and subjects them to an intense fresh water scrub before exhausting the gases through the emission stack. The freshwater fluoride abatement scrubber functions as an extra layer of insurance against fluoride emissions including HF. Figure 1 is a process block flow diagram of the XYZ granulation plants. Figure 2 is a schematic diagram of the XYZ granulation plant scrubber systems.

The fluoride abatement scrubber is a vertical spray chamber scrubber with fresh water sprays and a chevron type structured packing for mist elimination. Since it uses fresh water scrubbing exclusively, the abatement scrubber is believed to be unique to CF within the Phosphate Industry. The abatement scrubber pump sump is initially filled with non-process reuse water. Water from the abatement scrubber sump is pumped through ammonia vaporizer heat exchangers where the water is cooled before being sprayed in the abatement scrubber. Scrubber water is cooler than the process gases and causes condensation of fresh water from the stream of air and process gases entering the scrubber. This results in a continuous source of makeup fresh water to the scrubber and results in a subsequent blow down of the scrubber water without any other makeup water source.

## **2.1 Performance Indicators**

As an alternative to the Subpart BB monitoring it is proposed that the gas pressure drop across each of the scrubber segments (groups of scrubbers connected in series treating gases from the respective Fume, Dryer, Cooler, or Dust sources) be monitored and recorded continuously. Since the scrubbers in each segment are connected in series, the flow of gases through the entire segment can be monitored by the combined pressure drop across the segment. The liquid delivery pressure in the pond water cyclonic scrubbers will be measured and recorded manually. The liquid water flow and pH of the abatement scrubber water will be monitored and recorded continuously. The flow of the phosphoric acid scrubbing medium to the primary scrubbers will not be monitored, as these scrubbers do not function to remove fluorides from the gas stream.

## **2.2 Measurement Techniques**

The segment pressure drops will be measured using differential pressure transmitters. Pressure gauges will measure the nozzle delivery pressure in the pond water cyclonic scrubbers. Magnetic flow meters will be installed to measure the liquid flow to the fluoride abatement scrubber sprays. Existing pH probes will monitor the pH of the abatement scrubber water.

### **2.3 Monitoring Frequency**

The fluoride abatement scrubber liquid water flow and pH, and the pressure drop through each parallel segment, will be monitored continuously. An Aspen Data Historian will record the measured values every 30 seconds. The liquid delivery pressure to the nozzles in the pond water cyclonic scrubbers will be manually recorded in the Historian at the 2-hour intervals specified in the facility's Compliance Assurance Monitoring Plan.

### **2.4 Averaging time**

The Data Historian will convert the continuously-measured values to fifteen-minute block averages. The Historian will average the fifteen-minute values over three-hour periods for the determination of compliance. The Historian will calculate three-hour running averages of the liquid delivery pressures to the secondary scrubber nozzles.

## **3.0 "A" Granulation Plant**

Granulation Plant "A" (EU010) also produces granulated ammonium phosphate fertilizer products MAP and DAP, but is older and smaller than the "X,Y, and Z" Plants, and currently serves as a "back-up" unit for the other three plants. Alternative monitoring to the monitoring specified in the Subpart BB rule is being proposed for this plant as well, for the reasons explained in Sections 4.0 and 5.0.

The gas streams from this plant pass through a system of 8 individual scrubbers consisting of primary (phosphoric acid scrubbing medium) venturi and cyclonic scrubbers followed by fresh water spray downcomer scrubbers in the combined dust/dryer segment and the fume segment; a fresh water spray downcomer scrubber in the cooler segment, and a final, pH-controlled, freshwater, fluoride abatement scrubber. The pH-controlled abatement scrubber water is also used in the downcomer scrubber sprays. The fluoride abatement scrubber collects the gas streams from the fume, dust/dryer, and cooler scrubber segments and subjects them to an intense fresh water scrub before exhausting the gases through the emission stack. The freshwater fluoride abatement scrubber functions as an extra layer of insurance against fluoride emissions including HF. Figure 3 is a process block flow diagram of the "A" Granulation Plant. Figure 4 is a schematic diagram of the "A" Granulation Plant scrubber system.

The fluoride abatement scrubber is a vertical spray chamber scrubber with fresh water sprays and a chevron type structured packing for mist elimination. Since it uses fresh water scrubbing exclusively, the abatement scrubber is believed to be unique to CF within the phosphate industry. The abatement scrubber pump sump is initially filled with non-process reuse water. Water from the abatement scrubber sump is pumped through ammonia vaporizers where the water is cooled before being sprayed in the abatement scrubber. Scrubber water is cooler than the process gases and causes condensation of fresh water from the stream of air and process gases entering the scrubber. This results in a continuous source of

makeup fresh water to the scrubber and results in a subsequent blow down of the scrubber water without any other makeup water source.

### **3.1 Performance Indicators**

As an alternative to the Subpart BB monitoring it is proposed that the gas pressure drop across each of the scrubber segments be monitored and recorded continuously. Also it is proposed to continuously monitor and record the liquid water flow in the header line to the freshwater downcomer scrubber nozzles, the liquid water flow to the fluoride abatement scrubber, and the pH of the abatement scrubber water. The flow of the phosphoric acid scrubbing medium to the primary scrubbers will not be monitored, as these scrubbers do not function to remove fluorides from the gas stream.

### **3.2 Measurement Techniques**

The segment pressure drops will be measured using differential pressure transmitters. The liquid water flow to the downcomer sprays and to the abatement scrubber will be measured with magnetic flow meters. The existing pH probe will monitor the pH of the abatement scrubber water.

### **3.3 Monitoring Frequency**

The abatement scrubber pump liquid water flow and pH, the liquid water flow to the downcomer scrubber nozzles, and the gas pressure drop through each scrubber segment will be monitored and recorded continuously. An Aspen Data Historian will record the values every 30 seconds.

### **3.4 Averaging Time**

The Data Historian will convert the recorded values to fifteen-minute block averages, and will average the fifteen-minute values over three-hour periods for the determination of compliance.

## **4.0 Economic Justification For Alternative Monitoring**

Alternative monitoring of the granulation plant scrubbers is being proposed on the grounds that the Subpart BB scrubber monitoring called for under Rule 40 CFR 63 will not result in an appreciable environmental benefit through a reduction in HF emissions, requires a substantial expenditure of funds for the purchase and installation of monitoring equipment due to the unusually large number of scrubbers in the CF granulation plants, and therefore has an unreasonably high cost-to-benefit ratio in comparison with the acceptable ratio stated by the Environmental Protection Agency in the rule preamble. CF was proactive in installing the four unique fresh water fluoride abatement scrubbers in 1975 as extra fluoride emission control devices, and has been consistently meeting the Subpart BB emission standards since that time. Plant stack testing using Fourier Transform Infrared technology (FTIR) has been conducted (Appendix A – URS Report). That testing has demonstrated that the CF Plant City Complex has an estimated HF emission potential of 1.7 TPY HF from point sources (Table 2 – Calculation of Annual HF Emissions). The implementation of additional monitoring equipment called for under

the HF MACT Rule (Table 3 – Equipment List) would cost an estimated \$1,161,000 (Table 4 – Cost Estimate) and is expected to have negligible impact on actual HF emissions from the complex. In order to calculate a cost-to-benefit ratio (dollar cost of additional monitoring equipment divided by reduction in tons of HF emitted), CF has assumed that, if all monitoring called for in the HFMACT rule were implemented, rare upsets in scrubber performance caused by plugging or disruption of scrubber liquid or gas flows could be detected more quickly than they are with monitoring under other rules (Periodic Monitoring and Compliance Assurance Monitoring). If the additional monitoring over a 15-year instrument life were able to reduce the HF emissions from point sources by a conservative 10%, then the cost-to-benefit ratio would be calculated to be \$453,000 per ton of HF [ $\$1,161,000 / (10\% \times 1.7 \text{ TPY HF} \times 15 \text{ years})$ ]. This number is 9 times higher than the cost-to-benefit ratio stated to be “inappropriately high” and “unreasonable in terms of cost” in EPA’s example presented in the rule preamble at Federal Register Vol. 64, Page 31361 and on Page 31369. In that example EPA concluded that an expense of \$50,000 per ton of abated HF emissions would not be economically justified. Ergo, the much higher cost per ton ratio of the Subpart BB monitoring for the CF granulation plant scrubbers is not justified, and the allowance of an alternative monitoring plan is reasonable.

#### **5.0 Technical Justification For Alternative Monitoring**

The CF monitoring proposal provides the monitoring specified by 40 CFR 63 Subpart AA for Phosphoric Acid Plants “A” and “B”. It also provides the monitoring specified by 40 CFR 63 Subpart BB for the fresh water liquid flow rates to the fluorine abatement scrubbers at the four Granulation Plants “A”, “X”, “Y”, and “Z”. The alternative monitoring elements of the CF proposal are justified as follows.

(1) In each of the four granulation plants, continuous monitoring and recording of the fluorine abatement scrubber liquid pH is proposed in lieu of the pressure drop across the abatement scrubber. The pH of the scrubber liquid is controlled above pH 4.5 by caustic addition, in order to maintain the affinity of the liquid for fluoride gases and any phosphoric acid droplets coming from the upstream scrubber stages. The 4.5 minimum pH has been demonstrated to the Florida Department of Environmental Protection to be a viable limitation and is a condition of the current Title V permit. A high pH in the scrubbing liquid would not reduce the absorption of HF or other fluorides, so an upper range limit is not needed. CF proposes to retain the limit as it currently exists in the permit without further performance testing.

The pressure drop across the abatement scrubber is not proposed for measurement because it is an extremely low value and meaningful variations would not be detectable. The scrubber body is a spray chamber with no packing and the chevron-type structured mist eliminator packing at the scrubber exit is not susceptible to plugging or corrosion. Also, a loss of the gas flow through the scrubber is extremely unlikely, so there is no malfunction condition involving the gas flow to be detected by measuring the pressure drop.



(2) In each of the four granulation plants, the segment pressure drop for each of the parallel scrubber segments upstream of the fan and fluorine abatement scrubber is proposed to be continuously monitored and recorded, in lieu of the pressure drop across each scrubber. This provides a measurable indicator of the gas flow through all the scrubbers, or of any blockage that might occur in the scrubber segment. There is no significant opportunity for the gases to escape the system as they flow through the scrubber segment toward the fan, so pressure drop monitoring of the scrubber segment is a satisfactory substitute for the monitoring of the pressure drop across each scrubber..

(3) In Granulation Plant "A", continuous monitoring and recording of the liquid water flow through the header feeding the three downcomer scrubbers is proposed. Blockage or corrosion damage to any of the scrubber nozzles is unlikely in this neutralized fresh water system, but any such malfunction would affect the flow rate through the header line.

(4) In Granulation Plants "X, Y, and Z", the secondary scrubber liquid flow condition is proposed to be monitored by pressure gauges with the readings manually recorded at 2-hour intervals as proposed in the facility's Compliance Assurance Monitoring Plan. The continuous monitoring of this parameter is not needed due to the cost and the back-up effect provided by the fluoride abatement scrubber operating downstream.

(5) In each of the four granulation plants, CF proposes not to monitor the liquid flows to the primary scrubbers (venturi/cyclonic scrubber combinations using 28% phosphoric acid as a scrubbing medium) on the same basis that they are excluded from the Compliance Assurance Monitoring Rule provisions in 40 CFR 64; ie. that they are Inherent Process Equipment which serves the purpose of recovering product to the process. These units were stated by the design engineer to have the purpose of recovering ammonia and product dust from the gas stream and returning it to the production process (Appendix B – Design Engineer's Comments). Because they use phosphoric acid as a scrubbing liquid at the same concentration as is present in the phosphoric acid reactor, which is known to be a major source of fluoride gases, these scrubbers should be considered a source of fluoride gases rather than fluoride emission control equipment. The primary scrubbers are thus not HF control equipment, but inherent process equipment for recovering nitrogen and phosphate process materials.

Additionally, the monitoring of liquid flows to these scrubbers is extremely problematic due to constant scaling and pluggage of the monitoring devices with precipitating gypsum and fluosilicate compounds.

## TABLES

**TABLE 1**  
**Alternative Monitoring Plan Summary**

Scrubber	Liquid Monitoring	Gas Monitoring
<b>"A" &amp; "B" Phosphoric Acid Plants:</b>		
A-Phosphoric Acid Packed Bed Cross-Flow Scrubber	Liquid Flow, continuous	Pressure Drop, continuous
B-Phosphoric Acid Packed Bed Cross-Flow Scrubber	Liquid Flow, continuous	Pressure Drop, continuous
<b>"A" Granulation Plant:</b>		
Dryer Acid Cyclonic Scrubber		Segment* Pressure Drop, continuous
Dryer Acid Venturi Scrubber		Segment* Pressure Drop, continuous
Reactor Acid Cyclonic Scrubber		Segment* Pressure Drop, continuous
Reactor Acid Venturi Scrubber		Segment* Pressure Drop, continuous
Downcomer Fresh Water Fluoride Scrubber	Liquid Flow**, continuous	Segment* Pressure Drop, continuous
Fresh Water Fluoride Abatement Scrubber	Liquid Flow, continuous & pH, continuous	***
<b>"X", "Y", "Z" Granulation Plants:</b>		
Fume Acid Venturi Scrubber (3)		Segment* Pressure Drop, continuous
Fume Acid Cyclonic Scrubber (3)		Segment* Pressure Drop, continuous
Fume Pond Water Cyclonic Scrubber (3)	Delivery Pressure, 2-hour interval	Segment* Pressure Drop, continuous
Dryer Acid Venturi Scrubber (3)		Segment* Pressure Drop, continuous
Dryer Acid Cyclonic Scrubber (3)		Segment* Pressure Drop, continuous
Dryer Pond Water Cyclonic Scrubbers (3)	Delivery Pressure, 2-hour interval	Segment* Pressure Drop, continuous
Cooler Pond Water Cyclonic Scrubber	Delivery Pressure, 2-hour interval	Segment* Pressure Drop, continuous
Dust Acid Venturi Scrubber (3)		Segment* Pressure Drop, continuous
Dust Acid Cyclonic Scrubbers (3)		Segment* Pressure Drop, continuous
Fresh Water Fluoride Abatement Scrubber (3)	Liquid Flow, continuous & pH, continuous	***

\* A segment constitutes a train of scrubbers in series or a single scrubber, excluding the fresh water fluoride abatement scrubber.

\*\* One flow meter in the common header pipe delivers water to the three downcomer scrubbers.

\*\*\* Gas flow indicated by Segment Pressure Drop.

# TABLE 2

## CF Industries Inc. Plant City Phosphate Complex Emission Estimates For HF

Source/Unit	Point Source Total Allowable F (TPY)	HF Factor (HF/F) Ratio	Point Source Potential to Emit HF (TPY)	Estimated Fugitive HF (TPY)	Total HF Emission Potential (TPY)	Notes
A-DAP/MAP <sup>a</sup>	6.04	4.1%	0.25	0.12	0.37	Assumes 0.5% uncaptured fumes from all sources & 99% scrubber efficiency
X-DAP/MAP/GTSP <sup>a,c</sup>	6.70	4.1%	0.27	0.14	0.41	Assumes 0.5% uncaptured fumes from all sources & 99% scrubber efficiency
Y-DAP/MAP/GTSP <sup>b,c</sup>	9.60	5.8%	0.56	0.28	0.84	Assumes 0.5% uncaptured fumes from all sources & 99% scrubber efficiency
Z-DAP/MAP <sup>a</sup>	6.31	4.1%	0.26	0.13	0.39	Assumes 0.5% uncaptured fumes from all sources & 99% scrubber efficiency
A-PAP <sup>d</sup>	5.20	3.0%	0.16	0.18	0.34	Assumes 0.5% uncaptured fumes from reactor, 10% uncaptured fumes from filters and other sources, 99% scrubber efficiency, 93% of fumes from reactor. <sup>e</sup>
B-PAP <sup>a</sup>	4.60	3.0%	0.14	0.16	0.30	Assumes 0.5% uncaptured fumes from reactor, 10% uncaptured fumes from filters and other sources, 99% scrubber efficiency, 93% of fumes from reactor. <sup>e</sup>
Acid Clarification	1.23	4.7%	0.06	0.03	0.09	Assumes 0.5% uncaptured fumes from all sources & 99% scrubber efficiency
Shipping Scrubber <sup>c</sup>	NA	NA	NA	NA	NA	Assumes 0.5% uncaptured fumes from all sources & 99% scrubber efficiency
Misc HF Sources				0.107	0.107	Assumes 1.51 Lb HF/day/acre from the surface area of tanks and ditches with pond water. Vacuum Pump HF emissions per AP-42 1/95 Table 8.9-1; Controlled emission factor for Phosphoric Acid Plant filter vacuum pump
Process Water Cooling Ponds <sup>f</sup>	NA	NA	NA	0.85	0.85	Uses 0.02 µg/(m <sup>2</sup> -s) HF pond emission factor from the 1/7/94 Radian report. Assumes an average 6.8MPH wind speed, an average annual pond water temperature of 95°F, and a pond coverage area of 311 Acres.
<b>Total</b>			<b>1.70</b>	<b>2.00</b>	<b>3.70</b>	

<sup>a</sup>Note: While permitted for DAP & MAP, these plants have only produced DAP in the last 10+Yr. No testing was done in A and Z DAP/MAP. Therefore, the X-DAP HF emission factor was used.

<sup>b</sup>Note: This plant produces both DAP & MAP on a routine basis. The Y-MAP HF emission factor was used because it was higher than the X-DAP factor.

<sup>c</sup>Note: GTSP has not been produced in more than 10 years. If GTSP is produced in the future, emission factors will be developed and the facility's status as a HAP source will be re-evaluated.

<sup>d</sup>Note: No testing was done in A-PAP. The emission factor for B-PAP was used for A-PAP.

<sup>e</sup>Note: Past fume duct tests in A & B PAP have indicated that 93% of the fluoride fumes entering the scrubbers come from the reactor. The filter and other sources contribute only 7% of the fluorides.

<sup>f</sup>Note: See Appendix B for sample calculations.

**TABLE 3 - Monitoring Equipment List For HFMACT Rule - Specified Monitoring**

	Area	Loop #	DWG. #	New/Exist.	Flow meter req'd	Size	DP req'd	Description
1	APAP	2185	20-TW-035	Exist.				APAP Scrubber Process Water Supply Flow
2	APAP	2185	20-TW-035A	Exist.				APAP Scrubber Pressure
3	BPAP	3098		New	1	8"		BPAP Scrubber Process Water Supply Flow
4	BPAP	3099		New			1	BPAP Scrubber Pressure
5	X DAP	4547X	5.1-T-51	Exist.				X Dryer Scrubber Pressure
6	X DAP	4545X	5.1-T-53	Exist.				X Dust Scrubber Pressure
7	X DAP	4546X	5.1-T-52	Exist.				X Fume Scrubber Pressure
8	X DAP	4560X	5.1-T-54	Exist.				X Cooler Scrubber Pressure
9	X DAP	4330X		New	1	4"		X Dryer Secondary Scrubber Flow (pond water supply)
10	X DAP	4331X		New	1	4"		X Fume Secondary Scrubber Flow (pond water supply)
49	Z DAP	4340Z		new				Z Abatement Scrubber Flow (pond water supply)
50	A DAP	4333A		New	1	6"		A DAP Dryer Venturi Scrubber Flow (low pres. liquor supply)
51	A DAP	4334A		New	1	6"		A DAP Fume Venturi Scrubber Flow (low pres. liquor supply)
52	A DAP	4336A		New	1	4"		A DAP Dryer Primary (cyclonic) Scrubber Flow (high pres. liquor supply)
53	A DAP	4337A		New	1	4"		A DAP Fume Primary (cyclonic) Scrubber Flow (high pres. liquor supply)
54	A DAP	4547A	5.0-T-23	Exist.				A DAP Dryer Scrubber Pressure
55	A DAP	4546A	5.0-T-22	Exist.				A DAP Fume Scrubber Pressure
56	A DAP	4339A		New	1	14"		A DAP Abatement Scrubber Flow (pond water supply)
57	A DAP	4340A		New			1	A DAP Abatement Scrubber Pressure

**TABLE 4****ADDITIONAL SCRUBBER PROCESS MONITORING COST ESTIMATE**

	Qty.	Spares		Total
4" meters	22	1	\$5,000.00	\$115,000.00
6" meters	9	1	\$5,400.00	\$54,000.00
8" meters	1	1	\$6,050.00	\$12,100.00
14" meters	4	1	\$11,000.00	\$55,000.00
DP's	6	1	\$2,500.00	\$17,500.00
Enclosures	42		\$950.00	\$39,900.00
I/O cabinet	3		\$2,000.00	\$6,000.00
JB's	10		\$550.00	\$5,500.00
PLC's	3		\$15,000.00	\$45,000.00
I/O cards	3		\$2,500.00	\$7,500.00
Mech Eng.	1		\$65,000.00	\$65,000.00
Elect. Eng.	1		\$45,000.00	\$45,000.00
Software Eng.	1		\$25,000.00	\$25,000.00
Mech. Installation	42		\$5,350.00	\$224,700.00
Elect. Installation	58		\$4,400.00	\$255,200.00
Taxes				\$27,000.00
Freight				\$10,000
Subtotal				\$1,009,400.00
Contingency 15%				<u>\$151,410.00</u>
Total				<b>\$1,161,000.00</b>

## **APPENDIX A**

### **Extractive FITR Testing for Hydrogen Fluoride**

# Extractive FTIR Testing for Hydrogen Fluoride in the X-DAP, Y-MAP, B-PAP and ACU Stack Emissions

## Final Document

### Submitted to:

CF Industries, Inc.  
10608 Paul Buchman Hwy  
Plant City, FL 33565

### Submitted by:

Curtis T. Laush, Ph.D.  
URS Corporation  
9400 Amberglen Boulevard (78729)  
P.O. Box 201088  
Austin, Texas 78720-1088

May 2002



Report Titled:

**Extractive FTIR Testing for Hydrogen Fluoride in the X-DAP,  
Y-MAP, B-PAP and ACU Stack Emissions**

Pages: 1 through 27

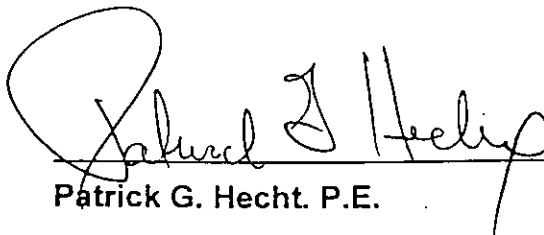
Reviewed & Sealed by:

Patrick G. Hecht. P.E.  
State of Florida, P.E. # 29507

URS Corporation — North Carolina  
General Contractor #50915

1600 Perimeter Park Drive  
Morrisville, NC 27560

September 2002

 9.30.2002  
Patrick G. Hecht. P.E. Date

Original Document In MS Word and secured in the Morrisville Office document  
management system as RTPDOCS-#6931-v3-ExtraTive\_FTIR\_Testing.DOC.

Copy #3

## 1.0 Executive Summary and Introduction

Measured hydrogen fluoride (HF) emissions from the phosphoric acid (B-PAP), acid clarification unit (ACU) and granulation process stacks are <1 ton/year, assuming:

- a conservative detection level of 36 ppbv at the X-train granulation stack (X-DAP);
- a measured average concentration of 246 ppbv at the B-PAP stack;
- a measured average concentration of 113 ppbv at the ACU stack;
- a measured average concentration 216 ppbv at the Y-train granulation stack (Y-MAP), and;
- Operations observed during measurement are typical for an 8760 hour year.

It is important to note that the stack chemistry also prohibits sample filtering at elevated temperatures, due to biasing effects caused by the chemical decomposition of particulates. A sampling probe and filter assembly maintained just above stack temperatures was used to prevent condensation losses and particulate dissociation, so that accurate reporting of HF emissions was ensured. The extractive FTIR method was validated by Method 301 spiking for HF monitoring at B-PAP and by EPA Method 320 spiking at the other stacks.

This document presents the results of a series of emission stack gas measurement tests performed by URS for CF Industries at the X-DAP, Y-MAP, ACU and B-PAP stacks. The measurements were made in a continuous and real-time fashion with an extractive-type Fourier Transform Infrared (FTIR) spectroscopic system. The system also included an aerosol/particulate filter assembly, with accommodations for spiking (diluting) the sample stream with certified gas standards per EPA Method 301 and 320.

The objective of this testing was to measure the gaseous HF emissions at each stack over a continuous three hour period during normal process conditions. The accuracy of the analytical monitoring method was validated by Method 301 to ensure that all the data were representative of actual stack emissions.

Testing took place between 10 April and 25 April 2002. The test schedule, sampling locations, and test conditions are summarized below in Table 1-1. The process and stack conditions are summarized in Table 1-2.

Table 1-1. Test Schedule – X-DAP, Y-MAP, B-PAP and ACU

Date	Activity	Test Conditions
10-Apr-02 thru 11-Apr-02	<ul style="list-style-type: none"> <li>Set-up and calibration of FTIR system at Y-MAP</li> <li>Sampling of Y-MAP stack emissions</li> <li>Spike tests with HF standard</li> </ul>	-Normal MAP process conditions -Contaminated extraction line
12-Apr-02 thru 15-Apr-02	<ul style="list-style-type: none"> <li>Set-up and calibration of FTIR system at X-DAP</li> <li>Method 320 pre-test spiking with HF standard</li> <li>Sampling of X-DAP stack emissions</li> <li>Method 320 post-test spiking with HF standard</li> </ul>	Normal DAP process conditions
16-Apr-02 thru 18-Apr-02	<ul style="list-style-type: none"> <li>Set-up and calibration of FTIR system at B-PAP</li> <li>Method 301 spiking at B-PAP</li> </ul>	Normal PAP process conditions
19-Apr-02	<ul style="list-style-type: none"> <li>Method 320 pre-test spiking with HF standard</li> <li>Sampling of B-PAP stack emissions</li> <li>Method 320 post-test spiking with HF standard</li> </ul>	Normal PAP process conditions
22-Apr-02 thru 23-Apr-02	<ul style="list-style-type: none"> <li>Set-up and calibration of FTIR system at Y-MAP again</li> <li>Method 320 pre-test spiking with HF standard</li> <li>Sampling of Y-MAP stack emissions</li> <li>Method 320 post-test spiking with HF standard</li> </ul>	Normal MAP Process conditions
24-Apr-02 thru 25-Apr-02	<ul style="list-style-type: none"> <li>Set-up and calibration of FTIR system at ACU</li> <li>Method 320 pre-test spiking with HF standard</li> <li>Sampling of ACU stack emissions</li> <li>Method 320 post-test spiking with HF standard</li> <li>Equipment pack-up</li> </ul>	Normal ACU conditions

**Table 1-2. CF Stack Testing – Process and Stack Conditions**  
(Provided by CF Industries, Inc.)

	Y-MAP 4/11/02	X-DAP 4/15/02	B-PAP 4/19/02	Y-MAP 4/23/02	Acid Clarification 4/25/02
	1:50 PM - 4:00 PM	11:09 PM - 3:40 PM	1:50 PM - 5:00 PM	10:15 AM - 4:40 PM	3:12 PM - 10:00 PM
Process Input Rate (TPH 100% P2O5)	37.0	36.6		30.9	
Process Input Rate (TPH 100% NH3)	7.9	15.9		8.3	
Process Output Rate @ 100% Recovery (TPH DAP)	71.9	80.4		60.2	
Fume Scrubbers Process Water Pressure (PSIG)	60	53		64	
Dryer Scrubbers Process Water Pressure (PSIG)	58	54		64	
Cooler Scrubbers Process Water Pressure (PSIG)	62	55		62	
Abatement Scrubber Water Pressure (PSIG)	38	42		38	
Dust Scrubber DP (Inches Water)	25	27		26	
Fume Scrubber DP (Inches Water)	30	25		30	
Dryer Scrubber DP (Inches Water)	24	27		26	
Cooler Scrubber DP (Inches Water)	10.0	5.8		8.0	
Abatement Scrubber pH	7.0	6.8		7.0	
B-PAP P2O5 Input From Phosphate Rock (TPH 100% P2O5)			82.7		
B-PAP Phosphate Rock Slurry Input (Wet Basis - TPH)			422.4		
B-PAP Sulfuric Acid Input (TPH 100% H2SO4)			213.6		
B-PAP Water Input From Sulfuric Acid (TPH)			16.1		
B-PAP Scrubber Outlet Temperature (°F)			105		
B-PAP Scrubber Water Pressure (°F)			50		
B-PAP Scrubber Fan Loading (Amperes)			211		
Acid Clarification Input Rate (TPH Acid)					422
Acid Clarification Scrubber Water Flow (GPM)					484
Acid Clarification Scrubber Fan Loading (Amperes)					95
Acid Clarification Scrubber Fan Temperature (°F)					99

## 2.0 Principles of FTIR Monitoring

Almost every chemical compound absorbs infrared (IR) light to some degree in a particular region of the mid-infrared spectrum. These absorption properties can be used to identify and quantify chemical compounds in a complex mixture of gases. As stated by Beer's Law, the magnitude of a compound's IR absorbance is directly proportional to the product of its concentration in the mixture and the sample cell optical path length. This is otherwise known as the compound's *optical depth*. The extractive FTIR instrument used by URS is able to achieve parts-per-billion (ppb) detection levels because the optical path length within the measurement cell is magnified many times by reflecting the IR beam between a series of mirrors before it reaches the detector. The mirrors provide a fixed optical path length best suited to the gas mixture being sampled. In this case, an optical path length of 20.1 meters was utilized.

### 2.1 The Spectrum Analysis Method

An infrared spectrum analysis is performed by matching the features of an observed spectrum to those of reference standards. If more than one feature is present in the same region, then a linear combination of references is used to match the compound feature. The standards are scaled to match the observed band intensities in the sample. This scaling also matches the unknown concentrations. An infrared spectrum can be collected and analyzed in approximately one second, but spectra are normally averaged over a one- or two-minute integration period to produce adequate signal-to-noise limits and ppb detection levels.

The scaled references are added together to produce a composite, which represents the best match with the sample. A classical least squares mathematical function is used to match the standards' absorption profiles with those of the observed spectrum in specified spectral analysis regions. The compounds of interest together with compounds expected to cause spectral interference are included in the analysis region.

#### 2.1.1 Creating the Spectrum Analysis Method

The spectrum analysis method used for the stack tests at CF Industries was developed by selecting the spectral regions and sub-regions that are least affected by primary IR absorbers ( $\text{H}_2\text{O}$  and  $\text{CO}_2$ , in this case) while also producing the best detection limit possible for the target compound (HF). Typically, an analysis method will be iteratively refined by using it to analyze a representative set of infrared spectra while varying the method. The optimum method is indicated when both the 95% confidence levels and the bias on the individual compounds are minimized. Table 2-1 lists the range of references included in the analysis method used by the

FTIR system for all stack tests. Each reference is described in terms of its optical depth (concentration times cell path length, or ppm\*m) range.

Table 2-1. Analysis Method Parameters for Major Contaminants and Spectroscopic Interferants

Compound	Optical Depth Range of References (ppm*m)	Estimate of Minimum Detection Limit (MDL)
H <sub>2</sub> O	28,870-27,509,700	N/A*
CO <sub>2</sub>	70.348-2110.430	N/A*
HF	1,000-2,000,000	18 ppbv

\* Determination of MDL not necessary because compound was always present in appreciable concentrations during sampling.

After setting up the FTIR instrument at each sampling location, signal-to-noise ratio (SNR) assessments were performed. This was determined on-site by measuring the noise equivalent absorbance (NEA) of each FTIR system while sampling nitrogen. The NEA is derived by ratioing two consecutive single beam spectra to produce a "zero" spectrum, then measuring the peak-to-peak absorbance at a frequency region of interest. This represents the noise level of the instruments under field conditions. By determining the concentration level for each contaminant that scales down its analyzed spectral features to the NEA (representing a SNR of 1 or better), the compound's SNR-limited minimum detection limit (MDL) can be estimated. These are listed in Table 2-1. *It should be noted that these values represent the lowest possible detection limits that the system hardware will allow.*

Therefore, it is important to note that these MDLs were estimated considering instrumental noise levels under field conditions *without* influences from the major spectroscopic interferants (H<sub>2</sub>O and CO<sub>2</sub>). When spectroscopic interferences *are* taken into account for those contaminants that have overlapping absorption features an increase in their MDLs are expected. A conservative estimate of that increase, based on experiences when sampling similar sources, is a factor of 2. This had come about by statistical analysis of those sources when it was known that the interferants were present at representative concentrations, but the contaminants of interest were known to be completely absent. Three times the standard deviation about the "zero" value ( $3\sigma$ ) for each contaminant resulted in an MDL twice as high as its corresponding SNR-limited MDL.

## 2.2 The Extractive FTIR and Sampling System

An extractive-type FTIR system was used for the stack testing conducted at CF Industries. An MKS (formerly, On-Line Technologies) FTIR spectrometer and sample cell were used to speciate and quantify the gaseous contaminants at each stack. Each sampling location was near the exit point of its respective stack, so the gas concentrations continuously monitored in real time were considered representative of what is emitted into the atmosphere (uniformly distributed in the stack with very little flow stratification). In general, the system components included a heated PFA-grade Teflon sample probe (3/8" OD), two heated mesh particulate filters (0.1  $\mu$ m pore size) in series, a heated PFA-grade Teflon extraction line, the On-Line FTIR spectrometer interfaced to a heated, nickel-coated sample cell, a sample pump and rotameter. A "tee" was placed either between the filters and the extraction line, or between the extraction line and sample cell, to allow the spiking of certified gas standards as near as possible to the point of stack gas extraction. The placement of the tee was determined by the stack chemistry (see Section 3.0). The schematic in Figure 2-1 displays the complete sampling system.

Given this configuration, real-time monitoring consisted of pulling a gas stream continuously from the sample port through the sampling system into the heated FTIR sample cell. Sample flow was maintained at approximately 5-15 liters per minute, depending on the isokinetic sampling requirements (see Section 3.0) by a diaphragm pump connected to the outlet of the FTIR cell. A heated rotameter at the sample cell exhaust was used to monitor the system sample flow.

Inside the FTIR cell, a set of optically matched gold-plated mirrors reflects an infrared beam through the sample gas multiple times. As the beam passes through the sample, the molecules in the sample absorb some of its energy. After exiting the cell, the infrared beam is directed to a liquid-nitrogen cooled mercury/cadmium/telluride (MCT) detector, a photoconductive device that produces an electrical voltage proportional to the amount of infrared light that strikes it. The strength of the absorption at particular frequencies is a measure of the compounds' concentration. The total distance traveled by the infrared beam inside the cell is the cell path length, and is an important variable used in determining sample concentrations. For this project, the cell path length was fixed at 20.1 meters.

The FTIR sample cell and extraction lines were maintained at a temperature of 150°C. The sample probe and filter assembly was maintained at a temperature slightly above stack conditions to preclude the chemical decomposition of fluoride-containing particulates (as per the *Test Plan for Quantification of Free Hydrogen Fluoride Emissions at CF Industries, Inc. Plant*

City, Florida submitted in February 2002, and approved with minor revision on April 9, 2002). Cell pressures were continuously recorded during measurement periods using a pressure sensor calibrated over the 0 – 900 torr range. Instrumental resolutions were set to  $0.5\text{ cm}^{-1}$  and signal averaging was performed over two-minute periods (per approved Test Plan).

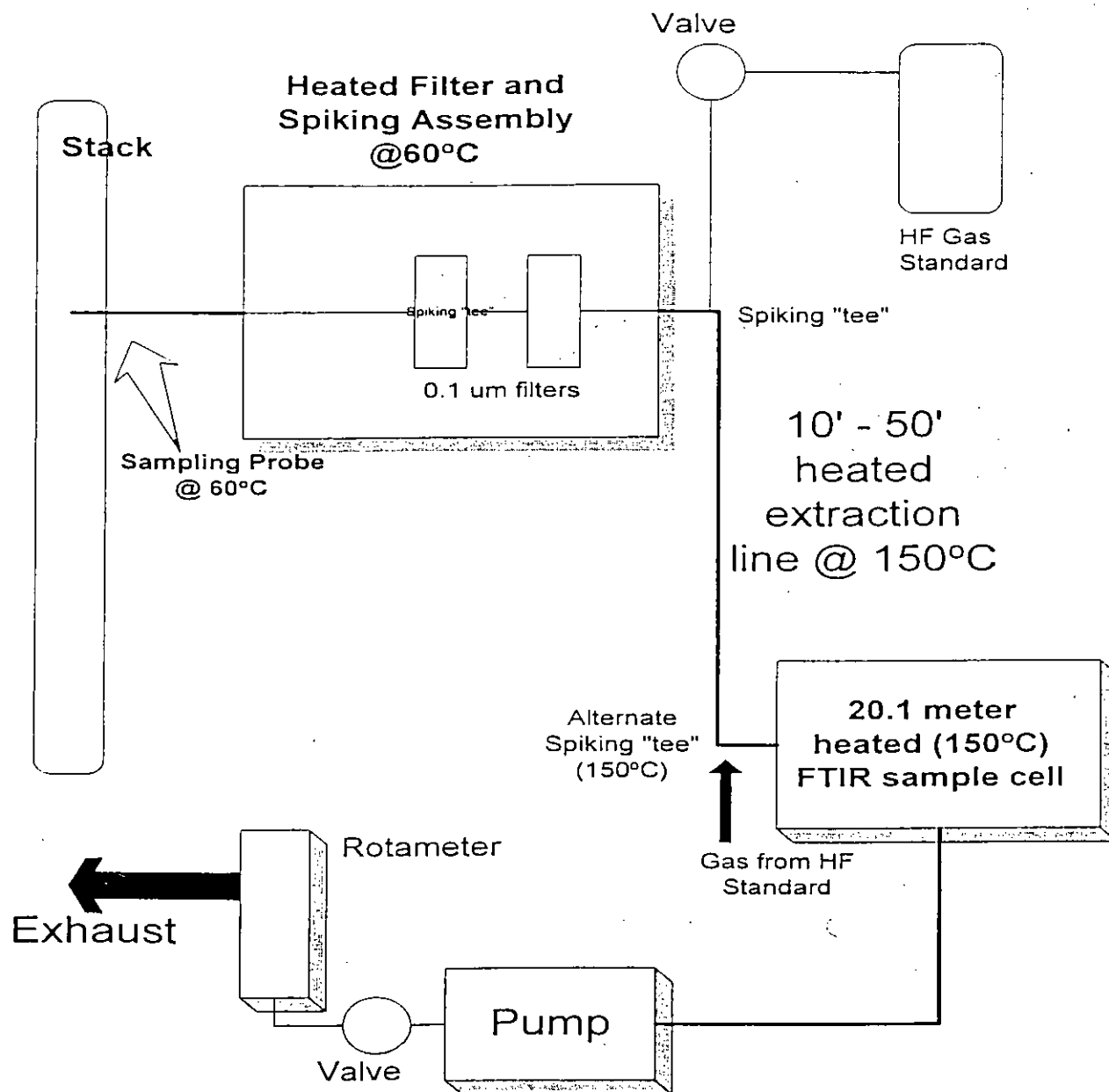


Figure 2-1. FTIR Sampling System Schematic



### 3.0 Stack Sampling Considerations

The stack chemistry at each location dictates how the sampling system must be configured to deliver representative gas streams to the FTIR sample cell. Regardless of sampling location, the sample probe and filter assembly must be maintained at a relatively low temperature (60-65°C), to preclude the dissociation of fluoride-containing particulates (aerosols) in the filters, but still above stack temperatures to prevent any condensation losses. It was the placement of the spiking tee that required special consideration at each stack because of the chemistry involved. The tee must be located at a point within the sampling system as close as possible to where stack gas is being initially extracted. Therefore, the spiking tee was located immediately downstream of the filters, but upstream of the extraction line, when sampling the B-PAP and ACU stacks.

For the granulation stacks, it was realized that HF recoveries would not be sufficient at this spiking tee location. The reason has nothing to do with the sampling system, but with the stack chemistry. The presence of  $\text{NH}_3$  in ppm-levels at Y-MAP requires the introduction of the HF standard into an extremely hot (well above 100°C) gas stream to prevent the reaction of the spike gas with ammonia to form additional  $\text{NH}_4\text{F}$ <sup>1</sup>. As a result, the spiking tee was placed further downstream within the sampling system, downstream of the extraction line but upstream of the sample cell. This location ensured mixing of the HF standard with stack gas under hot conditions.

It was requested that the stack gas be sampled under isokinetic conditions. This required matching the exhaust gas velocity within the stack to the sample probe extraction flow rate at each traverse point. EPA Method 1 determination of the number of traverse points gave the same result at most of the stacks: six points at each of two sampling ports situated 90° to each other. The ACU stack, however, required twelve points at each port. Table 3-1 summarizes the stack flow rate at each location and traverse point (as measured by CF Industries personnel via EPA Method 2 immediately prior to each FTIR sampling test) and the corresponding FTIR extraction flow rate, assuming a 0.116in. ID sample probe tip.

---

<sup>1</sup> For an overview of the reaction thermodynamics and kinetics associated with the formation of  $\text{NH}_4\text{F}$ , please refer to *Extractive FTIR Testing of the X-DAP, Y-MAP and B-PAP Emissions*, Section 5.0 and Appendix A, submitted in January 2002.

Table 3-1. Stack and Sample Extraction Flow Rates

Traverse Point #	X-DAP		Y-MAP		B-PAP		ACU	
	Stack flow	FTIR flow	Stack flow	FTIR flow	Stack flow	FTIR flow	Stack flow	FTIR flow
	ACFM	lpm	ACFM	lpm	ACFM	lpm	ACFM	lpm
1	148760	4.68	152515	4.80	35266	4.58	18766	3.77
2	153977	4.85	168535	5.30	40402	5.25	19626	3.95
3	159027	5.01	185065	5.83	42282	5.49	20179	4.06
4	180742	5.69	180743	5.69	41353	5.37	20981	4.22
5	177804	5.60	167110	5.26	38430	4.99	21241	4.27
6	171767	5.41	148760	4.68	29890	3.88	21753	4.37
7							22005	4.42
8							21753	4.37
9							21241	4.27
10							19626	3.95
11							18766	3.77
12							18766	3.77
1	135798	4.27	173150	5.45	35540	4.61	17554	3.53
2	174815	5.50	189123	5.95	39428	5.12	19904	4.00
3	180742	5.69	194774	6.13	42282	5.49	20717	4.16
4	171774	5.41	177804	5.60	42966	5.58	21499	4.32
5	159027	5.01	159033	5.01	40642	5.28	21499	4.32
6	141500	4.45	137726	4.33	34146	4.43	21499	4.32
7							22253	4.47
8							21753	4.37
9							21753	4.37
10							21753	4.37
11							21241	4.27
12							20179	4.06
Average Flow:	162977.8		169528.2		38552.25		20679.46	

## 4.0 Validations of the Analytical Method

EPA Method 320 procedures were followed during each FTIR sampling test, which require pre-test and post-test spiking of an HF gas standard while sampling native exhaust. The spikes were carried out at two distinct concentration levels immediately before the three-hour test, then immediately after the test to show that adequate system response and accuracy was maintained throughout. The location of the spiking tee within the sampling system was dictated by the stack chemistry (see Section 3.0) and the gas standard was injected in a continuous fashion through a mass flow controller. The gas standard contained HF at a relatively low concentration (3.5 ppm) and a tracer compound, SF<sub>6</sub> at 2.2 ppm, to allow for the precise determination of standard dilution. See Appendix A for a detailed description of the spiking procedure and calculations. It must be noted that the chemical reactivity associated with HF presents considerable challenges in the spiking procedure. Care was taken in sample line conditioning (passivation) before the spikes were delivered and sampling commenced. Enough time was allowed to elapse during the spikes to let the spike concentrations "level out".

An EPA Method 301 validation was performed at B-PAP to prove the applicability and accuracy of the extractive FTIR method for all the stacks tested. It consists of a series of 12 consecutive spikes at representative concentrations while sampling native exhaust. A statistical treatment of the 12-spiked/unspiked pairs determines the accuracy (acceptance criteria of  $\pm 30\%$ ), precision and bias factor (if needed) of the method. The B-PAP stack was chosen for this rigorous validation because it represented the worst-case testing scenario, i.e. an exhaust stream with representative concentrations of H<sub>2</sub>O and CO<sub>2</sub>, and the highest native concentrations of HF.

### 4.1 Instrument Calibrations and System Checks

A series of on-site calibration and system checks (outside of the gas standard validation spikes already discussed) was performed on the FTIR and sampling system prior to each test to ensure data of known quality. These tests consisted of the following:

- **Cell Leak Checks:** This test checks the integrity of the cell by pulling a vacuum on it and then monitoring the leak rate. The acceptance criteria for this test is a leak rate  $\leq 2$  torr/minute. The FTIR sample cell on-site was verified to have a leak rate well under 1 torr/minute at each of the four sampling locations (X-DAP, Y-MAP, B-PAP and ACU) prior to testing.
- **Infrared Detector Linearity Checks:** For best results, it must be assured that the infrared detector yields a linear response throughout a reasonable absorbance range and all the frequencies in a set of test spectra. A software linearizer is used to

continuously adjust the MCT detector preamp signal in order to achieve the desired response. To optimize the linearizer, background spectra are acquired without and with a polyethylene filmcard in the IR beam. Comparison of the strongly absorbing polyethylene bands in the low, mid and high frequency regions against a clean background enables the processor to appropriately set the linearizer terms (offset, linear, quad, cubic and delay). This procedure was run prior to the start of testing, and subsequent spectra were visually checked on a periodic basis to confirm that linearity was maintained.

- **Noise Equivalent Absorbance (NEA) or Signal-to-Noise Ratio (SNR) Tests:** This provides a measure of the sensitivity of the instrument for the specified spectral resolution (0.5 cm<sup>-1</sup>, in this case) and number of scans (108, or 1 minute of signal averaging, in this case). This is a measure of system noise. An NEA/SNR test was run upon set-up, then re-checked at each new sampling location. The results, which were used to assess the field detection limits listed in Table 2-1, were as follows:
  - Range = 1000-1100cm<sup>-1</sup>, RMS Noise=0.04%(0.194 mAU), SNR=2237
  - Range = 2400-2500cm<sup>-1</sup>, RMS Noise=0.04%(0.174 mAU), SNR=2487
  - Range = 4300-4400cm<sup>-1</sup>, RMS Noise=0.08%(0.338 mAU), SNR=1283
- **Path Length:** The sample cell used for these tests was geometrically fixed at 20.1 meters.
- **Spectrometer Frequency and Resolution Checks:** A real-time check of frequency position and resolution was performed prior to and directly after each round of testing by monitoring a specific water absorption line (present in ambient air). The position of this line must not deviate more than ±0.005 cm<sup>-1</sup> from the reference value and over the course of each test. Likewise, the line width (directly related to instrumental resolution) of this line must not deviate more than ±0.05 cm<sup>-1</sup> from the reference value and over the course of each test.
- **Spectral Background:** A spectral background is essentially a "blank spectrum" in that it does not contain any of the target compounds present in the sample. It was created by purging the cell with ultra-high-purity nitrogen while collecting a spectrum. This spectrum was then used by the analytical software to ratio against each sample spectrum to produce an absorbance spectrum for quantitative analysis. A new spectral background was generated prior to testing at each sampling location.

## 5.0 Stack Sampling Test Results

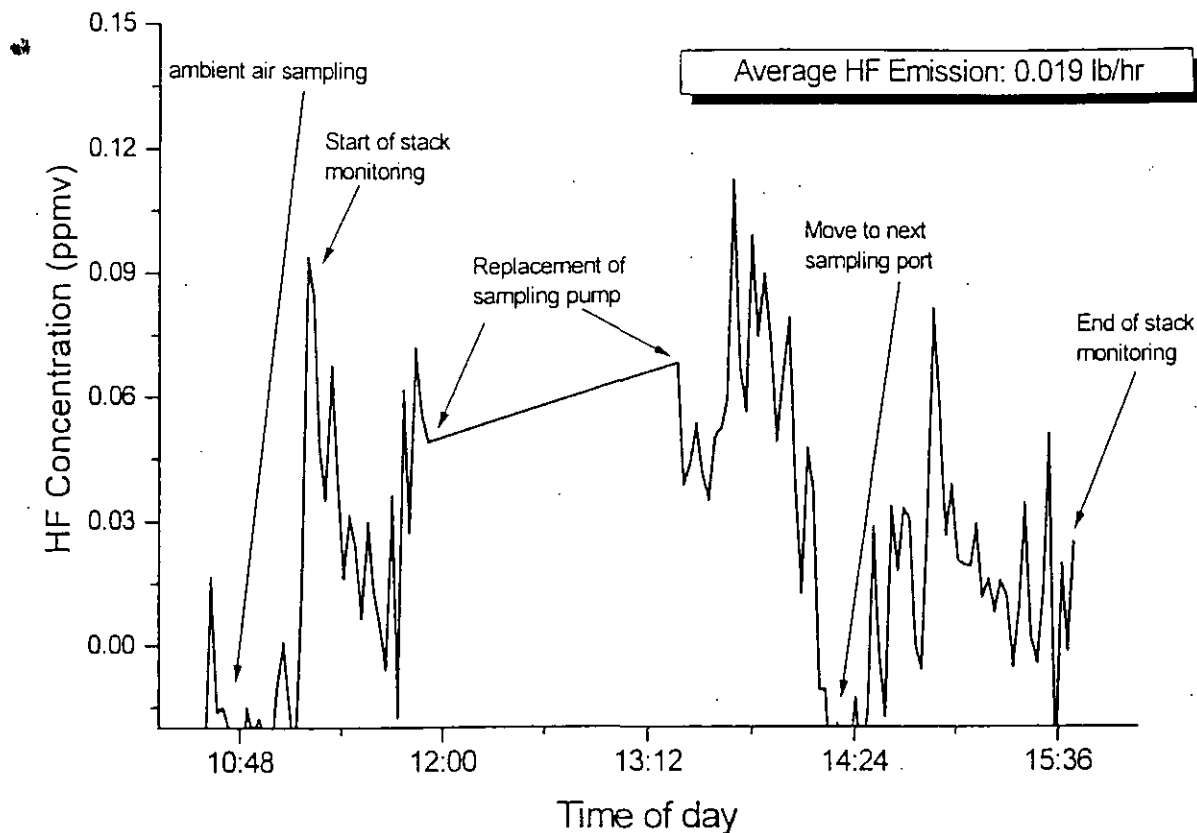
The results for each emissions test are reported in this section. They are categorized according to sampling location. Each FTIR sampling test consisted of a set of pre-test HF spikes (per Method 320), a continuous three-hour sampling run, with the sampling time at each traverse point equally divided, and a set of post-test HF spikes (per Method 320). See Sections 3.0 and 4.0 for details of the sampling system and method.

### 5.1 X-DAP Emissions Test

Extractive FTIR monitoring of HF at X-DAP was conducted on 15 April, 2002. The emission profile is plotted in Figure 5-1. Noted on the graph is when stack sampling began and ended, along with the times when the probe was out of the stack and ambient air was sampled (prior to the test and while the probe was moved from one stack sampling port to the other). The test was interrupted to allow for the replacement of the FTIR sampling pump (the original pump was beginning to fail) and is indicated in Figure 5-1. Upon averaging the concentrations reported in Figure 5-1, and factoring in the average stack flow rate reported in Table 3-1, an average HF mass emission rate of 0.019 lb/hr can be calculated. Following a convention often recommended by the EPA, a value of  $\frac{1}{2}$  the FTIR method MDL was assigned to each data point that was initially reported below the MDL for purposes of averaging. Given the conservative estimate of two times the SNR-limited MDL, or 36 ppbv, as the FTIR method MDL (see Section 2.1.1), a value of 18 ppbv was used.

HF spiking, per Method 320, was conducted prior to and immediately after this emissions test. The results are summarized in the following section.

Figure 5-1. X-DAP FTIR Emissions Test  
(15 April 2002)



#### 5.1.1 X-DAP Validation Spikes

The spiking of an HF certified gas standard was performed as stack gas was continuously extracted and analyzed at a central traverse point within X-DAP. It was necessary to deviate from the spiking procedure recommended by EPA Method 320, where the gas standard is injected close to the initial point of stack extraction, because of the stack chemistry. Since  $\text{NH}_3$  was present in the native exhaust at significant concentrations (roughly 40 ppmv, on average), it was critical to introduce the HF under elevated temperature conditions. This prevented the formation of  $\text{NH}_4\text{F}$ . Section 3.0 explains the need for the deviation in more detail and Figure 3-1 shows the alternate spiking "tee" location employed for the X-DAP tests. A gas standard containing HF (at 3.5 ppmv) was injected at constant flows (regulated by a mass flow controller) of 0.5 and 0.25 liters per minute over the sample gas. A spectroscopic tracer,  $\text{SF}_6$  (at 2.12 ppmv), was also in the gas standard blend to provide a precise means by which to calculate dilution ratios. Appendix A describes in detail how the tracer is used. Tables 5-1 and 5-2

summarize the results, which show good recovery of the expected HF concentration under stack dilution (using the EPA Method 320 allowances of 70%-130%), thereby validating the FTIR analysis method for this compound.

**Table 5-1. HF Spiking Parameters and Results at X-DAP: Pre-test**

Conc. SF <sub>6</sub> in gas cylinder (ppm), $C_{undil}$ :	2.12
Conc. SF <sub>6</sub> returned by method after analyte injection (ppm), $C_{dil}$ :	1 <sup>st</sup> spike: 0.32 2 <sup>nd</sup> spike: 0.17
Certified conc. of HF in gas cylinder (ppm), $T_{cert}$ :	3.5
Conc. native HF in stack, on average (ppm), $T_{native}$ :	0.018
Calculated conc. of HF after analyte injection (ppm), $T_{exp}$ :	1 <sup>st</sup> spike: 0.54 2 <sup>nd</sup> spike: 0.30
Measured conc. of HF by FTIR right before spike ends(ppm):	1 <sup>st</sup> spike: 0.50 2 <sup>nd</sup> spike: 0.28
% Recovery	1 <sup>st</sup> spike: 93% 2 <sup>nd</sup> spike: 93%

**Table 5-2. HF Spiking Parameters and Results at X-DAP: Post-test**

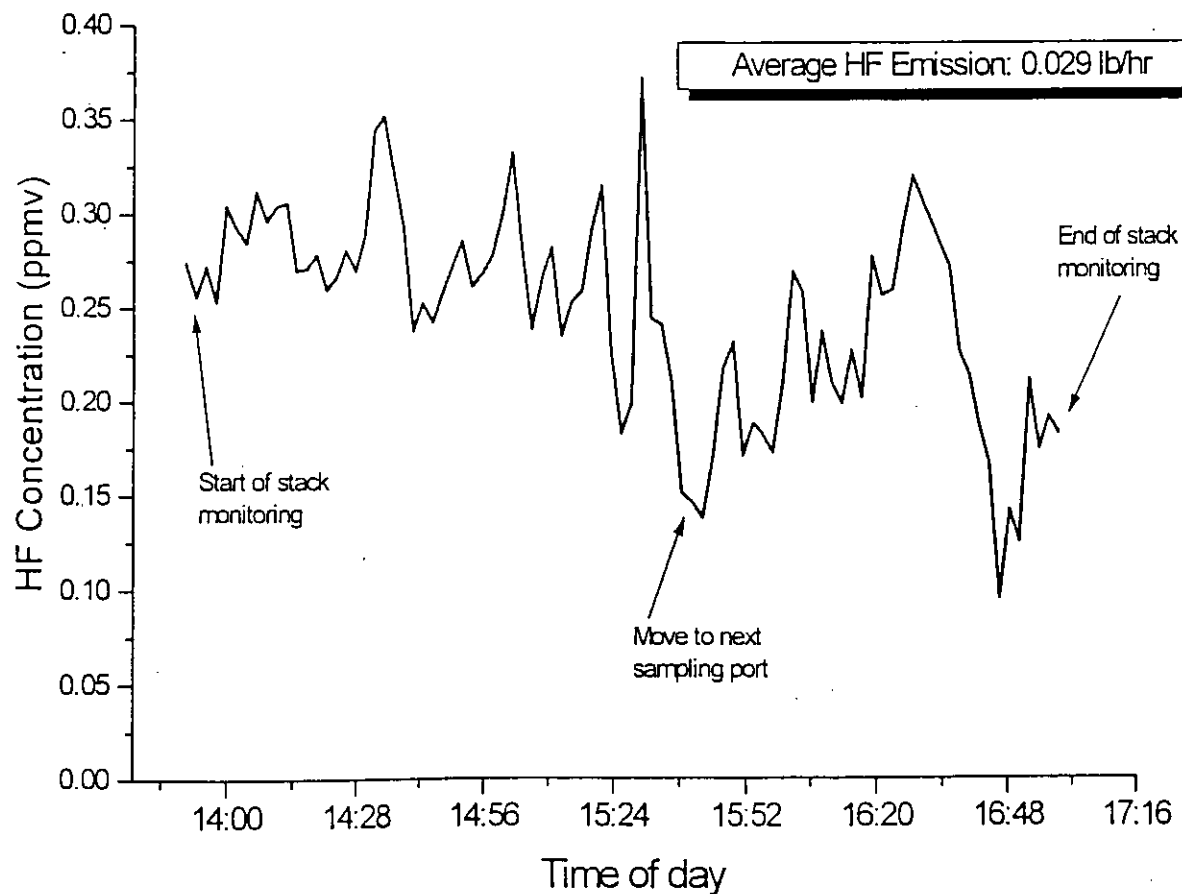
Conc. SF <sub>6</sub> in gas cylinder (ppm), $C_{undil}$ :	2.12
Conc. SF <sub>6</sub> returned by method after analyte injection (ppm), $C_{dil}$ :	1 <sup>st</sup> spike: 0.36 2 <sup>nd</sup> spike: 0.17
Certified conc. of HF in gas cylinder (ppm), $T_{cert}$ :	3.5
Conc. native HF in stack, on average (ppm), $T_{native}$ :	0.018
Calculated conc. of HF after analyte injection (ppm), $T_{exp}$ :	1 <sup>st</sup> spike: 0.61 2 <sup>nd</sup> spike: 0.30
Measured conc. of HF by FTIR right before spike ends(ppm):	1 <sup>st</sup> spike: 0.58 2 <sup>nd</sup> spike: 0.24
% Recovery	1 <sup>st</sup> spike: 95% 2 <sup>nd</sup> spike: 81%

## 5.2 B-PAP Emissions Test

Extractive FTIR monitoring of HF at B-PAP was conducted on 19 April, 2002. The emission profile is plotted in Figure 5-2. Noted on the graph is when stack sampling began and ended, along with the time when the probe was out of the stack and ambient air was sampled (while the probe was moved from one stack sampling port to the other). Upon averaging the concentrations reported in Figure 5-2, and factoring in the average stack flow rate reported in Table 3-1, an average HF mass emission rate of 0.029 lb/hr can be calculated.

HF spiking, per Method 320, was conducted prior to and immediately after this emissions test. The results are summarized in the following section.

Figure 5-2. B-PAP FTIR Emissions Test  
(19 April 2002)





### 5.2.1 B-PAP Validation Spikes

The spiking of an HF certified gas standard was performed as stack gas was continuously extracted and analyzed at a central traverse point within B-PAP. The gas standard was injected close to the initial point of stack extraction (no  $\text{NH}_3$  was present in this stack), per EPA Method 320. Section 3.0 explains the spiking procedure in more detail and Figure 3-1 shows the primary spiking "tee" location employed for the B-PAP tests. A gas standard containing HF (at 3.5 ppmv) was injected at constant flows (regulated by a mass flow controller) of 0.8 and 0.6 liters per minute over the sample gas. A spectroscopic tracer,  $\text{SF}_6$  (at 2.12 ppmv), was also in the gas standard blend to provide a precise means by which to calculate dilution ratios. Appendix A describes in detail how the tracer is used. Tables 5-3 and 5-4 summarize the results, which show good recovery of the expected HF concentration under stack dilution, thereby validating the FTIR analysis method for this compound. It should be noted that there were no means by which to simultaneously measure the native HF concentrations during the spike, so this value could only be extrapolated from the FTIR measurement immediately before the spike was injected.

Table 5-3. HF Spiking Parameters and Results at B-PAP: Pre-test

Conc. $\text{SF}_6$ in gas cylinder (ppm), $C_{\text{undil}}$ :	2.12
Conc. $\text{SF}_6$ returned by method after analyte injection (ppm), $C_{\text{dil}}$ :	1 <sup>st</sup> spike: 0.60 2 <sup>nd</sup> spike: 0.46
Certified conc. of HF in gas cylinder (ppm), $T_{\text{cert}}$ :	3.5
Conc. native HF in stack, before spike (ppm), $T_{\text{native}}$ :	0.20
Calculated conc. of HF after analyte injection (ppm), $T_{\text{exp}}$ :	1 <sup>st</sup> spike: 1.13 2 <sup>nd</sup> spike: 0.92
Measured conc. of HF by FTIR right before spike ends(ppm):	1 <sup>st</sup> spike: 0.92 2 <sup>nd</sup> spike: 0.83
% Recovery	1 <sup>st</sup> spike: 82% 2 <sup>nd</sup> spike: 91%

Table 5-4. HF Spiking Parameters and Results at B-PAP: Post-test

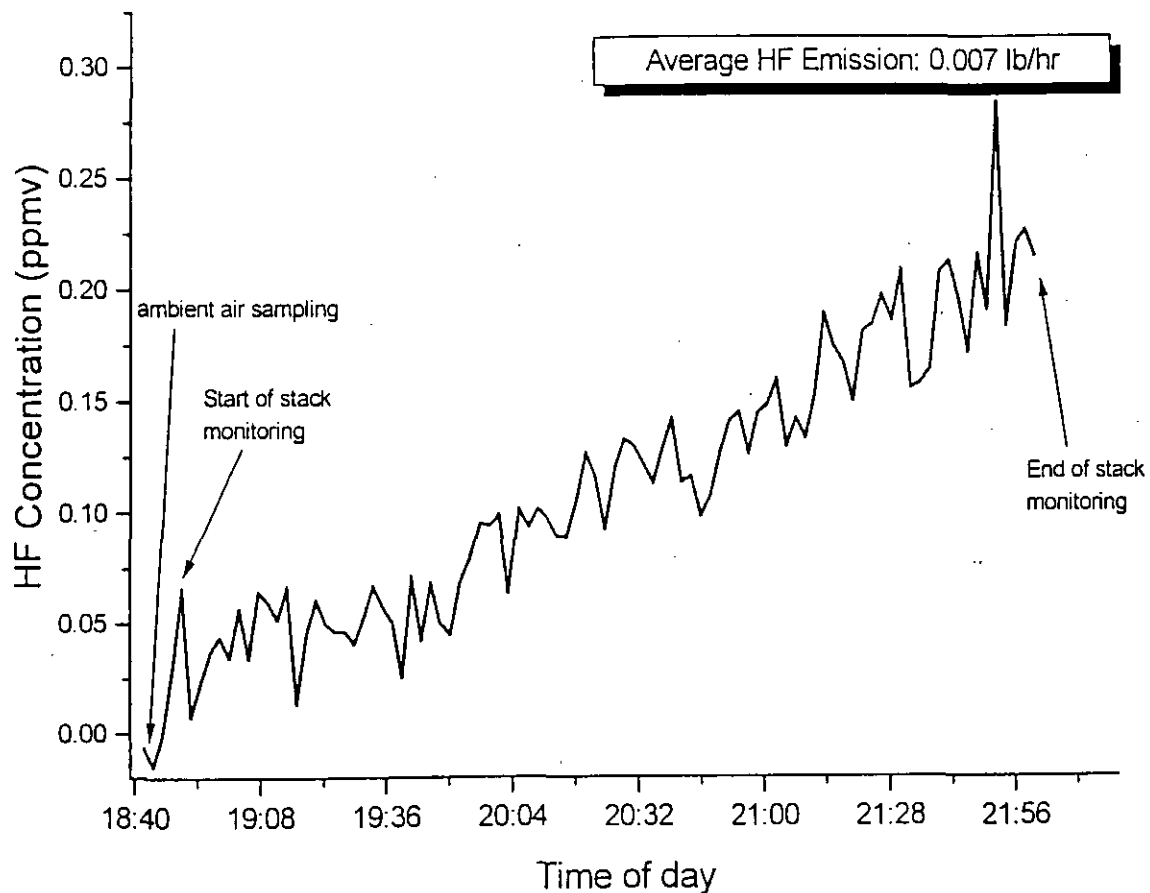
Conc. SF <sub>6</sub> in gas cylinder (ppm), $C_{undil}$ :	2.12
Conc. SF <sub>6</sub> returned by method after analyte injection (ppm), $C_{dil}$ :	1 <sup>st</sup> spike: 0.34 2 <sup>nd</sup> spike: 0.44
Certified conc. of HF in gas cylinder (ppm), $T_{cert}$ :	3.5
Conc. native HF in stack, on average (ppm), $T_{native}$ :	0.20
Calculated conc. of HF after analyte injection (ppm), $T_{exp}$ :	1 <sup>st</sup> spike: 0.73 2 <sup>nd</sup> spike: 0.89
Measured conc. of HF by FTIR right before spike ends(ppm):	1 <sup>st</sup> spike: 0.67 2 <sup>nd</sup> spike: 0.82
% Recovery	1 <sup>st</sup> spike: 92% 2 <sup>nd</sup> spike: 92%

### 5.3 ACU Emissions Test

Extractive FTIR monitoring of HF at ACU was conducted on 25 April, 2002. The emission profile is plotted in Figure 5-3. Noted on the graph is when stack sampling began and ended, along with the time when the probe was out of the stack and ambient air was sampled (prior to the test). Upon averaging the concentrations reported in Figure 5-3, and factoring in the average stack flow rate reported in Table 3-1, an average HF mass emission rate of 0.007 lb/hr can be calculated.

HF spiking, per Method 320, was conducted prior to and immediately after this emissions test. The results are summarized in the following section.

Figure 5-3. ACU FTIR Emissions Test  
(25 April 2002)



### 5.3.1 ACU Validation Spikes

The spiking of an HF certified gas standard was performed as stack gas was continuously extracted and analyzed at a central traverse point within ACU. The gas standard was injected close to the initial point of stack extraction (no  $\text{NH}_3$  was present in this stack), per EPA Method 320. Section 3.0 explains the spiking procedure in more detail and Figure 3-1 shows the primary spiking "tee" location employed for the ACU tests. A gas standard containing HF (at 3.5 ppmv) was injected at constant flows (regulated by a mass flow controller) of 0.8 and 0.6 liters per minute over the sample gas. A spectroscopic tracer,  $\text{SF}_6$  (at 2.12 ppmv), was also in the gas standard blend to provide a precise means by which to calculate dilution ratios. Appendix A describes in detail how the tracer is used. Tables 5-5 and 5-6 summarize the results, which show good recovery of the expected HF concentration under stack dilution, thereby validating the FTIR analysis method for this compound. It should be noted that there were no means by which

to measure exactly the native HF concentrations during the spike, so this value could only be estimated (by FTIR measurement immediately before the spike was injected).

**Table 5-5. HF Spiking Parameters and Results at ACU: Pre-test**

Conc. SF <sub>6</sub> in gas cylinder (ppm), $C_{multi}$ :	2.12
Conc. SF <sub>6</sub> returned by method after analyte injection (ppm), $C_{dil}$ :	1 <sup>st</sup> spike: 0.35 2 <sup>nd</sup> spike: 0.46
Certified conc. of HF in gas cylinder (ppm), $T_{cert}$ :	3.5
Conc. native HF in stack, on average (ppm), $T_{native}$ :	0.050
Calculated conc. of HF after analyte injection (ppm), $T_{exp}$ :	1 <sup>st</sup> spike: 0.62 2 <sup>nd</sup> spike: 0.80
Measured conc. of HF by FTIR right before spike ends(ppm):	1 <sup>st</sup> spike: 0.49 2 <sup>nd</sup> spike: 0.74
% Recovery	1 <sup>st</sup> spike: 79% 2 <sup>nd</sup> spike: 93%

**Table 5-6. HF Spiking Parameters and Results at ACU: Post-test**

Conc. SF <sub>6</sub> in gas cylinder (ppm), $C_{multi}$ :	2.12
Conc. SF <sub>6</sub> returned by method after analyte injection (ppm), $C_{dil}$ :	1 <sup>st</sup> spike: 0.32 2 <sup>nd</sup> spike: 0.42
Certified conc. of HF in gas cylinder (ppm), $T_{cert}$ :	3.5
Conc. native HF in stack, on average (ppm), $T_{native}$ :	0.200
Calculated conc. of HF after analyte injection (ppm), $T_{exp}$ :	1 <sup>st</sup> spike: 0.70 2 <sup>nd</sup> spike: 0.85
Measured conc. of HF by FTIR right before spike ends(ppm):	1 <sup>st</sup> spike: 0.62 2 <sup>nd</sup> spike: 0.80
% Recovery	1 <sup>st</sup> spike: 89% 2 <sup>nd</sup> spike: 94%

#### 5.4 Y-MAP Emissions Test

Extractive FTIR monitoring of HF at Y-MAP was conducted on 11 April, 2002 and again on 23 April, 2002. The emission profiles are plotted in Figures 5-4 and 5-5. Noted on the graphs are when stack sampling began and ended, along with the times when the probe was out of the stack and ambient air was sampled (prior to the test and while the probe was moved from one stack sampling port to the other). Y-MAP was re-tested because no Method 320 spikes were performed during the first test (no pre-test spiking because of time constraints and no post-test spiking because of insufficient HF recoveries due to extraction line contamination). Using the average of the concentrations reported in Figure 5-5, and factoring in the average stack flow rate reported in Table 3-1, an average HF mass emission rate of 0.119 lb/hr was calculated.

HF spiking, per Method 320, was conducted prior to and immediately after this emissions test. The results are summarized in the following section.

Figure 5-4. Y-MAP FTIR Emissions Test #1  
(11 April 2002)

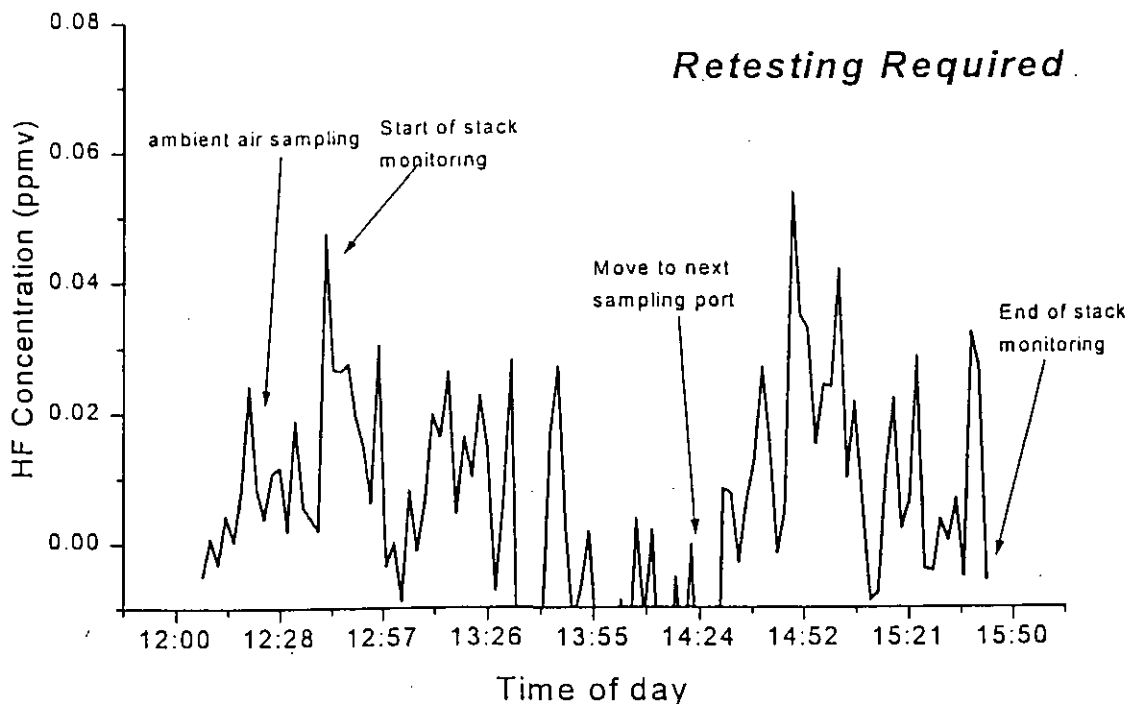
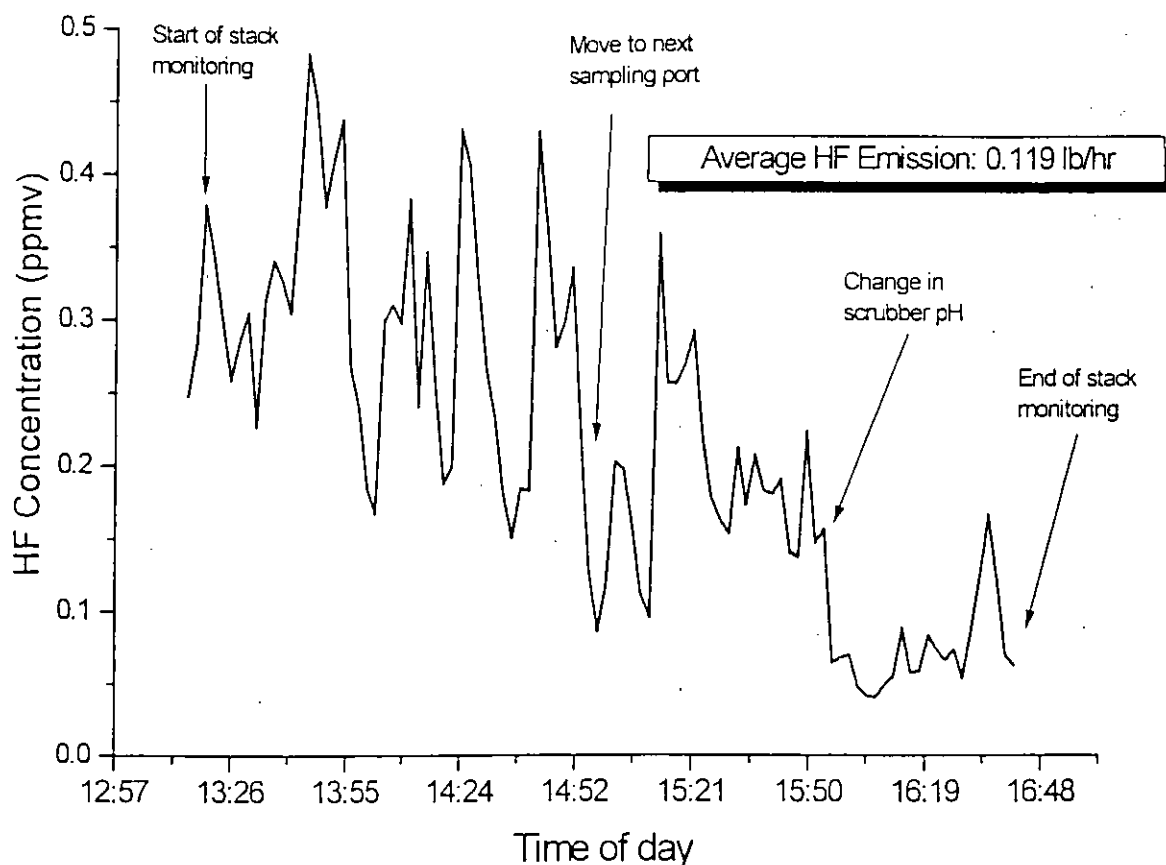


Figure 5-5. Y-MAP FTIR Emissions Test #2  
(23 April 2002)



#### 5.4.1 Y-MAP Validation Spikes

The spiking of an HF certified gas standard was performed as stack gas was continuously extracted and analyzed at a central traverse point within Y-MAP. The gas standard was injected close to the initial point of stack extraction (since only ~2 ppmv of  $\text{NH}_3$  was present in this stack), per EPA Method 320. Section 3.0 explains the spiking procedure in more detail and Figure 3-1 shows the primary spiking "tee" location employed for the Y-MAP tests. A gas standard containing HF (at 3.5 ppmv) was injected at constant flows (regulated by a mass flow controller) of 0.8 liters per minute over the sample gas. A spectroscopic tracer,  $\text{SF}_6$  (at 2.12 ppmv), was also in the gas standard blend to provide a precise means by which to calculate dilution ratios. Appendix A describes in detail how the tracer is used. Tables 5-7 and 5-8 summarize the results, which show good recovery of the expected HF concentration under stack dilution, thereby validating the FTIR analysis method for this compound.

Table 5-7. HF Spiking Parameters and Results at Y-MAP: Pre-test

Conc. SF <sub>6</sub> in gas cylinder (ppm), $C_{undil}$ :	2.12
Conc. SF <sub>6</sub> returned by method after analyte injection (ppm), $C_{dil}$ :	1 <sup>st</sup> spike: 0.49 2 <sup>nd</sup> spike: 0.44
Certified conc. of HF in gas cylinder (ppm), $T_{ceri}$ :	3.5
Conc. native HF in stack, on average (ppm), $T_{native}$ :	0.200
Calculated conc. of HF after analyte injection (ppm), $T_{exp}$ :	1 <sup>st</sup> spike: 0.96 2 <sup>nd</sup> spike: 0.89
Measured conc. of HF by FTIR right before spike ends(ppm):	1 <sup>st</sup> spike: 0.86 2 <sup>nd</sup> spike: 0.99
% Recovery	1 <sup>st</sup> spike: 89% 2 <sup>nd</sup> spike: 112%

Table 5-8. HF Spiking Parameters and Results at Y-MAP: Post-test

Conc. SF <sub>6</sub> in gas cylinder (ppm), $C_{undil}$ :	2.12
Conc. SF <sub>6</sub> returned by method after analyte injection (ppm), $C_{dil}$ :	1 <sup>st</sup> spike: 0.28*
Certified conc. of HF in gas cylinder (ppm), $T_{ceri}$ :	3.5
Conc. native HF in stack, on average (ppm), $T_{native}$ :	0.050
Calculated conc. of HF after analyte injection (ppm), $T_{exp}$ :	1 <sup>st</sup> spike: 0.51
Measured conc. of HF by FTIR right before spike ends(ppm):	1 <sup>st</sup> spike: 0.46
% Recovery	1 <sup>st</sup> spike: 91%

\*Only one spike was conducted due to time constraints

## 6.0 Method 301 Validation at B-PAP

The analyte spiking procedure outlined in the EPA document *Method 301-Field Validation of Pollutant Measurement Methods from Various Waste Media* was carried out at B-PAP on 18 April, 2002. Method 301 requires 24 test runs, 12 spiked and 12 unspiked, so this validation was completed upon the 12<sup>th</sup> paired HF spiking run when it was observed that the sampling trial met the necessary statistical allowances. The EPA method also calls for spiking as close as possible to the point of stack gas extraction, so the spiking "tee" was located in the primary position, as discussed in Section 3.0 and shown in Figure 3-1. A gas standard containing HF (at 3.5 ppmv) was injected at constant flows (regulated by a mass flow controller) on the order of 0.6 to 0.8 liters per minute over the sample gas. A spectroscopic tracer, SF<sub>6</sub> (at 2.12 ppmv), was also in the gas standard blend to provide a precise means by which to calculate dilution ratios. Appendix A describes in detail how the tracer is used.

Measurements consisted of comparing complete runs of unspiked and spiked analysis samples. The first run consisted of continuously monitoring the unspiked sample stream for a several-minute period, followed by a second run to continuously monitor the spiked sample stream for several minutes. The volume of spiked gas was limited to ~20-30% of the total sample gas volume.

The mean and standard deviation of the spiked members of the 12 pairs are dependent on the means and standard deviations of the analyte native to the stack exhaust and of the analyte spike itself. Since only one measurement system was used for this test, the variability in the concentrations within the stack background was combined with any variability from the instrument and cannot be separated. Table 6-1 shows the FTIR validation results for HF at B-PAP. Fortunately, the combined variances were not considered statistically significant. The validation statistics met all the allowable criteria for precision and accuracy without the need of a correction factor. A small negative bias was observed (possibly due to residual HF line effects after repeated spikes in a short time period), but was found to be statistically insignificant according to the t-statistic. Therefore, the FTIR system was deemed as an acceptable field analysis tool in reporting HF emissions. Table 6-2 shows the raw data collected during the Method 301 validation, in comparison with the expected HF spiking concentrations based on the tracer.



Table 6-1. EPA Method 301 Analyte Spiking: Statistical Results for HF

$S_m$ -mean of FTIR meas. spiked samples	1.4435	
$M_u$ -mean of FTIR meas. unspiked samp	0.5639	
$SD_s$ -std. dev. of FTIR meas. spiked samp	0.1040	
$SD_u$ -std.dev.of FTIR meas. unspiked samp	0.0781	
F-test	0.5638	For $n=12$ , if $0.288 < F < 3.474$ , calculate pooled SD
$SD_{pooled}$ -pooled std. dev.	0.0920	
RSD	0.0721	RSD must be $\leq 0.50$ for successful validation
RSD, if using pooled SD	0.1631	RSD must be $\leq 0.50$ for successful validation
B-bias at spike level	-0.0815	
t-statistic, $(n-2)=10$ degrees of freedom	2.1710	if t-stat. $\geq 2.776$ , then B is statistically significant
CF-correction factor if B stat. significant	1.0927	if $0.7 \leq CF \leq 1.3$ OR if B not statistically significant, then validation successful
Validation Successful		

Table 6-2. HF Validation at B-PAP: Spiking Parameters and Data

$SF_6$ concentration in gas cylinder (ppm)	2.12
Observed $SF_6$ concentration while line spiking (ppm), on average	0.582
Fraction of native scrubber exhaust in total spiked sample, on average	0.725
HF certified cylinder conc. (ppm)	3.50
Conc. of HF spiked into extracted scrubber exhaust (ppm), on average	0.961

HF Validation Data (ppm)

Run #	Unspiked Native Conc.	Calculated Native Plus Spiked Conc.	Measured Native Plus Spiked Conc.	% Recovery of Calc. vs Meas.
1	0.413	0.990	0.937	94.7
2	0.637	1.302	1.255	96.4
3	0.534	1.226	1.268	103.4
4	0.576	1.250	1.256	100.5
5	0.503	1.351	1.433	106.0
6	0.488	1.418	1.481	104.5
7	0.429	1.363	1.459	107.1
8	0.384	1.338	1.574	117.6
9	0.565	1.460	1.568	107.4
10	0.701	1.558	1.682	107.9
11	0.777	1.591	1.702	107.0
12	0.759	1.582	1.707	107.9
Mean Conc.	0.564	1.369	1.443	105.0

## 7.0 Summary and Conclusions

Table 7-1 summarizes the results for the FTIR hydrogen fluoride sampling tests at all the stacks tested at CF Industries in April 2002. Average HF emissions are reported in terms of volumetric concentrations (ppbv) and mass emission rates (lb/hr and ton/yr). Generally, these stacks emit relatively low amounts of pollutant (less than a total of 0.8 ton/yr) in the form of vaporous HF. The extractive FTIR monitoring method employed by URS Corporation was proven to be an accurate, continuous analysis tool upon validation by EPA Method 301.

Table 7-1. Average HF Concentrations Measured by FTIR at CFII Stacks

Stack Location	Average Concentration (ppbv)	Average Mass Emission (lb/hr)	Average Mass Emission (ton/yr)***
X-DAP	36*	0.017	0.07
B-PAP	246	0.027	0.12
ACU	113	0.007	0.03
Y-MAP #1	ND**	ND**	ND**
Y-MAP #2	216	0.106	0.46
TOTAL			0.68

\* Estimated detection limit of the FTIR test equipment.

\*\* Results not valid due to contaminated extraction line.

\*\*\* Projected based on measurements made under operating conditions present at the time of testing and 8760 hours/yr.

Appendix A  
Spiking/Validation Procedures

## Appendix A

### Spiking/Validation Procedures

Accuracy tests for the critical target compound (HF) were performed against the FTIR analysis method to assure the validity of the test data. This was accomplished by injecting measured volumes of certified gas into the extraction line as the FTIR system was drawing stack gas through its cell. A chemically inert compound known to possess a broad spectroscopic absorption pattern over a large range of concentrations ( $\text{SF}_6$ ) was included in the gas mixture to calibrate dilution ratios. The linear behavior of the  $\text{SF}_6$  concentrations returned by the analysis method provides a precise measure of the dilution factor associated with each analyte injection. The procedure used in calculating the concentrations expected during analyte spiking was as follows:

- The gas standard was introduced directly into the heated sample cell while bypassing the extraction line assembly. After the cell was sufficiently purged with the standard containing  $\text{SF}_6$ , the analysis method would return a value (called  $C_{undil}$ ) that represents the concentration of  $\text{SF}_6$  in the gas cylinder, as measured by the FTIR.
- The gas standard would then be injected into the extraction line as stack gas is drawn through the heated lines and sample cell. The analyte injection flow would be maintained at a low, constant rate with the aid of a mass flow controller. After the cell was sufficiently purged with the gas standard/stack gas mix, the analysis method would return a value (called  $C_{dil}$ ) that represents the concentration of  $\text{SF}_6$  diluted by stack gas, as measured by the FTIR.
- The expected concentration of the target compound,  $T_{exp}$  (which was also diluted by stack gas under the same proportions as  $\text{SF}_6$ ), during analyte injection is thus:

$$T_{exp} = \frac{C_{dil}}{C_{undil}} \times T_{cert} + \left(1 - \frac{C_{dil}}{C_{undil}}\right) \times T_{native}$$

Where:

$T_{cert}$  is the certified concentration of the target compound in the gas cylinder; and

$T_{native}$  is the average concentration of target compound present in the stack.

## Sample Calculations For FTIR HF Mass Flow Rates B-PAP 4/19/02

### Calculation of Mass: Mass Concentration of HF:

38,552 ACFM measured Air Flow

246 ppb<sub>v</sub> HF From FTIR Determination

177 ppb<sub>wt</sub> HF

ppb<sub>wt</sub> HF = ppb<sub>v</sub> X MW HF / MW Air at moist conditions or 246 X 20.00 / 27.87

### Calculation of Air Density at Sampling Conditions:

1.054 ρ<sub>Air</sub> g/l Moist Air at sampling conditions

Density(g/l) = 1.2929 X [273.13/(T(°K))] X [(B (mm Hg) - .3783 mm Hg X e )/760mm<sup>1</sup>

Using T=57.1 °C or 134.8 °F

Using measured barometric pressure of 768 mm Hg, 30.25"Hg

e=49.18 at a dew point of 57° C, 134°F Saturated Air Stream

1.2929 X [273.15/(273.15+57.1)] X 768 - [.3783 (49.18)]/760

0.0658 ρ<sub>Air</sub> Lb/Ft<sup>3</sup>

1.054g/l X 0.002205 Lb/g X 28.317 l/ft<sup>3</sup>

### Calculation of HF Mass Flow:

0.027 Lb HF /Hr

Mass Flow = Air Flow (ACFM) X ρ<sub>Air</sub> X [HF]ppb<sub>wt</sub> / 1X10<sup>9</sup> X 60 min/hr

# Sample Emission Estimate Calculations

## For Stack & Fugitive HF From B-Phosphoric Acid Unit

### CFI Plant City Phosphate Complex

	Column 1	Column 2	Column 3	Column 4	Column 5	
Source/Unit	Point Source Total Allowable F (TPY)	HF Factor (HF/F) Ratio	Point Source Potential to Emit HF (TPY)	Estimated Fugitive HF (TPY)	Total Potential HF Emission (TPY)	Notes
B-PAP	4.60	3.0%	0.14	0.16	0.30	Assumes 0.5% uncaptured fumes from reactor, 10% uncaptured fumes from filters and other sources, 99% scrubber efficiency, 93% of scrubber fumes come from reactor with the remaining 7% from filters & other sources.

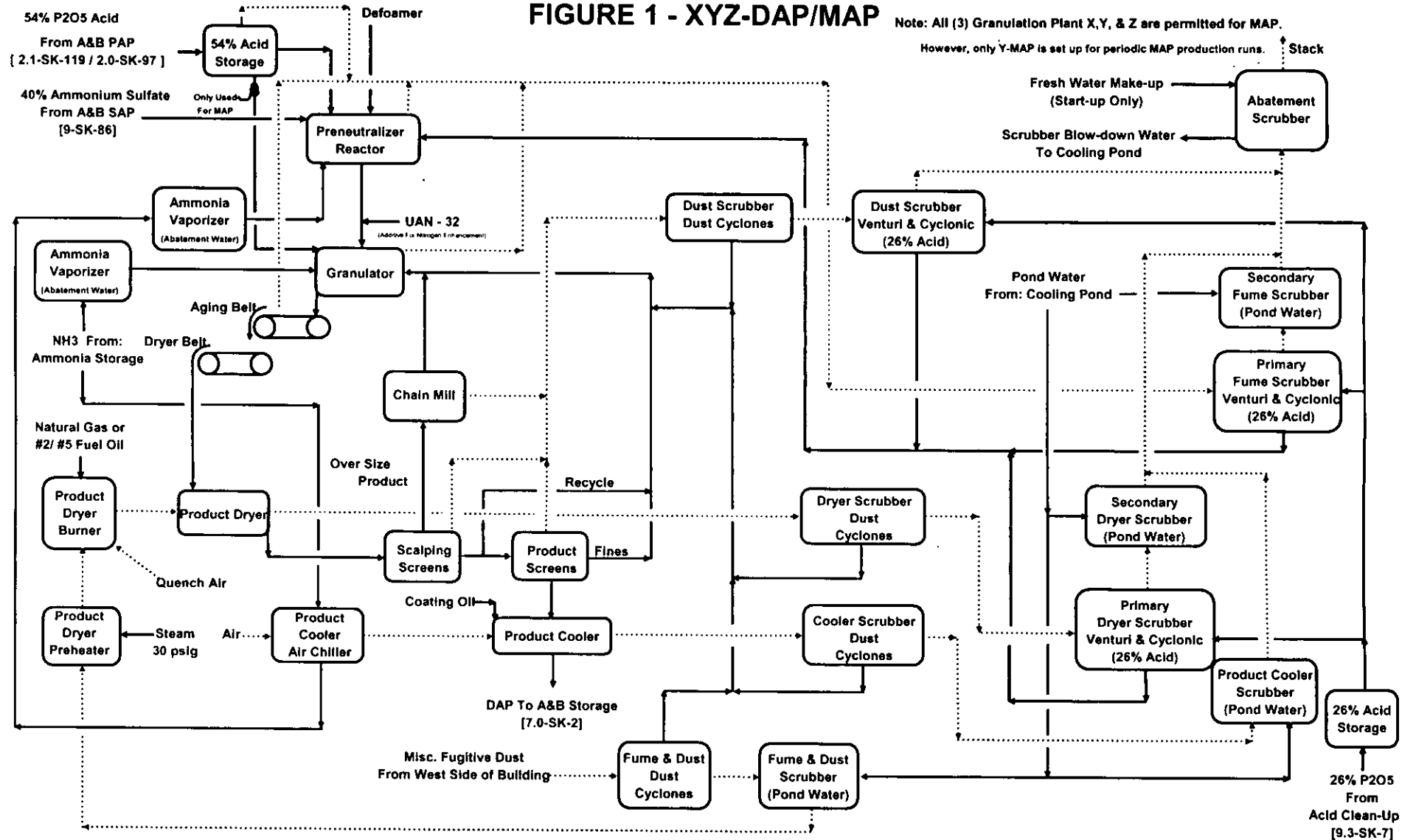
Column 1	This is the annual total allowable fluoride rate published in the Title V operating permit.
Column 2	This is the calculated ratio of HF specific fluorides to total fluorides measured simultaneous during FTIR and Method 13B testing. FTIR HF Rate (Lb/Hr) / Method 13B Total F Rate (Lb/Hr) 3.0% or 0.030 = 0.027 Lb HF/Hr / [(21.50 Lb F/Day X 1-Day/24-Hr) (See Table 2)]
Column 3	Point Source Potential to Emit HF = Permitted Allowable Total F X HF Factor 0.14 TPY HF = 4.6 TPY F X 0.030 Tons HF / Ton F
Column 4	This is the estimated fugitive emissions for B-PAP. The following assumptions were made.  Under normal operation the scrubber produces a vacuum on the reactor resulting in no fugitive HF. It was assumed that 10% of the time, build up in the scrubber system or upsets in the reactor may result in a slight positive pressure. When there is a positive pressure it was assumed that 5% of the fumes generated were uncaptured. Therefore, on an annualized basis 10% X 5% or 0.5% of reactor fumes are uncaptured.  The Bird & Belt filters have fume collection hoods that maintain a vacuum over the filter feed sections of the filters. Fluoride emissions from phosphoric acid are related the concentration of fluorides in the acid which in turn normally increases with the strength of the phosphoric acid. The fume hood collects fumes from strong acid feed boxes (26% P <sub>2</sub> O <sub>5</sub> ), and on the Belt filters it also collects fumes over the 1st wash box (8% P <sub>2</sub> O <sub>5</sub> ). The strength of acid/wash water in the four uncovered wash boxes on the Bird filters are approximately 8%, 5%, 2%, 2% P <sub>2</sub> O <sub>5</sub> and the strength of acid/pond water in the two uncovered wash boxes on the Belt filters is 5%, and 2%. It was assumed that 10% or the total filter fumes generated are uncollected.  Past plant testing has indicated that about 93% of the fluoride emissions reporting to the scrubber originate from the reactor and the other 7% come from the filter and tanks. Therefore, 93% X 0.5% Uncollected Reactor Fumes + 7% X 10% Uncollected Filter Fumes = 1.165% Overall Uncollected Fumes in the Phosphoric Acid Plants.  $\text{Estimated Fugitive HF} = \frac{\text{Permitted Allowable Total F} \times \text{HF Factor} \times \% \text{ Uncollected HF}}{(1 - \text{Scrubber Efficiency}) \times (1 - \% \text{ Uncollected HF})}$ 0.16 TPY HF = (4.6 TPY F X 0.030 Tons HF/Ton F X 0.01165) / [(1 - .99) X (1-0.01165)]
Column 5	Total HF Emission Potential = Point Source Potential to Emit HF + Estimated Fugitive HF 0.30 TPY HF = 0.14 TPY HF + 0.16 TPY HF

## FIGURES

FIGURE 1 - XYZ-DAP/MAP

Note: All (3) Granulation Plant X, Y, &amp; Z are permitted for MAP.

However, only Y-MAP is set up for periodic MAP production runs.



## Legend

..... Fume or Air Duct  
 ——— 26% / 40% P<sub>2</sub>O<sub>5</sub> Acid  
 ——— Ammonia  
 ——— Granular DAP/MAP  
 ——— Process Water

Other

## Revision By

Randy Charlot

## Date

1/27/04



## CF Industries, Inc.

Plant City Phosphate Complex  
 P.O. Drawer L

Plant City, Florida 33564

Phone: (813) 782-1591

Fax: (813) 788-9126

## Title

XYZ-DAP/MAP Granulation Block Flow Diagram

## DWR. NO

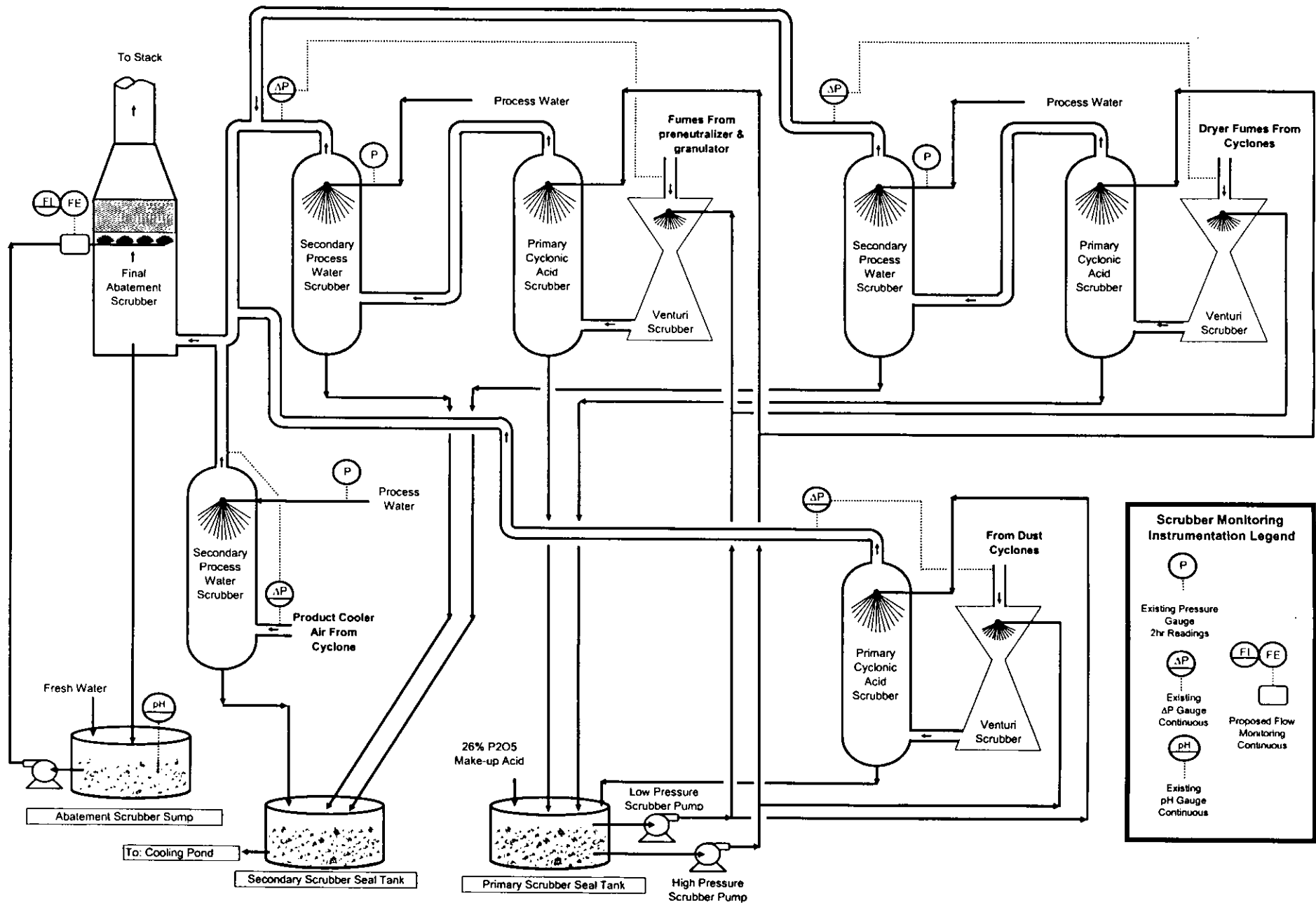
5.1-SK-57

51-06-07-21.0



**FIGURE 2**  
**XYZ DAP/MAP Granulation Scrubber Schematic - Single Granulation Train**

11



**Scrubber Monitoring Instrumentation Legend**

- Existing Pressure Gauge 2hr Readings:** Represented by a circle with 'P' inside.
- Existing  $\Delta P$  Gauge Continuous:** Represented by a circle with ' $\Delta P$ ' inside.
- Existing pH Gauge Continuous:** Represented by a circle with 'pH' inside.
- Proposed Flow Monitoring Continuous:** Represented by a square with 'FL' and 'FE' inside.

### FIGURE 3 - A-DAP/MAP

**Legend**

Line Style	Description	Other
—	Fume or Air Duct	
—	26% / 54% P <sub>2</sub> O <sub>5</sub> Acid	
—	Ammonia	
—	Granular DAP/MAP	
—	Abatement Water	

**Revision By**  
Randy Charlot

**Date**  
01/16/04

**CF Industries, Inc.**  
Plant City Phosphate Complex  
P.O. Drawer L  
Plant City, Florida 33564  
Phone: (813) 782-1591  
Fax: (813) 788-9126

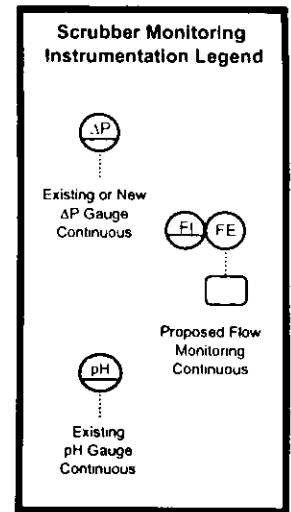
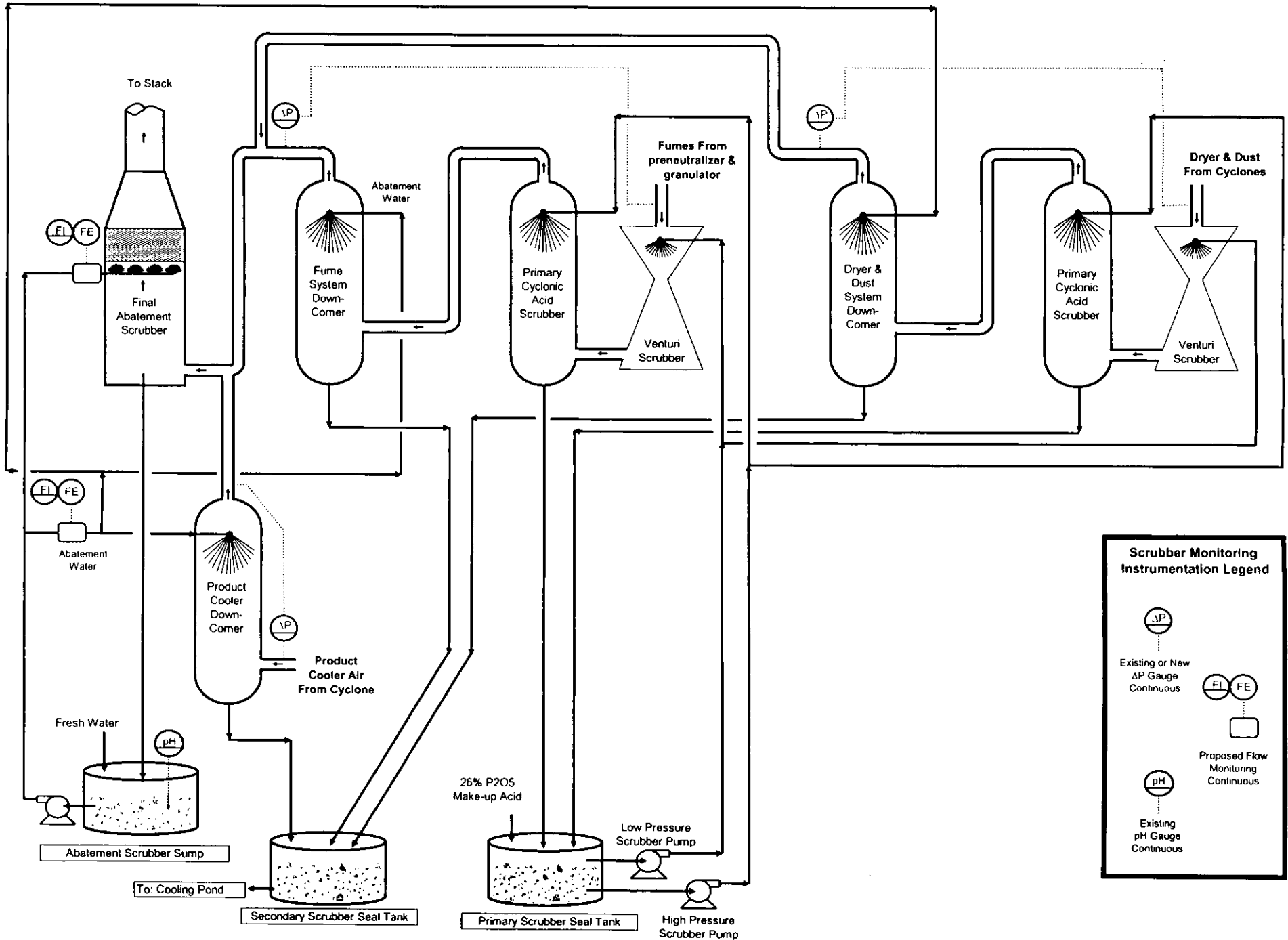
**Title**  
A-DAP/MAP Process Block Flow Diagram

**DWR. NO**  
5.0-SK-101

<b>Legend</b> _____ Fume or Air Duct _____ 26% / 54% P <sub>2</sub> O <sub>5</sub> Acid _____ Ammonia _____ Granular DAP/MAP _____ Abatement Water		<b>Revision By</b> Randy Charlot	<b>Date</b> 01/16/04	 <b>CF Industries, Inc.</b> Plant City Phosphate Complex P.O. Drawer L Plant City, Florida 33564 Phone: (813) 782-1591 Fax: (813) 788-9126	<b>Title</b> A-DAP/MAP Process Block Flow Diagram	<b>DWR. NO</b> 5.0-SK-101

**FIGURE 4**  
**"A" DAP/MAP Granulation Scrubber Schematic**

13



## **APPENDIX B**

### **Design Engineer's Comments on Purpose of Primary Scrubbers**



A

OPERATING MANUAL  
FOR  
CENTRAL PHOSPHATE, INC.  
SUBSIDIARY OF  
C F INDUSTRIES, INC.  
PLANT CITY PHOSPHATE COMPLEX  
PHASE - III  
DAP OPERATION MANUAL  
CONVERTED GRANULAR PLANT

PREPARED BY:

PEDONE ENGINEERING CORPORATION  
LAKELAND, FLORIDA  
JULY 1974



## DAP OPERATIONS MANUAL

### CONVERTED GRANULAR PLANT

#### 2.0 DESCRIPTION OF PROCESS

##### 2.1 GENERAL (cont.)

The portion of the product size which is directed to the Cooler Feed Conveyor (Item 5.02-5922) flows over this conveyor and is weighed by the Product Scale (Item 5.02-599) which is attached to the conveyor. It then flows to the top of the Product Cooler (Item 5.02-573), which is a counter-current fluid bed heat exchanger. The product then flows downward through the cooler and into the boot of the Product Elevator (Item 5.02-98). It is then elevated to Product Conveyor (Item 5.02-912) and is conveyed to storage.

Dust and fumes will be carried by all gases leaving the various sections of the plant and means have been provided for their recovery. All streams carrying dust first enter a dry cyclone system: Dryer Cyclone (Item 5.02-44) with Dryer Cyclone Valve (Item 5.02-5914); Dust Cyclone (Item 5.02-45) with Dust Cyclone Valve (Item 5.02-5915) and the Cooler Cyclone (Item 5.02-46) with Cooler Cyclone Valve (Item 5.02-5916). Collected solids are discharged to the Secondary Elevator (Item 5.02-95), which feeds the Granulating Drum (Item 5.02-51).

After the gases leave the dry cyclones, they are further scrubbed by the scrubbing system. This system employs a two stage scrubbing operation to first recover process values (DAP dust and ammonia) and then remove the pollutants from the air stream before discharging to the atmosphere.

Provision has been made to recover the collected dust particles and gases which have process value, consisting of the Reactor Fumes Scrubber (Item 5.02-43), the Dryer Fumes Scrubber (Item 5.02-47), and the Scrubber Liquor Tank (Item 5.01-83). In this section, a weak phosphoric acid solution is recirculated and returned to the process to reclaim any process values.

The pollution control section consists of the Cooler Downcomer (Item 5.02-37), the Dryer Downcomer (Item 5.02-86), the Reactor Downcomer (Item 5.02-85), the Fluorine Abatement Scrubber (Item 5.02-415), and the Scrubbing Solution Recirculation Tank (Item 5.02-35). In this section, a weak caustic solution is recirculated to absorb any pollutants before discharging the gases to the atmosphere. Sufficient caustic and fresh water are added to this solution to neutralize the acidic pollutants and maintain the pH at 5.5 to 6.5.



## DAP OPERATIONS MANUAL

### CONVERTED GRANULAR PLANT

#### 2.0 DESCRIPTION OF PROCESS

##### 2.1 GENERAL (cont.)

The volume of solution is maintained constant by continuously disposing of a small quantity of spent solution beyond the battery limits of the plant.

There are three (3) separate air streams which combine before entering the Fluorine Abatement Scrubber. One stream is drawn from the dust evacuation and dryer through the Dryer Fumes Scrubber, Dryer Downcomer, and Dryer Fan. A second stream is drawn from the Preneutralizer and Granulator through the Reactor Fumes Scrubber, Reaction Fumes Fan, and Reactor Downcomer. The third stream is drawn from the cooler through the Cooler Fan and Cooler Downcomer.

The scrubber solution flowing from the Reactor Fumes Scrubber (Item 5.02-43) and the Dryer Fumes Scrubber (Item 5.02-47), flows to the Scrubber Liquor Tank (Item 5.01-83). Solids are kept in suspension by Scrubber Liquor Tank Agitator (Item 5.02-554), which is attached to the tank. The solution is circulated from this tank back to the scrubbers by means of Scrubber Liquor Pump (Item 5.02-19) and the Scrubber Acid Booster Pump (Item 5.02-26). A measured amount of this scrubber solution is continuously transferred from this scrubber circulating system to the Preneutralizer (Item 5.02-531).

As the scrubber solution is withdrawn from the scrubber circulating system, makeup water and phosphoric acid is fed into the scrubber liquor tank. The water is fed through a level-flow control system, while the phosphoric acid is fed through a density-flow control system. These systems are arranged so that the combined system will be largely automatic once the controls are set.

The caustic scrubbing solution from the Reactor Downcomer (Item 5.02-85), the Dryer Downcomer (Item 5.02-86), and the Cooler Downcomer (Item 5.02-87) flows to a seal pot. It then flows by gravity to the Scrubbing Solution Recirculation Tank (Item 5.02-35) and mixes with the return from the Fluorine Abatement Scrubber (Item 5.02-413). The Caustic Metering Pump (Item 5.02-29) feeds 50% NaOH to this tank and controls to a pH of approximately 5.5 to 6.5 with a pH flow controller. Scrubbing solution is pumped to the Downcomers, Abatement Scrubber and Battery Limits



## DAP OPERATIONS MANUAL

### CONVERTED GRANULAR PLANT

#### 2.0 DESCRIPTION OF PROCESS

##### 2.5 TECHNICAL DISCUSSION (cont.)

##### 2.5.5 Cycloning and Scrubbing System (cont.)

##### 2.5.5.6 Reactor Fume Scrubber (cont.)

###### b. Description (cont.)

and the remainder is rubber lined. It has two Weir boxes for liquid introduction, separator with tangential gas inlet and outlet, manhole and wash connections. There are six wash boxes with six sprays each located near the inlet to the cyclonic section.

###### c. Operation

Air and fumes from the granulating drum and the preneutralizer are drawn through this scrubber by the reactor fume fan. As the air and fumes enter the scrubber they are joined by the recycled scrubber effluent which enters on either side of the inlet.

The quantity of scrubber liquor on each side may be balanced by slightly adjusting the valves on each line. These valves should be fully open when the pump is started.

The gas and liquid pass at high velocity through the narrow venturi throat where liquid is broken down into droplets and an intimate gas-liquid contact takes place, with consequent absorption of ammonia into the liquid. The gas-liquid mixture then passes into the cyclonic acid scrubber where scrubber liquor is sprayed to further scrub the gases then cyclonic action of the ascending air sends the liquid droplets to the wall





## DAP OPERATIONS MANUAL

### CONVERTED GRANULAR PLANT

#### 2.0 DESCRIPTION OF PROCESS

##### 2.5 TECHNICAL DISCUSSION (cont.)

##### 2.5.5 Cycloning and Scrubbing System (cont.)

##### 2.5.5.7 Dryer Fume Scrubber (cont.)

###### b. Description

This was an Airetron combination venturi-cyclonic scrubber, with a 4'-8" SQ inlet by 13' long venturi section, and a 11'-0" diameter by 30' high cyclonic section. The Venturi, flooded elbow and cyclonic entry panel have been replaced with the Venturi and entry panel being 316L stainless steel. The remainder is rubber lined. Two pipe manifolds for liquid introduction, a venturi throat and a cyclonic scrubber with tangential gas inlet and outlet, and 10 tangential nozzles with ramp bottom sprays, manhole and wash connections.

###### c. Operation

Air and fumes from the dryer cyclone and the dust cyclone are pulled through this scrubber by the dryer fan. As air and fumes enter the scrubber they are joined by the recycled scrubber liquor which flows from pipe manifolds on either side on the inlet. The gas and liquid pass at high velocity through the narrow venturi throat where the liquid is broken down into droplets and an intimate gas liquid contact takes place with consequent absorption of ammonia into the liquid. The gas liquid mixture then passes into the cyclonic acid scrubber where scrubber liquor is sprayed to further scrub the gases then cyclonic action of the ascending air sends the liquid droplets to the wall where they run down to the bottom discharge and to



## DAP OPERATIONS MANUAL

### CONVERTED GRANULAR PLANT

#### 2.0 DESCRIPTION OF PROCESS

#### 2.5 TECHNICAL DISCUSSION (cont.)

##### 2.5.5 Cycloning and Scrubbing System (cont.)

##### 2.5.5.8 Reactor Downcomer (cont.)

###### b. Description

This is a sixty inch diameter fiber-glass reinforced plastic downcomer with side inlet at the top and three spray boxes with four Spraying Systems Co. Vee Jet (R)  $H\frac{1}{4}$  US070 nozzles in each for caustic recirculation solution.

###### c. Operation

Scrubbed gas from the reactor fume scrubber, discharged by the reactor fume fan, enters at the top and passes through a shower of droplets of caustic recirculating solution, which absorbs some of the flourine and partially saturates the gases, before discharging to the flourine abatement scrubber. The caustic solution discharges at the bottom to a seal pot and flows to the scrubbing solution recirculating tank.

###### d. Instrumentation

Pressure Indicator PI-377 is located in the caustic solution line to the sprays.

##### 2.5.5.9 Dryer Downcomer

###### a. Location

This is Item 5.02-86, located outside of the building, it is the eastern-most of the three downcomers north of the dryer fan.



## DAP OPERATIONS MANUAL

### CONVERTED GRANULAR PLANT

#### 2.0 DESCRIPTION OF PROCESS

#### 2.5 TECHNICAL DISCUSSION (cont.)

##### 2.5.5 Cycloning and Scrubbing System (cont.)

##### 2.5.5.9 Dryer Downcomer (cont.)

###### b. Description

This is an 84" diameter fiberglass reinforced plastic downcomer with side inlet at the top and four spray boxes with five Spraying Systems Co. Vee Jet (R) H<sub>4</sub> U8070 nozzles in each for caustic recirculating solution.

###### c. Operation

Scrubbed gas from the dryer fume scrubber enters at the top and passes through a shower of droplets of caustic recirculating solution which absorbs some of the flourine and partially saturates the gases before discharging to the Dryer Fan (Item 5.02-25). The caustic solution discharges at the bottom to a seal pot and flows to the scrubbing solution recirculation tank.

###### d. Instrumentation

Pressure Indicator PI-378 is located in the caustic solution line to the sprays.

##### 2.5.5.10 Cooler Gas Downcomer

###### a. Location

This is Item 5.02-87, located outside of the building, it is the western-most of the three downcomers north of the dryer fan.



## DAP OPERATIONS MANUAL

### CONVERTED GRANULAR PLANT

## 2.0 DESCRIPTION OF PROCESS

### 2.5 TECHNICAL DISCUSSION (cont.)

#### 2.5.5 Cycloning and Scrubbing System (cont.)

##### 2.5.5.10 Cooler Gas Downcomer (cont.)

###### b. Description

This is a 54 inch diameter fiberglass reinforced plastic downcomer with side inlet at the top and three spray boxes with three Spraying Systems Co. Vee Jet (R) H $\frac{1}{4}$  U8070 nozzles in each for caustic recirculation solution.

###### c. Operation

Gas from the product cooler cyclones enters at the top and passes through a shower of droplets of caustic recirculation solution which absorbs some of the flourine and partially saturates the gases, before discharging to the flourine abatement scrubber. The caustic solution discharges at the bottom to a seal pot and flows to the scrubbing solution recirculation tank.

###### d. Instrumentation

Pressure Indicator PI-379 is on the caustic solution line to the sprays.

##### 2.5.5.11 Flourine Abatement Scrubber

###### a. Location

This is Item 5.02-413, located outside of the building on the west side of the scrubbing area.



## DAP OPERATIONS MANUAL

### CONVERTED GRANULAR PLANT

#### 2.0 DESCRIPTION OF PROCESS

##### 2.5 TECHNICAL DISCUSSION (cont.)

###### 2.5.5 Cycloning and Scrubbing System (cont.)

###### 2.5.5.11 Flourine Abatement Scrubber (cont.)

###### b. Description

This is a Ducon size 15-28 flourine abatement scrubber with internal spray piping and nozzles, an external distribution header, packed mist elimination section, and a vertical discharge to stack.

###### c. Operation

Air and gas discharged from the downcomers enters the Flourine Abatement Scrubber at the bottom and passes through a shower of droplets of caustic recirculating solution, which absorbs the remaining flourine and dust. The gas then passes into a packed mist eliminator section and up the stack. Caustic recirculating solution discharges at the bottom and returns to the Scrubbing Solution Recirculation Tank.

###### d. Instrumentation

Flow Indicator Controller FIC-173, Temperature Indicator TI-571 and Pressure Indicator PI-580 are located in the recirculating solution line to the sprays. The flow control valve has a by-pass line for emergency use.

###### 2.5.5.12 Scrubber Liquor Tank

###### a. Location

This is Item 5.01-83 located at grade level outside of building between the dryer fume scrubber and the reactor fume scrubber.

OPERATING MANUAL

12

GRANULAR FERTILIZER PRODUCTION

FOR

C. F. INDUSTRIES, INC.

ZEPHYR HILLS, FLORIDA

Prepared by

*J. J. Easley*

Approved by

*E. K. Landgraf*

J-2053

1 June 1974

DORR-OLIVER ENGINEERING LTD.



## DORR-OLIVER

## OPERATING MANUAL

## GRANULAR FERTILIZER PRODUCTION

PAGE 18

The discharge from the Dryer is conveyed and elevated for screening by gravity on two single-deck electrically vibrated "Hum-mer" type Process Scalping Screens. Oversize material is crushed and returned to the Granulator. A controlled portion of the material passing through the Scalping Screens is fed to the Process Product Screens, also of the "Hum-mer" type. Excess material passing through the Scalping Screens overflows back to the Granulator along with the fines from the Product Screens.

The on-size material from the Product Screens is conveyed to the rotary Product Cooler where it is cooled by a countercurrent sweep of ambient air. The cooler discharge is elevated and passed through a gyratory Polishing Screen and conveyed to storage.

The gases from the Dryer, the Cooler and the Dust system all pass through dry Cyclones before entering the scrubbing systems. The gases from the Preneutralizer, the Granulator and the Aging Belt pass directly to the Fume Scrubbing system.

The Dryer and Fume Scrubbing systems handle gases containing appreciable quantities of dust, ammonia vapor and fluoride gases. Accordingly they consist of primary Venturi and Cyclonic stages using phosphoric acid scrubbing liquor to capture ammonia vapor and dust particles and secondary Cyclonic stages using strained pond water scrubbing liquid to capture fluoride gases.

The Dust Scrubbing system handles gases containing appreciable quantities of dust and ammonia vapor but only minor quantities of fluoride gases. The Dust Scrubbing system, accordingly consists only of primary Venturi and cyclonic stages using phosphoric acid scrubbing liquor to capture the dust and ammonia vapor.

The Cooler Scrubbing system handles gases containing minimal amounts of dust, ammonia vapor and fluoride gases. The Cooler Scrubbing system thus consists only of a single stage cyclonic unit using strained pond water to remove these contaminants with no attempt at ammonia or dust recovery.

The Dryer Fan, the Fume Fan, the Cooler Fan and the Dust Fan are all on the downstream side of the corresponding Scrubbing systems. These fans all discharge through a large Abatement Scrubber in which the gases are scrubbed with a recirculated caustic-adjusted solution prior to their discharge to the atmosphere via the exhaust Stack.

DORR-OLIVER  
OPERATING MANUAL

## GRANULAR FERTILIZER PRODUCTION

PAGE 36

2.7 SCRUBBING

The production of granular fertilizer materials is accompanied by the release of waste products that are potential environmental pollutants. These are mainly dusts and fluorides and to a lesser degree ammonia and sulfur oxides. The dusts are basically fertilizer material ultrafines and phosphate rock ground feed material. The fluorides are a minor constituent of the dusts emitted and a major constituent of the gases evolved in the various reactions. Gaseous ammonia evolved in the production of DAP must be recovered for plant economy reasons. Sulfur oxides arise mostly from the burning of fuel oil to supply heat for the dryer.

Most of the dust generated in the processing of the fertilizer materials is captured dry in high efficiency cyclones. Dust generated in the handling of the ground phosphate rock is captured in baghouse devices with up to 99% capture. The fertilizer material dust not captured in the dry cyclones is practically all removed from the carrying air in the multistage wet scrubbing units.

The fluoride gases evolved in the various reactors producing triple super phosphate must be absorbed by the liquid media in the scrubber units. This absorption is promoted by low liquid temperatures and by long residence times.

The gaseous ammonia evolved in the various steps of producing diammonium phosphate must be absorbed by phosphoric acid scrubbing media in the primary stage scrubbers for the dryer, reactor and dust air streams. Only minor quantities of fluoride gases are evolved in the basic ammoniation reaction vessels, but ammonia recovery in the scrubber units is most effective at low pH values (that is, below 5.0) and the reaction is exothermic so that the scrubber solution temperature is generally maintained above 160°F. At these conditions of pH and temperature, fluoride gases are often stripped from the phosphoric acid before it reaches the preneutralizer. Thus the second stages of the dryer, reactor and dust scrubbers receive fluoride enriched gases during diammonium phosphate production.



**DORR-OLIVER**  
OPERATING MANUAL

GRANULAR FERTILIZER PRODUCTION

PAGE 87

3. Fill the Fluorine Abatement Scrubber Sump with fresh water. When the agitator blades are adequately covered, start the Abatement Scrubber Sump Agitator (1A-166); use the local start pushbutton. As the sump level approaches the overflow point, adjust the fresh water flow rate to approximately 9 gpm by controller (FRC-4131) and adjust the level controller (LIC-4318) to maintain a pre-set liquid level. Start fresh water flow to the pump bearings and start the Fluorine Abatement Circulating Pump (IP-168) from the local start pushbutton; adjust the pump discharge valve so that the pressure gauge (PI-4538) reads at or slightly over 20 psig. Check the pump motor current draw (II-4249). Start the Caustic Metering Pump (IP-361) feeding about 3 gph of 50% NaOH solution to the Fluorine Abatement Scrubber Sump, and periodically check the pH of the solution. When the pH reaches 5.5 put the caustic feed on automatic pH control. Start exporting Abatement Scrubber solution to the Liquor Effluent Tank (IS-265) by level control instrumentation (LIC-4318) to maintain the liquid level slightly below overflow.
4. Start the large air handling fans once the above liquid flows have been established in the various scrubbers. Close tight the three fan discharge dampers and start fresh water flow to the fan bearings. For the Z-Train only, follow the fan startup procedure outlined in Paragraph 3 of Section 5.5 below excepting that the selector switch is to be in the "TSP" position. For the X and Y-Trains, start the Dust Fan (1B-263), the Reactor Fan (1B-262) and the Dryer Fan (1B-261) from the Process Control Panel start pushbuttons. Check the current draw indicated by the Control Panel Ammeters (II-4250, II-4251 and II-4252) and gradually open the three fan discharge dampers to bring the current draw up to about 90 percent of full load current. Adjust the Venturi Scrubber throats to obtain approximately 15" w.g. differential pressure readings on gauges (PDI-4545, PDI-4546 and PDI-4547).

Project: J-2053

1 June 1974

DORR-OLIVER  
OPERATING MANUAL

PAGE 110

## GRANULAR FERTILIZER PRODUCTION

Agitator blades, stop the Agitator. Stop the Scrubber Effluent Pump when it loses suction. Stop the Scrubber Water Return Pump when it loses suction. Rotate the spectacle flange at the overflow nozzle for its full open setting if the Z-Train is to be restarted on GTSP product.

- 11) Stop the caustic solution addition to the Fluorine Abatement Scrubber Sump by stopping the Caustic Metering Pump and stop fresh water addition to the Scrubber Sump. Pump down the Fluorine Abatement Scrubber Sump by opening the bypass valve around the Level Control Valve (LV4318Z) until the Circulating Pump loses suction. Shut off the level control bypass valve and refill the sump with fresh water through the 1 1/2 inch feed bypass line with valve wide open. Repeat this sequence several times, with the Circulating Pump, the Abatement Scrubber piping and the Scrubber Sump being successively flushed out with more-and-more dilute scrubber solution. Stop the Abatement Scrubber Sump Agitator (1A-166Z) and pump the sump down as far as possible with the Circulating Pump (1P-168Z). Stop the Circulating Pump. Empty the sump with a portable water pump to prepare it for cleanout.
- 12) Perform all of the maintenance and cleanup tasks in accordance with plant practice for a regularly scheduled "turn-around". Among others this generally includes; descaling the Preneutralizer and inspecting the brickwork, washing out the Dryer, washing out acid and slurry lines and pumps, inspecting and cleaning fans, ducts, chutes, hoppers and scrubbers, cleaning the screens, fixing leaks, steaming granulator sparger and spray nozzles, mechanical and instrument maintenance and general cleanup of plant floors, stairways, platforms etc. The plant is then ready for restarting according to the procedure outlined in Section 5.5 above for DAP production or with a bare iron cleaning per Section 5.6 above for GTSP production.

## **APPENDIX C**

### **HF MACT Initial Performance Test Plan**

**HF MACT INITIAL PERFORMANCE  
TEST PLAN  
for  
*CF INDUSTRIES, INC.*  
*PLANT CITY, FL***

**Prepared For:  
CF Industries, Inc.  
Plant City, Florida**

**Prepared By:  
Golder Associates Inc.  
6241 NW 23rd Street, Suite 500  
Gainesville, Florida 32653-1500**

**February 2005**

**0437520**

**DISTRIBUTION:  
7 Copies - CF Industries  
1 Copies - Golder Associates Inc.**

## TABLE OF CONTENTS

<u>SECTION</u>	<u>PAGE</u>
1.0 INTRODUCTION.....	1-1
2.0 PROCESS DESCRIPTION .....	2-1
2.1 "A" AND "B" PHOSPHORIC ACID PLANTS.....	2-1
2.1.1 PHOSPHORIC ACID PLANT A .....	2-1
2.1.2 PHOSPHORIC ACID PLANT B.....	2-1
2.2 "A" DAP/MAP .....	2-2
2.3 "X", "Y" AND "Z" DAP/MAP .....	2-3
3.0 INITIAL PERFORMANCE TESTING .....	3-1
3.1 TEST METHODS.....	3-1
3.1.1 "A" AND "B" PHOSPHORIC ACID PLANTS.....	3-1
3.1.2 "A" DAP/MAP PLANT .....	3-2
3.1.3 "X", "Y" AND "Z" DAP/MAP PLANTS .....	3-3
3.2 TEST SCHEDULE .....	3-5
4.0 DATA QUALITY OBJECTIVES .....	4-1
5.0 INTERNAL AND EXTERNAL QUALITY ASSURANCE.....	5-1
5.1 INTERNAL QUALITY ASSURANCE .....	5-1
5.2 EXTERNAL QUALITY ASSURANCE .....	5-1
5.2.1 PRETEST.....	5-1
5.2.2 IN THE FIELD .....	5-3
5.2.3 POST TEST .....	5-5
6.0 CALCULATIONS AND REPORTING .....	6-1
6.1 CALCULATIONS .....	6-1
6.2 REPORTING .....	6-1

## 1.0 INTRODUCTION

CF Industries, Inc. (CF Industries) operates a phosphate fertilizer production facility located near Plant City, Hillsborough County, Florida. The CF Industries facility consists of the following major plant areas: molten sulfur handling and storage, sulfuric acid production, phosphoric acid ( $\text{H}_3\text{PO}_4$ ) production, diammonium phosphate (DAP) production, monoammonium phosphate (MAP) production, and MAP/DAP storage and shipping. The facility is currently permitted under Permit No. 0570005-007-AV.

CF Industries has agreed to accept a determination by the Florida Department of Environmental Protection that the Plant City Phosphate Complex is a major source of hazardous air pollutants (HAPs), until such time as process pond monitoring demonstrates that it is not. Therefore, the  $\text{H}_3\text{PO}_4$  and MAP/DAP production sources at the facility are regulated under Title 40 of the Code of Federal Regulations, Part 63 (40 CFR 63), Subpart AA: National Emission Standards for Hazardous Air Pollutants from Phosphoric Acid Manufacturing Plants, and 40 CFR 63, Subpart BB: National Emission Standards for Hazardous Air Pollutants from Phosphate Fertilizers Production Plants. These standards reflect the maximum achievable control technology for these sources, and are therefore referred to as the "MACT" standards. The sources at the CF Industries facility that are regulated under Subpart AA consist of the "A" and "B" Phosphoric Acid Plants. The sources regulated under Subpart BB consist of the "A", "X", "Y", and "Z" DAP/MAP Plants. All these plants are currently meeting the MACT emission limits based on annual stack compliance test results.

The MACT standards regulate hydrogen fluoride (HF) emissions. The MACT regulations set emission limits for total fluorides (F), i.e., the total of both particulate fluorides and gaseous fluorides, as a surrogate parameter for HF, and require specific compliance testing and monitoring.

According to Subparts AA and BB, the individual source emission limits for F are as follows:

- For existing  $\text{H}_3\text{PO}_4$  plants: 0.020 pound of F per ton (lb/ton) of phosphorous pentoxide equivalent (expressed as  $\text{P}_2\text{O}_5$ ) input;
- For existing DAP/MAP plants: 0.060 lb/ton of  $\text{P}_2\text{O}_5$  equivalent input.

CF Industries has been negotiating an alternative MACT monitoring plan with the Florida Department of Environmental Protection (FDEP). The FDEP has determined that the proposed monitoring plan varies from the rule-specified monitoring sufficiently that it requires U.S. Environmental Protection Agency (EPA) approval before it can be incorporated into the facility's Title V permit. Once the alternative monitoring plan is approved, CF Industries will have 180 days in which to install the monitoring equipment and perform the initial performance testing. The test report must be submitted to the FDEP and the EPA within 60 days of completing the initial performance testing on the operating plants. Since the "A" DAP/MAP plant is on stand-by status and is currently idle, CF proposes to perform the initial performance test for that plant within 60 days following its future start-up.

The following sections describe the MACT sources located at the CF Industries facility, initial performance test procedures, test methods, schedule, data quality objectives, internal and external quality assurance, calculations, and reporting to comply with the MACT standards and to determine control device operating parameters necessary to comply with the F emission limits for the affected sources.

## 2.0 PROCESS DESCRIPTION

### 2.1 "A" AND "B" PHOSPHORIC ACID PLANTS

#### 2.1.1 PHOSPHORIC ACID PLANT A

"A" Phosphoric Acid Plant has a maximum permitted process input rate of 59 tons per hour (TPH) and 1,416 tons per day (TPD) as 100-percent rock  $P_2O_5$ . F emissions from this plant are controlled by a cyclonic scrubber followed by a packed bed scrubber with "Kimre" packing or equivalent packing. Typical gas flow rate through the scrubbers is approximately 43,000 dry standard cubic feet per minute (dscfm). The scrubber system uses pondwater as the scrubbing liquid. The scrubber system's approximate normal operating parameters are: liquid flow rate to the packed bed scrubber = 1,210 gallons per minute (gpm) at 40 pounds per square inch gauge (psig) and total gas pressure drop across the scrubbers = 9 inches w.g. (approximately 7 inches w.g. across the cyclonic scrubber and 2 inches across the packed bed scrubber).

F emissions from the "A" Phosphoric Acid Plant are regulated under MACT. The F emission standard from the MACT regulations is 0.020 lb/ton  $P_2O_5$  input, equivalent to 1.18 pounds per hour (lb/hr) F and 5.2 tons per year (TPY). These are the same limits that are currently in the facility's permit.

#### 2.1.2 PHOSPHORIC ACID PLANT B

The maximum permitted process input rate to this plant is 87.8 TPH and 2,107 TPD as 100-percent rock  $P_2O_5$ . Fluoride emissions from this plant are controlled by a North American Steel packed bed scrubber with "Kimre" packing or equivalent packing. Typical gas flow rate through the scrubber is approximately 48,000 actual standard cubic feet per minute (ascfm). The scrubber uses pond water as the scrubbing liquid. The packed bed scrubber's approximate normal operating parameters are: maximum outlet temperature of 120 degrees Fahrenheit ( $^{\circ}F$ ) and minimum fan amps of 80.

F emissions from the "B" Phosphoric Acid Plant are regulated under MACT. The F emission standard from the MACT regulations is 0.020 lb/ton  $P_2O_5$  input, equivalent to 1.76 lb/hr F. However, the plant is limited by an existing permit condition to 1.04 lb/hr and 4.6 TPY.



## 2.2 "A" DAP/MAP

The "A" DAP/MAP plant consists of a reactor, granulator, dryer, product cooler, mills, and screens. The dryer is fired with natural gas or No. 5 fuel oil, or a better grade, i.e., No. 2, 3, or 4 (back-up); at a maximum heat input rate of 28.5 million British thermal units per hour (MMBtu/hr). The maximum permitted  $P_2O_5$  input rates, based on a 12-hour average, are as follows:

<u>Production</u>	<u><math>P_2O_5</math> Input, TPH</u>
DAP	29.53
MAP	33.30

Emissions from the reactor and granulator are controlled by the following pollution control equipment, respectively:

- Scrubber Stage I: Ducon Envir. Tech. Series 435X-RL 9-foot (ft) outside diameter (O.D.), 27-ft long scrubber with  $H_3PO_4$  as the scrubbing liquid.
- Scrubber Stage II: Fume Downcomer consisting of duct work with fresh water sprays. The water is from the abatement scrubber.
- Abatement Scrubber: Ducon Envir. Tech. 15 ft x 28 ft spray chamber scrubber with fresh water as the scrubbing liquid.

Emissions from the dryer, mills, and screens are controlled by the following pollution control equipment, respectively:

- Dust Cyclones: Fly Ash Arrestor Corp. Four, 59 3/8-inch diameter each.
- Scrubber Stage I: Ducon Envir. Tech. 11-ft O.D. x 30-ft scrubber with  $H_3PO_4$  as the scrubbing liquid.
- Scrubber Stage II: Fume Downcomer consisting of duct work with fresh water sprays. The water is from the abatement scrubber.
- Abatement Scrubber: (same as above)

Emissions from the product cooler are controlled by the following pollution control equipment, respectively:

- Dust Cyclones: Fly Ash Arrestor Corp. Two 65-inch diameter each.
- Cooler Scrubber: Fume Downcomer consisting of duct work with fresh water sprays. The water is from the abatement scrubber
- Abatement Scrubber: (same as above)

Note: All equipment gases pass through the same abatement scrubber.

F emissions from the "A" DAP/MAP Plant are regulated under MACT. The F emission standard from the MACT regulations is 0.060 lb/ton  $P_2O_5$  input, equivalent to 1.78 lb/hr F for DAP production, and 2.00 lb/hr for MAP production. However, the plant is limited by an existing permit condition to 1.38 lb/hr and 6.04 TPY.

### 2.3 "X", "Y" AND "Z" DAP/MAP

Each of the "X, Y, and Z" granulation plants consists of a reactor, granulator, aging belt, product cooler, mills, and screens. Granular Triple Superphosphate (GTSP) is currently permitted for "X" and "Y", but will be deleted from the renewed/revised permit due to lack of use. The following are the maximum permitted input limits for the X Train:

**RAW MATERIAL INPUT (TPH)**

Mode	$P_2O_5$ Input	Phos. Acid ( $H_3PO_4$ )	Ammonia ( $NH_3$ )	Operating Time (hr/yr)
DAP	48.7	122.3	23.1	7,884
MAP	55.0	130.6	14.1	6,091

The following are the maximum permitted input limits for the Y Train:

**RAW MATERIAL INPUT (TPH)**

Mode	$P_2O_5$ Input	Phos. Acid ( $H_3PO_4$ )	Ammonia ( $NH_3$ )
DAP	48.7	122.3	23.1
MAP	55.0	130.6	14.1

The following are maximum permitted input limits for the Z train:

**RAW MATERIAL INPUT (TPH)**

Mode	$P_2O_5$ Input (TPH)	Phos. Acid ( $H_3PO_4$ )	Ammonia ( $NH_3$ )
DAP	48.7	122.3	23.1
MAP	55.0	130.6	14.1

The dryers are fired with natural gas or No. 5 fuel oil or lower fuel oil (back-up) at a maximum heat input rate for each plant as follows:

"X" Train DAP/MAP	49.7 MMBtu/hr
"Y" Train DAP/MAP	49.5 MMBtu/hr
"Z" Train DAP/MAP	42.75 MMBtu/hr

In each of the three plants, emissions from the reactor, granulator, and aging belt are controlled by the following pollution control equipment, respectively:

Scrubber Stage I:	Ducon Envir. Tech. Series 550, 9-ft 9-inch O.D., 36-ft 10½-inch-high scrubber with H <sub>3</sub> PO <sub>4</sub> as the scrubbing liquid.
Scrubber Stage II:	Ducon Envir. Tech. Series 550, 9-ft 9-inch O.D., 35-ft 4½-inch-high scrubber with pond water as the scrubbing liquid.
Abatement Scrubber:	Ducon Envir. Tech. Size: 15-ft x 35-ft scrubber with fresh water as the scrubbing liquid.

Emissions from the dryer are controlled by the following pollution control equipment, respectively:

Dust Cyclones:	Ducon Envir. Tech. 810/175 Type VM
Scrubber Stage I:	Ducon Envir. Tech. Series 555, 10-ft 2-inch O.D., 38-ft 4½-inch-high scrubber with H <sub>3</sub> PO <sub>4</sub> as the scrubbing liquid.
Scrubber Stage II:	Ducon Envir. Tech. Series 555, 10-ft 2-inch O.D., 36-ft 10½-inch-high scrubber with pond water as the scrubbing liquid.
Abatement Scrubber:	(same device as the reactor/granulator abatement scrubber)

Emissions from the mills and screens are controlled by the following pollution control equipment, respectively:

Dust Cyclones:	Ducon Envir. Tech. 810/175 Type VM
Dust Scrubber:	Ducon Envir. Tech., Series 535, 8-ft 8-inch O.D., overall height 34 ft 3 inches with H <sub>3</sub> PO <sub>4</sub> as the scrubbing liquid.
Abatement Scrubber:	(same device as the reactor/granulator abatement scrubber)

Emissions from the product cooler are controlled by the following pollution control equipment, respectively:

- Dust Cyclones: Ducon Envir. Tech. 810/175 Type VM Size 4-355 cyclone.
- Cooler Scrubber: Ducon Envir. Tech., Series 550, 9-ft 9-inch O.D., 35-ft 4½-inch high scrubber with pond water as the scrubbing liquid.
- Abatement Scrubber: (same device as the reactor/granulator abatement scrubber)

Note: All equipment gases pass through the same abatement scrubber.

F emissions from the "X", "Y" and "Z" DAP/MAP Plants are regulated under MACT. The F emission standard from the MACT regulations is 0.060 lb/ton P<sub>2</sub>O<sub>5</sub> input. However, the plants are limited by existing permit conditions to the following:

The "X" Plant shall not exceed any of the following maximum allowable F emissions rates:

FLUORIDE EMISSION RATE			
Production Mode	lb F/ton P <sub>2</sub> O <sub>5</sub>	lb/hr	TPY
DAP	0.035	1.70	6.70
MAP	0.04	2.20	6.70

The combined total fluoride emission rate for DAP and MAP from the X Plant shall not exceed 6.70 TPY.

The Y Plant shall not exceed any of the following maximum allowable F emissions rates:

FLUORIDE EMISSION RATE			
Production Mode	lb F/ton P <sub>2</sub> O <sub>5</sub>	lb/hr	TPY
DAP	0.06	2.2	9.6
MAP	0.06	2.2	9.6

The Z plant shall not exceed any of the following maximum allowable F emission rates based on the design capacity of 24 TPH of  $P_2O_5$  input.

**FLUORIDE EMISSION RATE**

Production Mode	lb F/ton $P_2O_5$	lb/hr	TPY
DAP	0.06	1.44	6.31
MAP	0.06	1.44	6.31

### 3.0 INITIAL PERFORMANCE TESTING

#### 3.1 TEST METHODS

The following parameters will be measured during the initial performance test, as required by MACT regulations and approved under the alternative MACT monitoring plan.

##### 3.1.1 "A" AND "B" PHOSPHORIC ACID PLANTS

CF will use historic test data from "A" Phosphoric Acid Plant to establish baseline average values for pressure drop and scrubber liquid flow rate across each scrubber in the "A" Phosphoric Acid Plant, as allowed by 40 CFR 63.605(d)(2).

CF will conduct performance testing to establish baseline average values for the scrubbers in the "B" Phosphoric Acid Plant. The testing will utilize the following procedures:

1. Total F using EPA Method 13B.
  - a. A minimum of two test runs will be performed. A minimum of one test run will be performed at the lower end of the scrubber pressure drop and liquid flow rate range, and a minimum of one test run will be performed at the upper end of the scrubber pressure drop and liquid flow rate range. This procedure will establish the "allowable range" of scrubber parameters.
  - b. Sampling time for each run will be a minimum of 60 minutes.
  - c. Sampling volume for each run will be a minimum of 30 dry standard cubic feet (dscf).
2. For determining sample port location and number of traverse points, EPA Method 1 will be used.
3. Volumetric gas flow rate measured out the stack using EPA Method 2.
4. Moisture content of stack gas using EPA Method 4.
5. Mass flow of phosphate-bearing materials, measured in tons per hour, using process data and factors unique to this process.
6. P<sub>2</sub>O<sub>5</sub> content of the feed, using as appropriate the methods specified in 40 CFR 63.626(c)(3).
7. Monitor pressure drop across the scrubber. The pressure drop will be recorded in 15-minute block averages during each run. The monitoring system will be certified to be accurate within ±5 percent over its operating range. The average pressure drop during

each of the runs will be determined. The minimum 1-run average and the maximum 1-run average will be used to establish the baseline range for pressure drop.

8. Monitor scrubber liquid flow rate. The scrubber liquid flow rate will be recorded in 15-minute block averages during each run. The monitoring system will be certified to be accurate within  $\pm 5$  percent over its operating range. The average liquid flow rate during each of the runs will be determined. The minimum 1-run average and the maximum 1-run average will be used to establish the baseline range for liquid flow rate.

### 3.1.2 "A" DAP/MAP PLANT

CF will use historic test data from "A" DAP/MAP Plant to establish baseline average values for pH of the scrubber water to the freshwater abatement scrubber in the "A" DAP/MAP Plant, as allowed by 40 CFR 63.625(f)(2).

CF will conduct performance testing to establish baseline average values for pressure drop across each scrubber segment in the "A" DAP/MAP Plant, and to establish baseline average values for scrubber liquid flow to the freshwater downcomers and the fresh water abatement scrubber in the "A" DAP/MAP Plant. The testing will utilize the following procedures:

1. Total F using EPA Method 13B.
  - a. A minimum of two test runs will be performed. A minimum of one test run will be performed at the lower end of the scrubber pressure drop and liquid flow rate range, and a minimum of one test run will be performed at the upper end of the scrubber pressure drop and liquid flow rate range. This procedure will establish the "allowable range" of scrubber parameters.
  - b. Sampling time for each run will be a minimum of 60 minutes.
  - c. Sampling volume for each run will be a minimum of 30 dscf.
2. For determining sample port location and number of traverse points, EPA Method 1 will be used.
3. Volumetric gas flow rate measured out the stack using EPA Method 2.
4. Moisture content of stack gas using EPA Method 4.
5. Mass flow of phosphate-bearing materials, measured in tons per hour, using process data and factors unique to this process.
6. P<sub>2</sub>O<sub>5</sub> content of the feed, using as appropriate the methods specified in 40 CFR 63.626(c)(3).

7. Monitor pressure drop across each scrubber segment: reactor/granulator, dryer/mills/screens, and product cooler (excludes final abatement scrubber). The pressure drop will be recorded in 15-minute block averages during each run. The monitoring system will be certified to be accurate within  $\pm 5$  percent over its operating range. The average pressure drop during each of the runs will be determined. The minimum 1-run average and the maximum 1-run average will be used to establish the baseline range for pressure drop.
8. Monitor scrubber liquid flow rates to freshwater downcomers and fresh water abatement scrubber. The scrubber liquid flow rates will be recorded in 15-minute block averages during each run. The monitoring system will be certified to be accurate within  $\pm 5$  percent over its operating range. The average liquid flow rates during each of the runs will be determined. The minimum 1-run average and the maximum 1-run average will be used to establish the baseline range for liquid flow rate.
9. Monitor pH of the scrubber water to the freshwater abatement scrubber. The minimum baseline average pH value will be determined from historic compliance test data. However, the pH range shall be limited only to a minimum of 4.5, regardless of the baseline average value, with no upper range limit. This limit is based on past demonstrations of scrubbing effectiveness and on fluoride chemistry.

### 3.1.3 "X", "Y" AND "Z" DAP/MAP PLANTS

CF will use historic test data from "X", "Y" and "Z" DAP/MAP Plants to establish baseline average values for pressure drop across each scrubber segment, and to establish baseline average values for pH of the scrubber water to the freshwater abatement scrubber, in the "X", "Y" and "Z" DAP/MAP Plants, as allowed by 40 CFR 63.625(f)(2).

CF will conduct performance testing to establish baseline average values for delivery pressure to each pond water cyclonic scrubber in the "X", "Y" and "Z" DAP/MAP Plants, and to establish baseline average values for scrubber liquid flow rate to the final abatement scrubber in the "X", "Y" and "Z" DAP/MAP Plants. The testing will utilize the following procedures:

1. Total F using EPA Method 13B.
  - a. A minimum of two test runs will be performed. A minimum of one test run will be performed at the lower end of the delivery pressure and liquid flow rate range, and a minimum of one test run will be performed at the upper end of the delivery pressure



and liquid flow rate range. This procedure will establish the "allowable range" of scrubber parameters.

- b. Sampling time for each run will be a minimum of 60 minutes.
- c. Sampling volume for each run will be a minimum of 30 dscf.
2. For determining sample port location and number of traverse points, EPA Method 1 will be used.
3. Volumetric gas flow rate measured out the stack using EPA Method 2.
4. Moisture content of stack gas using EPA Method 4.
5. Mass flow of phosphate-bearing materials, measured in tons per hour, using process data and factors unique to this process.
6. P<sub>2</sub>O<sub>5</sub> content of the feed, using as appropriate the methods specified in 40 CFR 63.626(c)(3).
7. Monitor pressure drop across each scrubber segment: reactor/granulator, dryer, mills/screens, and product cooler (excludes final abatement scrubber). Historic compliance test data will be used to establish the baseline average pressure drop value.
8. Monitor liquid delivery pressure to pond water cyclonic scrubbers. The scrubber liquid delivery pressure will be recorded once every 15 minutes during each run. The monitoring system will be certified to be accurate within  $\pm 5$  percent over its operating range. The average liquid delivery pressure during each of the runs will be determined. The minimum 1-run average and the maximum 1-run average will be used to establish the baseline range for liquid flow rate.
9. Monitor scrubber liquid flow rate to final abatement scrubber. The scrubber liquid flow rate will be recorded in 15-minute block averages during each run. The monitoring system will be certified to be accurate within  $\pm 5$  percent over its operating range. The average liquid flow rate during each of the runs will be determined. The minimum 1-run average and the maximum 1-run average will be used to establish the baseline range for liquid flow rate.
10. Monitor pH of the scrubber water to the freshwater abatement scrubber. The minimum baseline average pH value will be determined from historic compliance test data. However, the pH range shall be limited only to a minimum of 4.5, regardless of the baseline average value, with no upper range limit. This limit is based on past demonstrations of scrubbing effectiveness and on fluoride chemistry.

### 3.2 TEST SCHEDULE

The test schedule will be set after approval of the alternative MACT monitoring plan. Testing will occur on each plant within thirty days after the installation and successful operation of the necessary monitoring equipment and data management systems. FDEP and EPA will be notified of the approximate test dates at least 60 days in advance of the testing.

#### 4.0 DATA QUALITY OBJECTIVES

The initial performance testing and indicator monitoring data will meet the precision and accuracy that is required in the MACT requirements and the specific test methods.

## 5.0 INTERNAL AND EXTERNAL QUALITY ASSURANCE

### 5.1 INTERNAL QUALITY ASSURANCE

CF Industries has implemented the following quality assurance (QA) procedures, which will also be followed during the MACT testing:

- Equipment is calibrated at least annually;
- Gauges are checked at least annually;
- Systems are inspected prior to testing;
- Flow meters are calibrated at least annually; and
- Malfunctioning equipment is repaired and recalibrated as soon as practicable.

### 5.2 EXTERNAL QUALITY ASSURANCE

All stack sampling will be conducted by the CF Industries, Inc., Environmental Laboratory or Southern Environmental Sciences, Inc., of Plant City, Florida. The analysis of the samples will be performed by the CF Industries, Inc., Environmental Laboratory. The QA program is broken down into the following categories:

#### 5.2.1 PRETEST

##### Calibrations

The CF Industries Environmental Laboratory uses a dedicated Rockwell dry gas meter (Serial No. JA631105) as a calibration standard. Calibrations are performed annually against a wet test meter. The calibrations are performed at five points in triplicates according to EPA specifications.

All original calibration data and updates as well as the calibration curve, are presented in Appendix B of all test reports.

Field meters are calibrated against this standard annually by Southern Environmental Sciences, Inc. The field meters are recalibrated anytime a post calibration test check yields results which deviate by more than five percent (EPA requires recalibration at  $\pm 5$  percent).

The thermometers and thermocouples are calibrated annually and spot checked frequently (post test calibrations).

Pitot tubes are constructed to EPA specifications and are calibrated by measurement technique. Each pitot is visually inspected for proper alignment and possible damage prior to each use.

All calibration data are included in Appendix B of the test reports. Past calibration logs are available for inspection in CF Industries and Florida Department of Environmental Protection files.

#### *Analytical Instruments*

All instruments used by the CF Industries Environmental Laboratory for stack compliance testing are maintained and calibrated strictly by the manufacturers' recommended procedures. Documentation of each instrument's Performance Specifications, Interference Response, and Accuracy Verification are included in each report.

#### Tare Weights

Particulate filters and beakers are tare weighed in CF Industries' laboratory weight room. The weight room is humidity controlled and maintained at 30- to 50-percent relative humidity. The weighing balance is a Mettler AT200 Model. It is serviced and calibrated annually or as needed by Mettler service personnel.

Filters are visually inspected for irregularities, numbered, oven fired at 200°F for 2 hours and desiccated for 24 hours.

Beakers are washed with warm soapy water, rinsed with tap water, and final rinsed with distilled water. They are then drip dried, oven dried at 200°F for 2 hours, and desiccated for 24 hours.

Prior to use, the Mettler level bubble is checked and the balance is zeroed. Linearity is checked with 0.5-, 10.0-, and 100.0-gram Type S certified weights. The certified weight checks along with temperature, humidity, date, time, and technician's name performing the weighing are recorded in the tare weight book. Filters and beakers are then weighed and recorded in the tare weight book. The weighed items are then replaced in desiccators and reweighed at a minimum of 6 hours elapsed time. Weights that vary no more than 0.5 milligram (mg) are considered constant. Two acceptable weighings are averaged for the final tare weight. Beakers are kept in desiccators until needed. Filters are either placed directly in sealed filter holders for field use or sealed in petri dishes and Ziplock™ bags for future use.

### *Sample Bottles*

Dedicated Teflon sample bottles are rinsed with tap water and then with distilled water. The bottles are visually inspected for particulate residue and allowed to air dry. They are then tightly sealed and taped for use in the field.

### Silica Gel

Upon purchase, silica gel is inspected for proper color and mesh size. The silica gel is weighed into the test impingers and then tightly sealed for field use.

### *Acetone*

Pesticide-grade acetone is used as a rinse reagent. The acetone is stored in glass containers. Before opening a new container of rinse reagent, it is thoroughly shaken, and three 100-milliliter (mL) aliquots are taken. These samples are treated as field blanks to ensure the quality of our clean-up reagents. Bad acetone is returned to the supplier.

## **5.2.2 IN THE FIELD**

The CF Industries Laboratory field team leader is responsible for all QA in the field.

### Leak Checks

The meter box is leak checked (inclusive of post pump portions) at 15+ inches of water (H<sub>2</sub>O) pressure to insure meter integrity during transit.

Both sides of the pitot tube are leak checked at 3+ inches H<sub>2</sub>O pressure.

When the sampling train is assembled, all components are leak checked at 15+ inches mercury (Hg) vacuum. If any leaks are detected, they are corrected before any sampling is initiated. All required leak checks are repeated after each sampling run. Both pre- and post-test leak check results are recorded on the first page of the "Compliance Test Field Sheet".

### Nozzle Calibration

Nozzle calibration is performed in the laboratory by a CF Environmental Analyst or Technician. Three different diameters of the nozzle opening are measured with calipers and averaged. These measurements are recorded on the "Probe Nozzle Calibration Data" sheet.

**Field Testing**

The names of the test participants, coordinator, and agency observers are also recorded on the field data sheets.

The barometric pressure is obtained from the National Oceanic and Atmospheric Administration (NOAA).

Field calculations are made at the conclusion of each sample run to insure isokinetic limits have been met and that moisture content and flow rates are within the expected performance of the unit tested. This procedure detects any tube leaks and fan imbalances that can be detrimental in meeting compliance standards.

**Sample Recovery**

Upon completion of a sample run, the probe is placed in a secure position and the exterior of the nozzle is carefully wiped clean. After the leak check, the nozzle is removed and rinsed with acetone (or water) into a prepared sample bottle. The nozzle is then thoroughly brushed and rinsed until all particulate has been captured. The sample bottle is then securely closed and the liquid level is marked. The bottle is labeled with the run number and date. It is then placed in an upright position in the sample box.

The equipment is then transported to the on-site environmental laboratory where condensate collected in the first, second, and third impingers is carefully measured and recorded on the first page of the field data sheet. Any unusual characteristics (color, odor, etc.) are noted. The silica gel in the fourth impinger is carefully recovered and placed in its original container and labeled with the run number and date.

Used silica gel is also kept in the sample box.

The filter holder is then removed from the probe. It is securely sealed at both ends and labeled the same as the sample bottle. All filter recovery is performed at the CF Industries Environmental Laboratory.

The holder is carefully opened and the filter is removed. A spatula and a nylon bristle brush are used to recover any pieces of the filter adhering to the gasket or filter holder. The filter is placed in a plastic Petri dish, sealed, and labeled. The sample side of the holder is then washed and thoroughly brushed. The wash is added to the nozzle wash sample bottle and the liquid level is remarked. All samples are kept in the sample box.

#### **Blanks**

A filter and an acetone sample blank are run in the environmental laboratory alongside the field samples.

### **5.2.3 POST TEST**

#### **Analysis**

Nozzle, probe, and filter holder washes are checked for liquid loss. They are then thoroughly shaken and poured into tared beakers. The container is rinsed with acetone or water and the contents are added to the beaker and weighed. The total volume is recorded on the laboratory data sheet. Beakers are evaporated to dryness at ambient temperature and pressure, oven dried at 200°F for 2 hours, and finally desiccated until cool.

Filters are placed in glass petri dishes; oven dried at 105°C for 2 hours; and desiccated until cool. Final weights are determined using the same procedure as the tare weighing process. Time, date, temperature, humidity, and the name of the technician are recorded on the laboratory data sheet for each weighing. A laboratory data sheet is completed for each run.

#### **Chain of Custody**

The chain of custody is initiated at the time of sample recovery. Run number, container number, and comments are all noted on the chain-of-custody sheet. Technicians performing recovery and analysis sign the chain of custody sheet. This sheet is included in Appendix B of the test reports.

#### **Post-Test Calibrations**

Post-test calibration checks are performed on the dry gas meter. This check is made under conditions approximating the actual field test.



The meter is checked in triplicate at the maximum vacuum encountered during sampling. The stack thermocouple is compared to a mercury-in-glass thermometer at the average stack temperature and the meter temperature is checked at ambient conditions prior to meter use. The post test calibration sheet is signed by the technician performing the calibrations and is included in all stack reports.

#### **5.2.4 REPORTS**

The CF Industries, Inc., Environmental Laboratory uses a report format that is acceptable to all regulatory agencies. The reports are prepared by the Environmental Laboratory Supervisor and are reviewed by the Chief Environmental Services and the Superintendent Environmental Affairs for document completeness and accuracy.

## 6.0 CALCULATIONS AND REPORTING

### 6.1 CALCULATIONS

The emission rate (E) of total F shall be computed for each run using the following equation:

$$E = \frac{C_s \times Q_s \times 60 \text{ min/hr}}{P \times K}$$

- where:
- E = Emission rate of total F, (lb/ton) of equivalent  $P_2O_5$  feed.
  - $C_s$  = Concentration of total F from emission point, (grains/dscf).
  - $Q_s$  = Volumetric flow rate of effluent gas from emission point (dscf/min).
  - P = Equivalent  $P_2O_5$  feed rate, TPH.
  - K = Conversion factor, (7,000 grains/lb).

The equivalent  $P_2O_5$  feed rate (P) shall be computed using the following equation:

$$P = M_p R_p$$

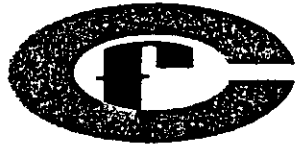
- where:
- $M_p$  = Total mass flow rate of phosphorus-bearing feed, (tons/hr).
  - $R_p$  =  $P_2O_5$  content, decimal fraction.

### 6.2 REPORTING

The results of the stack tests will be submitted to FDEP within 45 days of completion of the tests while the results of the initial performance test will be submitted to the Administrator before the close of business on the 60<sup>th</sup> day following the completion of the performance test. The report will include:

- The F emissions limits for the tested sources, determined from the initial performance test;
- The calculations and supporting documentation used to determine the F emissions limits for the tested sources;
- The average baseline scrubber parameters for the tested sources established during these initial performance tests; and
- Data and information demonstrating good QA.

P.O. Drawer L.  
Plant City, Florida 33564-9007  
Telephone: 813/782-1591



**CF Industries, Inc.**  
Plant City Phosphate Complex

May 3, 2004

RECEIVED  
MAY 6 2004  
Department of Air Monitoring  
& Environmental Sciences

Mr. Douglas Neeley  
Chief, Air Toxics and Monitoring Branch  
U.S. Environmental Protection Agency  
Region IV  
61 Forsyth Street, S.W.  
Atlanta, Georgia 30303-8960

Re: CF Industries, Inc.  
Application for Approval of Alternative Monitoring

Dear Mr. Neeley:

Please accept this letter and the accompanying attachments as CF Industries, Inc.'s (CFI's) application to the Environmental Protection Agency (EPA) for approval of an alternative monitoring plan pursuant to 40 CFR §63.8, in regard to CFI's Plant City Phosphate Complex in Hillsborough County, Florida.

CFI first submitted a proposal for an alternative monitoring plan to the Florida Department of Environmental Protection (FDEP) in a letter dated June 5, 2003. (Attachment 1.) As you will see, this letter provides substantial background information concerning the Plant City Complex. At the time that this letter was sent, CFI and FDEP were addressing the development of a protocol for quantifying fugitive hydrogen fluoride (HF) emissions from the plant's pond system, because the amount of fugitive HF emissions from the ponds, insofar as the fugitive emissions are quantifiable, is dispositive as to whether the Plant City Phosphate Complex constitutes a "major source" that is subject to 40 CFR Part 63, Subparts AA and BB. CFI requested consideration of an alternative monitoring plan in the event the Plant City Phosphate Complex is determined to be a major source.

CFI's submittal to FDEP stated (p.8):

In the event that the Plant City Phosphate Complex is determined to be subject to the HF MACT standards, CF requests that the DEP take into account the unique fresh water fluoride abatement scrubbing already in place, the record of past compliance with fluoride emission permit limits that equal the MACT emission standards, the

excessive cost:benefit ratio of the Part 63 monitoring, and the technically comparable parametric monitoring already in use, and accept the Alternative Monitoring Plan provided in Appendix E as alternative monitoring allowed under Rule 40 CFR 63.8(f).

Subsequently, CFI and FDEP agreed to resolve the disagreement over whether the Plant City Phosphate Complex is a major source subject to Part 63, Subparts AA and BB by adding language to the determination of major source status (in the Title V permit) stating that CFI may request that major source status be revisited based on additional testing and modeling. FDEP also agreed to work with CFI in developing a mutually acceptable alternative monitoring plan. (See Attachments 2 and 3.)

We are forwarding these materials and applying to EPA for approval of an alternative monitoring plan because FDEP informed us on March 26, 2004 that under the delegation agreement EPA has retained authority to rule on some of the types of proposed alternative monitoring methods CFI proposed.

Also enclosed, for EPA's consideration, is CFI correspondence dated October 31, 2003 (Attachment 4), December 31, 2003 (Attachment 5), and February 6, 2004 (Attachment 6), responding to FDEP's questions and information requests on CFI's proposed alternative monitoring plan. Finally, Attachment 7 summarizes CFI's summary of the alternative monitoring plan proposal that it now requests EPA to consider.

CFI would sincerely appreciate the opportunity to confer with appropriate representatives of EPA Region IV regarding this proposed alternative monitoring plan. We would like to present a brief overview of our proposal and answer all questions. The appropriate contact at CFI is Tom Edwards; he can be reached by telephone at 813-364-5608.

Thank you for considering CFI's proposed alternative monitoring plan.

Sincerely,



Herschel E. Morris  
Vice President Phosphate Operations and  
General Manager

cc: Michael Cooke, FDEP  
Trina Vielhauer, FDEP  
Errin Pichard, FDEP  
Gerald Kissell, FDEP  
Jerry Campbell, EPCHC  
David Buff, Golder Assoc.  
J.S. Alves, HGS

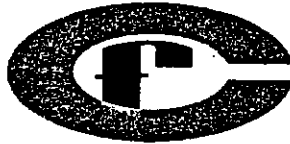
ATTACHMENT 1

JUNE 5, 2003 LETTER

MORRIS TO KISSEL

TAE

P.O. Drawer L.  
Plant City, Florida 33564-9007  
Telephone: 813/782-1591



**CF Industries, Inc.**  
Plant City Phosphate Complex

June 5, 2003

Mr. Gerald Kissel, P.E.  
Air Permitting Supervisor  
Southwest District Office  
Department of Environmental Protection  
3804 Coconut Palm Drive  
Tampa, Florida 33619

RE: Hydrogen Fluoride NESHAP Applicability and  
Alternative Monitoring - CF Industries, Inc.,  
Plant City Phosphate Complex, Permit No.  
0570005-007-AV

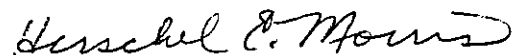
Dear Mr. Kissel:

CF Industries, Inc., provides the enclosed information as agreed in an April 22, 2003 meeting with FDEP and HCEPC personnel at the Plant City Phosphate Complex.

This submittal includes a re-evaluation of process fugitive HF emissions, a justification and proposed test plan for the determination of process water pond HF emissions, and a proposed alternative monitoring plan with justification rationale. CF Industries, Inc., proposes that the Title V air permit be issued with conditions requiring (1) the site specific testing of the process water ponds to determine the applicability of the HF NESHAP rule, and (2) the implementation of the alternative monitoring plan at such time as the rule is conclusively shown to be applicable.

Please review those materials and provide any questions or comments to Bob May or Tom Edwards.

Sincerely,

A handwritten signature in cursive script, reading "Herschel E. Morris".

Herschel E. Morris  
General Manager

cc: Winston Smith, USEPA  
John Glunn, DEP  
Al Linero, FDEP Tallahassee  
W. Douglas Beason, Esq., DEP OGC  
Jerry Campbell, HCEPC  
J.G. Sampson, CFI  
Jim Alves, HGS

PROPOSAL FOR PHOSPHORIC ACID PROCESS POND HF TESTING AND  
CONTINGENCY ALTERNATIVE MONITORING PROVISIONS  
CF INDUSTRIES, INC. - PERMIT NO. 0570005-007-AV

I. Introduction

The CF Industries, Inc., Plant City Phosphate Complex (CF) was initially constructed in 1964-1965 to produce primarily run-of-pile triple superphosphate and diammonium phosphate fertilizers. CF Industries, Inc., acquired the facility in 1970, and received permits to expand the facility in 1973. As a condition of the permit approvals, CF installed fluoride emission scrubbing capacity designed to remove 99.5 to 99.8% of the fluoride emissions from the granulation processes (Appendix A - Letter, Department of Pollution Control). The gas scrubbing trains on each of the four granulation plants include a final, fresh water, fluoride-abatement scrubber using caustic addition to maintain a neutral pH and ensure a high degree of fluoride removal.

The history of compliance tests shows the total fluoride emissions from the phosphoric acid, granulation, and storage building stacks to be typically in the range of 50% to 80% lower than required under the New Source Performance Standards, amply meeting the emission standards set forth in 40 CFR 63 Subparts AA and BB as Maximum Achievable Control Technology (MACT). The fresh-water, fluoride abatement scrubbers are believed to be unique to CF within the industry, and therefore provide an extra level of control against hydrogen fluoride (HF) as well as total fluoride emissions.

The CF Industries, Inc., Title V Air Permit No. 0570005-007-AV currently includes the periodic monitoring of operating parameters for routine control of its pollution control equipment. Additionally, CF has recently proposed a Compliance Assurance Monitoring Plan in accordance with 40 CFR 64. Both of these parametric monitoring programs have the purpose of ensuring continuing pollution control performance during periods between emission stack compliance tests. When the HF NESHAP (National Emission Standards for Hazardous Air Pollutants) rule sought to



impose additional costly parametric monitoring, CF questioned the need for the additional monitoring (continuous liquid flow and pressure drop measurement on all scrubbers). CF also questioned the applicability of the rule to the Plant City Phosphate Complex, recognizing the extra pollution control assurance provided by the existing freshwater abatement scrubbers.

In order to obtain site-specific data for the determination of MACT rule applicability, CF first sampled its emission stacks for fluoride, silicon, and ammonia to determine if the stack gases contained sufficient silicon and ammonia to combine with all the fluoride present. An excess of silicon and/or ammonia would imply that all the fluoride could exist as chemical compounds with these two substances, and not as HF. These tests did indicate excesses of ammonia and silicon in all the stack gases.

CF then contracted with URS Corporation to sample the stacks using Fourier-Transform Infrared Spectroscopy (FTIR) to determine whether an actual concentration of HF could be detected and measured. This testing concluded that small concentrations of HF were present, but at a much lower HF to F ratio than was assumed by EPA (Federal Register Volume 64, Page 31363) during the development of Subpart AA and BB rules. The measured concentration of HF was actually 3% to 5.8% of Total F, not 33% as assumed by EPA. The total HF emissions from the facility using the measured stack gas concentrations in combination with the estimated fugitive HF emissions, were less than the 10 ton per year threshold for applicability of the rule. This was reported to the Department of Environmental Protection (DEP) in a written report on October 14, 2002.

In subsequent meetings with the DEP and the Hillsborough County Environmental Protection Commission (EPC), the agencies questioned the values used by CF for HF fugitive emissions. These questions focused on (1) the HF fugitive emissions from process equipment and exposed process materials in the manufacturing area of the Plant City Complex, and (2) the process water pond HF flux (CF had used a flux similar to that estimated by a consultant for The

Fertilizer Institute and accepted by EPA during the rule development). In order to resolve the first question, CF has sampled the pre-scrubber gases from its processes to determine the silicon, ammonia, and fluoride concentrations in the fugitive gases, calculated the area of exposed process material surfaces, and revised its estimate of process fugitive HF emissions based on the new data. Regarding the second question, CF proposes to conduct rigorous measurement and modeling of HF emissions from its process water ponds to develop an improved estimate for that source.

CF also proposes an alternative monitoring plan, pursuant to 40 CFR 63.8(f), to be implemented if the facility is ultimately shown to be a major source of HF emissions as defined by 40 CFR 63. The alternative monitoring proposed is justified by an analysis of the ratio of the cost of the monitoring equipment to the pollutant reduction expected, - i.e., the cost per ton of reduced emissions, as well as the technical comparability between the proposed approach and the MACT requirements. The ratio calculated for the flow and pressure drop monitoring specified by the rule is greatly in excess of EPA cost/benefit guidelines (re: discussion in Part IV, below). CF has already invested in pollution control equipment that is in excess of the general industry practice (the freshwater fluoride abatement scrubbers), already has a significant parametric monitoring program in place, and already meets the MACT emission limits. Consequently, the expenditure for the additional monitoring equipment is neither economically nor technically justified, whether or not the facility meets the major source threshold.

## II. Point Source and Process Fugitive Emissions Determination

### A. Point Source Emissions

The point source emissions were sampled first by CF Industries personnel using a method that extracts a gas sample from the stack and collects it in a series of impingers. The solutions from the impingers were analyzed for fluoride, silicon, and ammonia, all substances that were

known to be present in the gas streams. The concentrations of silicon and ammonia were found to be in excess of the amount necessary to react with all the fluoride present and form silicon tetrafluoride ( $\text{SiF}_4$ ) or ammonium bifluoride ( $\text{NH}_4\text{HF}_2$ ). These results were the first indication that HF point source emissions could be expected to be lower than the EPA assumed ratio (1HF:3 Total F).

CF then contracted URS Corporation to measure the HF concentrations in the stacks using FTIR methodology on an extracted sample. DEP and EPC provided input to the test plan. The tests were conducted with EPA Methods 301 and 320 for method validation and quality assurance. EPA Method 13B sampling for Total Fluoride was conducted simultaneously with the FTIR testing so the HF:Total F ratios could be calculated. The resulting ratios were then applied to the allowable fluoride limits in the permits to determine the HF Potential to Emit (PTE) for the facility's point sources.

These results were provided to the agencies in an October 14, 2002, report. The PTE was found to be 1.70 tons per year from these sources.

#### B. Process Fugitive Emissions

The HF fugitive emissions from the manufacturing area of the facility were estimated using the following assumptions:

- (1) The fumes from process equipment that is designed to be evacuated to a scrubbing system are collected and scrubbed 99.5% of the time, since the equipment is under negative pressure except when duct flow is occasionally restricted by pluggage.
- (2) Scrubber efficiency is 99% (per design and previous inlet/outlet sampling).
- (3) The phosphoric acid filters and other sources in the phosphoric acid plants are responsible for 10% of the fugitive

emissions from those plants, 90% of the fugitives are from the reactor during flow restriction episodes.

- (4) The HF:F ratio in the fugitive emissions is the same as in the scrubbed point source emissions.

The resulting process fugitive emissions were calculated to be 1.04 tons per year. This was also reported in the October 14, 2002, submittal.

In subsequent meetings, the above assumptions were questioned by DEP and EPC personnel, and CF agreed to review them and do additional testing of the scrubber inlet gases to determine whether silicon and ammonia were in excess at that point, and therefore in the process fugitives.

Based on its review, CF provides the following comments:

- (1) The 99.5% collection efficiency is based upon long-term operator experience and best engineering judgment. There is no basis for changing this assumption.
- (2) The scrubber efficiency of 99% is based on design parameters agreed to by CF during the initial permitting of the scrubbers and upon inlet/outlet sampling previously conducted. There is no basis for changing this assumption.
- (3) Miscellaneous fugitive emissions from exposed process material surfaces including phosphoric acid filter areas not under the collection hood, sewer ditches, seal tanks, and vacuum pump exhausts, have been calculated. The actual surface areas of the exposed surfaces were calculated and totaled, and a conservative HF flux estimate was applied. The emission factor for vacuum pump exhaust was taken from the AP-42 data compilation. The total from these sources is 0.107 tons per year. This amount has

been added to the previous total, as shown in the revised Table 3, Appendix B.

- (4) The scrubber inlet gases from both phosphoric acid plants, a DAP granulation plant, and a granular product storage building were sampled for silicon, ammonia, and fluoride. The silicon and ammonia concentrations were found to be in excess of the fluoride concentration in each case, just as they were in the scrubbed stack gases. Therefore it is reasonable to assume the same HF:F ratios in the process fugitive emissions as were found by the FTIR method in the point source stack emissions.

Taking the above review into account, it is appropriate to change the estimated process fugitive emission total from 1.04 to 1.15 tons per year. The total estimate of point source potential to emit and process fugitive emissions is 2.85 tons HF per year. This was provided to the agencies by letter report on May 22, 2003.

### III. Rule Applicability

In order to determine the applicability of Rule 40 CFR 63, Subparts AA and BB, to the Plant City Phosphate Complex, the total HF emission from all sources at the facility must be determined to exceed 10 tons per year. The emissions from point sources and process fugitives are stated above to be 2.85 tons per year. The remaining source to be considered is the flux from the process water cooling pond and storage ponds.

In the October 14, 2002 submittal, CF used the HF flux determined in a 1993 FTIR study of its cooling pond. This study was very similar to the TFI study accepted by EPA during the rule-making. The flux for the CF pond was 0.02 lb.HF per acre per day, resulting in an emission estimate of 0.85 tons HF per year from the pond surfaces. DEP has declined to accept this flux determination and emission estimate due to concerns with the air dispersion modeling used. Consequently, CF proposes to conduct a thorough, site-specific, process water pond study using a combination of the FTIR methodology and TDL (Tunable Diode Laser)

methodology to arrive at CF's pond emissions flux. The test plan, provided by ARCADIS/Geraghty and Miller, is attached for agency review (Appendix C). This plan includes adequate validation and quality assurance checks to provide confidence in the results of the study. If the results of the study show pond emissions to be 7.15 tons per year or greater, then the total HF emission from the facility will be in the major source range and the rule will be applicable to the Plant City Phosphate Complex. If the results of the study show pond emissions to be less than 7.15 tons per year, then the facility will not be a major source of hazardous air pollutants.

In order to provide assurance to CF and the agencies that the proposed study, upon completion, will resolve the applicability question, CF proposes that the study be made a condition of the final Title V air operation permit and be conducted upon the issuance of the final permit.

#### IV. Parametric Monitoring

If the proposed process water pond study shows that the Plant City Phosphate Complex is not a major source of HF, then the monitoring requirements of 40 CFR 63 will not apply. However, if the facility is shown to be a major source, CF has determined that the implementation of parametric monitoring as prescribed by the rule would cost \$1,161,000. This determination is attached in Appendix D.

CF has also conservatively estimated the incremental reduction in HF emissions that could result from the added monitoring at approximately 10% of the current point source potential to emit, or about 0.17 tons per year. The reduction logically could result from the detection of occasional scrubber performance problems a few minutes to a few hours earlier than they are now detected by the existing parametric monitoring program. The improvement in the detection time could then foreseeably result in an improvement in the response time for the correction of dips in scrubber performance. Significantly, however, the Part 63 monitoring would barely affect the total HF emission from the complex.

Based on the above implementation cost and HF emission reduction, the calculated cost to benefit ratio of the additional monitoring is \$6.8 million per ton of HF, more than 130 times the \$50,000 per ton figure stated by EPA to be "inappropriately high" and "unreasonable in terms of cost" (Federal Register Vol. 64, Pages 31361 and 31369). Even if the entire point source emission were to be eliminated by the additional monitoring, the cost would still be several times the stated EPA guideline and typical economic feasibility thresholds in other project evaluations, and would not be justified by the negligible pollutant reduction.

In the event that the Plant City Phosphate Complex is determined to be subject to the HF MACT standards, CF requests that the DEP take into account the unique fresh water fluoride abatement scrubbing already in place, the record of past compliance with fluoride emission permit limits that equal the MACT emission standards, the excessive cost:benefit ratio of the Part 63 monitoring, and the technically comparable parametric monitoring already in use, and accept the Alternative Monitoring Plan provided in Appendix E as alternative monitoring allowed under Rule 40 CFR 63.8(f).

CF requests that a condition be included in the final permit specifying that the proposed Alternative Monitoring Plan is to be implemented in the event the process pond testing proposed in Section III, above, shows the Plant City Phosphate Complex to be a major source of HF. CF also requests that the condition specify a period of 120 days from the date of issuance of the test report for procurement and installation of the monitoring equipment specified in the Alternative Monitoring Plan, and an additional 90 days for stack testing to establish the parametric control compliance ranges.

APPENDIX A

LETTER - DEPARTMENT OF POLLUTION CONTROL





B

STATE OF FLORIDA  
DEPARTMENT OF  
POLLUTION CONTROL  
INTEROFFICE COMMUNICATION

M E M O R A N D U M

TO: Peter P. Baljet  
FROM: K. K. Huffstutler  
DATE: March 5, 1973  
SUBJECT: Hillsborough County AP  
C. F. Industries Inc.  
Phosphate Fertilizer Industry

I. Type of Permit

C. F. Industries, Inc., Phosphate Fertilizer Plant located 10 miles north of Plant City has applied for permit to construct air pollution control devices on existing plants and to increase the production by installing new plants in some cases. A total of seven applications were submitted.

II. Basic Details of the Project

The seven applications are listed below with a brief description of each.

1. Sulfuric Acid Plants

Two existing plants 1000 TPD  $H_2SO_4$  each will be improved by modifying the scrubbers and addition of Brinks demisters.

Two new 1500 TPD  $H_2SO_4$  each are double absorption type and final gas scrubbers are not required.

2. Phosphoric Acid Plants. Expansion of existing facility from 630 TPD to 1620 TPD phosphoric acid production. Additional scrubbers will be designed for 99.5% efficiency.

3. Granular Shipping and Storage. Additional storage and shipping building will have a dry cyclone followed by a packed scrubber. Will be designed for 10#/day maximum emission.

Hillsborough County AP (cont'd)

-2-

C. F. Industries Inc.

Phosphate Fertilizer Industry

4. Granular Triple Super Phosphate. Additional scrubbers designed for overall efficiency of 99.8% will handle expanded capacity.
5. Diammonium Phosphate-Cyclone scrubbers followed by spray type scrubbers.
6. Rock Grinding and Handling-Additional bag-type collectors with 99.8% efficiency.
7. Mixed Grade Triple Superphosphate-Modify existing scrubbers and add two more scrubbers of proprietary design to give 99.6% efficiency.

All these modifications will meet the July 1, 1975 specifications by that time.

### III. Coordination by Department of Pollution Control

Local program Hillsborough County Pollution Control Commission reviewed the applications and has no objection to their approval.

L. G. Kerner, Regional Engineer DPC, reviewed the applications and offers no objections.

### IV. Evaluation

This plant is in Hillsborough County and therefore is under a moratorium for new sources of particulate and SO<sub>2</sub> pollution. Therefore, the following information is submitted to show a reduction in SO<sub>2</sub> and at least an even break in particulates.

There will be <sup>no</sup> an increase in fluorine emissions but still within the limits of Chapter 17-2.

A table of all emissions is presented here for clarification:

SO<sub>2</sub> emissions from 5000 TPD

Sulfuric Acid Plants

#/day per applications

#/day per Ch. 17-2  
New plants

20,000

20,000

Last year (1972) with production rate of 2000 TPD SO<sub>2</sub> emissions were reported 35,000 to 40,000 #/day. Therefore the new construction would increase H<sub>2</sub>SO<sub>4</sub> production from 2000 TPD to 5000 TPD and actually cut SO<sub>2</sub> emissions in half.

Hillsborough County AP (cont'd) -3-  
 C. F. Industries Inc.  
 Phosphate Fertilizer Industry

Fluorine from	#/day application	#/day 17-2 New plants
Granular Storage & shipping 2670 TPD 2232 TPD acid	30	53.40
Phosphoric Acid 1620TPD	22	32.40
Granular triple Super phosphate 1837TPD 1224 TPD acid	60	73.44
Mixed granular triple super phosphate 467TPD acid	50	56.04
DiAmmonium phosphate 369TPD acid	21	22.14
Dust(particulate) from	Per application #/day	Per 17-2 #/day weight table
Granular storage & shipping 2670TPD	186	866.64
Granular triple super phosphate 1837TPD	366	836.40
Mixed granular super phosphate 700TPD	171	816.00
DiAmmonium phosphate 833TPD	97	720
Grinding 8296TPD	140	1030

V. Recommendation

The staff recommends approval of the project and construction permits to make the modifications.

APPENDIX B

REVISED TABLE 3

FROM THE OCTOBER 14, 2002, REPORT

Table 3

## CF Industries Inc. Plant City Phosphate Complex Emission Estimates For HF

Source/Unit	Point Source Total Allowable F (TPY)	HF Factor (HF/F) Ratio	Point Source Potential to Emit HF (TPY)	Estimated Fugitive HF (TPY)	Total HF Emission Potential (TPY)	Notes
A-DAP/MAP <sup>a</sup>	6.04	4.1%	0.25	0.12	0.37	Assumes 0.5% uncaptured fumes from all sources & 99% scrubber efficiency
X-DAP/MAP/GTSP <sup>a,c</sup>	6.70	4.1%	0.27	0.14	0.41	Assumes 0.5% uncaptured fumes from all sources & 99% scrubber efficiency
Y-DAP/MAP/GTSP <sup>b,c</sup>	9.60	5.8%	0.56	0.28	0.84	Assumes 0.5% uncaptured fumes from all sources & 99% scrubber efficiency
Z-DAP/MAP <sup>a</sup>	6.31	4.1%	0.26	0.13	0.39	Assumes 0.5% uncaptured fumes from all sources & 99% scrubber efficiency
A-PAP <sup>d</sup>	5.20	3.0%	0.16	0.18	0.34	Assumes 0.5% uncaptured fumes from reactor, 10% uncaptured fumes from filters and other sources, 99% scrubber efficiency, 93% of fumes from reactor. <sup>e</sup>
B-PAP <sup>d</sup>	4.60	3.0%	0.14	0.16	0.30	Assumes 0.5% uncaptured fumes from reactor, 10% uncaptured fumes from filters and other sources, 99% scrubber efficiency, 93% of fumes from reactor. <sup>e</sup>
Acid Clarification	1.23	4.7%	0.06	0.03	0.09	Assumes 0.5% uncaptured fumes from all sources & 99% scrubber efficiency
Shipping Scrubber <sup>c</sup>	NA	NA	NA	NA	NA	Assumes 0.5% uncaptured fumes from all sources & 99% scrubber efficiency
Misc HF Sources				0.107	0.107	Assumes 1.51 Lb HF/day/acre from the surface area of tanks and ditches with pond water. Vacuum Pump HF emissions per AP-42 1/95 Table 8.9-1; Controlled emission factor for Phosphoric Acid Plant filter vacuum pump
Process Water Cooling Ponds <sup>f</sup>	NA	NA	NA	0.85	0.85	Uses 0.02 µg/(m <sup>2</sup> -s) HF pond emission factor from the 1/7/94 Radian report. Assumes an average 6.8MPH wind speed, an average annual pond water temperature of 95°F, and a pond coverage area of 311 Acres.
Total			1.70	2.00	3.70	

<sup>a</sup>Note: While permitted for DAP & MAP, these plants have only produced DAP in the last 10+Yr. No testing was done in A and Z DAP/MAP. Therefore, the X-DAP HF emission factor was used.

<sup>b</sup>Note: This plant produces both DAP & MAP on a routine basis. The Y-MAP HF emission factor was used because it was higher than the X-DAP factor.

<sup>c</sup>Note: GTSP has not been produced in more than 10 years. If GTSP is produced in the future, emission factors will be developed and the facility's status as a HAP source will be re-evaluated.

<sup>d</sup>Note: No testing was done in A-PAP. The emission factor for B-PAP was used for A-PAP.

<sup>e</sup>Note: Past fume duct tests in A & B PAP have indicated that 93% of the fluoride fumes entering the scrubbers come from the reactor. The filter and other sources contribute only 7% of the fluorides.

<sup>f</sup>Note: See Appendix B for sample calculations.

APPENDIX C

PROCESS WATER POND

TEST PLAN

## **Proposal to CF Industries, Plant City, Florida**

### **Determination of HF fluxes from Cooling Pond by Optical Remote Sensing**

**ARCADIS**

**PO Box 13109**

**Research Triangle Park, NC 27709**

#### **INTRODUCTION**

ARCADIS is pleased to have the opportunity to propose CF Industries air monitoring services to make measurement-based determinations of the emission rate of HF from a cooling pond (and other HF sources as time permits), using two different Optical Remote Sensing (ORS) measurement technologies. The measurements will take place over a period of one week, consisting of five working days (Monday through Friday). On each day the weather forecast will be noted to determine which of measurement configuration will be optimum under the given wind conditions for the purpose of determining the emission rates for hydrogen fluoride at different segments of the pond. Priority will be given to making measurements to determine the emissions from the cooling pond. If these measurements are completed before the end of the five-day period, other emission sources within CF Industries facility will be investigated. Measurements could also be made on or outside the CF fenceline, upon request.

#### **COST**

**One-Week Monitoring Service.** Five days of emissions measurements using both a scanning Tunable Diode Laser, an Open-Path FTIR sensor and a weather station. For any wind condition, the configuration of the measurement will be optimum for determining quantitative and reliable HF emission fluxes from the cooling pond. Any other measurement of facility fugitive emissions or other ponds will be conducted as time and wind conditions allow .....\$29,000

**Extended Monitoring Service.** CF Industries may elect (based on preliminary information from the first several days of measurement) to extend the monitoring service beyond the five-day period for the purpose of monitoring other emission sources.....\$3,000 per day

#### **METHOD**

In most of the configurations, a segment of the pond is chosen and the Tunable Diode Laser (TDL), tuned to an HF absorption line in the wavelength region of 1.5 micrometers, is set up on the downwind side of the selected lagoon-segment. The OP-FTIR is set up on the upwind side of the segment. A weather station will set up near the TDL beams to make wind speed and direction measurements that are simultaneous to the HF measurements.

The TDL and OP-FTIR sensors transmit the infrared beams to corner-cube retroreflector arrays that return the beams back to the respective sensors. Thus, each sensor will receive a beam that has passed through the plume twice. This in effect doubles the signal level, improving the detection sensitivity and the measurement precision. The TDL will be multiplexed to make simultaneous path-integrated HF concentration measurements to two different retroreflectors. One retroreflector, designated as the ground-level retro, is set up at ground level (~1-meter elevation) and the second retroreflector, designated as the elevated-level retro, is setup on a

scissor jack at an elevation between 10 and 17 meters. The beams from the TDL to the two retroreflectors form a vertical plane that is roughly normal to the wind direction. The path-integrated concentrations from the two beam paths are input to an optimization algorithm that calculates the vertical concentration gradient in the vertical plane. The emission flux through the measurement plane is determined from the determined area-integrated concentrations times the wind speed component normal to the plane. This method has been validated in controlled-release studies, sponsored by USEPA, DOD and DOE. The path-integrated measurement of the HF by the OP-FTIR system, along the upwind boundary of the chosen pond segment, will be used to facilitate the determination of the HF flux into the pond segment. The net flux from the segment is determined by subtracting the upwind contribution from the CT-determined flux through the downwind vertical plane.

We have designed ten different scanning measurement configurations for CF Industries Cooling Pond, and one configuration for the facility complex fugitive emissions. These configurations will provide optimum monitoring coverage for any given wind direction. In all setups, the multiplexed TDL beam will be aligned to both the ground-level retro and to the elevated retro to make simultaneous measurements over the two beam paths. At the same time the OP-FTIR will either be in an "upwind" configuration, fixed to a single ground-level retro and making repeated one-minute measurements, or be setup in the middle of the pond scanning to several retroreflectors to locate and quantify hot spots. In the latter scenario, the OP-FTIR sensor will be aligned alternatively to each of several ground-level retro, dwelling one each for a one-minute measurement time. These ground-level retros will be strategically placed to facilitate the mapping of the concentrations of hydrogen fluoride over the pond surface.

## **SOUTH WIND**

When the wind is from the South, each of three proposed configurations will be set up and measurements will be made in sequence. The three configuration are labeled South-Configuration 1, South-Configuration 2, South-Configuration 3 and are shown in Figures 1, 2, and 3, respectively.

### **South-Configuration 1**

When the wind is determined to be from a southerly direction, the TDL, OP-FTIR and the retroreflectors will be set up in *South-Configuration 1*, as shown in Figure 1. This configuration was designed to determine the emission flux from the hot well, and thus has the highest priority of the three south-wind configurations. The TDL will scan a ground-level retro and an elevated retro. The elevated retro will be at a lower height (10 meters) in this configuration because the beam will be fairly close to the emission source. The beams to the two retroreflectors lie on the vertical plane through which the HF flux will be determined by the optimization algorithm. The OP-FTIR measurements of HF on the upwind side of the hot well will determine whether any of the flux measured by the TDL sensor originated from sources outside of the hot well and pond. If it is determined that there is an upwind source of HF, the determination will be used to estimate the input flux to the hot well area, so that this component can be removed from the TDL determination to yield a net flux from the hot well.



### South-Configuration 2

When the *South-Configuration 1* is completed (after a 90-minute measurement period), sensors and retroreflectors will be setup in *South-Configuration 2*, as shown in Figure 2. This configuration was designed to determine the emission flux from the segment of the pond just north of the hot well, in the region between the OP-FTIR beam on the upwind side and the TDL beams on the downwind side. The elevated retro will be raised to a higher elevation, ~ 17 meters, because the plane is now further from the upwind emission sources in the pond. The optimization algorithm will determine the total HF flux through the vertical plane defined by the TDL beams.

The vertical plane defined by the TDL beams in *South-Configuration 1*, downwind of the hot well, is the upwind plane for the south-central pond segment being covered by *South-Configuration 2*. If the wind and emission conditions do not change significantly from the time of the *South-Configuration 1* measurements, the downwind vertical-plane flux determination from *South-Configuration 1* can be used as the upwind input flux to the south-central pond segment. The OP-FTIR beam path in *South-Configuration 2* is identical to the TDL ground-level beam path in *South-Configuration 1* determination for the beam path to the ground-level retro, thus the respective OP-FTIR measurement can be compared to the earlier TDL ground-level measurement. If there is agreement, the total output flux determined in *South-Configuration 1* can be used as the input flux for the south-central pond segment. If the OP-FTIR indicates a change in the ground-level path-integrated concentration of HF, the input flux can be estimated by assuming a proportionate change in the flux. The net flux from the emission in the south-central pond segment is determined by subtracting the input flux from the total output flux.

### South-Configuration 3

When the measurements using *South-Configuration 2* is completed (after a measurement period of 90 minutes), the equipment will be set up in *South-Configuration 3* as shown in Figure 3. This configuration was designed to determine the HF flux from the emissions from the northern segment of the pond shown between the OP-FTIR beam on the upwind side and the TDL beams on the downwind perimeter of the pond. Once the setup is complete, the same procedures will be followed as described for *South-Configuration 2*.

### NORTH WIND

When the wind is from the north, each of three other configurations will be set up and measurements made in sequence. The three configurations are labeled *North-Configuration 1*, *North-Configuration 2*, and *North-Configuration 3* and are shown in Figures 4, 5, and 6, respectively.

### North-Configuration 1

As in the case of southerly winds, the first priority is to determine net flux from the hot well. The sensors and retroreflectors will first be set up in *North-Configuration 1* as shown in Figure 4. This configuration is similar to *South-Configuration 1*, except that the positions of the vertical scanning TDL and the OP-FTIR have been switched to maintain the vertical scan on the downwind side of the measurement pond segment. The procedures to determine the net flux of HF from the hot well are the same as for *South-Configuration 2*. The input flux will be

determined by comparing the OP-FTIR determinations in this configuration with the subsequent measurement of the downwind flux by the vertical scanning TDL in *North-Configuration 2*.

#### **North-Configuration 2**

Upon completion of the *North-Configuration 1* measurements, the equipment will be setup in *North-Configuration 2* as shown in Figure 5. This configuration was designed to determine the HF flux from the same pond segment as by *South-Configuration 2*, and is identical except that the positions of the TDL and OP-FTIR sensors are swapped to maintain the TDL scanned vertical plane on the downwind side of the segment. The procedure is the same as for *South-Configuration 2*, except that the OP-FTIR determinations will be compared to the subsequent downwind flux measurement in *North-Configuration 3* to estimate the input flux of this segment.

#### **North-Configuration 3**

The *North-Configuration 3*, shown in Figure 6, was designed to determine the net HF flux from the northern segment of the pond. Since there are no HF sources in the upwind direction, to the north, total flux measurement at the TDL vertical plane is from the emissions from this segment. Thus the OP-FTIR is free to perform another task, to determine locations in the pond with high HF emissions and to provide a rough map of the concentration distribution over the entire pond. The OP-FTIR will be performing a horizontal scan over the pond for the central position provided by the north-south road that penetrates the pond. The three to five retroreflectors will be placed strategically around the perimeter of the pond. The locations of the OP-FTIR retroreflectors shown in Figure 6 are examples to display the concept. The exact locations will be determined at the site based on observations during other measurements.

#### **WEST WIND**

When the wind is from the West, two of three proposed configurations will be set up and measurements will be made in sequence to determine the hydrogen fluoride emissions from the southern and the north segments of the cooling pond. If sufficient measurement data is collected for the purpose of determining emissions, a third configuration will be setup for the purpose of determining the emission flux of HF from the facility complex that lies west of the southern portion of the cooling pond. The three configurations are labeled *West-Configuration 1*, *West-Configuration 2*, *West-Configuration 3* and are shown in Figures 7, 8, and 9, respectively.

#### **West Configuration 1**

The sensors and retroreflectors will first be set up in *West-Configuration 1* as shown in Figure 7 to determine emission flux from the southern portion of the cooling pond. The OP-FTIR will be setup on the east (upwind) side to estimate the input flux from the direction of the facility complex.

#### **West Configuration 2**

Upon completion of the *West Configuration 1* measurements, the equipment will be setup in *West-Configuration 2* as shown in Figure 8, to determine the HF emission flux from the northern portion of the cooling pond.

### **West Configuration 3**

If the winds persist in the westerly direction after completion of *West Configuration 1* and 2, or sufficient cooling pond emission data is collected at any other configuration, the equipment will be setup in *West-Configuration 3*, as shown in Figure 9. for the purpose of determining directly the emission flux from the facility complex. The multiplexed TDL sensor will be set up with a vertical plane that is downwind of the CF Industries facilities, but upwind of the pond. The TDL is set up at the westward bend in pond perimeter, just north of the southwest corner of the pond. The scissor jack will be set up on the hill directly to the south. This will provide extra elevation in order to measure HF emissions from higher-elevations in the facility. The OP-FTIR sensor will collect data to a retro located at the southwest corner of the cooling pond to account for ground level fugitive emissions.

### **EAST WIND**

When the wind is from the East, two proposed configurations will be set up and measurements will be made in sequence to determine the hydrogen fluoride emissions from the southern and the north segments of the cooling pond. The two configurations are labeled *East-Configuration 1*, and *East-Configuration 2*, and are shown in Figures 10 and 11, respectively.

#### **East Configuration 1**

The sensors and retroreflectors will first be set up in *East-Configuration 1* as shown in Figure 10 to determine emission flux from the southern portion of the cooling pond. The OP-FTIR will be setup on the east (upwind) side to estimate the input flux from the direction of the facility complex.

#### **East Configuration 2**

Upon completion of the *East Configuration 1* measurements, the equipment will be setup in *East-Configuration 2* as shown in Figure 11, to determine the HF emission flux from the northern portion of the cooling pond.

If the winds persist in any one direction after the completion of the measurements leading to emission flux determinations for that wind direction, the equipment will either be setup on the hill to the east of the cooling pond to determine HF emissions from the elevated ponds to the east or, upon request by CF Industries, at other sites. Other sites could include other ponds, the western (downwind) side of the facility complex, or at or beyond the facility fenceline.

## **CHEMICAL ANALYSIS**

### **The Tunable Diode Laser**

The Tunable Diode Laser is tuned over a single absorption line of hydrogen fluoride. The concentration of HF is determined from a least-squares fit of the measured detector response to a calibrated response curve. The presence of HF is determined from the cross-correlation coefficient for the measured and calibrated response curve.

The calibration can be performed automatically at any time. The detector response is recorded while before and during the introduction of a known amount of HF into a gas cell that is always

in the laser beam path. The baseline response is recorded before the HF is introduced to the cell and after the HF is purged from the cell. The calibration is rejected if the before and after baseline responses do not agree. The detector response with the HF present in the cell is recorded as the calibrated response curve.

Quality Assurance (QA) can be achieved by performing a calibration check periodically and recording any amplitude discrepancy between the new calibrated response and the one prior to the QA check.

### **Open-Path FTIR**

The OP-FTIR measurements and spectroscopic analysis will follow the procedures in the USEPA Compendium Method TO-16, "Long-Path Open-Path Fourier Transform Infrared Monitoring of Atmospheric Gases."

The raw data are interferograms that are converted to absorbance spectra in which chemicals that passed through the infrared beam leave absorption bands in which the absorbance values follow a linear relationship to the concentration-pathlength product. These bands have intricate structure and shapes that are unique to each of the absorbing molecular species. The qualitative analysis is performed by a multi-variant regression program that fits the shape of the bands in the measured spectra to the shapes of reference spectra for both hydrogen fluoride and water vapor.

The reference spectra are used as a quantitative calibration set; the chemical concentration for each reference was measured and recorded. The path-integrated concentration is obtained from the least-squares fitting parameter for HF. The detection limits are determined for each measurement the standard error of the fit, propagated to the concentration determination. In cases of non-detects, the measurement-based determination of the detection limit provides an upper limit to the path-integrated concentration.

The calibration of the spectral reference for HF will be checked against HF references in several different libraries and the OP-FTIR concentration determination will be cross calibrated against the TDL instrument sharing the same optical path.

### **FINAL REPORT**

All of the results will be detailed and summarized in a report. The hydrogen fluoride measurements will be tabulated with the general wind direction. Each one-minute average determination will listed along with the standard error of the regression fit to the reference HF spectrum. In the measurements in which HF is not detected, the detection limit, determined from the standard error, will be recorded as the upper limit to the HF concentration. The report will include a table with all the determinations of the emission rate of HF along with the wind direction and wind speed.

Method validation and quality assurance (QA) procedures on both the TDL and the OP-FTIR measurements will be discussed. The quality assurance procedures will lead to an error analysis. The analysis will include all possible sources of systematic and random error propagated to the chemical measurements and to the emission rate determinations.

Detailed calculation of the yearly emission rate in ton/year will be presented in the report based on the temporally resolved emission rate measurement from the target cooling pond. If emission rates from the other HF source will be successfully completed in this measurement campaign, the same yearly calculation will be performed for this site also.

Figure 1. South Configuration 1. A Scanning Configuration for a southerly wind to determine HF Flux from the hot well. The retroreflectors labeled retro are at ground level and the retroreflector on the scissor jack is elevated to 10 meters.

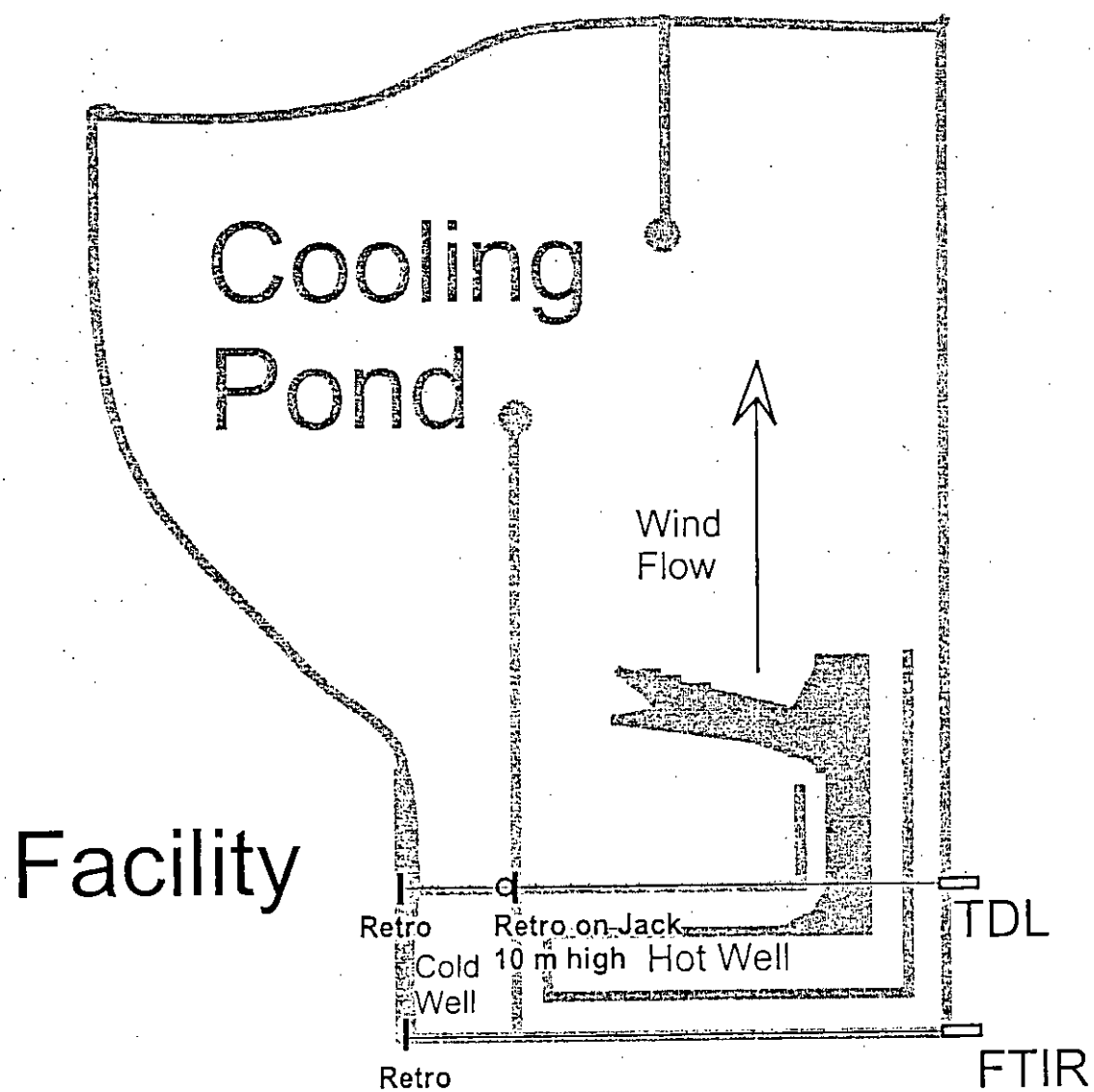


Figure 2. South Configuration 2. A Scanning Configuration for a southerly wind to determine HF Flux from the pond segment just north of the hot well. The retroreflectors labeled retro are at ground level and the retroreflector on the scissor jack is elevated to ~17 meters.

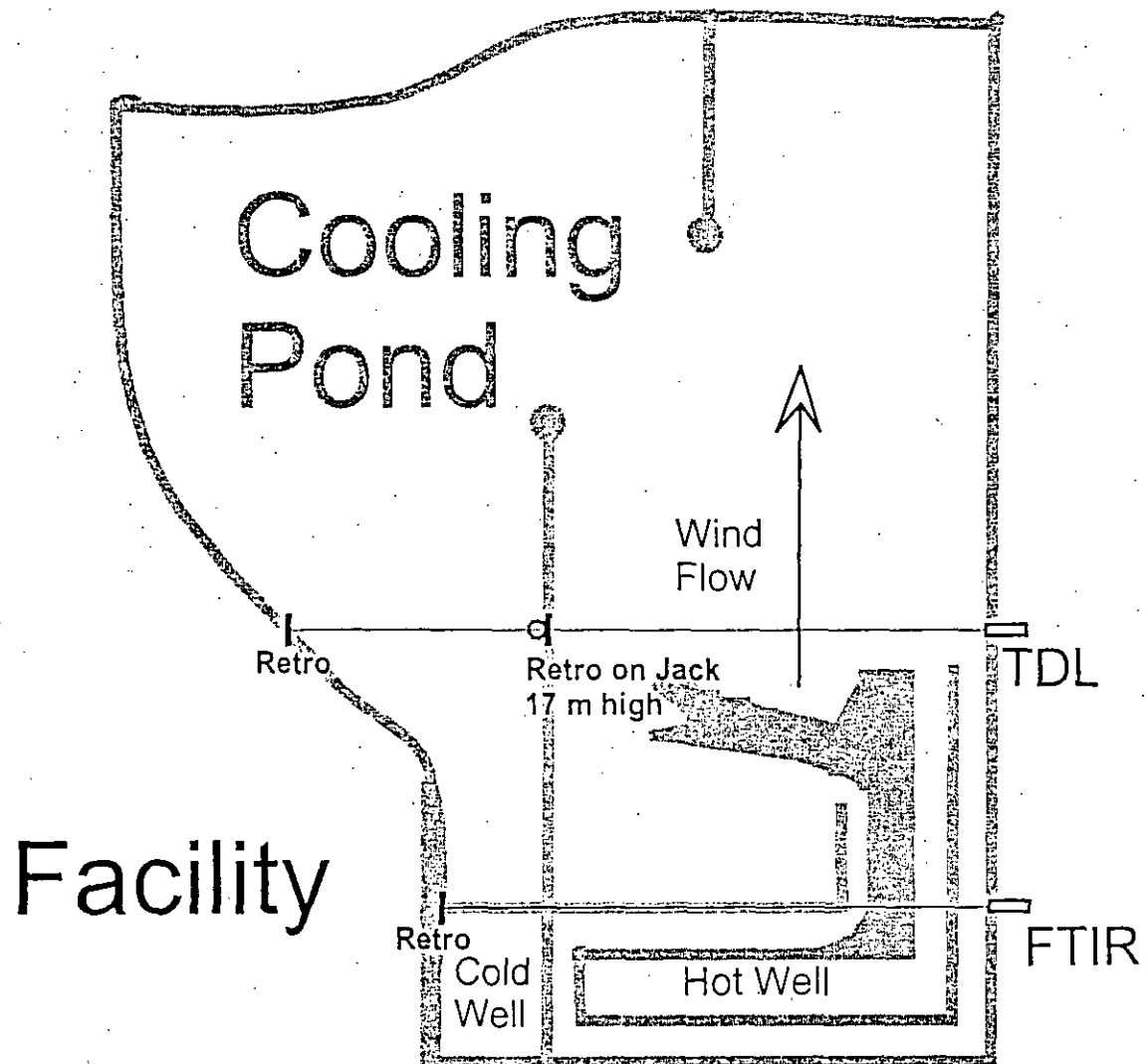


Figure 3. South Configuration 3. A Scanning Configuration for a southerly wind to determine HF Flux from the northern segment of the pond. The retroreflectors labeled retro are at ground level and the retroreflector on the scissor jack is elevated to ~17 meters.

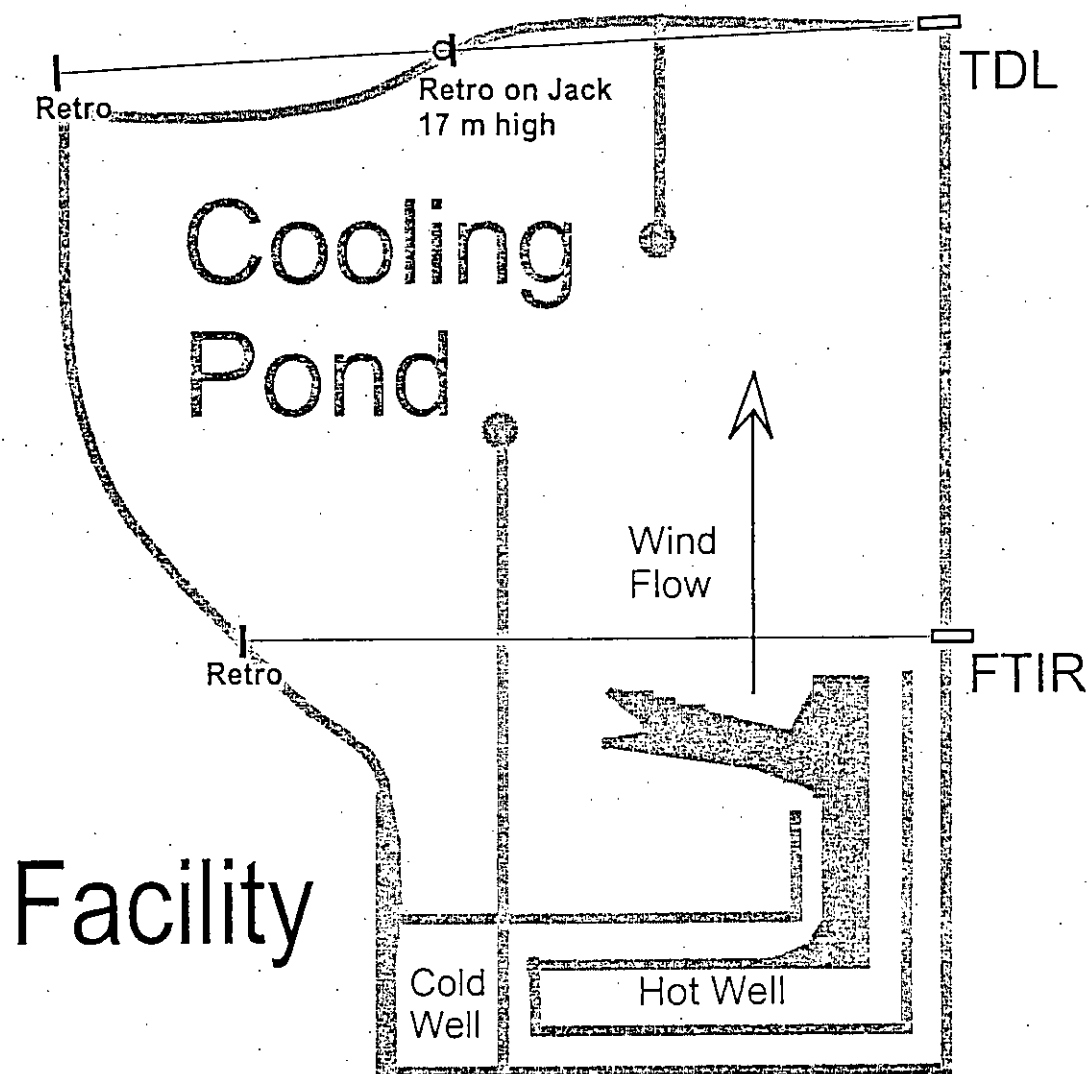




Figure 4. North Configuration 1. A Scanning Configuration for a northerly wind to determine HF Flux from the hot well. The retroreflectors labeled retro are at ground level and the retroreflector on the scissor jack is elevated to ~17 meters.

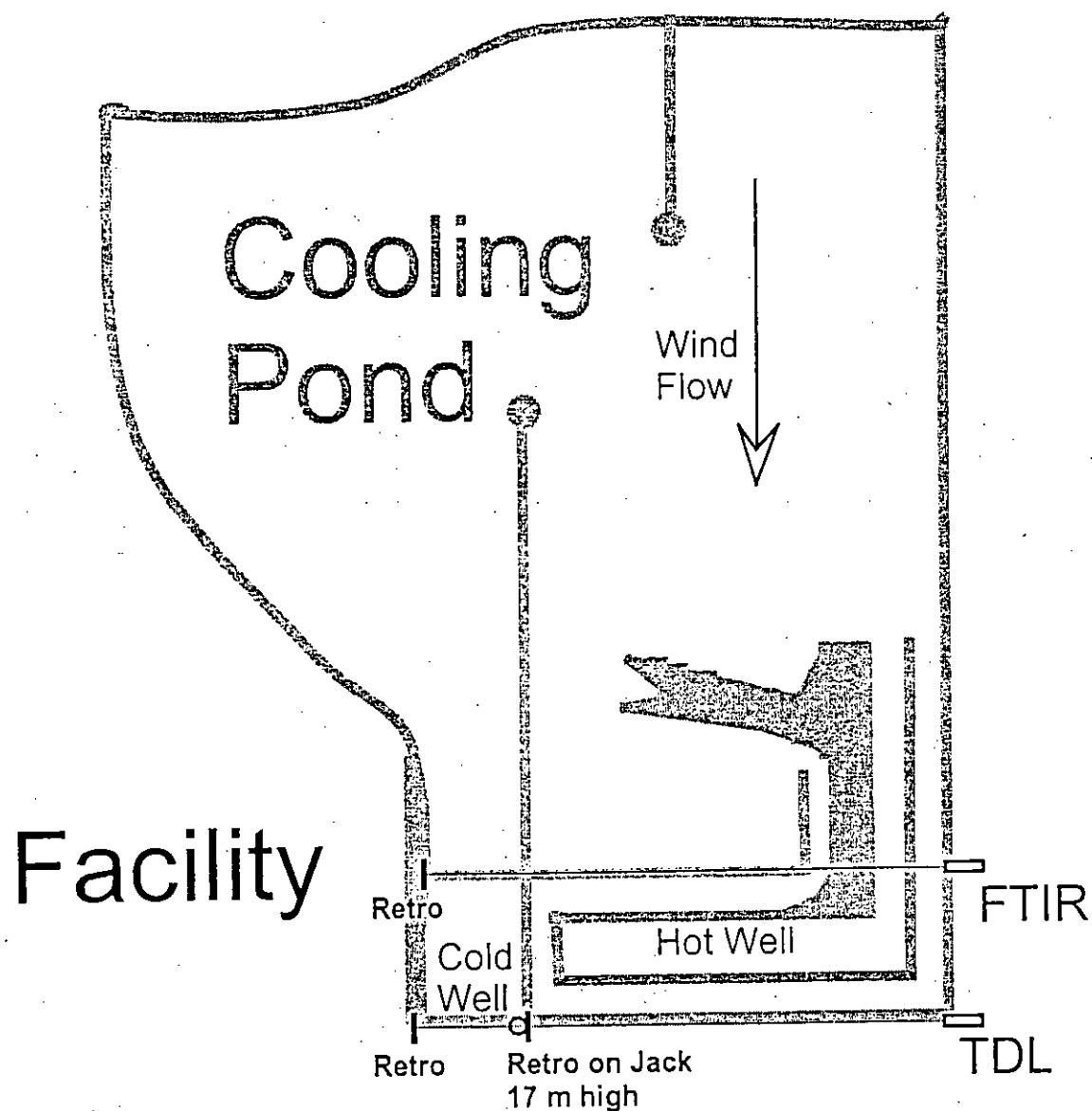


Figure 5. North Configuration 2. A Scanning Configuration for a northerly wind to determine HF Flux from the pond segment just north of the hot well. The retroreflectors labeled retro are at ground level and the retroreflector on the scissor jack is elevated to ~17 meters.

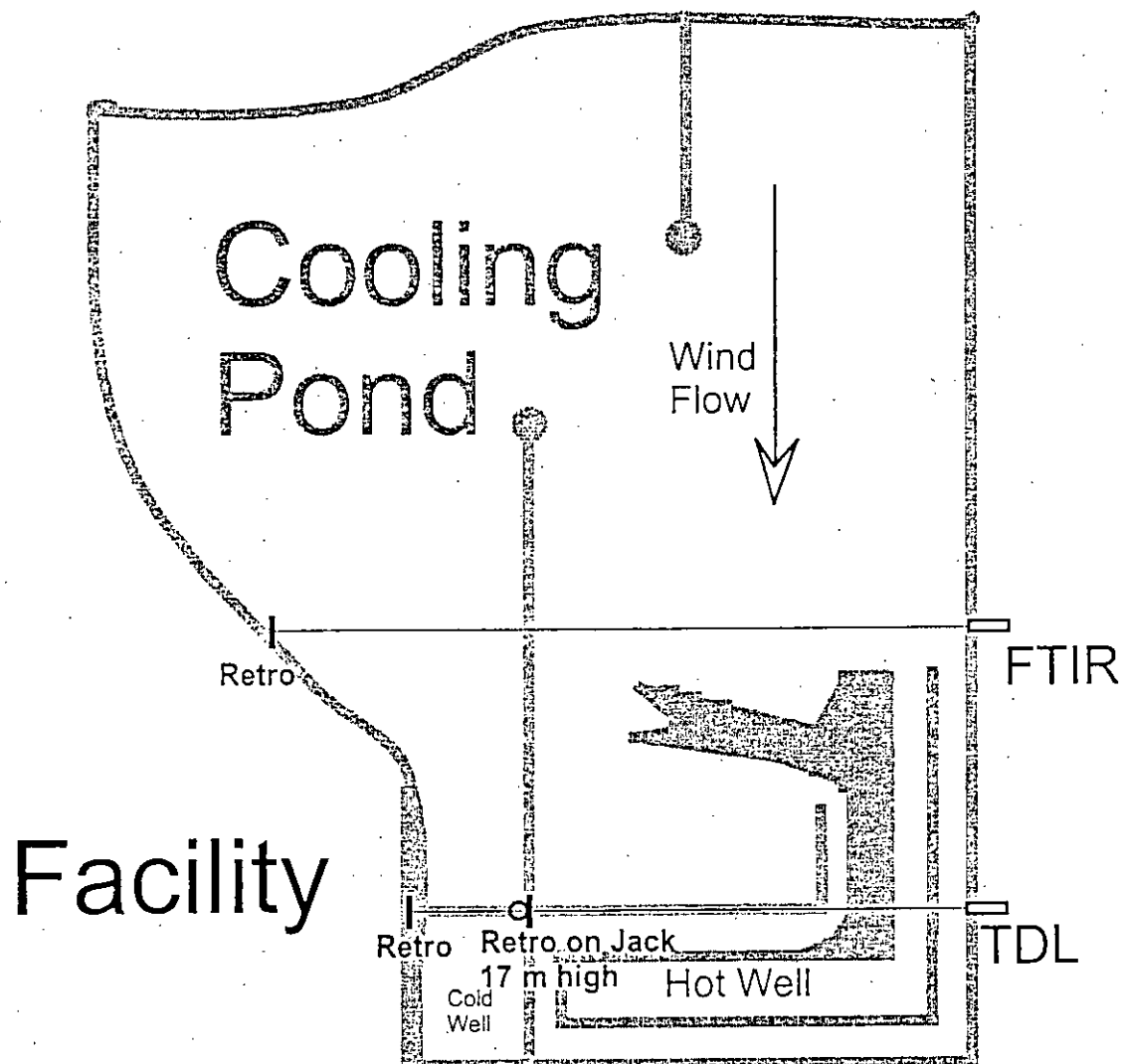


Figure 6. North Configuration 3. A Scanning Configuration for a northerly wind to determine HF Flux from the northern segment of the pond. The retroreflectors labeled retro are at ground level and the retroreflector on the scissor jack is elevated to 17 meters. The OP-FTIR scans to several ground-level retroreflectors to identify and quantify regions of the pond that have higher emissions ("hot spots").

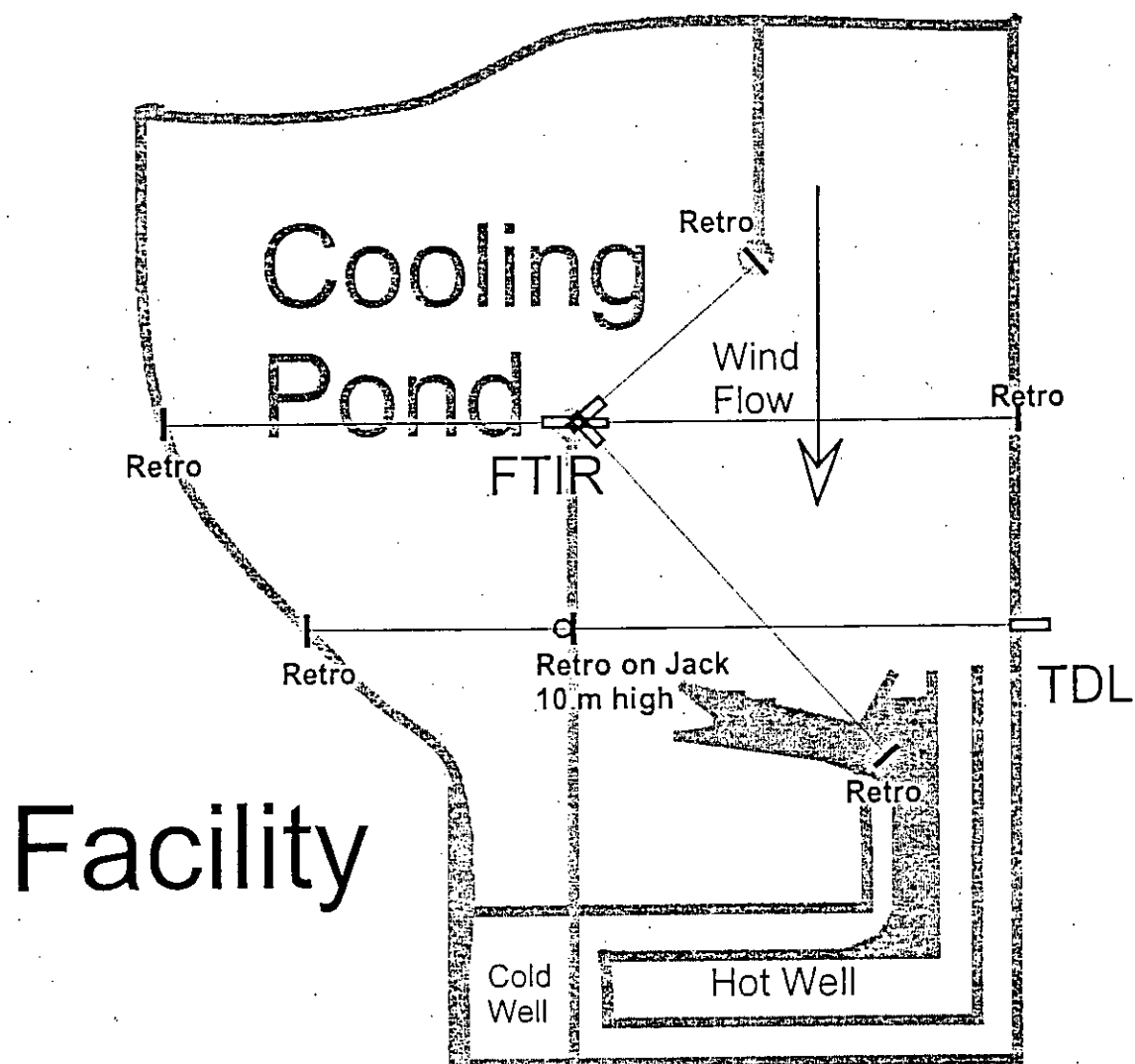


Figure 7. West Configuration 1. A Scanning Configuration for a westerly wind to determine HF Flux from the southern segment of the pond. The retroreflectors labeled retro are at ground level and the retroreflector on the scissor jack is elevated to ~10 meters.

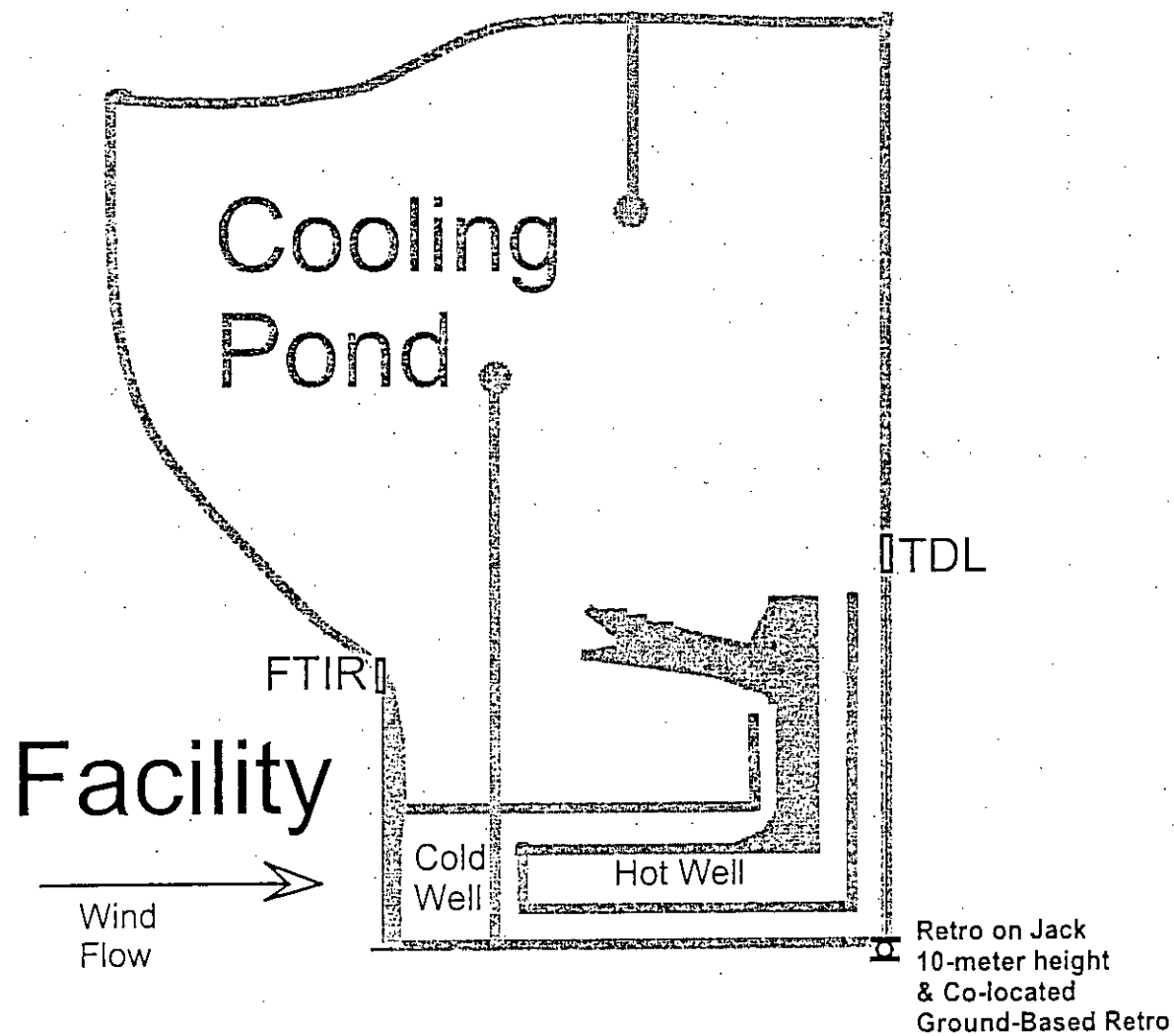


Figure 8. West Configuration 2. A Scanning Configuration for a westerly wind to determine HF Flux from the northern segment of the pond. The retroreflectors labeled retro are at ground level and the retroreflector on the scissor jack is elevated to ~17 meters.

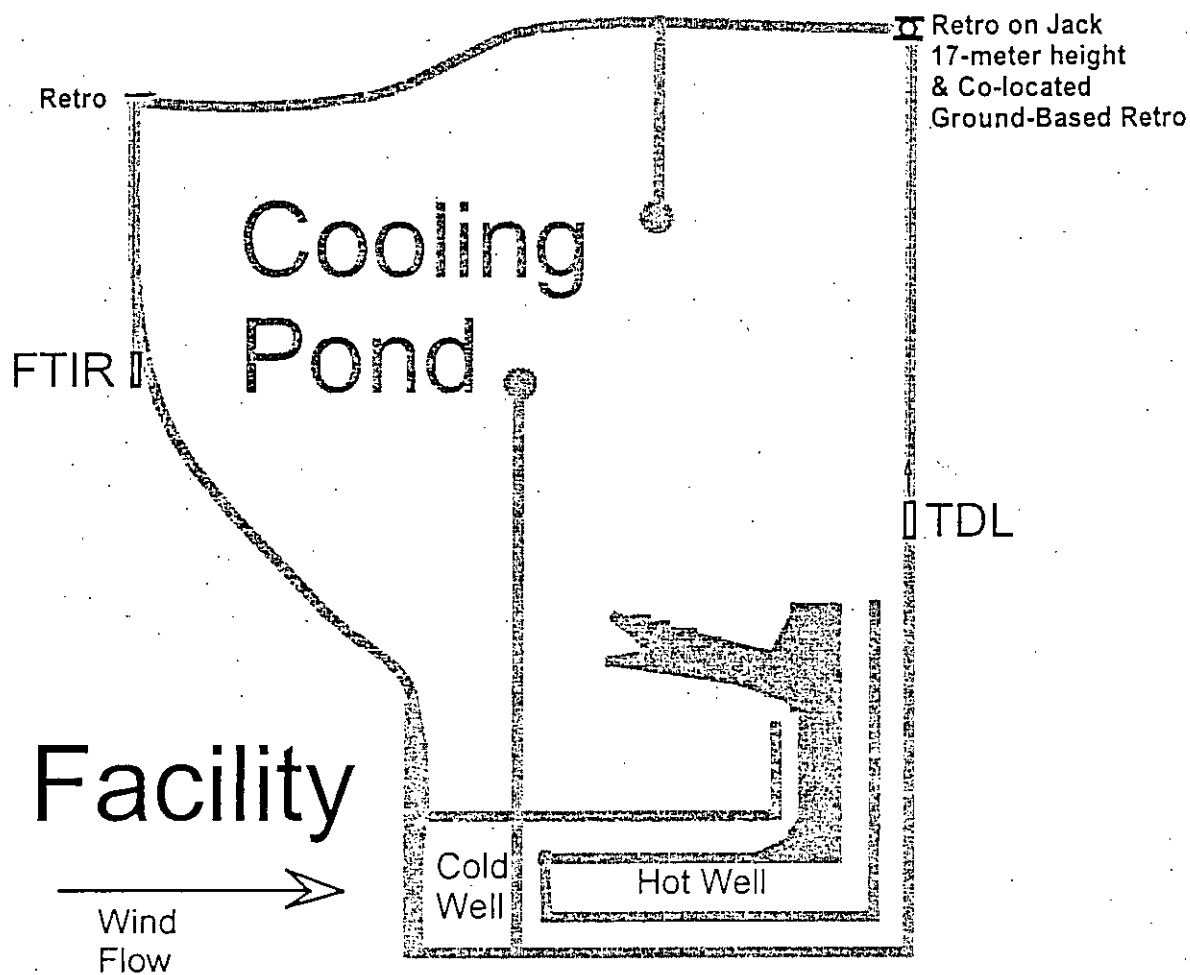


Figure 9. West Configuration 3. A Scanning Configuration for a westerly wind to determine HF Flux from the facility.

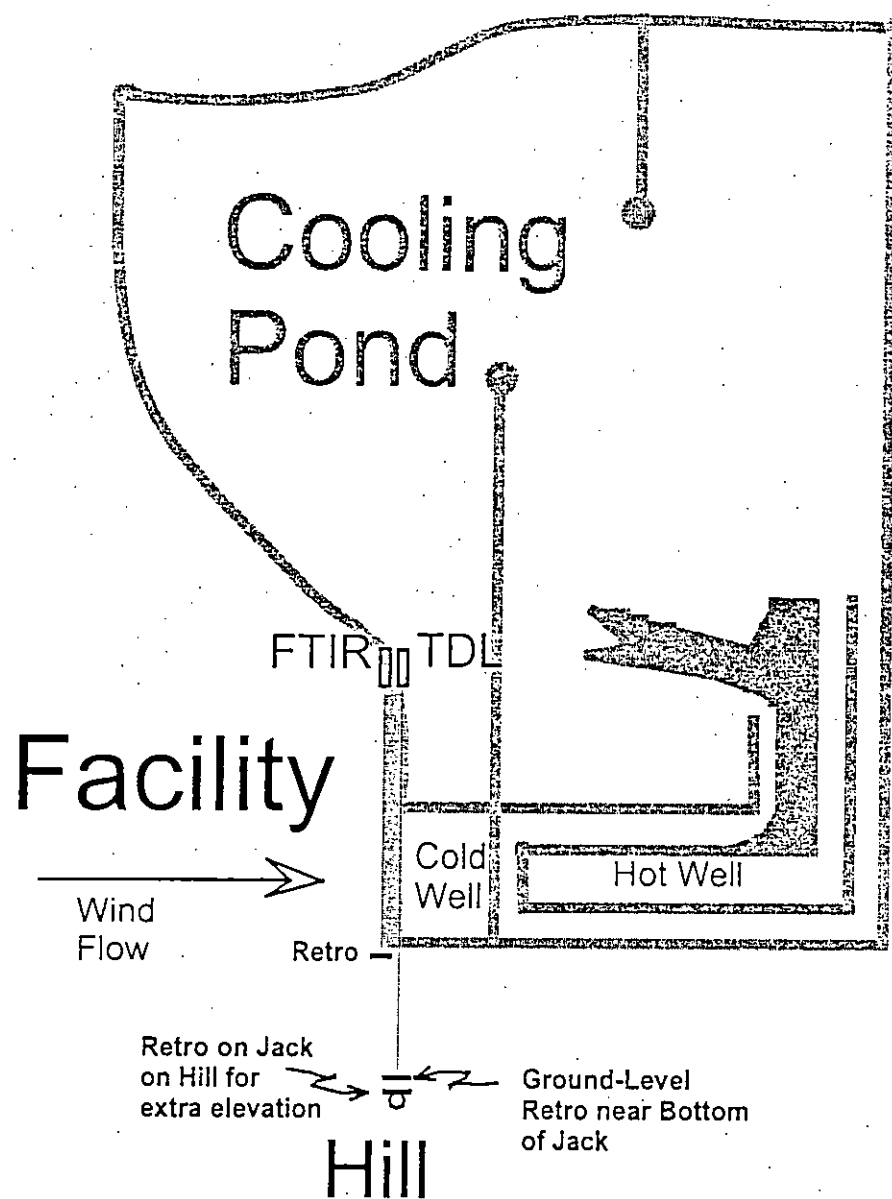


Figure 10. East Configuration 1. A Scanning Configuration for an easterly wind to determine HF Flux from the southern segment of the pond. The retroreflectors labeled retro are at ground level and the retroreflector on the scissor jack is elevated to ~10 meters.

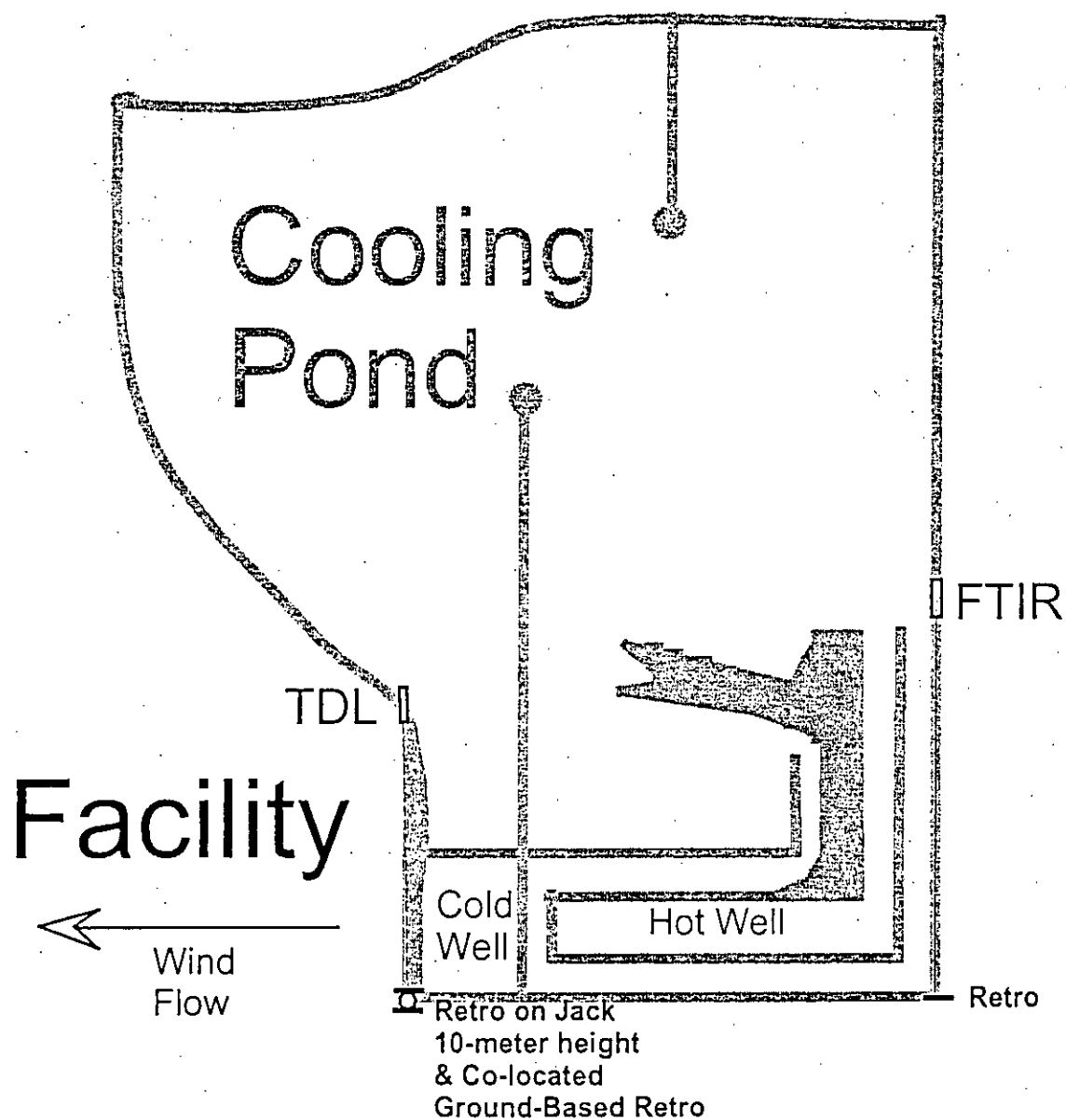
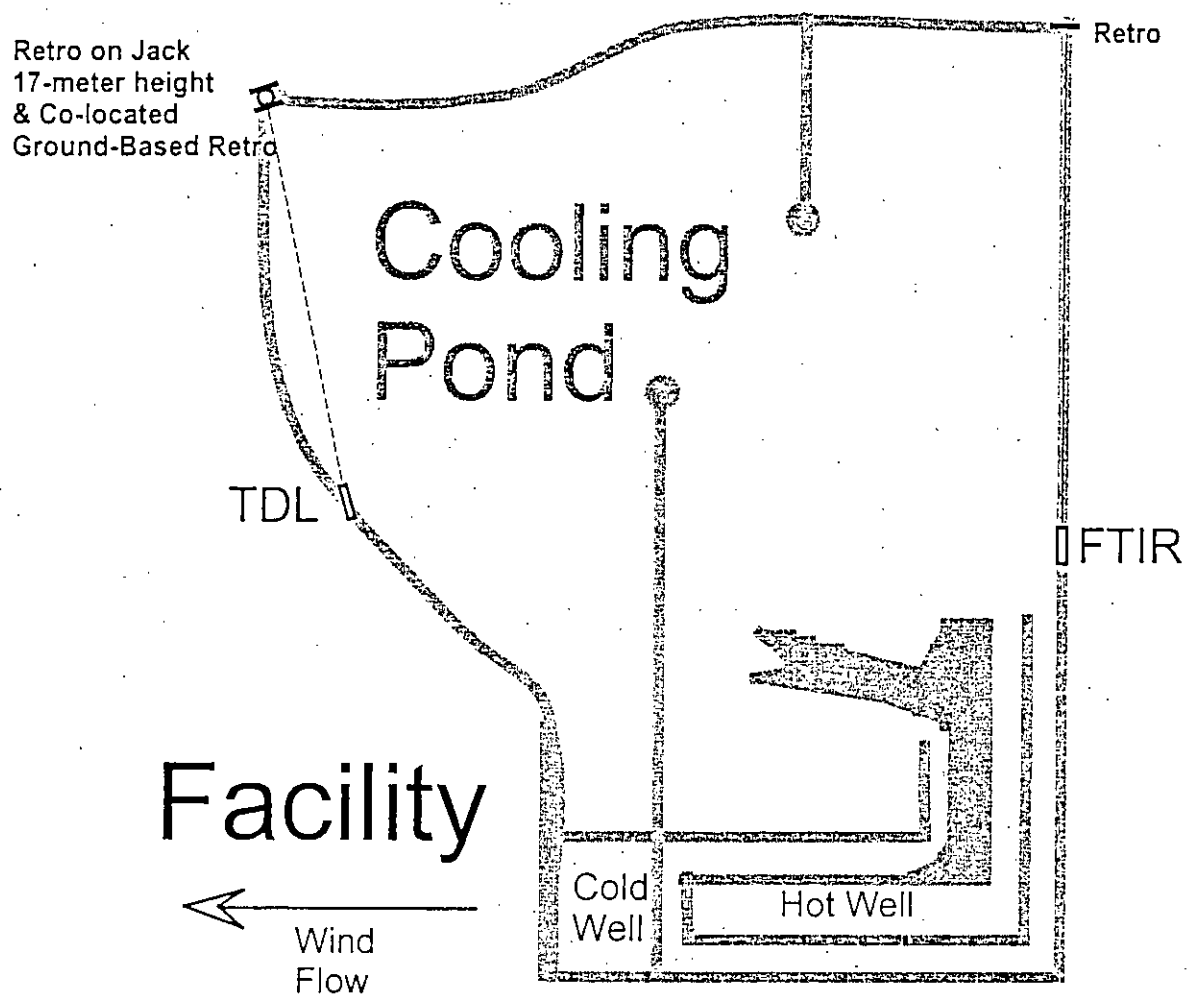


Figure 11. East Configuration 2. A Scanning Configuration for an easterly wind to determine HF Flux from the northern segment of the pond. The retroreflectors labeled retro are at ground level and the retroreflector on the scissor jack is elevated to ~17 meters.





## **Appendix A System Concept**

### **Tunable Diode Laser (TDL) Air Monitor**

The TDL scans the laser frequency over a single HF absorption line. The response at the center of the line will decrease with an increase in path-integrated concentration. The path-integrated concentration is determined from a least-squares fit of the detector response as a function of the laser frequency to a calibrated detector response curve. The presence of HF in the laser beam is determined from the correlation coefficient for the detection response to the measurement and the calibrated response curve.

### **Open-Path FTIR (OP-FTIR) Air Monitor**

The OP-FTIR systems are essentially the same in principal as a laboratory FTIR spectrometer. The main difference is that instead of measuring an infrared spectrum in a gas cell, the OP-FTIR measures the spectrum of a long path of an infrared beam that passes through the atmosphere. An infrared light beam, modulated by a Michaelson interferometer is transmitted from a single telescope to a retroreflector target, which usually is set up at a range of 100 to 500 meters. The single telescope receives the returned light signal. The light is absorbed by the molecules in the beam path as the light propagates to the retroreflector and again as the light is reflected back to the analyzer. Thus, the round-trip path of the light doubles the chemical absorption signal.

### **Configuration for Emission Rate Calculation**

ARCADIS proposes to use a path integrated air monitor configure with two beams in a vertical plane downwind of the investigated pond area. One beam is at a ~ 1-meter height and parallel to the ground, and the second beam is along the slant path from the ORS sensor head to a retroreflector that is elevated to ~ 15 meters on a scissor jack. The vertical concentration gradient is determined from the two beam paths and an area-integrated concentration for a cross-section of the plume, is calculated from the measurements of the path-integrated concentrations along the two paths. The HF flux is equal to the area-integrated concentration times the normal component of the wind speed.

APPENDIX D .

COST OF PRESCRIBED MONITORING,

RULE 40 CFR 63, SUBPARTS AA AND BB

EQUIPMENT FOR HF MACT SCRUBBER MONITORING

	Area	Loop #	DWG. #	New/Exist.	Flow meter req'd	Size	DP req'd	Description
1	APAP		20-TW-035	Exist.				APAP Scrubber Process Water Supply Flow
2	APAP	2185	20-TW-035A	Exist.				APAP Scrubber Pressure
3	BPAP	3098		New	1	8"		BPAP Scrubber Process Water Supply Flow
4	BPAP	3099		New			1	BPAP Scrubber Pressure
5	ACU	9392		New			1	ACU Scrubber Pressure
6	X DAP	4547X	5.1-T-51	Exist.				X Dryer Scrubber Pressure
7	X DAP	4545X	5.1-T-53	Exist.				X Dust Scrubber Pressure
8	X DAP	4546X	5.1-T-52	Exist.				X Fume Scrubber Pressure
9	X DAP	4560X	5.1-T-54	Exist.				X Cooler Scrubber Pressure
10	X DAP	4330X		New	1	4"		X Dryer Secondary Scrubber Flow (pond water supply)
11	X DAP	4331X		New	1	4"		X Fume Secondary Scrubber Flow (pond water supply)
12	X DAP	4332X		New	1	6"		X Cooler Secondary Scrubber Flow (pond water supply)
13	X DAP	4333X		New	1	6"		X Dryer Venturi Scrubber Flow (low pres. liquor supply)
14	X DAP	4334X		New	1	6"		X Fume Venturi Scrubber Flow (low pres. liquor supply)
15	X DAP	4335X		New	1	6"		X Dust Venturi Scrubber Flow (low pres. liquor supply)
16	X DAP	4336X		New	1	4"		X Dryer Primary (cyclonic) Scrubber Flow (high pres. liquor supply)
17	X DAP	4337X		New	1	4"		X Fume Primary (cyclonic) Scrubber Flow (high pres. liquor supply)
18	X DAP	4338X		New	1	4"		X Dust Primary (cyclonic) Scrubber Flow (high pres. liquor supply)
19	X DAP	4339X		New	1	14"		X Abatement Scrubber Flow
20	X DAP	4340X		New			1	X Abatement Scrubber Pressure
21	Y DAP	4547Y	5.1-T-171	Exist.				Y Dryer Scrubber Pressure
22	Y DAP	4545Y	5.1-T-169	Exist.				Y Dust Scrubber Pressure
23	Y DAP	4546Y	5.1-T-170	Exist.				Y Fume Scrubber Pressure
24	Y DAP	4560Y	5.1-T-172	Exist.				Y Cooler Scrubber Pressure

	Area	Loop #	DWG. #	New/Exist.	Flow meter req'd	Size	DP req'd	Description
25	Y DAP	4330Y		New	1	4"		Y Dryer Secondary Scrubber Flow (pond water supply)
26	Y DAP	4331Y		New	1	4"		Y Fume Secondary Scrubber Flow (pond water supply)
27	Y DAP	4332Y		New	1	4"		Y Cooler Secondary Scrubber Flow (pond water supply)
28	Y DAP	4333Y		New	1	6"		Y Dryer Venturi Scrubber Flow (low pres. liquor supply)
29	Y DAP	4334Y		New	1	6"		Y Fume Venturi Scrubber Flow (low pres. liquor supply)
30	Y DAP	4335Y		New	1	4"		Y Dust Venturi Scrubber Flow (low pres. liquor supply)
31	Y DAP	4336Y		New	1	4"		Y Dryer Primary (cyclonic) Scrubber Flow (high pres. liquor supply)
32	Y DAP	4337Y		New	1	4"		Y Fume Primary (cyclonic) Scrubber Flow (high pres. liquor supply)
33	Y DAP	4338Y		New	1	4"		Y Dust Primary (cyclonic) Scrubber Flow (high pres. liquor supply)
34	Y DAP	4339Y		New	1	14"		Y Abatement Scrubber Flow
35	Y DAP	4340Y		New			1	Y Abatement Scrubber Pressure
36	Z DAP	4547Z	5.1-T-236	Exist.				Z Dryer Scrubber Pressure
37	Z DAP	4545Z	5.1-T-234	Exist.				Z Dust Scrubber Pressure
38	Z DAP	4546Z	5.1-T-235	Exist.				Z Fume Scrubber Pressure
39	Z DAP	4560Z	5.1-T-237	Exist.				Z Cooler Scrubber Pressure
40	Z DAP	4330Z		New	1	4"		Z Dryer Secondary Scrubber Flow (pond water supply)
41	Z DAP	4331Z		New	1	4"		Z Fume Secondary Scrubber Flow (pond water supply)
42	Z DAP	4332Z		New	1	4"		Z Cooler Secondary Scrubber Flow (pond water supply)
43	Z DAP	4333Z		New	1	6"		Z Dryer Venturi Scrubber Flow (low pres. liquor supply)
44	Z DAP	4334Z		New	1	6"		Z Fume Venturi Scrubber Flow (low pres. liquor supply)
45	Z DAP	4335Z		New	1	4"		Z Dust Venturi Scrubber Flow (low pres. liquor supply)
46	Z DAP	4336Z		New	1	4"		Z Dryer Primary (cyclonic) Scrubber Flow (high pres. liquor supply)
47	Z DAP	4337Z		New	1	4"		Z Fume Primary (cyclonic) Scrubber Flow (high pres. liquor supply)
48	Z DAP	4338Z		New	1	4"		Z Dust Primary (cyclonic) Scrubber Flow (high pres. liquor supply)
49	Z DAP	4339Z		New	1	14"		Z Abatement Scrubber Flow
50	Z DAP	4340Z		New			1	Z Abatement Scrubber Pressure

	Area	Loop #	DWG. #	New/Exist.	Flow meter req'd	Size	DP req'd	Description
51	A DAP	4333A		New	1	6"		A DAP Dryer Venturi Scrubber Flow (low pres. liquor supply)
52	A DAP	4334A		New	1	6"		A DAP Fume Venturi Scrubber Flow (low pres. liquor supply)
53	A DAP	4336A		New	1	4"		A DAP Dryer Primary (cyclonic) Scrubber Flow (high pres. liquor supply)
54	A DAP	4337A		New	1	4"		A DAP Fume Primary (cyclonic) Scrubber Flow (high pres. liquor supply)
55	A DAP	4547A	5.0-T-23	Exist.				A DAP Dryer Scrubber Pressure
56	A DAP	4546A	5.0-T-22	Exist.				A DAP Fume Scrubber Pressure
57	A DAP	4339A		New	1	14"		A DAP Abatement Scrubber Flow (pond water supply)
58	A DAP	4340A		New			1	A DAP Abatement Scrubber Pressure

# ADDITIONAL SCRUBBER PROCESS MONITORING COST ESTIMATE

	Qty.	Spares		Total
4" meters	22	1	\$5,000.00	\$115,000.00
6" meters	9	1	\$5,400.00	\$54,000.00
8" meters	1	1	\$6,050.00	\$12,100.00
14" meters	4	1	\$11,000.00	\$55,000.00
DP's	6	1	\$2,500.00	\$17,500.00
Enclosures	42		\$950.00	\$39,900.00
I/O cabinet	3		\$2,000.00	\$6,000.00
JB's	10		\$550.00	\$5,500.00
PLC's	3		\$15,000.00	\$45,000.00
I/O cards	3		\$2,500.00	\$7,500.00
Mech Eng.	1		\$65,000.00	\$65,000.00
Elect. Eng.	1		\$45,000.00	\$45,000.00
Software Eng.	1		\$25,000.00	\$25,000.00
Mech. Installation	42		\$5,350.00	\$224,700.00
Elect. Installation	58		\$4,400.00	\$255,200.00
Taxes				\$27,000.00
Freight				\$10,000
Subtotal				\$1,009,400.00
Contingency 15%				<u>\$151,600.00</u>
Total				<u>\$1,161,000.00</u>

APPENDIX E

PROPOSED CONTINGENCY

ALTERNATIVE MONITORING PLAN

## **0.0 Proposed Alternative Monitoring Plan Summary**

The proposed monitoring in the phosphoric acid plants is expected to meet the requirements of the HF MACT Rule. However, in the granulation plants (A,X,Y,Z) substantial changes to the HF MACT Rule monitoring are being proposed in the alternative monitoring plan. See Table 1 for a summary of the current and planned scrubber monitoring in the alternative monitoring plan. Sections 4.0 and 5.0 discuss the economic and technical justification for alternative monitoring in the granulation plants.

### **1.0 Phosphoric Acid Plants**

In the phosphoric acid plants (EU 004, EU 009) there are no planned deviations from the monitoring required in the HF MACT Rule Subparts AA and BB. These plants operate horizontal cross flow packed bed scrubbers and utilize process water for the scrubbing medium. The "A" Phosphoric Acid Plant (EU 004) has the existing installed equipment required to monitor scrubber water flow and pressure drop across the scrubber. In the "B" Phosphoric Acid Plant (EU 009), a scrubber water flow meter and differential pressure transmitter will have to be installed on the scrubber in order to meet the MACT HF requirements.

#### **1.1 Monitoring Frequency and Recording**

The scrubber water flows and pressure drops will be continuously monitored. An Aspen Data Historian will record the values every 30 seconds, convert them to 15-minute block averages, and calculate three-hour averages for determination of compliance.

#### **1.2 Operating Ranges and Limits**

In order to provide reasonable assurance that the pollution control equipment is operating properly, acceptable operating range limits will be specified as a condition of compliance. The operating range limits will be determined using baseline averages taken during performance testing using the methodology described in 40 CFR 63.625(f).

### **2.0 "X,Y,Z" Granulation Plants**

In the granulation plants (EU011, EU012, EU013) alternatives to the monitoring required in the HF MACT Rule Subparts AA and BB are being proposed. The "X", "Y", and "Z" Granulation Plants each operate a system of 10 individual scrubbers consisting of pond water cyclonic scrubbers on the fume, cooler, and dryer systems; acid cyclonic scrubbers on the fume, dryer, and dust systems; and venturi scrubbers on the dryer, fume, and dust systems. The effluent gases that pass through these scrubbers enter into a final freshwater spray abatement scrubber which functions as an extra layer of insurance against fluoride emissions including HF. See Figure 1 for a schematic of the XYZ granulation plant scrubber systems and Figure 2 for a process block flow diagram of the XYZ granulation plants.

The abatement scrubber is a vertical cross flow scrubber with fresh water sprays with a chevron type structured packing for mist elimination. Since it uses fresh water scrubbing, the abatement scrubber is believed to be unique to CF within the Phosphate Industry.

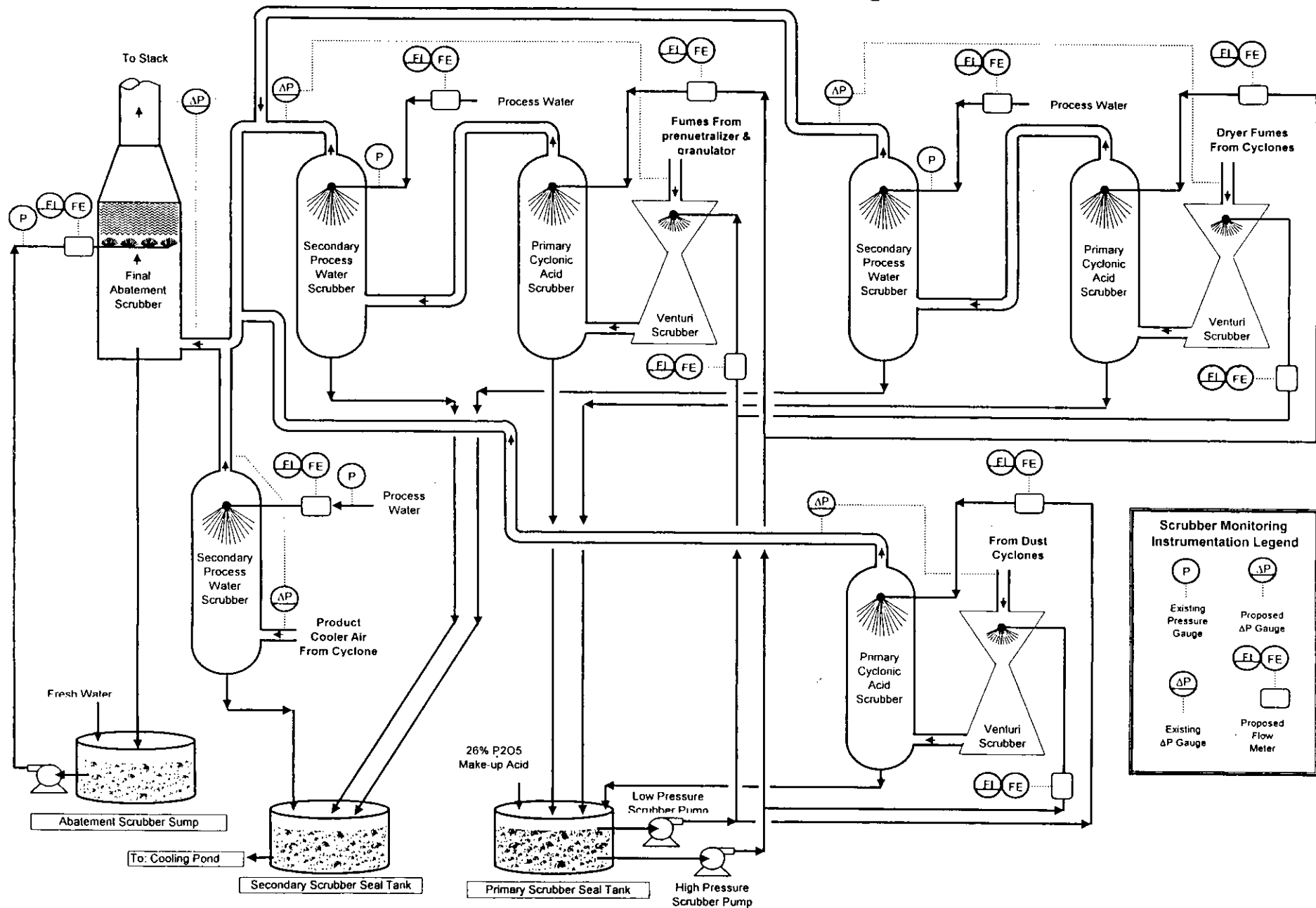


**Table 1**

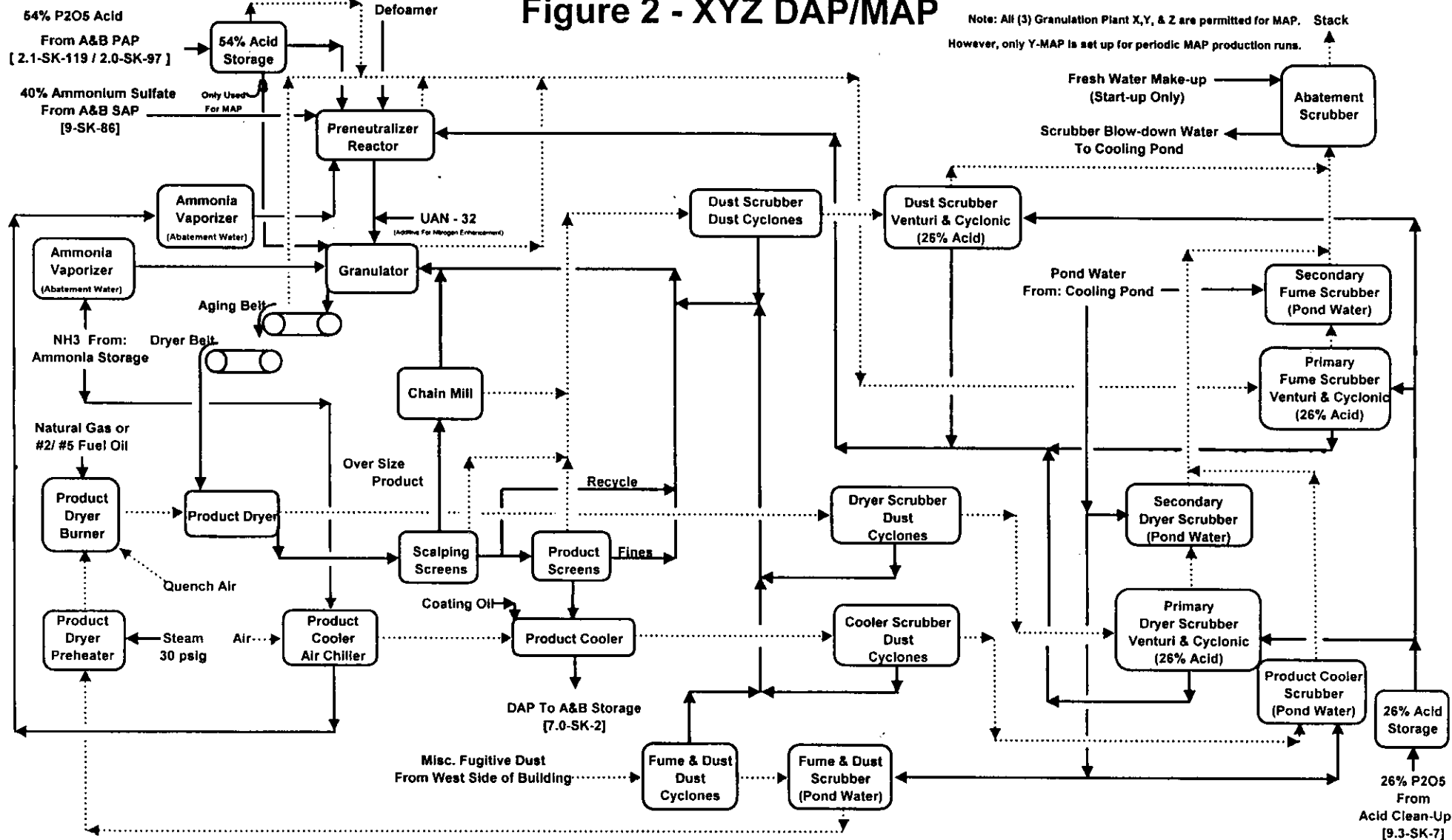
	<u>Location</u>	<u>Description</u>	<u>New/ Existing</u>	<u>Variable Range</u>
1)	A-PAP	Continuous Scrubber $\Delta$ P Monitoring & Recording	Existing	TBD
2)	A-PAP	Continuous Scrubber Process Water Flow Monitoring & Recording	Existing	TBD
3)	B-PAP	Continuous Scrubber $\Delta$ P Monitoring & Recording	New	TBD
4)	B-PAP	Continuous Scrubber Process Water Flow Monitoring & Recording	New	TBD
5)	XDAP/MAP	Continuous Abatement Scrubber Water* Pressure Monitoring & Recording	New	TBD
6)	XDAP/MAP	Continuous Abatement Scrubber Air Pressure Monitoring & Recording (Pre-Packing)	New	TBD
7)	YDAP/MAP	Continuous Abatement Scrubber Water* Pressure Monitoring & Recording	New	TBD
8)	YDAP/MAP	Continuous Abatement Scrubber Air Pressure Monitoring & Recording (Pre-Packing)	New	TBD
9)	ZDAP/MAP	Continuous Abatement Scrubber Water* Pressure Monitoring & Recording	New	TBD
10)	ZDAP/MAP	Continuous Abatement Scrubber Air Pressure Monitoring & Recording (Pre-Packing)	New	TBD
11)	ADAP/MAP	Continuous Abatement Scrubber Water* Pressure Monitoring & Recording	New	TBD
12)	ADAP/MAP	Continuous Abatement Scrubber Air Pressure Monitoring & Recording (Pre-Packing)	New	TBD

\*Note: The abatement towers are initially filled with non-process reuse water. Circulated water from the abatement scrubber sump gets cooled in ammonia vaporizers. Scrubber water is cooler than the stack gases and causes fresh water condensing in the stack gases entering the scrubber. This results in a continuous source of additional fresh water to the scrubber and a subsequent blow down of the scrubber water.

Figure 1 - XYZ Granulation Scrubber Schematic - Single Granulation Train



# Figure 2 - XYZ DAP/MAP



## Legend

-----	Fume or Air Duct	-----	Other
-----	26% / 40% P <sub>2</sub> O <sub>5</sub> Acid	-----	
-----	Ammonia	-----	
-----	Granular DAP/MAP	-----	
-----	Process Water	-----	

## Revision By

## Date

Randy Charlot	08/28/01
Randy Charlot	11/1/02



## CF Industries, Inc.

Plant City Phosphate Complex  
P.O. Drawer L  
Plant City, Florida 33564  
Phone: (813) 782-1591  
Fax: (813) 788-9126

## Title

XYZ-DAP/MAP Granulation Block Flow Diagram

## DWR. NO

5.1-SK-57

91-SK-47-218

The abatement scrubber pump sump is initially filled with non-process reuse water. Water from the abatement scrubber sump is pumped through ammonia vaporizer heat exchangers where the water is cooled before being sprayed in the abatement scrubber. Scrubber water is cooler than the stack gases and causes fresh water condensing in the stack gases entering the scrubber. This results in a continuous source of makeup fresh water to the scrubber and results in a subsequent blow down of the scrubber water.

The existing Title V permit requires the pressure drop across fume, dust, dryer, and cooler scrubber systems be continuously monitored and recorded. The permits also require a minimum pond water pressure of 45psig on all of the pond water cyclonic scrubbers. The permit also specifies a minimum pressure of 18psig for the abatement scrubber spray header and an abatement scrubber pH >4.9.

As an alternative to the HF MACT Rule monitoring it is proposed that the current monitoring, range limits, and frequency of monitoring/recording specified in the Title V permit be continued. In addition, the TDH of the abatement scrubber pump will be continuously monitored and recorded along with the abatement scrubber pressure upstream of the packing. See section 4.0 and 5.0 for a discussion on the economic and technical justification.

### **2.1 Monitoring Frequency and Recording**

The abatement scrubber pump TDH and scrubber effluent gas pressure upstream of the packing will be continuously monitored. An Aspen Data Historian will record values every 30 seconds, convert them to 15-minute block averages, and calculate three-hour averages for determination of compliance.

### **2.2 Operating Ranges and Limits**

In order to provide reasonable assurance that the pollution control equipment is operating properly, acceptable operating range limits for the abatement water pump TDH and abatement scrubber pressure will be specified as a condition of compliance. The operating range limits will be determined using baseline averages taken during performance testing using the methodology described in 40 CFR 63.625(f).

## **3.0 "A" Granulation Plant**

In the Granulation Plant (EU010) alternative monitoring to the monitoring required in the HF MACT rule Subparts AA and BB is being proposed. The "A" Granulation Plant operates a system of 5 individual scrubbers consisting of acid cyclonic scrubbers, venturi scrubbers and freshwater spray downcomer scrubbers on the fume, dryer and dust systems. The effluent gases that pass through these scrubbers enter into a final abatement scrubber that functions as a secondary redundant scrubber. See Figure 3 for a process block flow diagram of the "A" Granulation Plant.

The abatement scrubber is a vertical cross flow scrubber with fresh water sprays with chevron type structured packing for mist elimination. Since it uses a fresh water scrubbing, the abatement scrubber is believed to be unique to CF within the phosphate industry. The abatement scrubber pumping sumps are initially filled with non-process

reuse water. Water from the abatement scrubber sump gets pumped through ammonia vaporizers where the water is cooled before being sprayed in the abatement scrubber. Scrubber water is cooler than the stack gases and causes fresh water condensing in the stack gases entering the scrubber. This results in a continuous source of makeup fresh water to the scrubber and results in a subsequent blow down of the scrubber water.

The existing Title V permit requires the pressure drop across fume, dust, dryer, and cooler scrubber systems to be continuously monitored and recorded. Title V also specifies a minimum pressure of 18psig for the abatement scrubber spray header and an abatement scrubber pH >4.9.

As an alternative to the HF MACT monitoring it is proposed that the current monitoring, range limits, and frequency of monitoring/recording specified in the Title V permit be continued. In addition, the Total Dynamic Head (TDH) of the abatement scrubber pump will be continuously monitored and recorded along with the abatement scrubber pressure upstream of the packing. See section 4.0 and 5.0 for a discussion on the economic and technical justification.

### **3.1 Monitoring Frequency and Recording**

The abatement scrubber pump TDH and scrubber effluent gas pressure upstream of the packing will be continuously monitored. An Aspen Data Historian will record the values every 30 seconds, convert them to 15-minute block averages, and calculate three-hour averages for determination of compliance.

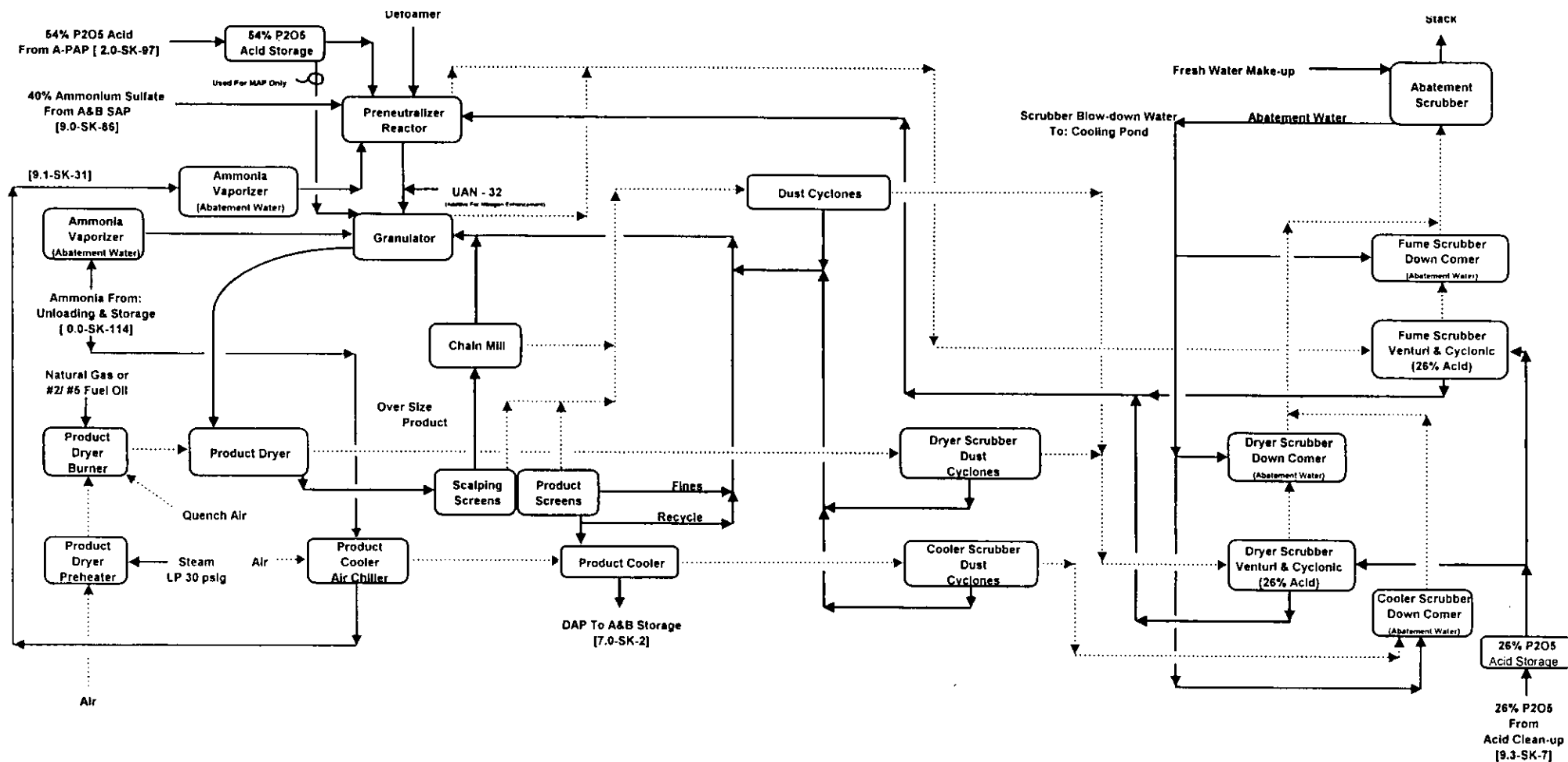
### **3.2 Operating Ranges and Limits**

In order to provide reasonable assurance that the pollution control equipment is operating properly, acceptable operating range limits for the abatement water pump TDH and abatement scrubber pressure will be specified as a condition of compliance. The operating range limits will be determined using baseline averages taken during performance testing using the methodology described in 40 CFR 63.625(f).

## **4.0 Economic Justification For Alternative Monitoring**

Alternative monitoring of phosphoric acid plant and granulation plant scrubbers is being proposed on the grounds that the HF MACT scrubber monitoring called for under the rule will not result in any appreciable environmental benefit through reduction in HF emissions and therefore has an unreasonably high cost to benefit ratio as outlined in the rule. Plant stack testing using FTIR has indicated that the CF Plant City Complex has an estimated HF emission potential of 1.7 TPY HF from point sources. The implementation of additional monitoring equipment called for under the HF MACT Rule would cost an estimated \$1,161,000 and is expected to have negligible impact on actual HF emissions from the complex. Rare upsets in scrubber performance caused by plugging or loss of scrubber liquor flow could possibly be caught sooner if all monitoring called for in the HF MACT rule were implemented. If additional monitoring were able to reduce the potential to emit HF from point sources by a conservative 10% then the cost to benefit ratio could be calculated to be \$6.8 million per ton of HF [ $\$1,161,000 / (10\% \times 1.7 \text{ TPY HF})$ ]. This number is 136 times higher than the HF cost to benefit example presented in

# Figure 3 - "A" DAP/MAP

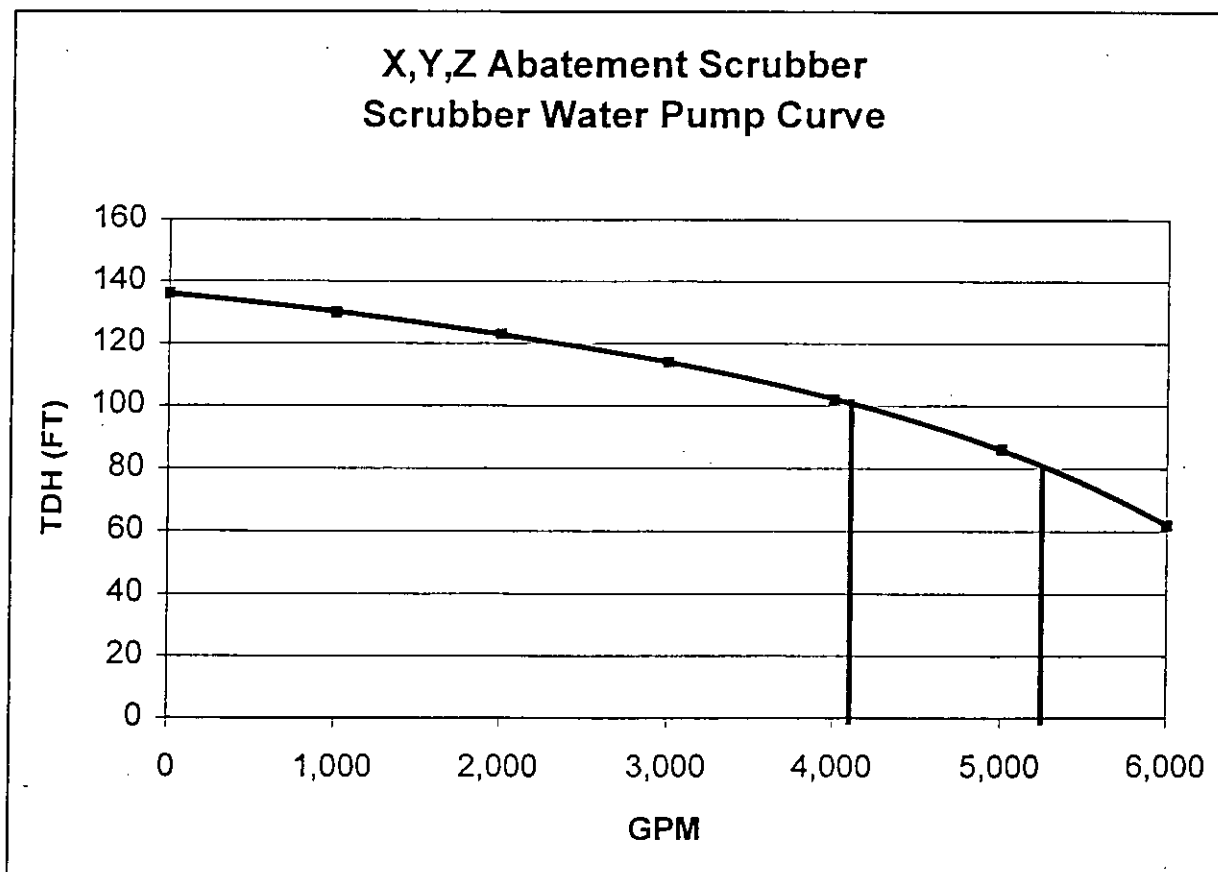


the HF MACT preamble at Federal Register Vol. 64, Page 31361, Paragraph 1. In that example they concluded that an expense of \$50,000 per ton of abated HF emissions would not be economically justified.

#### 5.0 Technical Justification For Alternative Monitoring

In lieu of monitoring of actual flow of the abatement scrubber water it is being proposed that the abatement scrubber water supply pump TDH be continuously monitored and recorded. Each abatement scrubber includes an independent pump that is used solely for circulation of scrubber water to the sprays in the scrubber. For any given centrifugal pump the TDH of the pump (discharge pressure minus suction pressure) has a unique flow defined by the performance curve for the pump. Plugging of the spray nozzles or changes in downstream valves will not change the relationship defined by the performance curve. For example, if the TDH of the abatement water pumps was maintained between 100ft (43.4psig) and 80ft (34.7psig) then the flow to the sprays would be restricted to the range of 4,158GPM and 5,283GPM respectively, see Figure 4. The actual operating range limits will be determined using baseline averages taken during performance testing using the methodology described in 40 CFR 63.625(f).

Figure 4



As an alternative measurement of the actual pressure drop across the scrubber, it is being proposed that the absolute pressure upstream of the scrubber be monitored and permanently recorded. The absolute pressure is being proposed in lieu of differential pressure because of the small pressure drops inherent in the chevron type packing in the scrubber. Typically the upstream pressure in the scrubber would be 0.5" H<sub>2</sub>O and the pressure downstream of the packing would be 0.3" H<sub>2</sub>O resulting in a pressure drop of only 0.2" H<sub>2</sub>O. Variations in pressure drop at this level would be insignificant. The actual operating range limits for the upstream pressure will be determined using baseline averages taken during performance testing using the methodology described in 40 CFR 63.625(f).



ATTACHMENT 2

FEBRUARY 26, 2004 LETTER

VIELHAUER TO EDWARDS



Jeb Bush  
Governor

# Department of Environmental Protection

Twin Towers Office Building  
2600 Blair Stone Road  
Tallahassee, Florida 32399-2400

David B. Struhs  
Secretary

February 26, 2004

Tom Edwards  
CF Industries, Inc.  
Post Office Drawer L  
Plant City, Florida 33564

RE: CF Industries Plant City Facility

Dear Mr. Edwards:

This letter is to confirm our conversation yesterday regarding resolution of the outstanding litigation regarding the applicability of the phosphate MACT to the above-referenced facility. As we discussed, to resolve this litigation, the Department will add the following language to the Department's determination of major source status for HAPs in the Title V permit:

***If additional testing and modeling demonstrate that the facility is not and has never been a major source of hazardous air pollutants since at least June 10, 2002, the permittee shall have the right to request that the Department revise the permit to remove those requirements and conditions that are applicable because the facility is a major source of hazardous air pollutants as determined by the Department.***

In addition, the Department will work with CF on an alternate monitoring plan for this facility. We can discuss the timing of the withdrawal of the extension of time to petition for hearing, issuance of the Title V revision and the Title V renewal when we meet at your facility. If you have any questions, please do not hesitate to contact me at 850/921-9503.

Sincerely,

Trina L. Vielhauer  
Chief,  
Bureau of Air Regulation

"More Protection, Less Process"

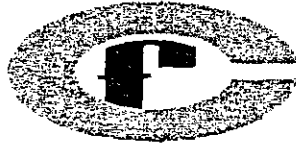
Printed on recycled paper.

ATTACHMENT 3

MARCH 3, 2004 LETTER

MORRIS TO VIELHAUER

P.O. Drawer L.  
Plant City, Florida 33564-9007  
Telephone: 813/782-1591



**CF Industries, Inc.**  
Plant City Phosphate Complex

March 3, 2004

Ms. Trina Vielhauer  
Chief, Bureau of Air Regulation  
Florida Department of Environmental Protection  
Department of Air Resources Management  
2600 Blair Stone Road, MS 5500  
Tallahassee, Florida 32399-2400

Re: CF Industries, Inc., Proposed Alternative Monitoring Plan,  
Letter of February 9, 2004

Dear Ms. Vielhauer:

Based on the recently expressed assurance of the Department that a mutually-agreeable alternative monitoring plan will be developed for compliance with the Hydrogen Fluoride NESHAP rules, and based on the agreement that the language suggested in your February 25, 2004 electronic mail will be applied to the CF Plant City Phosphate Complex, CF agrees not to object to the Department's determination that the facility is a major source of HAPs.

CF believes that the DEP plant tour and meetings currently being scheduled for the Plant City Complex will be beneficial to the Title V permit processing effort. We encourage the Department to involve in the meetings as many as possible of the permitting personnel who will be active in the development of the facility's permit renewal.

Sincerely,

Herschel E. Morris,  
Vice President Phosphate Operations and  
General Manager

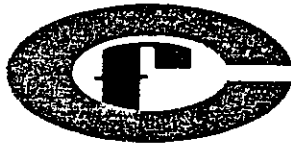
cc: Alan Bedwell, DEP Deputy Secretary  
Michael Cooke, BAR  
Errin Pichard, BAMMS  
Jerry Kissel, SWD  
Jerry Campbell, EPCHC

ATTACHMENT 4

OCTOBER 31, 2003 LETTER

MORRIS TO PICHARD

P.O. Drawer L.  
Plant City, Florida 33564-9007  
Telephone: 813/782-1591



**CF Industries, Inc.**  
Plant City Phosphate Complex

October 31, 2003

Errin Pichard, P.E., Administrator  
Emissions Monitoring Section  
Bureau of Air Monitoring and Mobile Sources  
Florida Department of Environmental Protection  
2600 Blair Stone Road  
Tallahassee, FL 32399-2400

RE: DEP Letter of September 29, 2003, "Proposed  
Alternative Monitoring Plan."

Dear Administrator Pichard:

The attached information is provided in response to the information requests of your September 29, 2003 letter regarding the Alternative Monitoring Plan proposed by CF Industries, Inc., (CF) on June 5, 2003. The letter asked for confirmation of your understanding of the CF Industries Alternative Monitoring Plan proposal, and asked a number of questions regarding the proposed monitoring plan elements. The letter also expressed disagreement with CF's position on the issue of the cost-effectiveness of the MACT monitoring requirements.

After you have reviewed these responses, you are welcome to call Tom Edwards or Bob May at 813-782-1591 for further discussion or clarification.

Sincerely,

A handwritten signature in cursive script that reads "Herschel E. Morris".

Herschel E. Morris  
Vice President,  
Phosphate Operations and  
General Manager

cc: Jerry Kissel, Southwest District

**Owner/Authorized Representative or Responsible Official**

1. Name and Title of Owner/Authorized Representative or Responsible Official: Herschel E. Morris, General Manager
2. Owner/Authorized Representative or Responsible Official Mailing Address: Organization/Firm: CF Industries, Inc. Street Address: P. O. Box Drawer L City: Plant City State: FL Zip Code: 33564
3. Owner/Authorized Representative or Responsible Official Telephone Numbers: Telephone: ( 813 ) 782 - 1591 Fax: ( 813 ) 788 - 9126
4. Owner/Authorized Representative or Responsible Official Statement: <i>I, the undersigned, am the owner or authorized representative*(check here [ ], if so) or the responsible official (check here [ X ], if so) of the Title V source addressed in this application, whichever is applicable. I hereby certify, based on information and belief formed after reasonable inquiry, that the statements made in this application are true, accurate and complete and that, to the best of my knowledge, any estimates of emissions reported in this application are based upon reasonable techniques for calculating emissions. The air pollutant emissions units and air pollution control equipment described in this application will be operated and maintained so as to comply with all applicable standards for control of air pollutant emissions found in the statutes of the State of Florida and rules of the Department of Environmental Protection and revisions thereof. I understand that a permit, if granted by the Department, cannot be transferred without authorization from the Department, and I will promptly notify the Department upon sale or legal transfer of any permitted emissions unit.</i>  <div style="display: flex; justify-content: space-between;"><div>Signature <u>Herschel E. Morris</u></div><div>Date <u>10/31/03</u></div></div>

\* Attach letter of authorization if not currently on file.

**Professional Engineer Certification**

1. Professional Engineer Name: David A. Buff Registration Number: 19011
2. Professional Engineer Mailing Address: Organization/Firm: Golder Associates Inc.* Street Address: 6241 NW 23rd Street, Suite 500 City: Gainesville State: FL Zip Code: 32653-1500
3. Professional Engineer Telephone Numbers: Telephone: ( 352 ) 336 - 5600 Fax: ( 352 ) 336 - 6603

\*Board of Professional Engineers Certificate of Authorization # 00001670

4. Professional Engineer Statement:

*I, the undersigned, hereby certify, except as particularly noted herein\*, that:*

*(1) To the best of my knowledge, there is reasonable assurance that the air pollutant emissions unit(s) and the air pollution control equipment described in this Application for Air Permit, when properly operated and maintained, will comply with all applicable standards for control of air pollutant emissions found in the Florida Statutes and rules of the Department of Environmental Protection; and*

*(2) To the best of my knowledge, any emission estimates reported or relied on in this application are true, accurate, and complete and are either based upon reasonable techniques available for calculating emissions or, for emission estimates of hazardous air pollutants not regulated for an emissions unit addressed in this application, based solely upon the materials, information and calculations submitted with this application.*

*If the purpose of this application is to obtain a Title V source air operation permit (check here [X], if so), I further certify that each emissions unit described in this Application for Air Permit, when properly operated and maintained, will comply with the applicable requirements identified in this application to which the unit is subject, except those emissions units for which a compliance schedule is submitted with this application.*

*If the purpose of this application is to obtain an air construction permit for one or more proposed new or modified emissions units (check here [ ], if so), I further certify that the engineering features of each such emissions unit described in this application have been designed or examined by me or individuals under my direct supervision and found to be in conformity with sound engineering principles applicable to the control of emissions of the air pollutants characterized in this application.*

*If the purpose of this application is to obtain an initial air operation permit or operation permit revision for one or more newly constructed or modified emissions units (check here [ ], if so), I further certify that, with the exception of any changes detailed as part of this application, each such emissions unit has been constructed or modified in substantial accordance with the information given in the corresponding application for air construction permit and with all provisions contained in such permit.*

David A. Buff  
Signature

10/29/03  
Date

(seal)

\* Attach any exception to certification statement.



CF Industries, Inc., responses to Department of Environmental Protection Requests, September 29, 2003:

With regard to the proposed monitoring, it is correct that CF, if the 40 CFR 63 Subparts AA and BB rules are determined to be applicable, proposes to monitor the two phosphoric acid plant scrubbers using the rule-specified instrumentation and procedures.

In the four granulation plants, CF proposes to use the monitoring strategy that will be specified in the Compliance Assurance Monitoring (CAM) Plan being finalized under EPA Rule 40 CFR 64, as part of its Alternative Monitoring Plan. This CAM Plan was submitted to DEP on May 28, 2003, and is being modified and supplemented as it is processed through the DEP review of the Title V permit renewal application. CF is currently developing proposals for pollution control parametric ranges as a part of this plan development. Ranges for the parameters monitored with newly installed equipment will be developed after the equipment is installed.

In addition to the CAM provisions, CF proposes to continuously monitor the freshwater abatement scrubbers for scrubber liquid delivery pressure and for gas pressure upstream of the scrubber packing, as described in the June 5, 2003, CF submittal. The entire CF monitoring proposal, including the CAM provisions, is compiled in Table 1.

The June 5 "Proposed Contingency Alternative Monitoring Plan" presented only the existing periodic monitoring because that is the currently permitted monitoring system approved by DEP, and the CAM Plan had not proceeded very far into the review process. CF intended, however, that the displacement of the existing monitoring procedures with the CAM Plan would occur and would be acceptable to DEP as a logical procedural occurrence, since DEP approval of the CAM Plan is required.

RESPONSE TO QUESTION 1

DEP requests justification for placing no upper limit on the scrubber liquid delivery pressure in the acid and process water scrubbers in the granulation plants.

CF will establish upper limits for the delivery pressure parameters in the CAM Plan.

DEP requests a description of the variation of delivery pressure with changes in flow rate of the scrubber liquor.

Changes in the scrubber liquor flow rate will be reflected in the backpressure from the scrubber spray nozzles and therefore in the scrubber liquor pressure. Nozzle performance curves are provided in Appendix A to illustrate the relationship of liquid pressure to liquid flow through a nozzle. The spray nozzles shown in Appendix A are common to the fume, dryer, dust, and cooler scrubber systems.

RESPONSE TO QUESTION 2:

DEP requests information regarding the pressure drop across each scrubber in each system, with data to demonstrate the effect of each individual scrubber on the overall reduction of hydrogen fluoride (HF) emissions.

The requested data has never been generated and is not available. If CF is demonstrated to be a major source of HF, CF proposes to rely on the freshwater fluoride abatement scrubber in each plant as justification for alternative monitoring. These scrubbers provide extra insurance against excess HF emissions, because of the affinity of HF for pH-neutral fresh water. The freshwater abatement scrubbers are believed to be unique to CF within the phosphate industry and constitute an extra "layer" of pollution control for HF. The existence of and proposed parametric monitoring for these scrubbers, along with the compliance assurance monitoring proposed for the other component scrubbers in the system, should constitute abundant parametric monitoring to meet the spirit and purpose of the HF Maximum Achievable Control Technology (MACT) rule.

Preceding the freshwater abatement scrubbers, each granulation plant scrubber system consists of four independent scrubber trains which discharge into the common abatement scrubber before discharging to atmosphere. The four independent trains are designated as the Fume, Dryer, Dust, and Cooler Systems. Furthermore, these four trains contain various combinations of venturi, acid cyclonic, and pond water cyclonic components that are configured in series. The total pressure drop across each independent train is currently monitored. Any operational problem with an individual component will be reflected in the pressure drop for the train, and therefore, pressure drop monitoring

of the individual components is not necessary to detect an operational problem.

CF urges DEP to take into account the cost-effectiveness analysis provided in the June 5, 2003, submittal; the existing Title V permit limits for fluoride which are already at the MACT levels; and the extra layer of pollution control assurance provided by the freshwater fluoride abatement scrubbers, in considering the alternative monitoring proposal.

### RESPONSE TO QUESTION 3

DEP requests justification for the use of upstream air pressure monitoring in lieu of pressure drop monitoring in the freshwater abatement scrubbers.

Upstream air pressure is proposed in lieu of pressure drop for the abatement scrubbers because the pressure drop in these scrubbers is so low as to prevent a meaningful detection of variations. The monitoring of upstream pressure is proposed because the upstream pressure measurement provides a higher value than the pressure drop (0.5 inches of water as compared with 0.2) and provides an increased probability of detecting a significant variation in the event of an operational problem. A reduction in the gas flow or water flow to the scrubber would be expected to cause a drop in the pressure reading upstream of the chevron packing, while a pluggage of the packing itself would cause an increase in the pressure reading.

Monitoring of the downstream pressure of the abatement scrubber is not necessary since the abatement scrubber discharges to a 110" diameter stack open to the atmosphere. The stack is not subject to pluggage or a buildup in pressure.

### RESPONSE TO OTHER COMMENTS AND REQUESTS

The Department states that it disagrees with CFI's position that the monitoring required by the MACT standards is not cost-effective.

The federal rule states that requests for approval of alternative monitoring plans should address considerations such as the "economic infeasibility" or "impracticality" of requiring the affected source to meet the otherwise applicable monitoring requirements. 40 CFR sec. 63.8 (f)(4)(ii). The June 5, 2003 proposal addressed these considerations by comparing costs to projected air emission impacts. We respectfully submit that the disparity between costs and environmental benefits should guide the agency's discretion in considering the proposed alternative monitoring plan.

CF requests an explanation of the Department's rationale for disagreement with the CF position.

The Department requests additional information related to process parameters that are currently monitored.

Information on process parameters currently monitored is provided in Appendix B, "Information on Pollution Control Parameters Currently Monitored."

The Department requests a color schematic of the granulation train.

The requested color schematic is attached as Appendix C.

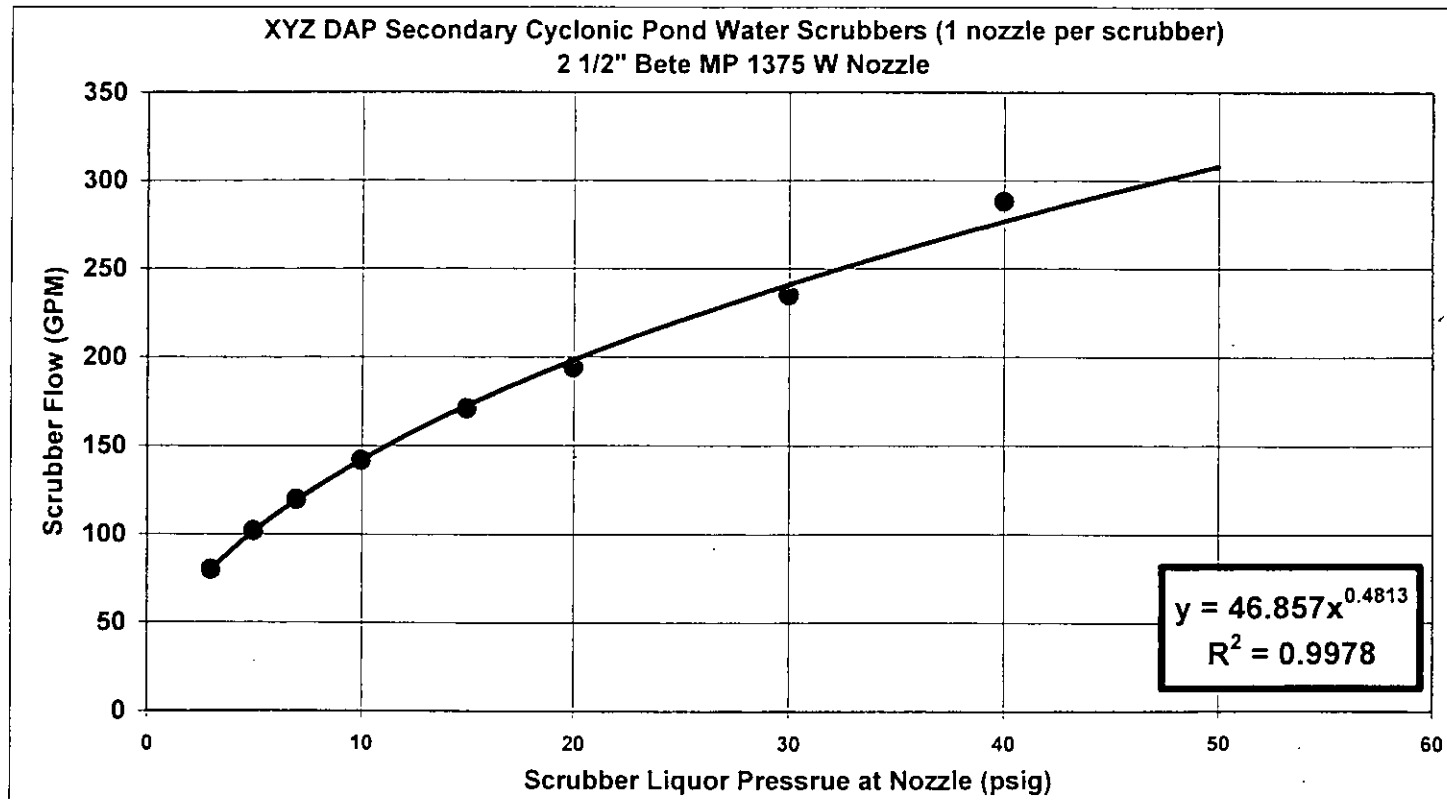
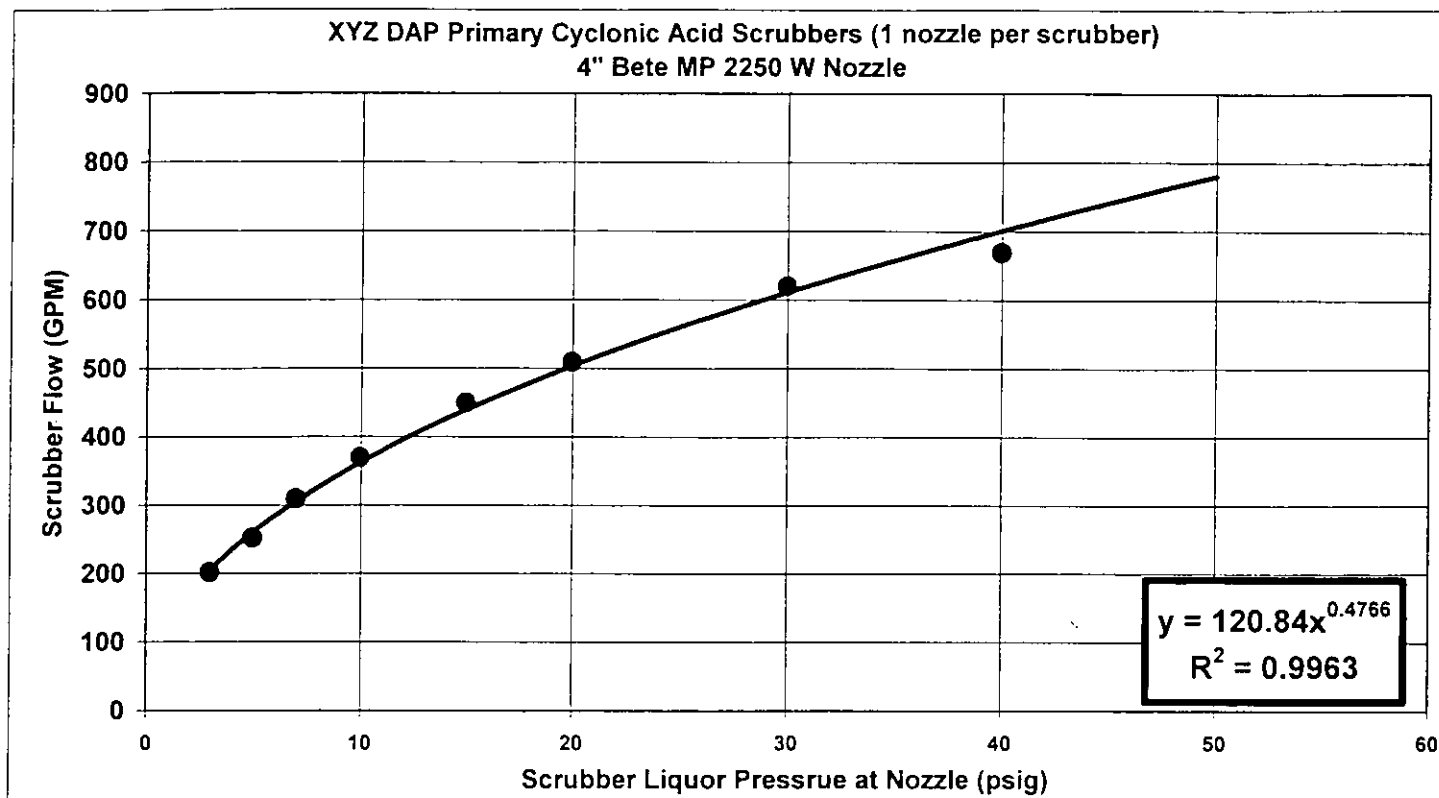
**TABLE I**  
**PROPOSED ALTERNATIVE MONITORING PLAN ELEMENTS**

SCRUBBER	LIQUID MONITORING	GAS MONITORING
A-Phosphoric Acid Packed Bed Cross-flow Scrubber	Liquid Flow, continuous	Pressure Drop, continuous.
B-Phosphoric Acid Packed Bed Cross-flow scrubber	Liquid Flow, continuous	Pressure Drop, continuous.
<b>X,Y,Z Granulation Plants:</b>		
Fume Venturi Scrubbers (3)	Delivery Pressure, 2-hr. interval.	Segment* Pressure Drop, continuous
Fume Acid Cyclonic Scrubbers (3)	Delivery Pressure, 2-hr. interval.	Segment* Pressure Drop, continuous
Fume Pondwater Cyclonic Scrubbers (3)	Delivery Pressure, 2-hr. interval.	Segment* Pressure Drop, continuous
Dryer Venturi Scrubbers (3)	Delivery Pressure, 2-hr. interval.	Segment* Pressure Drop, continuous
Dryer Acid Cyclonic Scrubbers (3)	Delivery Pressure, 2-hr. interval.	Segment* Pressure Drop, continuous
Dryer Pondwater Cyclonic Scrubbers (3)	Delivery Pressure, 2-hr. interval.	Segment* Pressure Drop, continuous
Cooler Cyclonic Scrubbers (3)	Delivery Pressure, 2-hr. interval.	Segment* Pressure Drop, continuous
Dust Venturi Scrubbers (3)	Delivery Pressure, 2-hr. interval.	Segment* Pressure Drop, continuous
Dust Cyclonic Scrubbers (3)	Delivery Pressure, 2-hr. interval.	Segment* Pressure Drop, continuous
Freshwater Fluoride Abatement Scrubbers (3)	Delivery Pressure, continuous. pH, continuous.	Gas pressure upstream of packing, continuous.

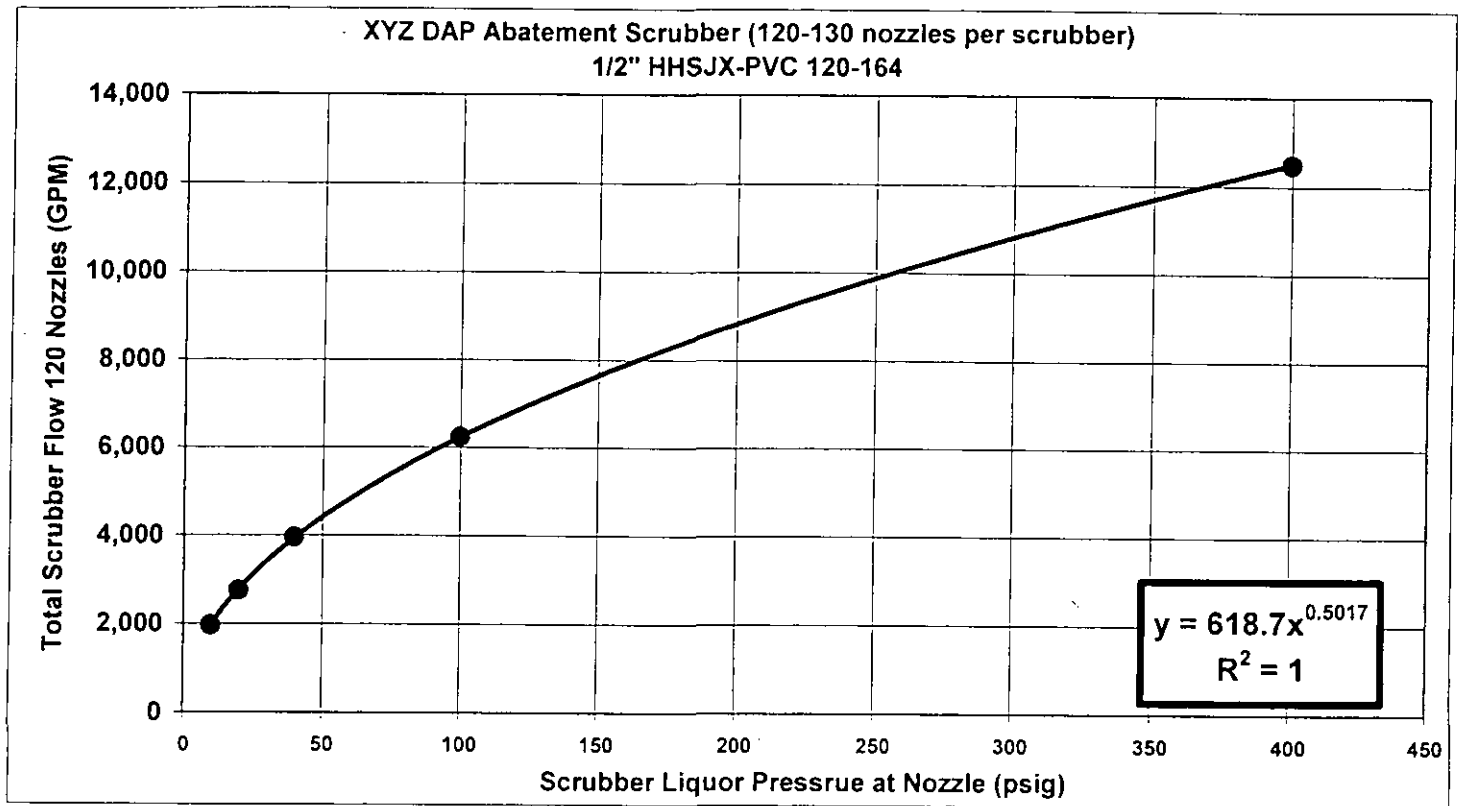
- A segment constitutes a train of scrubbers in series or a single scrubber, excluding the fresh water fluoride abatement scrubber.

APPENDIX A- NOZZLE DESIGN CURVES

## Appendix A - Page 1



Appendix A - Page 2

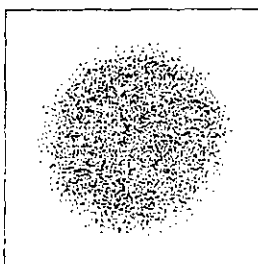




# *SpiralJet*™ SPRAY NOZZLES EXTRA LARGE FREE PASSAGE

**C**  
38

GENERAL PURPOSE  
FULL CONE



## COMMON APPLICATIONS

- Flue gas scrubbing
- Gas cooling
- Washing & rinsing processes
- Fire suppression & prevention

## HHSJX

threaded/hex  
3/8"-2" NPT or BSPT (M)



## HHSJX

threaded/flats  
3/8"-2" NPT or BSPT (M)



## HHSJX

threaded/round  
3/8"-2" NPT or BSPT (M)



## DESIGN FEATURES

Maximum free passage SpiralJet nozzles minimize the possibility of plugging in high-flow pollution control applications. With a simple one-piece design, the inlet orifice is the smallest opening that liquid passes through. The outlet helix orifice is proportionately larger than the inlet opening. This virtually eliminates plugging and allows for maximum liquid throughput.

Maximum free passage SpiralJet nozzles are available in brass, 316SS, and polypropylene. Additional materials such as TEFLON, silicon carbide, ceramic, and PVC are available upon request.

Type HHSJX SpiralJet nozzles are available with either 90° or 120° spray angle with full-cone spray patterns. The HHSJX

nozzle is available in threaded hex, threaded round, and threaded flats. Maximum operating pressure depends on material, size and application.

## PERFORMANCE DATA

Pipe Size NPT or BSPT (M)	Spray Angle at 10 psi		Capacity Size	Orifice Diam. inches	Free Passage Diam. inches	CAPACITY (gallons per minute)					Nozzle Length 90° & 120°
	90°	120°				10 psi	20 psi	40 psi	100 psi	400 psi	
3/8	•	•	66	1/16	1/16	3.6	4.2	6.0	9.5	19.0	2 3/4"
	•	•	40	3/32	3/32	4.0	5.7	8.0	12.6	25	
	•	•	53	1/8	1/8	5.3	7.5	10.6	16.8	34	
	•	•	82	3/16	3/16	8.2	11.6	16.4	26	52	
1/2	•	•	120	1/4	1/4	12.0	17.0	24	38	76	3 1/4"
	•	•	164	5/16	5/16	16.4	23	33	52	104	
3/4	•	•	210	3/8	3/8	21	30	42	66	133	5 1/4"
1	•	•	340	1/2	1/2	34	48	68	108	215	5 1/4"
	•	•	470	5/8	5/8	47	66	94	149	297	
1-1/2	•	•	640	3/4	3/4	64	91	128	202	405	6 3/4"
	•	•	820	1	1	82	116	164	259	519	
	•	•	960	1 1/8	1 1/8	96	136	192	304	607	
	•	•	1400	1 1/2	1 1/2	140	198	280	443	885	
2	•	•	1780	1 3/4	1 3/4	178	252	356	563	1125	10 1/4"
	•	•									

Material	Material Code
•	no material code = Brass
•	SS = Cast 316 Stainless Steel
•	PP = Polypropylene

Additional materials upon request.

## ACCESSORIES

Adjustable Ball Fittings



Split-Eyelet Connector



Other Accessories

- Pressure Regulators
- Control Valves
- Solenoid Valves
- Swivel Connectors

SEE SECTION G FOR  
COMPLETE INFORMATION.

## ORDERING INFORMATION

COMPLETE NOZZLE  
ASSEMBLY

3/8 HHSJX-SS 120 30

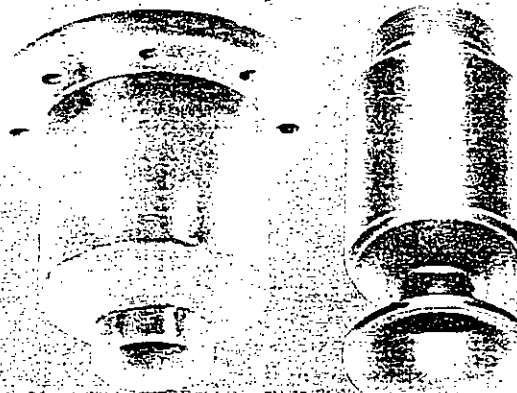
Pipe Nozzle Material Spray Capac.

# Appendix A - Page 4

SERIES

Maximum  
Clear Passage  
Full Cone

MAXI-PASS™



Full Cone 90° M

Full Cone 120° W

## DESIGN

Ultimate non-clogging design.  
Two unique S-shaped internal vanes  
allow free passage of particles.  
HIGH ENERGY EFFICIENCY.  
Easily handles dirty, lumpy and  
stringy liquids.

## SPRAY CHARACTERISTICS

High velocity discharge.  
Square patterns to special order.  
Spray pattern - full cone  
Spray angles - 30°, 60°, 90°, and 120°  
Flow rates - .68 to 670 gpm  
Flow rates up to 4500 gpm available.  
Call our Engineering Department for details.  
High reliability spray performance under  
most difficult conditions.

## MATERIALS

PVC  
Polypropylene  
Polyurethane  
Teflon  
Brass  
Hastelloy C  
316 Stainless Steel  
Stellite 6  
Other materials on application

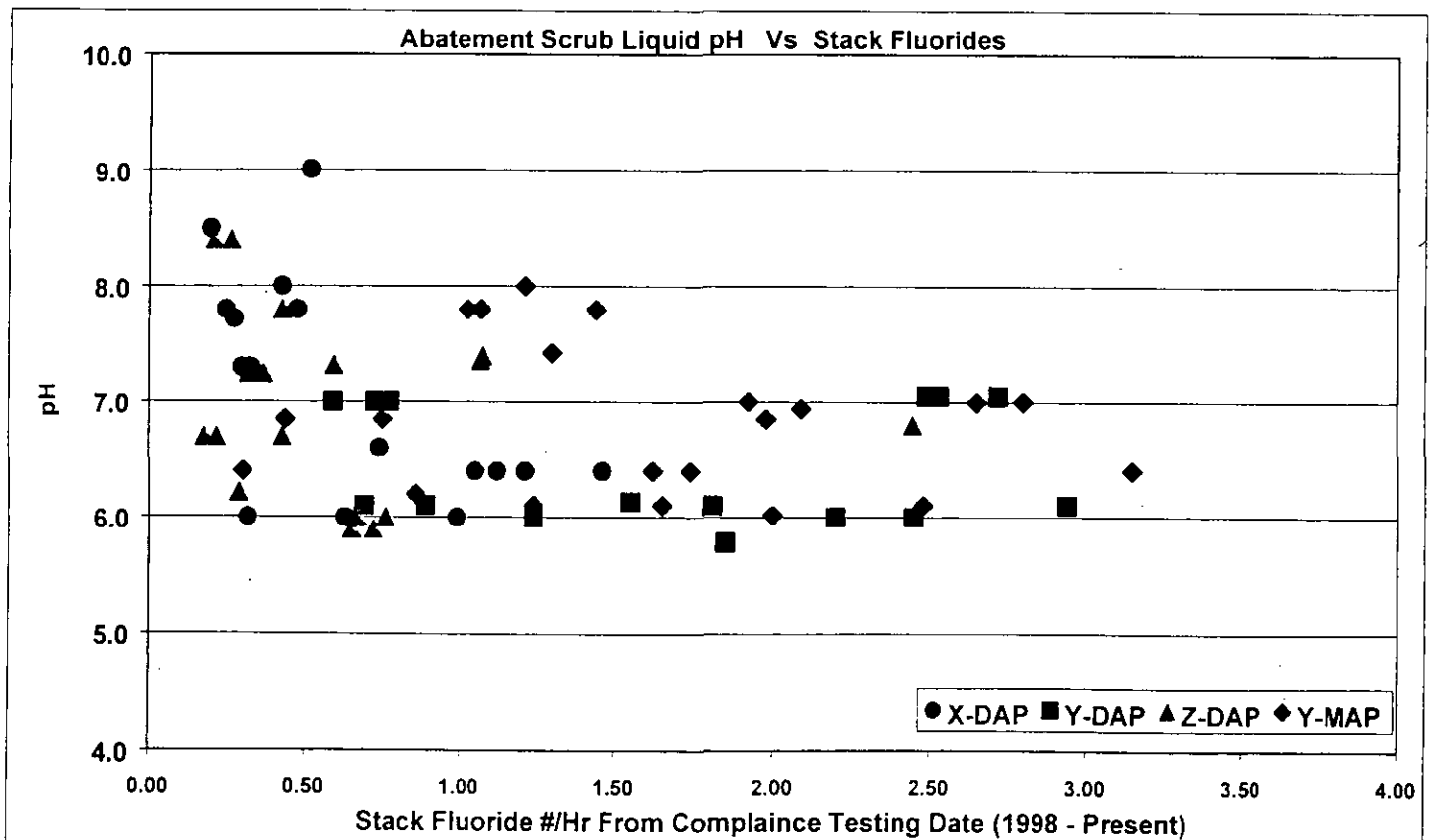
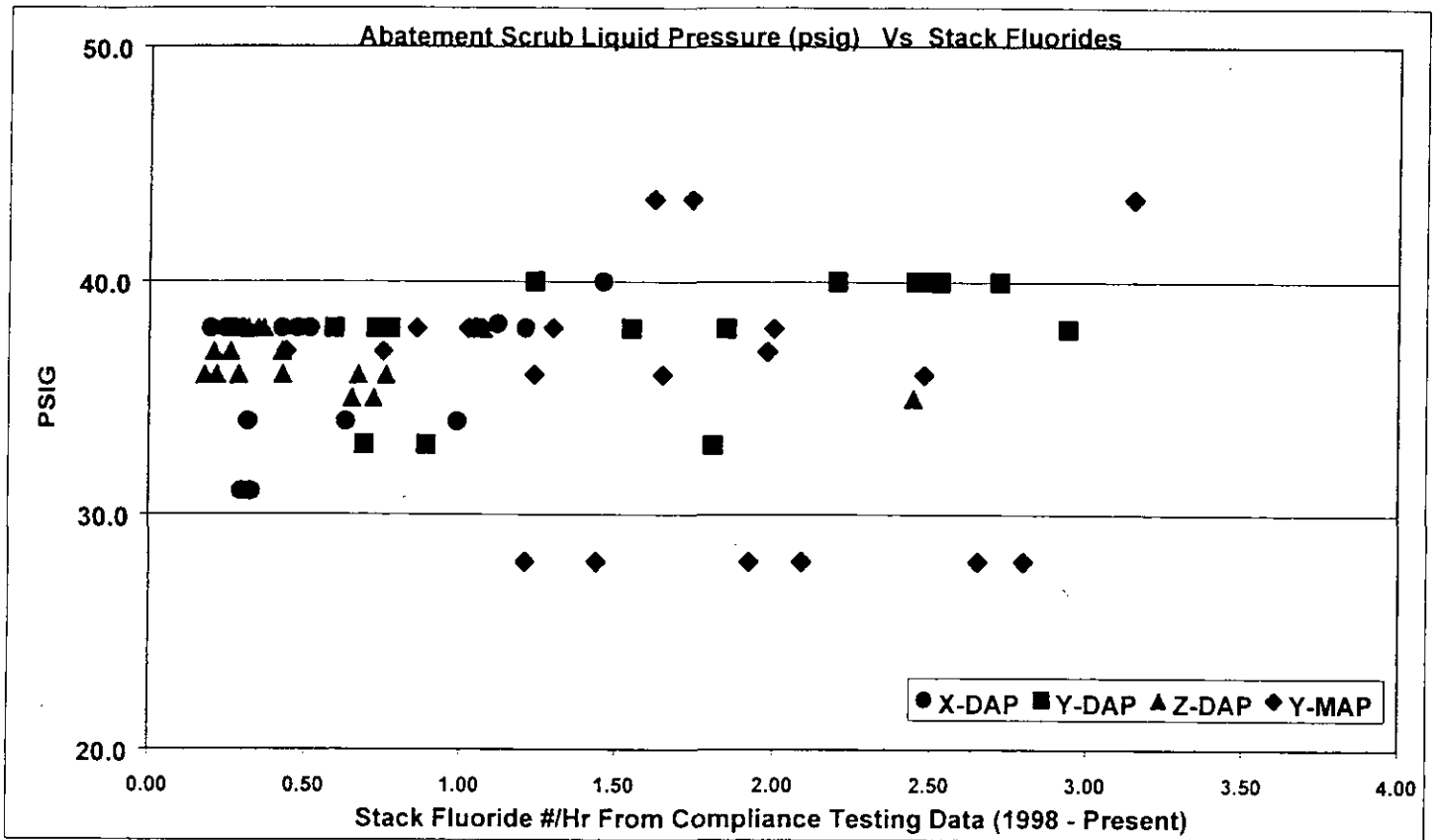
## FULL CONE

Spray Angle	Port Size	Male Hose Number	Female Hose Number	Clear Passage Inch	Overall Length Male	Overall Length Female	Hex O'Round Male	Hex O'Round Female	GALLONS PER MINUTE @ PSI									
									7	8	10	15	20	30	40	50	60	70
120°	3/8	MP125W	FMP125W	1.8	1.12	1.12	7/8	7/8	65	65	10	12	15	17	21	24		
		MP156W	FMP156W	5.52	1.12	1.12	7/8	7/8	105	105	16	19	23	27	33	38		
		MP187W	FMP187W	7.15	1.12	1.12	7/8	7/8	125	125	20	24	29	34	41	47		
	1/2	MP187W	FMP187W	3.75	1.75	1.75	1	1	115	115	23	28	34	39	47	53		
		MP218W	FMP218W	7.52	1.75	1.75	1	1	145	145	31	37	44	51	62	71		
		MP250W	FMP250W	11	1.75	1.75	1	1	175	175	41	50	60	70	84	100		
	3/4	MP281W	FMP281W	9.22	2.38	2.38	1.12	1.12	215	215	51	61	74	86	106	124		
		MP312W	FMP312W	9.16	2.38	2.38	1.12	1.12	245	245	62	74	90	104	126	147		
		MP343W	FMP343W	11.32	2.38	2.38	1.12	1.12	275	275	75	90	110	127	156	180		
		MP375W	FMP375W	13.8	2.38	2.38	1.12	1.12	305	305	90	110	135	155	192	220		
	1	MP375W	FMP375W	13.8	2.516	2.516	1.12	1.12	335	335	100	120	150	175	212	240		
		MP406W	FMP406W	15.72	2.516	2.516	1.12	1.12	365	365	115	136	168	195	233	260		
		MP437W	FMP437W	17.16	2.516	2.516	1.12	1.12	395	395	130	150	180	210	250	300		
	1 1/4	MP437W	FMP437W	17.16	3.38	3.38	2	2	435	435	150	180	210	240	280	320		
		MP500W	FMP500W	19.4	3.38	3.38	2	2	465	465	170	200	230	260	300	340		
		MP531W	FMP531W	17.32	3.38	3.38	2	2	495	495	190	220	250	280	320	360		
		MP562W	FMP562W	19.16	3.38	3.38	2	2	525	525	210	240	270	300	340	380		
	1 1/2	MP562W	FMP562W	21.16	4.18	4.18	2 1/4	2 1/4	565	565	230	260	290	320	360	400		
		MP593W	FMP593W	19.32	4.18	4.18	2 1/4	2 1/4	595	595	250	280	310	340	380	420		
		MP625W	FMP625W	15.6	4.18	4.18	2 1/4	2 1/4	625	625	270	300	330	360	400	440		
		MP656W	FMP656W	21.34	4.18	4.18	2 1/4	2 1/4	655	655	290	320	350	380	420	460		
120°	2	MP687W	FMP687W	15.75	4.18	4.18	2 1/4	2 1/4	685	685	310	340	370	400	440	480		
		MP750W	FMP750W	15.4	6.12	6.12	3 1/4	3 1/4	715	715	330	360	390	420	460	500		
		MP812W	FMP812W	15.16	6.12	6.12	3 1/4	3 1/4	745	745	350	380	410	440	480	520		
	2 1/2	MP875W	FMP875W	15.16	6.12	6.12	3 1/4	3 1/4	775	775	370	400	430	460	500	540		
		MP937W	FMP937W	15.16	6.12	6.12	3 1/4	3 1/4	805	805	390	420	450	480	520	560		
		MP1000W	FMP1000W	15.16	6.12	6.12	3 1/4	3 1/4	835	835	410	440	470	500	540	580		
	3	MP1125W	FMP1125W	15.16	6.12	6.12	3 1/4	3 1/4	865	865	430	460	490	520	560	600		
		MP1250W	FMP1250W	15.16	8.316	8.316	4 3/8	4 3/8	895	895	450	480	510	540	580	620		
		MP1375W	FMP1375W	15.16	8.316	8.316	4 3/8	4 3/8	925	925	470	500	530	560	600	640		
		MP1500W	FMP1500W	15.16	8.316	8.316	4 3/8	4 3/8	955	955	490	520	550	580	620	660		
	4	MP1500W	FMP1500W	15.16	10.38	10.38	4 7/8	4 7/8	985	985	510	540	570	600	640	680		
		MP1625W	FMP1625W	15.16	10.38	10.38	4 7/8	4 7/8	1015	1015	530	560	590	620	660	700		
		MP1750W	FMP1750W	15.16	10.38	10.38	4 7/8	4 7/8	1045	1045	550	580	610	640	680	720		
120°	4	MP1750W	FMP1750W	15.16	12.516	12.516	6 3/16	6 3/16	1075	1075	570	600	630	660	700	740		
		MP1875W	FMP1875W	15.16	12.516	12.516	6 3/16	6 3/16	1105	1105	590	620	650	680	720	760		
		MP2000W	FMP2000W	15.16	12.516	12.516	6 3/16	6 3/16	1135	1135	610	640	670	700	740	780		
		MP2125W	FMP2125W	15.16	12.516	12.516	6 3/16	6 3/16	1165	1165	630	660	690	720	760	800		
120°	4	MP2250W	FMP2250W	15.16	12.516	12.516	6 3/16	6 3/16	1195	1195	650	680	710	740	780	820		
		MP2375W	FMP2375W	15.16	12.516	12.516	6 3/16	6 3/16	1225	1225	670	700	730	760	800	840		

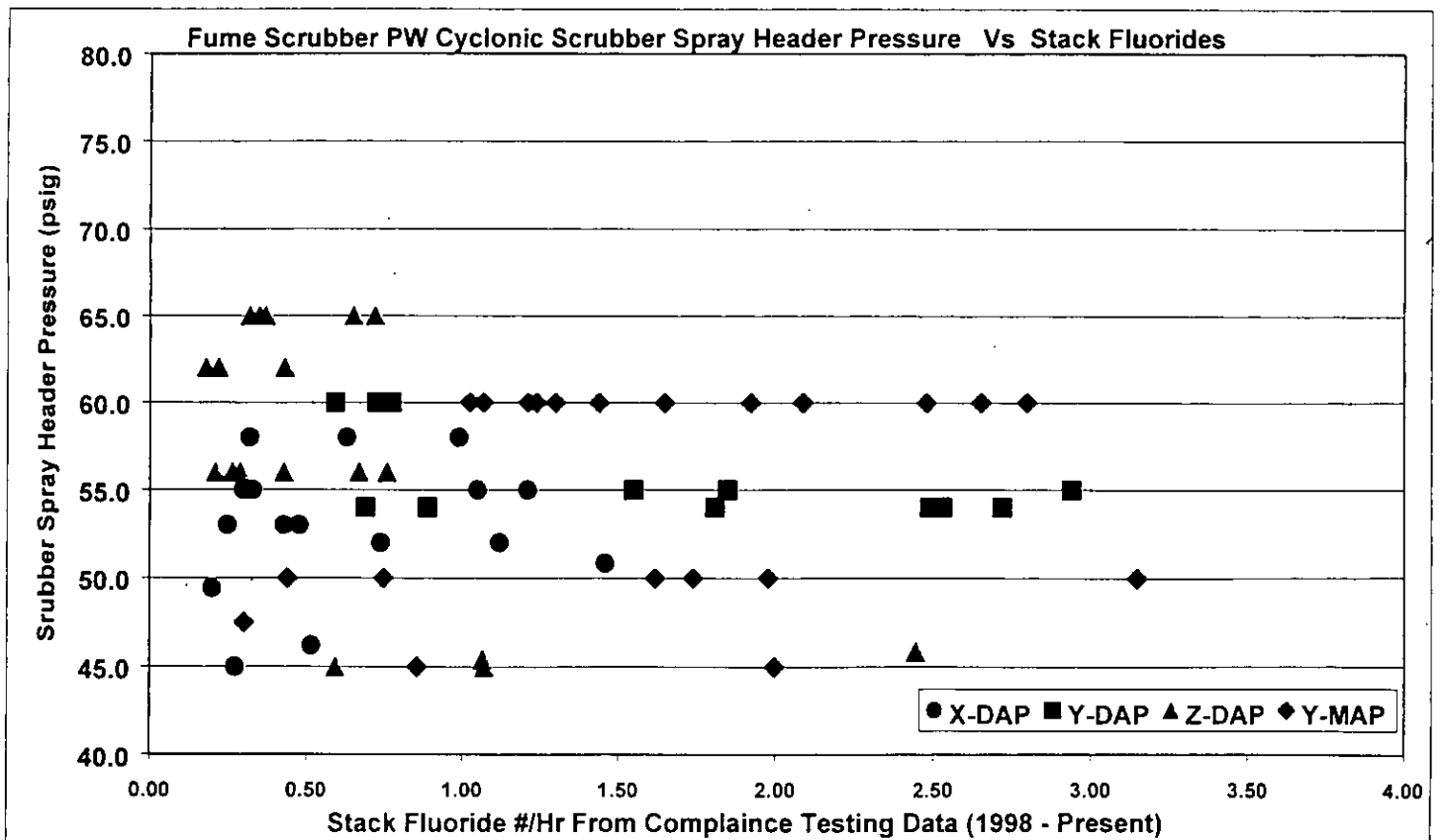
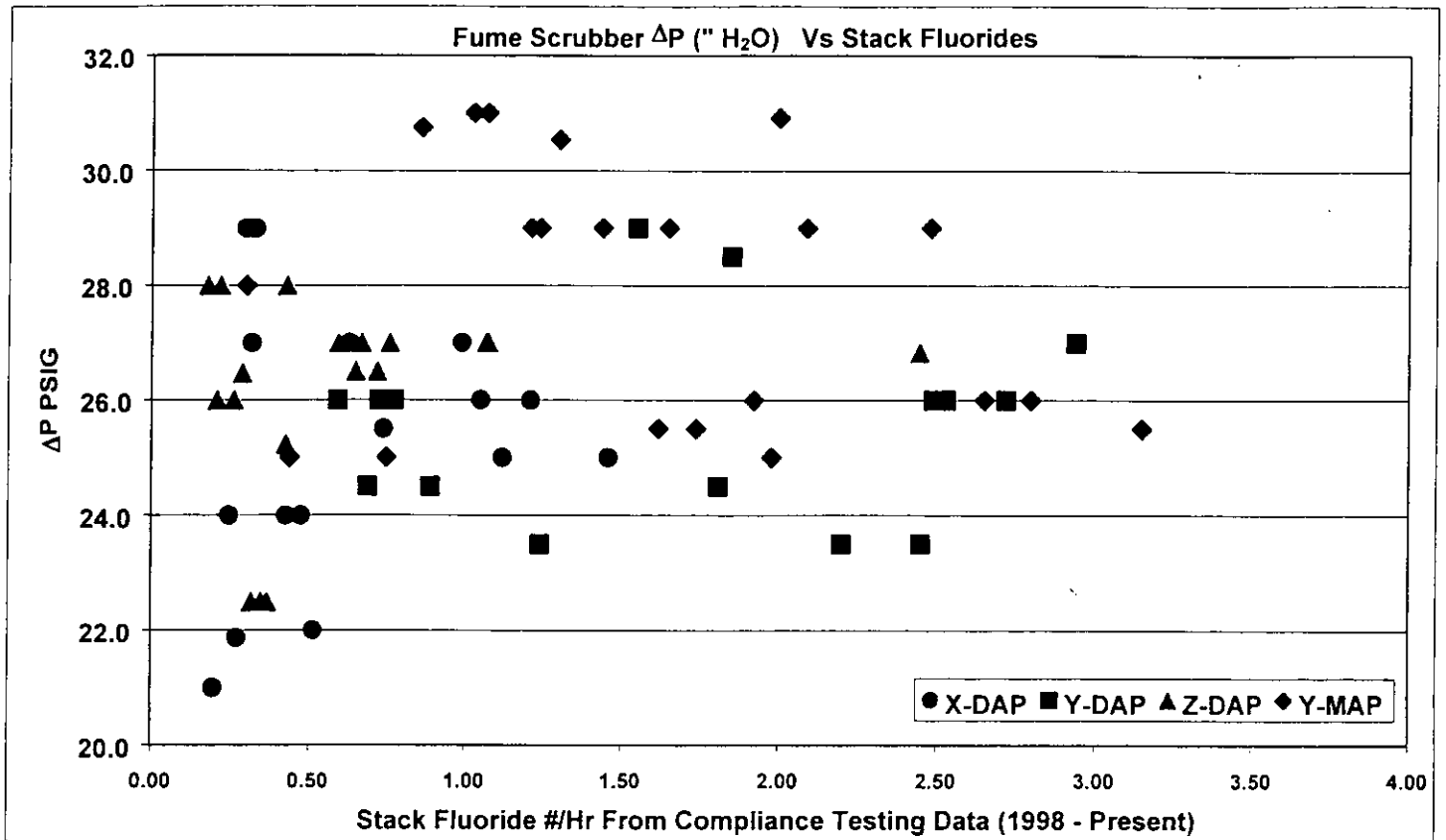
242

APPENDIX B- INFORMATION ON POLLUTION CONTROL  
PARAMETERS CURRENTLY MONITORED

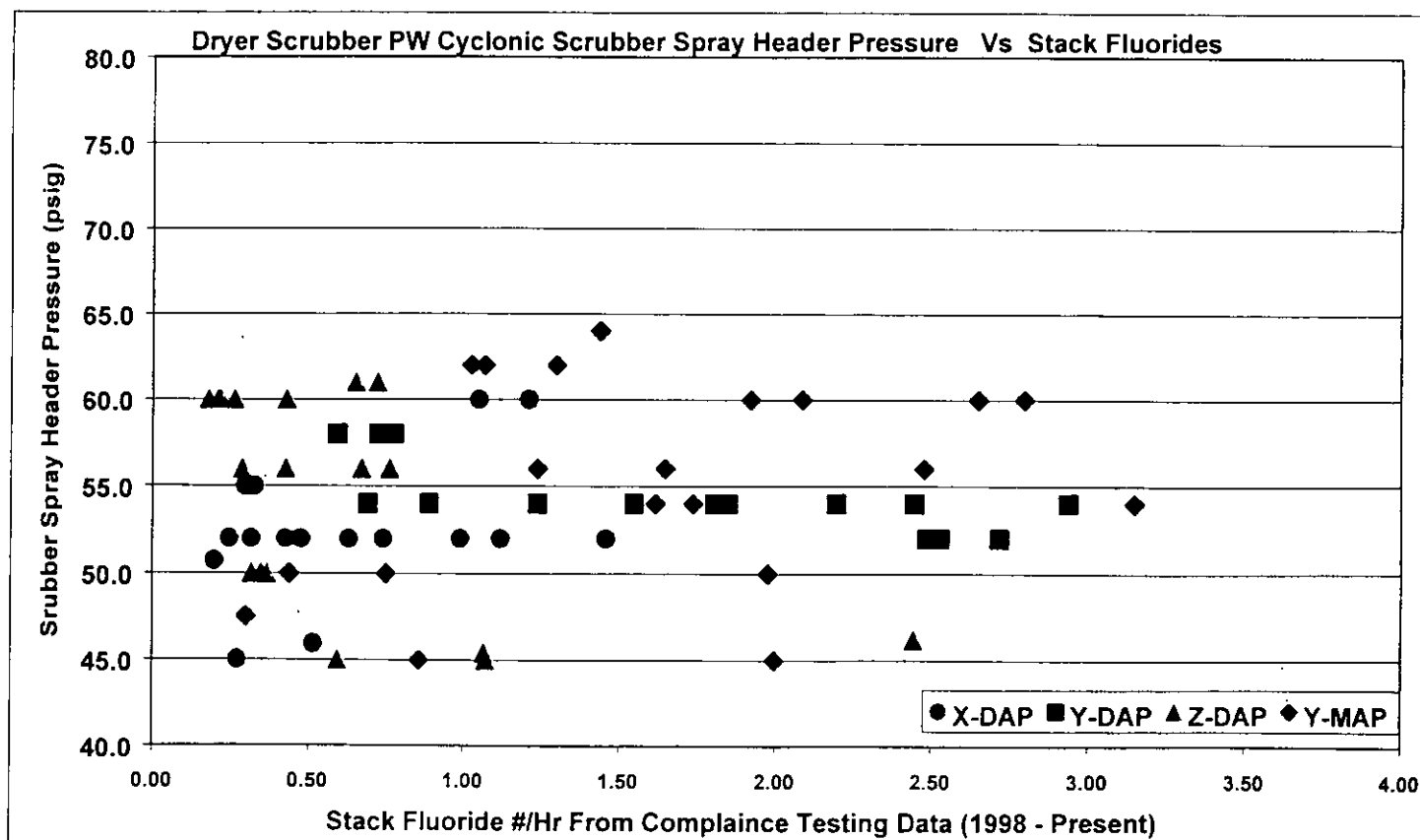
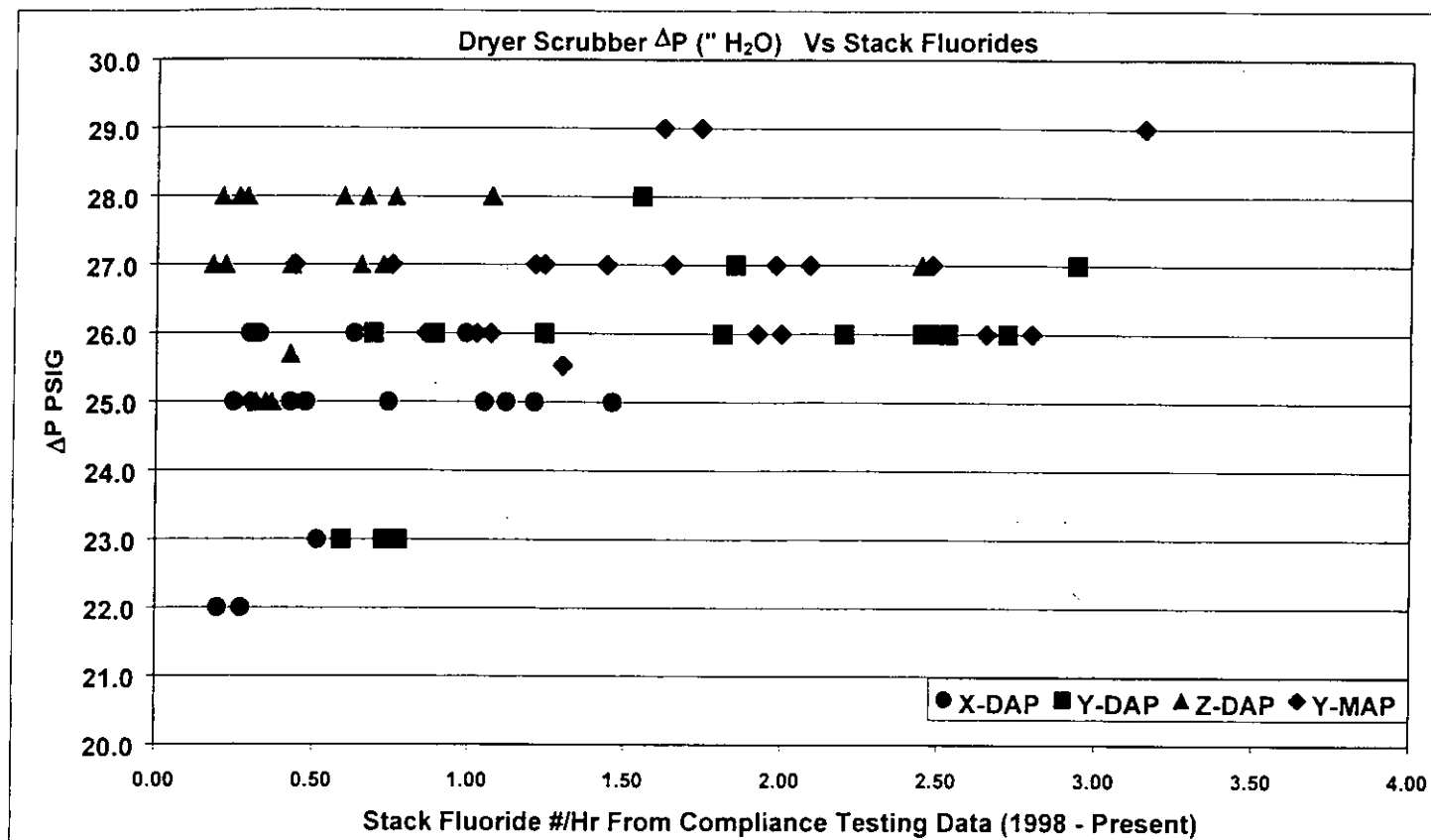
# Appendix B - Page 1



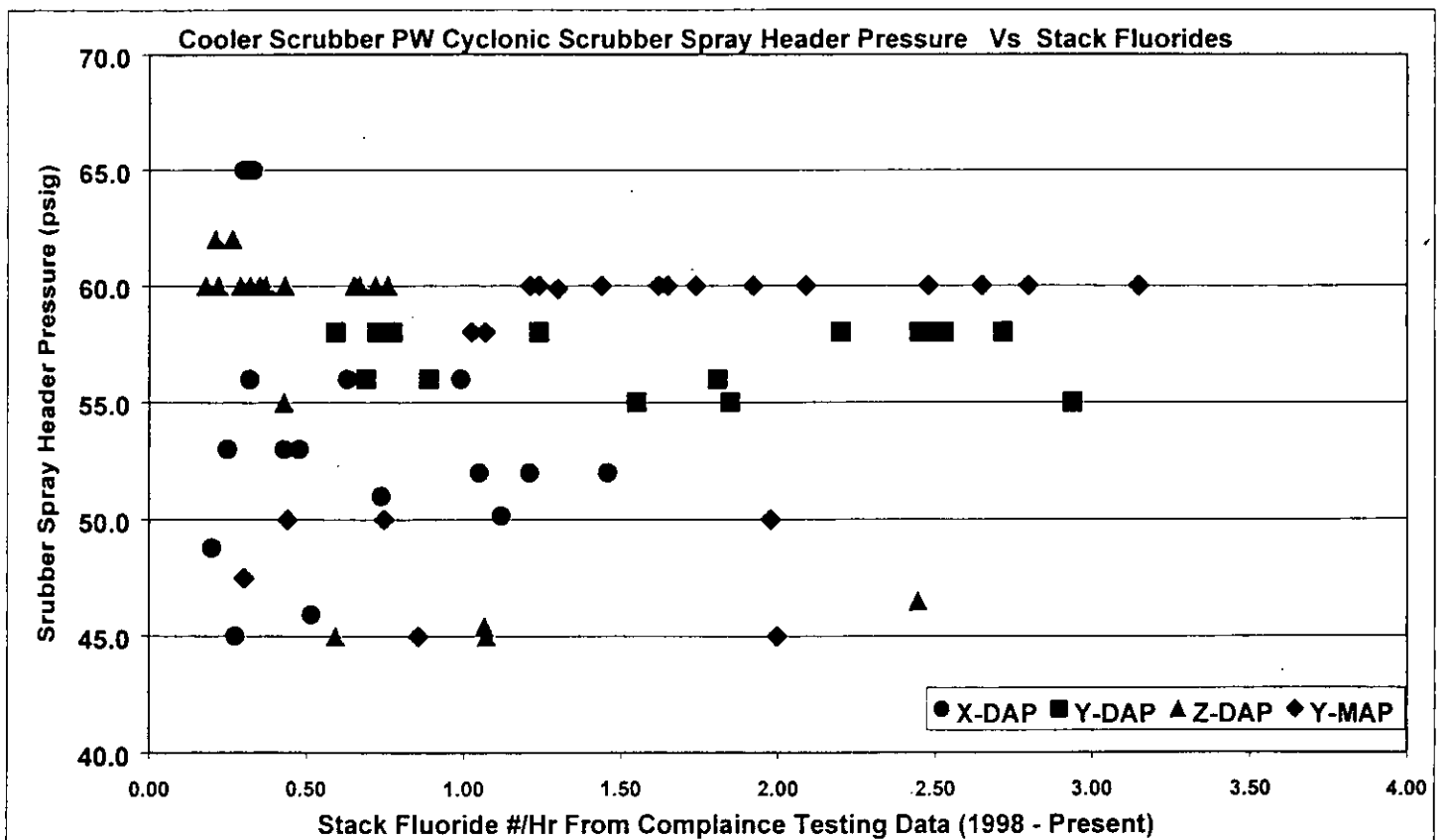
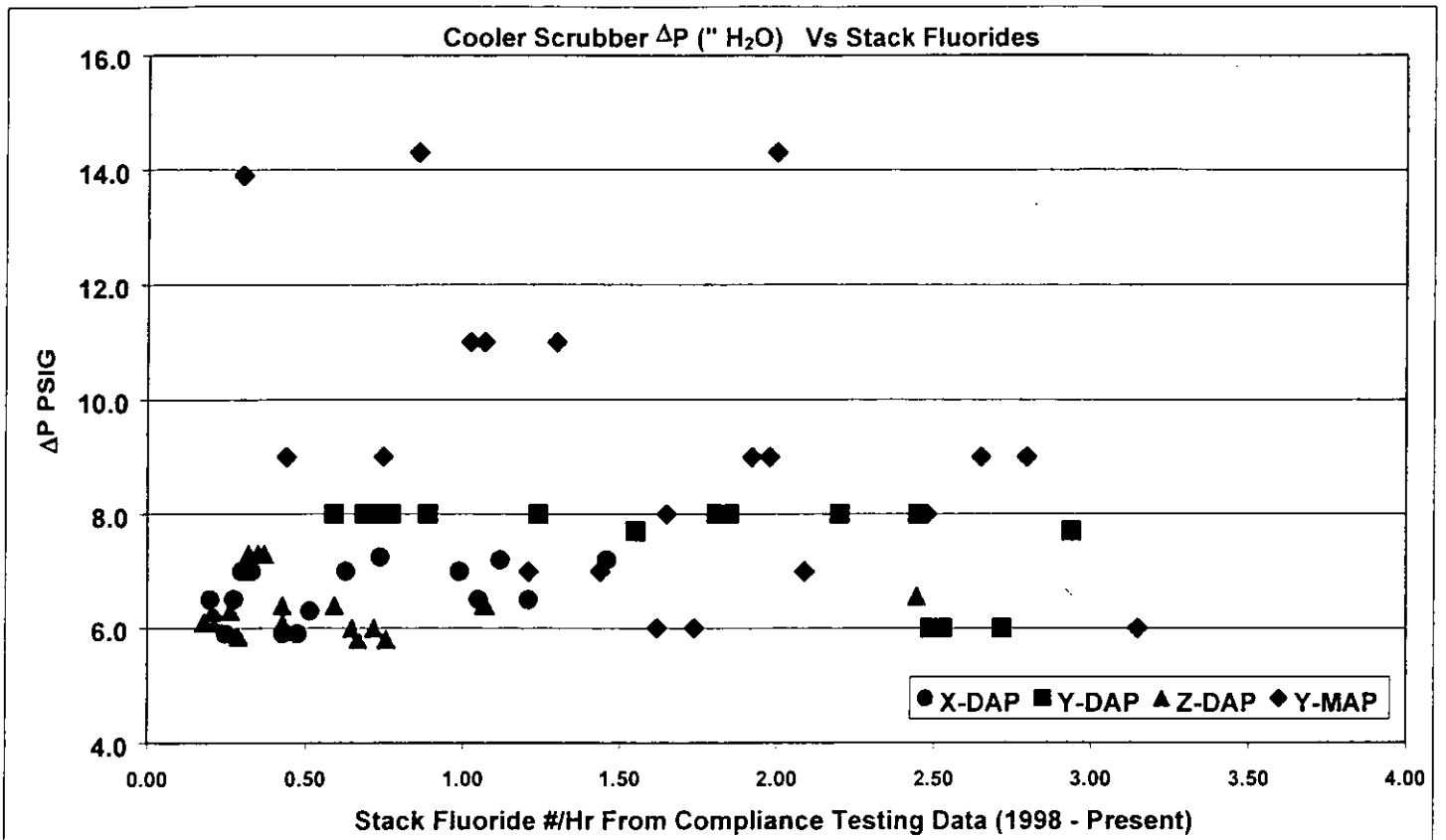
# Appendix B - Page 2

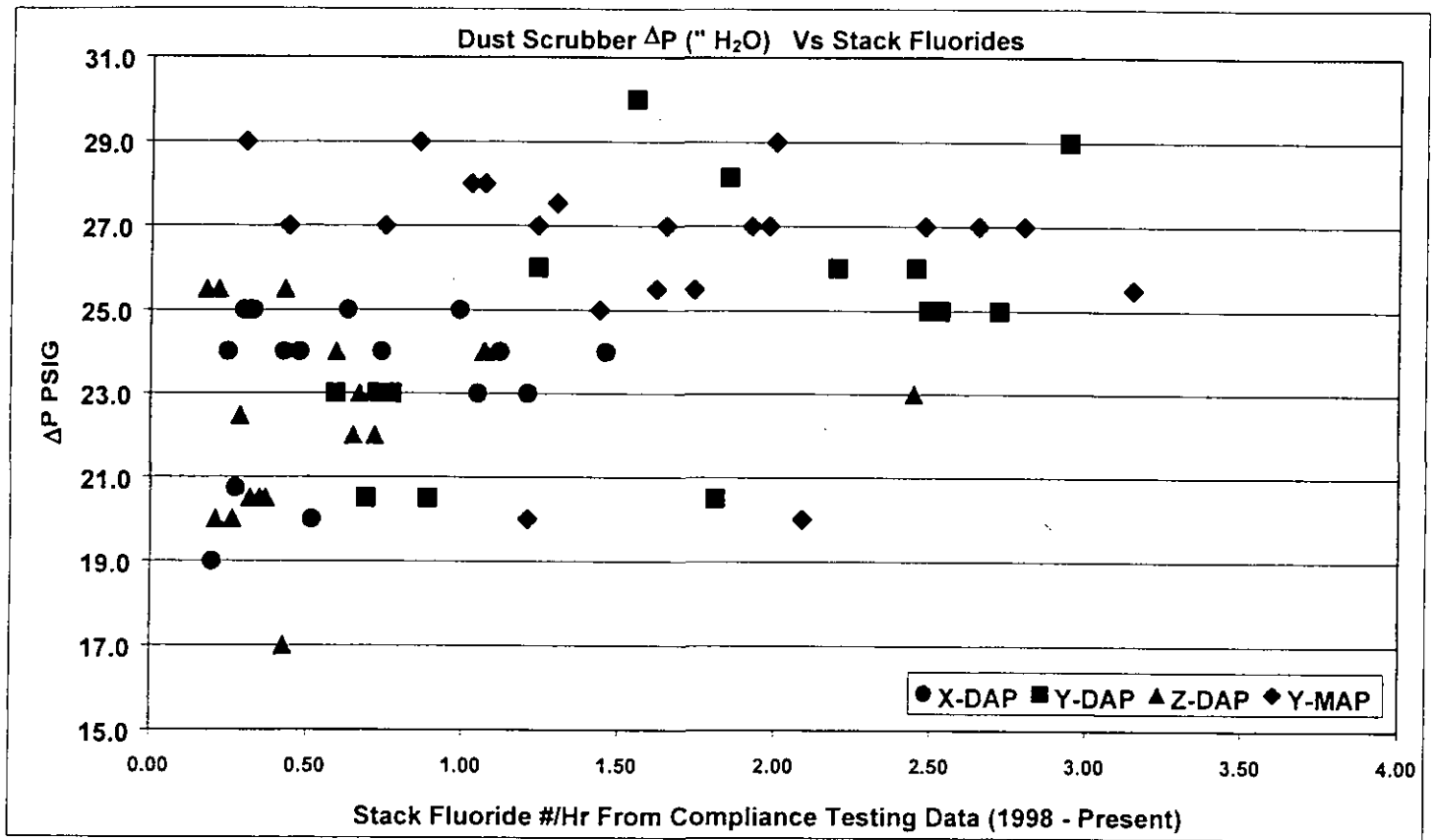


# Appendix B - Page 3



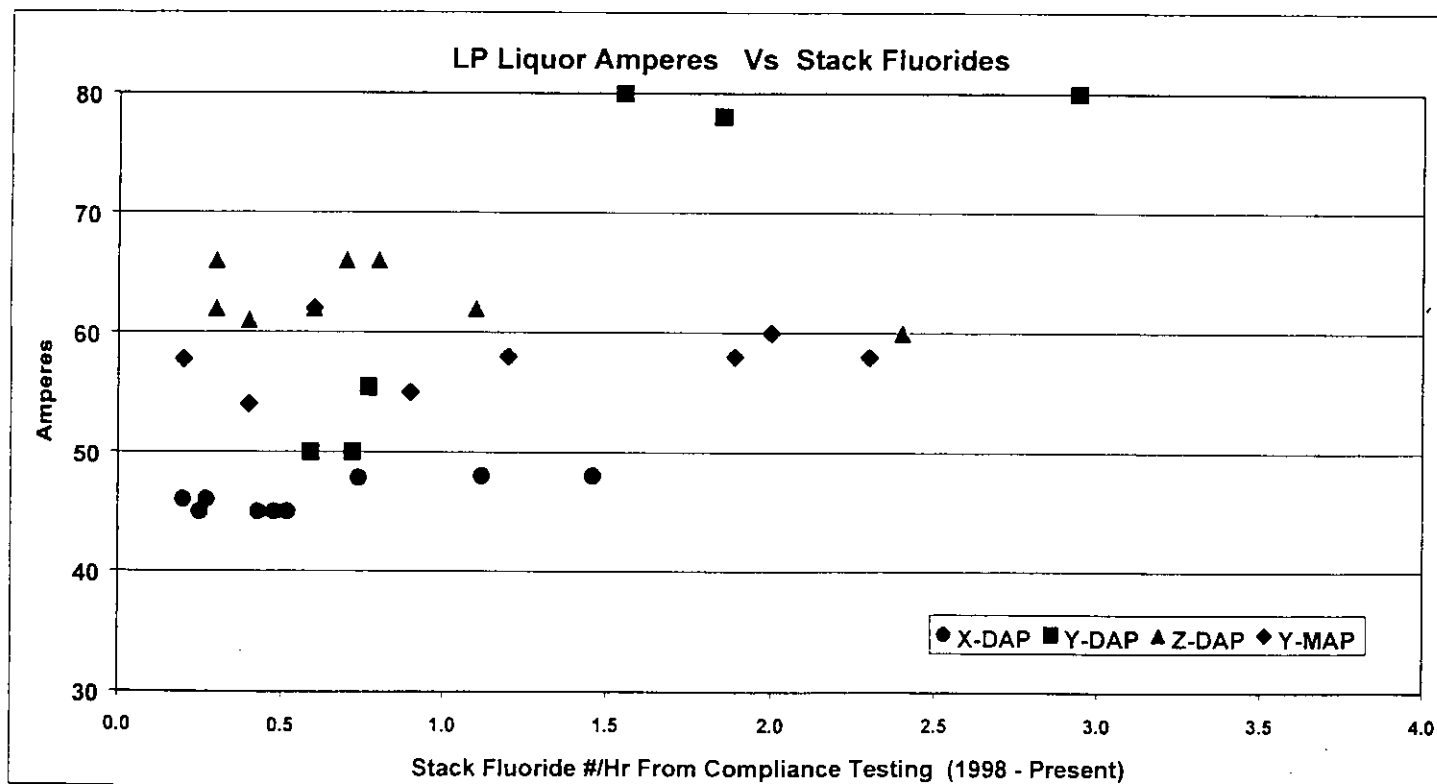
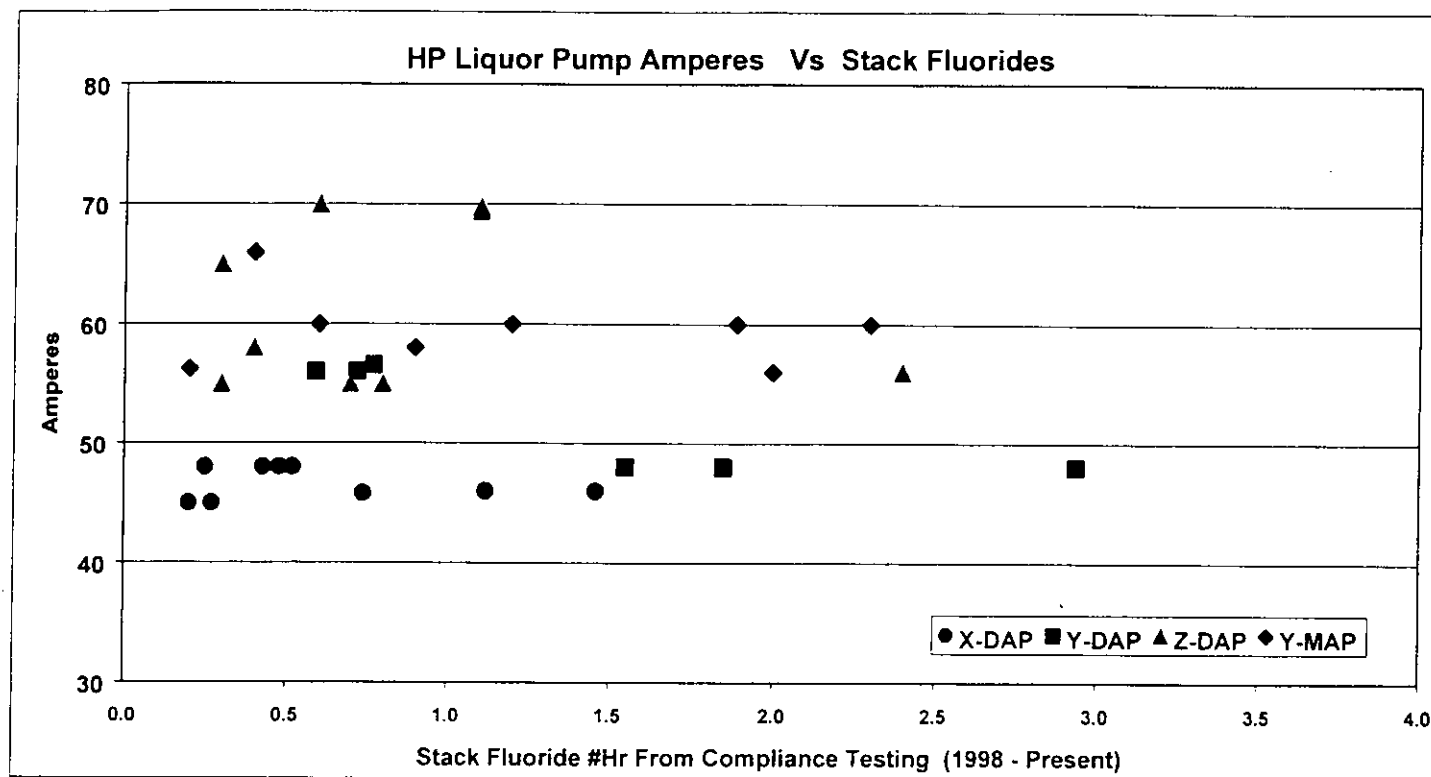
# Appendix B - Page 4

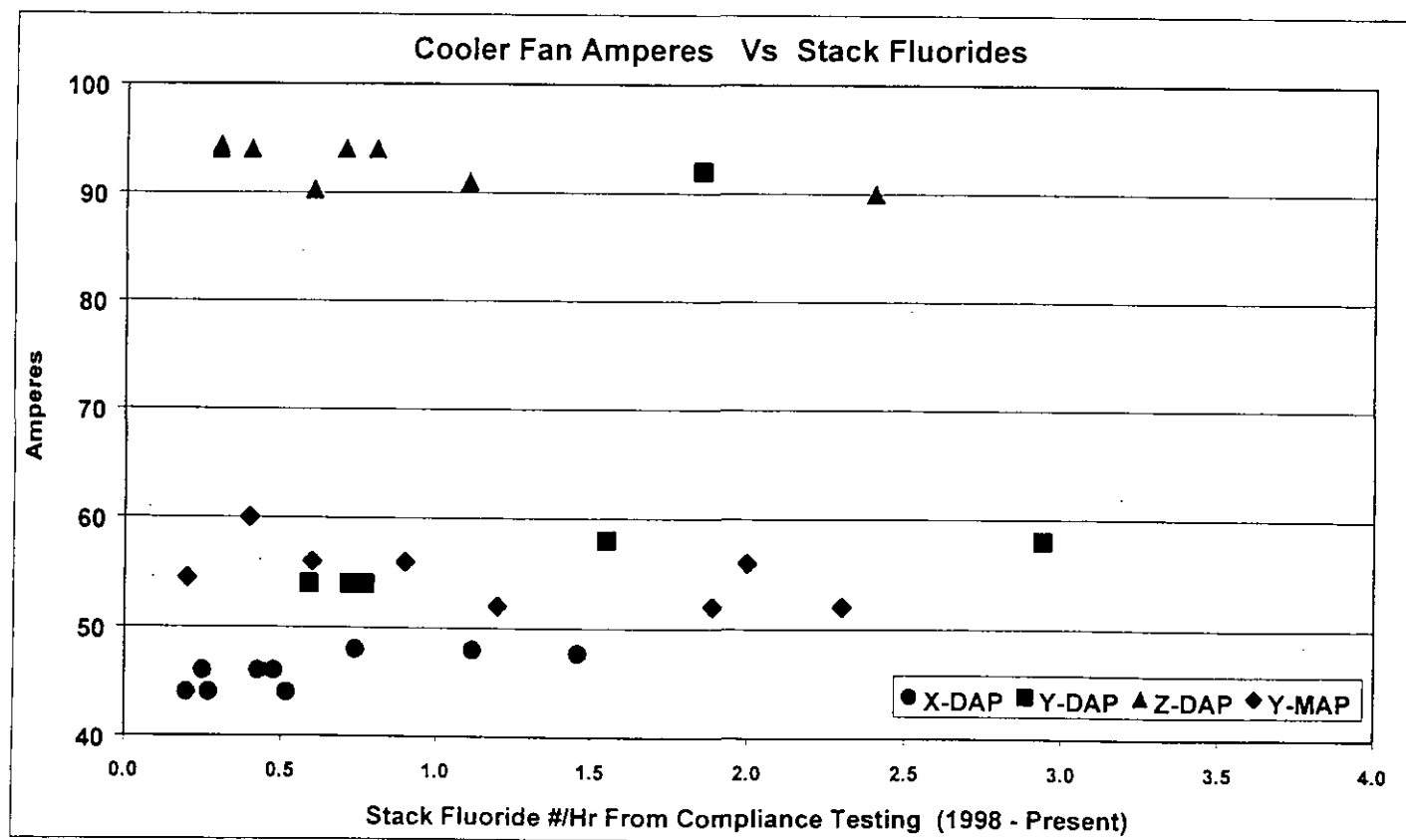
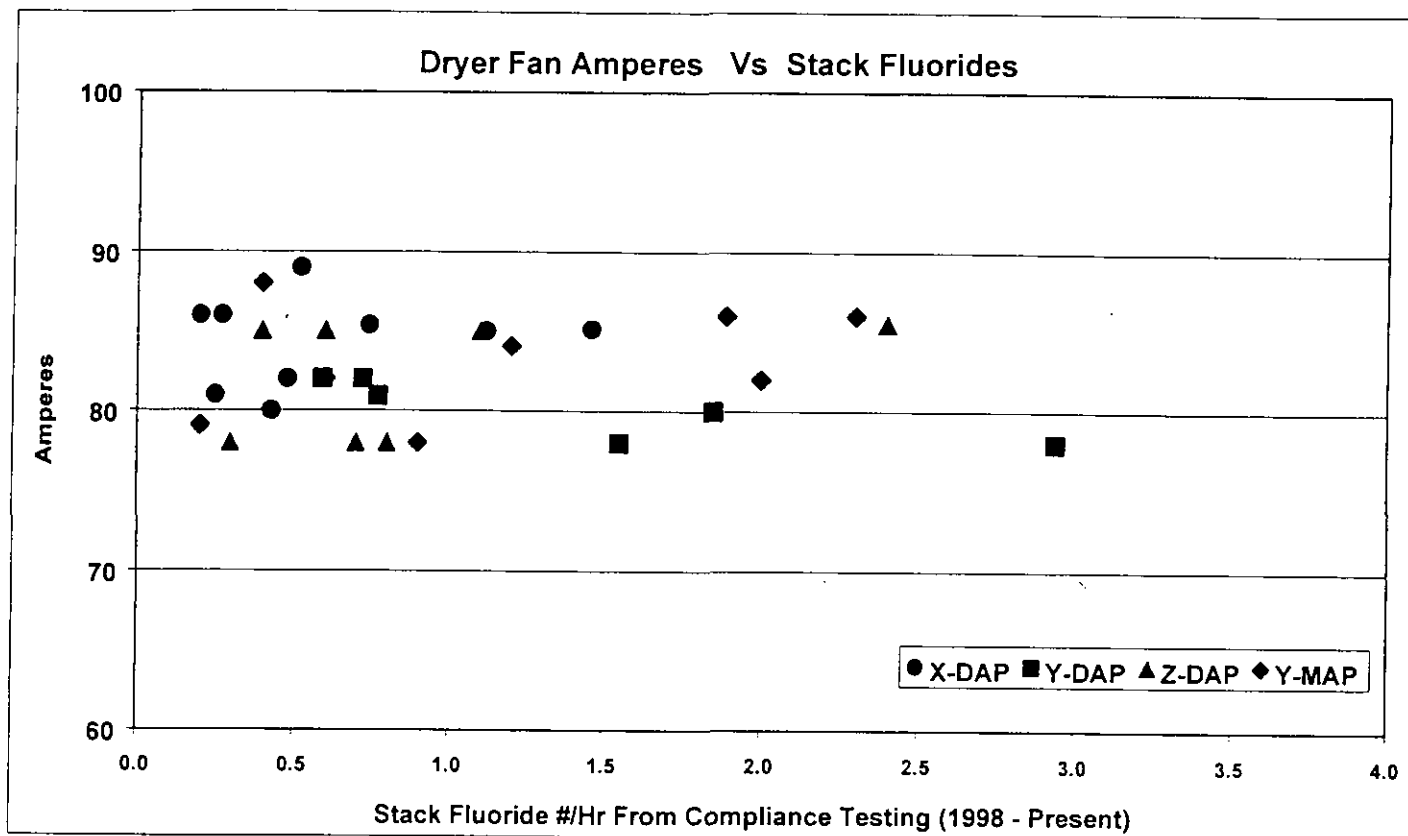


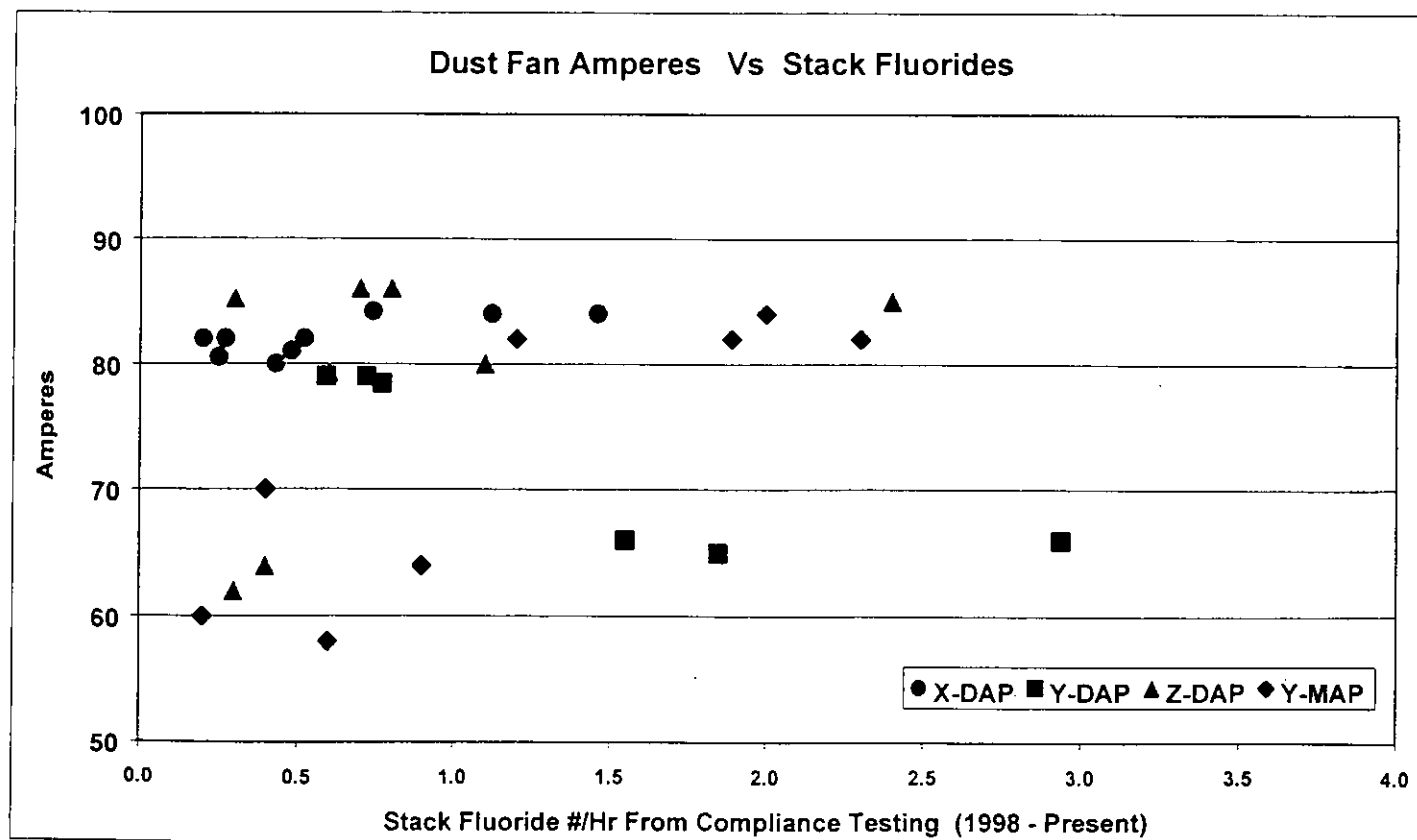
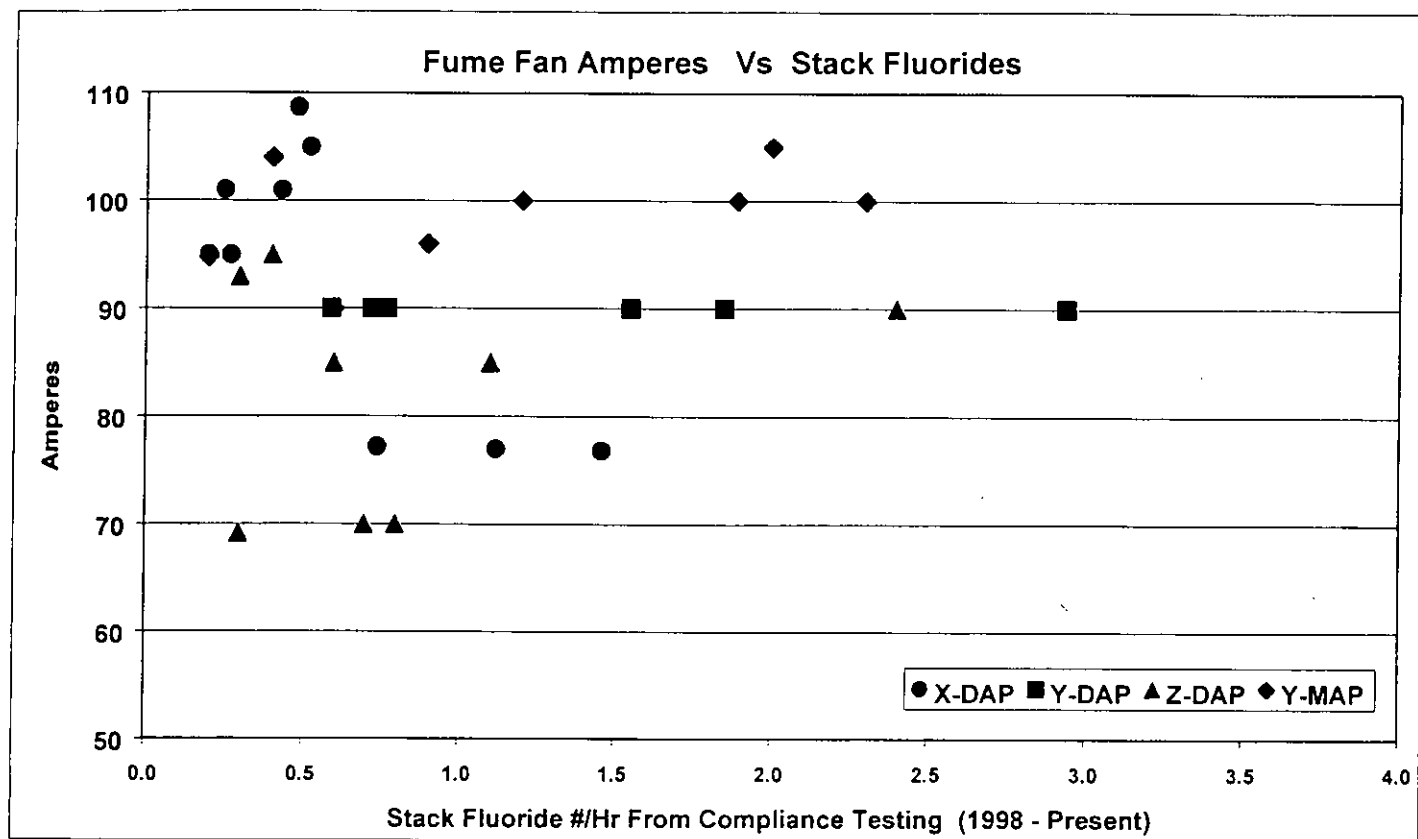




# Appendix B - Page 6



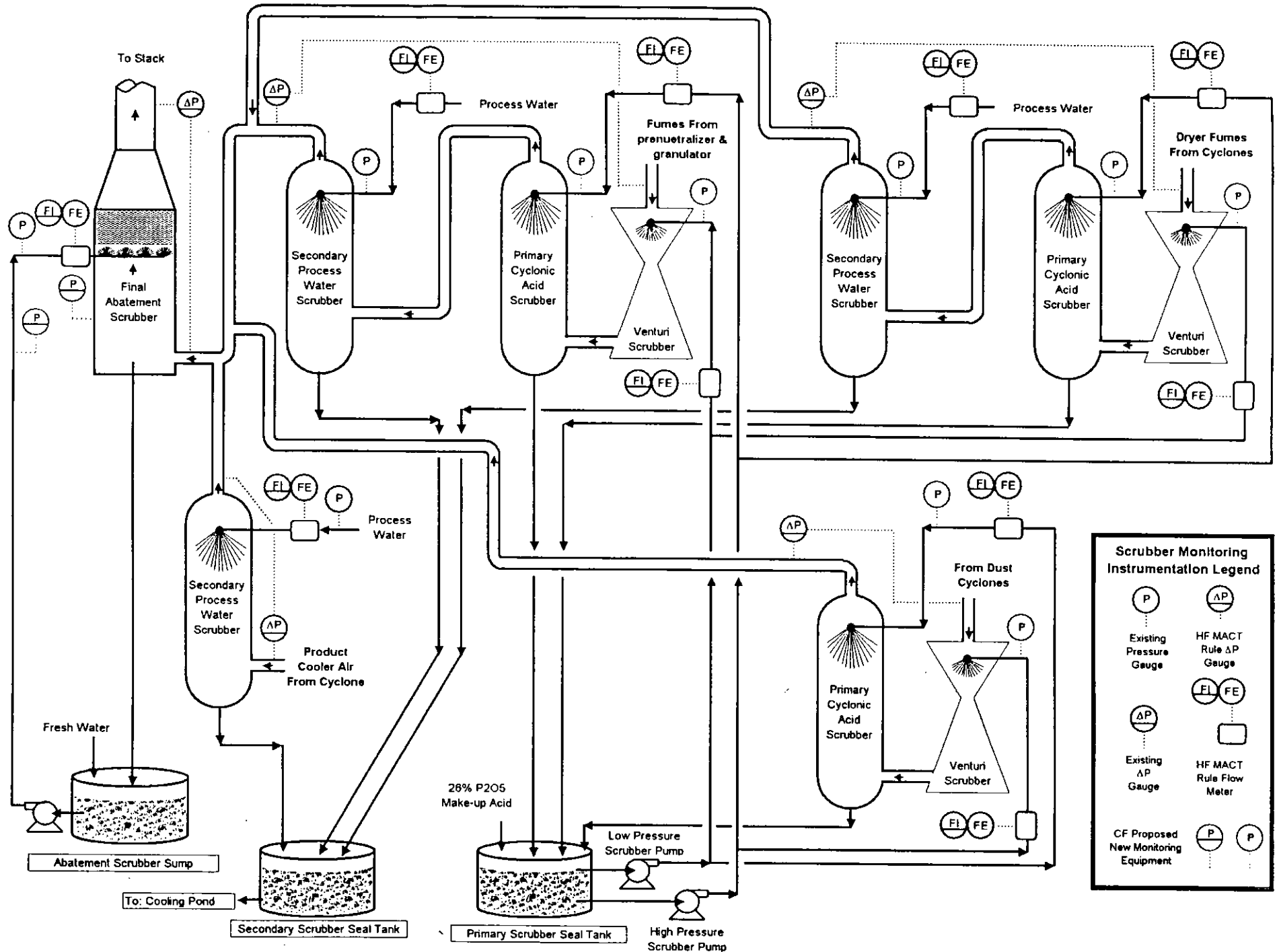




APPENDIX C

COLOR SCHEMATIC DIAGRAM

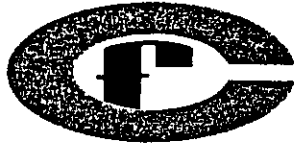
## Appendix C - XYZ Granulation Scrubber Schematic - Single Granulation Train



ATTACHMENT 5

DECEMBER 31, 2003 LETTER

MORRIS TO PICHARD



**CF Industries, Inc.**  
Plant City Phosphate Complex

December 31, 2003

Errin Pichard, P.E., Administrator  
Emissions Monitoring Section  
Bureau of Air Monitoring and Mobile Sources  
Florida Department of Environmental Protection  
2600 Blair Stone Road  
Tallahassee, FL 32399-2400

RE: DEP Letter of December 3, 2003, "Proposed  
Alternative Monitoring Plan."

Dear Administrator Pichard:

The attached information is provided in response to the information requests of your December 3, 2003 letter regarding the Alternative Monitoring Plan proposed by CF Industries, Inc., (CF) on October 31, 2003.

Regarding comments on the description of the nozzle pressure/flow curves: The nozzle pressure/flow curves are based on a clean nozzle, i.e. no scale, buildup, or nozzle restriction. Flow restrictions in the nozzle due to scale buildup will cause higher pressure and lower flow. The proposed nozzle pressure indicator ranges of +/- 20% will allow the operator to react to the restriction before the system is out of compliance and take corrective action.

Regarding CF's request to monitor only the upstream pressure of the abatement scrubber: CF currently has no upstream pressure monitoring or differential pressure monitoring instrumentation on the abatement scrubbers to provide supporting data. CF reserves the right to modify the Alternative Monitoring Plan once actual continuous data becomes available. However, the upstream and downstream pressures are expected to be very consistent. The abatement scrubber discharges directly into the stack with minimal connecting ductwork. The accuracy of the pressure gauge is expected to be +/- 0.2% of span.

Regarding the revised Table I: Table I has been revised to include the "A" Granulation Plant in the proposed Alternative Monitoring Plan.

Regarding questions related to Total Dynamic Head (TDH): CF is withdrawing its request to monitor TDH. TDH as a monitoring parameter is being deleted in favor of delivery pressure. Total Dynamic head is measured at the discharge of the abatement tower scrubber water-circulating pump, as compared to delivery pressure, which is measured at the nozzle header. The selection of delivery pressure avoids potential effects associated with isolation valves.

Regarding the issue of continuous monitoring of liquid delivery pressure: As shown in Table I, CF is proposing "2-hour interval" monitoring for the Dryer, Fume, Cooler, and Dust System acid scrubber components. Continuous monitoring is proposed for the fresh water abatement scrubber liquid delivery pressure and pH, and gas upstream pressure. CF believes this "Alternative Monitoring Plan" is consistent with the intent stated in 40 CFR 63.8(f)(2), which allows the approval of "any monitoring methods or procedures". Furthermore, CF believes it is appropriate that the proposed Alternative Monitoring Plan be approved because the very low measured HF emissions from the subject plants implies that the change from the proposed 2-hour monitoring to continuous monitoring will result in a negligible reduction in emissions. The deviation from "continuous" is justified, and within the context of "alternative" monitoring.

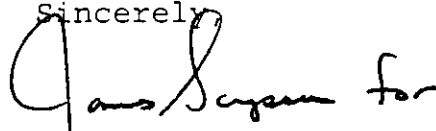
Regarding CF's position on the appropriateness of an economic test: CF believes that an economic test is appropriate whether for new control equipment or monitoring instrumentation. There logically should be no distinction. CF's position is founded in the fact that potential HF emissions as reported in the October 13, 2002 letter to Jerry Kissel were 1.70 tons HF per year. Actual HF emissions are significantly lower. These facts coupled with the already extensive current monitoring of plant scrubber systems leads one to conclude that additional monitoring will result in benefits that are immeasurably small. In addition, CF provides an extra measure of protection through the already existing fresh water fluoride abatement scrubbers. These scrubbers are not in common use in the industry and represent a significant investment in capital and operating costs. However, in order to comply with the intent of the HF MACT standard, CF has proposed the enhanced monitoring contained in the proposed Alternative Monitoring Plan. This Plan improves on current monitoring practices and procedures by adding



continuous monitoring, where appropriate, and adding additional 2-hour interval scrubber liquid monitoring for the granulation plants. CF contends that the proposed Plan will improve monitoring of plant scrubber systems without being an unjustified economic burden.

After you have reviewed these responses, you are welcome to call Tom Edwards or Bob May at 813-782-1591 for further discussion or clarification.

Sincerely,

A handwritten signature in dark ink, appearing to read "Herschel E. Morris for". The signature is fluid and cursive, with a large initial "H" and a stylized "E".

Herschel E. Morris  
Vice President,  
Phosphate Operations and  
General Manager

cc: Jerry Kissel, Southwest District

PROPOSED ALTERNATIVE MONITORING PLAN ELEMENTS

TABLE I

SCRUBBER	LIQUID MONITORING	GAS MONITORING
A-Phosphoric Acid Packed Bed Cross-flow Scrubber	Liquid Flow, continuous	Pressure Drop, continuous.
B-Phosphoric Acid Packed Bed Cross-flow scrubber	Liquid Flow, continuous	Pressure Drop, continuous.
<b>"A" Granulation Plant:</b>		
Dryer Acid Cyclonic Scrubber	Delivery Pressure, 2-hr. Interval	Segment* Pressure Drop, continuous
Dryer Acid Venturi Scrubber	Delivery Pressure, 2-hr. Interval	Segment* Pressure Drop, continuous
Reactor Acid Cyclonic Scrubber	Delivery Pressure, 2-hr. Interval	Segment* Pressure Drop, continuous
Reactor Acid Venturi Scrubber	Delivery Pressure, 2-hr. Interval	Segment* Pressure Drop, continuous
Downcomer Freshwater Fluoride Scrubber	Delivery Pressure, 2-hr. Interval	None
Freshwater Fluoride Abatement Scrubber	Delivery Pressure & pH, continuous	Gas pressure upstream of packing, continuous
<b>X,Y,Z Granulation Plants:</b>		
Fume Venturi Scrubbers (3)	Delivery Pressure, 2-hr. interval.	Segment* Pressure Drop, continuous
Fume Acid Cyclonic Scrubbers (3)	Delivery Pressure, 2-hr. interval.	Segment* Pressure Drop, continuous
Fume Pondwater Cyclonic Scrubbers (3)	Delivery Pressure, 2-hr. interval.	Segment* Pressure Drop, continuous
Dryer Venturi Scrubbers (3)	Delivery Pressure, 2-hr. interval.	Segment* Pressure Drop, continuous
Dryer Acid Cyclonic Scrubbers (3)	Delivery Pressure, 2-hr. interval.	Segment* Pressure Drop, continuous
Dryer Pondwater Cyclonic Scrubbers (3)	Delivery Pressure, 2-hr. interval.	Segment* Pressure Drop, continuous
Cooler Cyclonic Scrubbers (3)	Delivery Pressure, 2-hr. interval.	Segment* Pressure Drop, continuous
Dust Venturi Scrubbers (3)	Delivery Pressure, 2-hr. interval.	Segment* Pressure Drop, continuous
Dust Cyclonic Scrubbers (3)	Delivery Pressure, 2-hr. interval.	Segment* Pressure Drop, continuous
Freshwater Fluoride Abatement Scrubbers (3)	Delivery Pressure, continuous. pH, continuous.	Gas pressure upstream of packing, continuous.

- A segment constitutes a train of scrubbers in series or a single scrubber, excluding the fresh water fluoride abatement scrubber.

ATTACHMENT 6

FEBRUARY 6, 2004 LETTER

EDWARDS TO PICHARD

P.O. Drawer L.  
Plant City, Florida 33564-9007  
Telephone: 813/782-1591  
Fax: 813/715-0851



# CF Industries, Inc.

Phosphate Operations

February 6, 2004

Mr. Errin Pichard, P.E., Administrator  
Emissions Monitoring Section  
Bureau of Air Monitoring and Mobile Sources  
Florida Department of Environmental Protection  
2600 Blair Stone Road  
Tallahassee, FL 32399-2400

RE: Proposed Alternative Monitoring Plan;  
Pichard E-mail Letter of January 13, 2004

Dear Mr. Pichard:

The enclosed information is provided in response to the information requests in your January 13 E-mail letter. The requests are repeated in the same order as in the E-mail, followed by the information requested.

CF has addressed the matters of economic justification and the request for acquiescence to major source status designation in a January 29, 2004, letter. It is our hope that you will be able to continue to process the alternative monitoring proposal while allowing the source status to be determined as described in the draft settlement stipulation originally proposed by the Department and revised by CF Industries (OGC Case No. 02-0587) on January 5, 2004.

We look forward to meeting with you as we have discussed before, once you have reviewed the enclosed materials.

Sincerely,

Thomas A. Edwards  
Superintendent, Environmental Affairs

cc: Joseph Kahn, DARM  
Russell Wider, DARM  
Cindy Phillips, DARM  
Scott Shaplak, DARM

Jason Waters, DEP, SW District  
J.S. Alves, HGS  
J.G. Sampson

1. Pump curves, with typical operating points, for the scrubbers.

A common pond water supply header supplies the secondary pond water. There are six vertical Hazleton pumps delivering 13,000 GPM each (78,000GPM total) into the pond water supply header. The supply header provides pond water for a multitude of uses plant wide. See Figure 1 for a pump curve.

The acid cyclonic scrubbers are supplied by Wilfley A7 8X6-15 pumps with 150HP("X" train) or 250HP("Y" & "Z" Train) 1750 RPM direct drive motors. Each plant uses a single pump to supply the acid cyclonic scrubbers for the fume, dryer, and dust systems. See Figure 2 for the pump curve.

The venturi scrubbers are supplied by Durco 3K8X6-16 pumps with 75HP 1180-RPM direct drive motors. Each plant uses a single pump to supply venturi scrubbers for the fume, dryer, and dust systems. See Figure 3 for the pump curve.

Each plant has a single abatement scrubber pump that circulates water through a shell and tube ammonia vaporizer heat exchanger before being sprayed in the abatement scrubber. The pumps are Hazleton 10: BN Type VS with 100HP 1175 rpm direct drive motors. See Figure 4 for the pump curve.

2. A more detailed description of the abatement scrubber sumps, i.e., the rate of freshwater make-up, typical pH levels, F or HF concentrations, and a comparison to the pond water pH and F/HF concentrations.

The abatement sumps in X, Y, and Z granulation plants typically only get freshwater make-up during start-up. Abatement water is continuously recycled through a shell and tube heat exchanger used to vaporize ammonia prior to being sprayed in the abatement scrubber. The ammonia vaporizer cools the abatement scrubber water. When the cooled water is sprayed in the abatement scrubber it causes water vapor in the stack gas to cool and condense. The constant condensing of stack gas water vapor eliminates the need for fresh water make-up and results in a continuous over-flow (blow-down) from the sump. In A-DAP the abatement water used in the dryer and cooler downcomers is single use and is not returned to the abatement sump. Because of this, there is an estimated 50-100 GPM of continuous fresh water make-up to the A-DAP abatement scrubber sump.

The abatement sumps have a typical operating pH range of 5.0 – 8.0. The upper end of the pH range is irrelevant to fluoride emissions and scrubbing efficiency. Only low pH causes the emission of fluorides from the liquid. See Figure 5 for a scatter diagram showing a 3-year history of the average daily low and high abatement sump pH for the X, Y, and Z Granulation Plants.

The abatement water is not routinely analyzed. Two samples from "X" & "Y" were recently collected and analyzed. The fluoride concentration was between 60-70 ppm F<sup>-</sup>. At the pH values operated in the scrubber, none of the fluoride would exist in the form of HF.

In the last part of this question you requested "**a comparison to the pond water pH and F/HF concentrations**". This question appears to be out of context with the discussion of this specific question, abatement scrubbers. Pond water is not used in the abatement scrubbers. However, to address your question the pond water pH is typically in a range 1.1 to 1.8 with total fluoride concentration of 5,000 to 10,000 ppm. The abatement scrubber water ranges from 5.0 to 10.0 pH with total fluoride concentration in the 50 to 100 ppm range.

3. More detailed information regarding the "A" granulation train. In particular -
- Revised Table I included with CF's latest letter indicates a single "downcomer freshwater fluoride scrubber", but the schematic depicts separate scrubbers for the dryer, cooler and reactor trains. Which is correct? Are these similar to the "secondary process water scrubbers" shown on the XYZ granulation schematic?
  - It is unclear from the "A" granulation train schematic what happens to the water from the freshwater abatement scrubber. Does it go to the cooling pond? To the downcomer scrubber or scrubbers? Both?
  - The "A" granulation schematic does not indicate a dedicated acid scrubber for the dust train. Is this correct or a drawing error?

The dryer, cooler and fume systems all have individual downcomer scrubbers. Table I of the previous submittal indicated a single pressure reading for all three downcomers because they are located adjacent to each other and share a common supply header. For this reason only one supply pressure is recorded. See Figure 6 for details. The downcomers in A-DAP use abatement scrubber water for scrubbing medium whereas the secondary cyclonic pond water scrubbers in XYZ use pond water for a scrubbing medium. Also the secondary pond water scrubbers in "XYZ" are cyclonic whereas the downcomers do not utilize cyclonic mixing in their design.

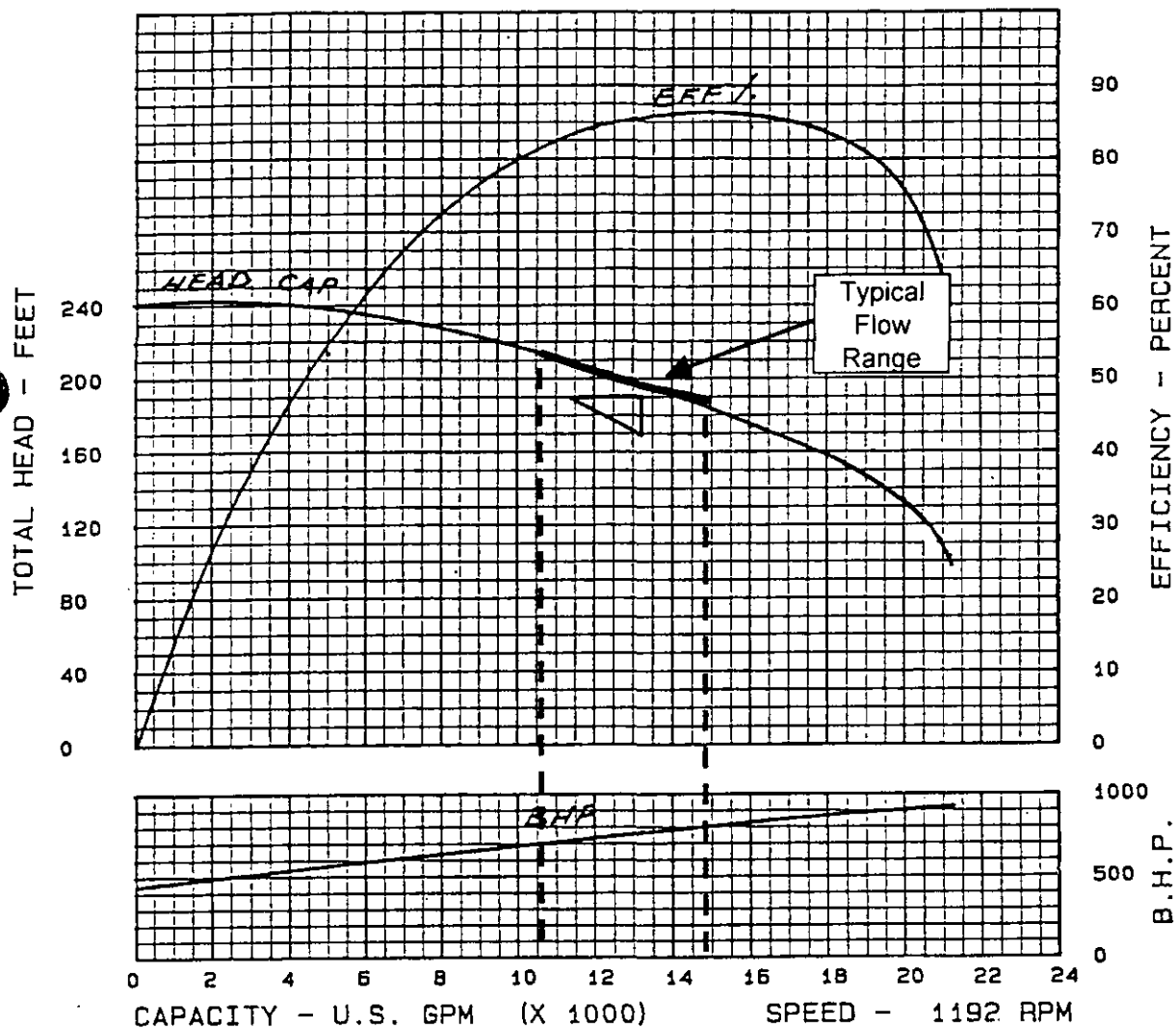
The freshwater abatement scrubber water system is a closed circuit system except for the dryer and cooler downcomers, which use once through abatement water that discharges to the pond. Figure 7 has been revised to better illustrate where the abatement water goes.

The "A" granulation schematic is correct. The dust system pickups are pulled through the dryer scrubbers.

# Figure 1

## Process Water Supply Pumps - 1 of 6 in Parallel

CASD12131B P12131 V12131A- 24.25B-IMP12073 P12073 V12073- 4- 22.75T  
M= 94.5 %



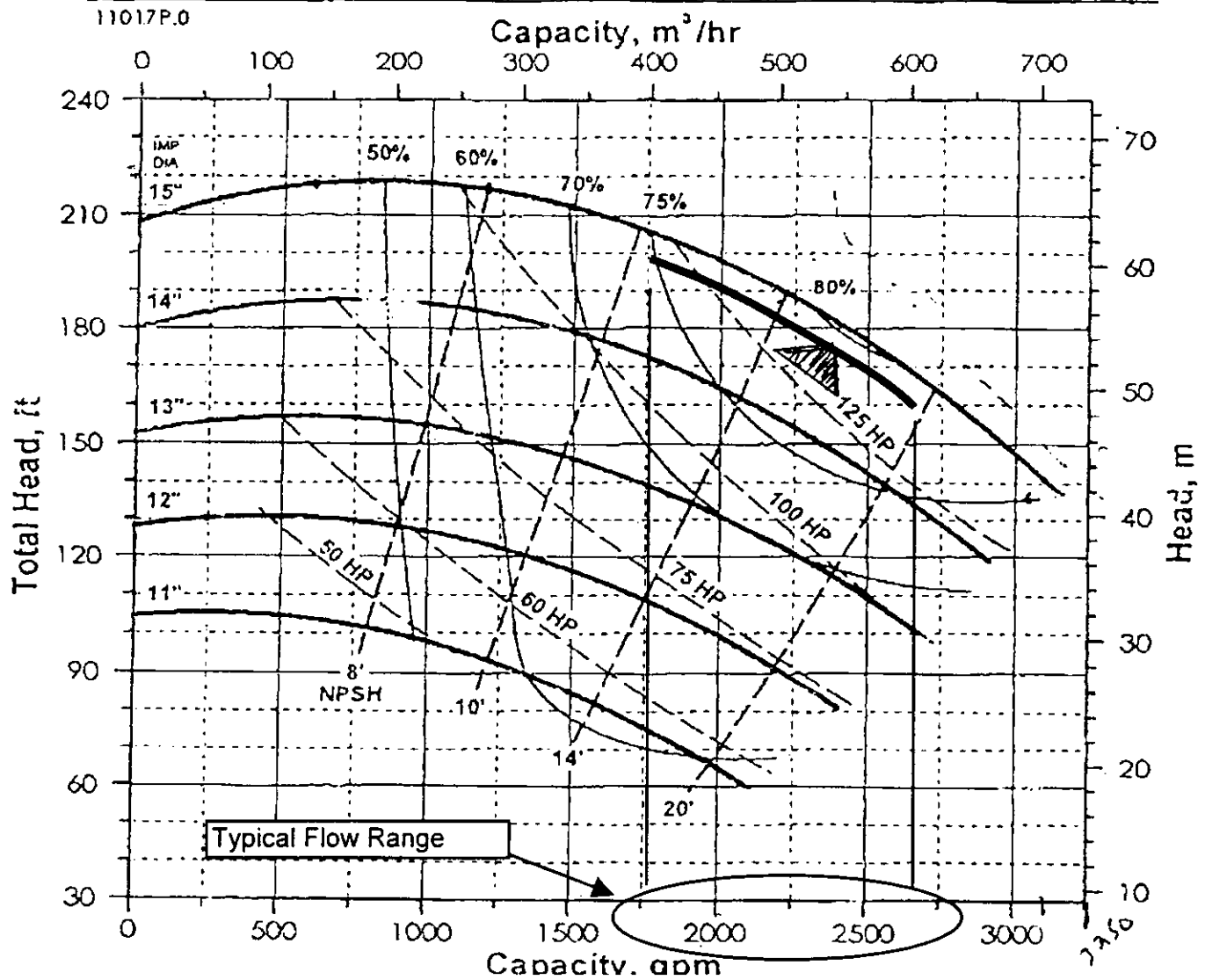
# Figure 2

## Acid Cyclonic Scrubber Liquor Pumps

**WILFLEY**

MODEL A7

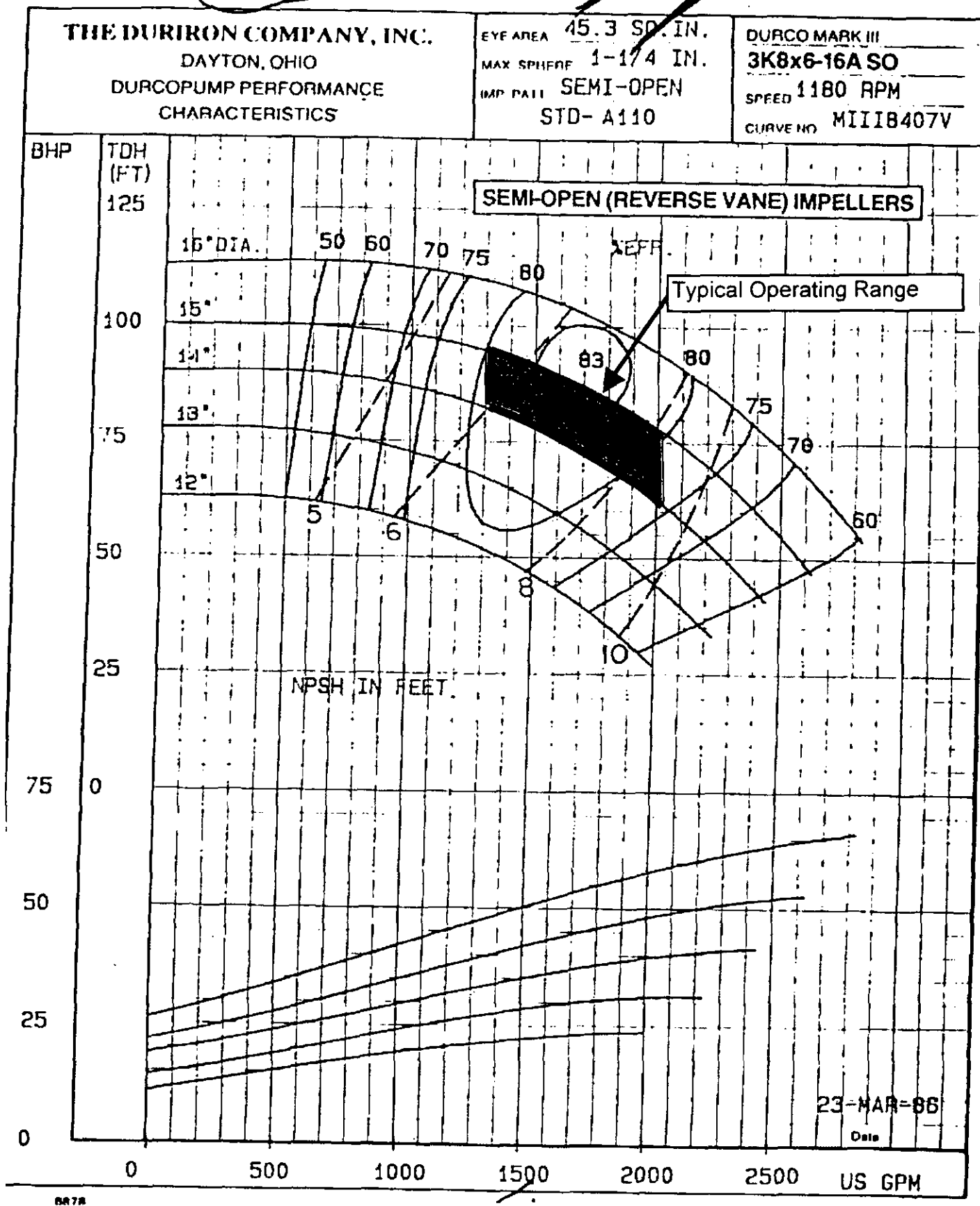
8 x 6 - 15 ANSI A110-15  
1750 RPM  
S.G.=1.0





# Figure 3

## Acid Venturi Scrubber Liquor Pumps



# Figure 4 - Abatement Circulating Pump HAZLETON PUMPS, INC.

CHARACTERISTIC CURVE  
10" BN TYPE VS PUMP  
HAZLETON PUMPS, INC.  
HAZLETON, PA.

1,174 RPM AT 16.005" DESIGN IMPELLER

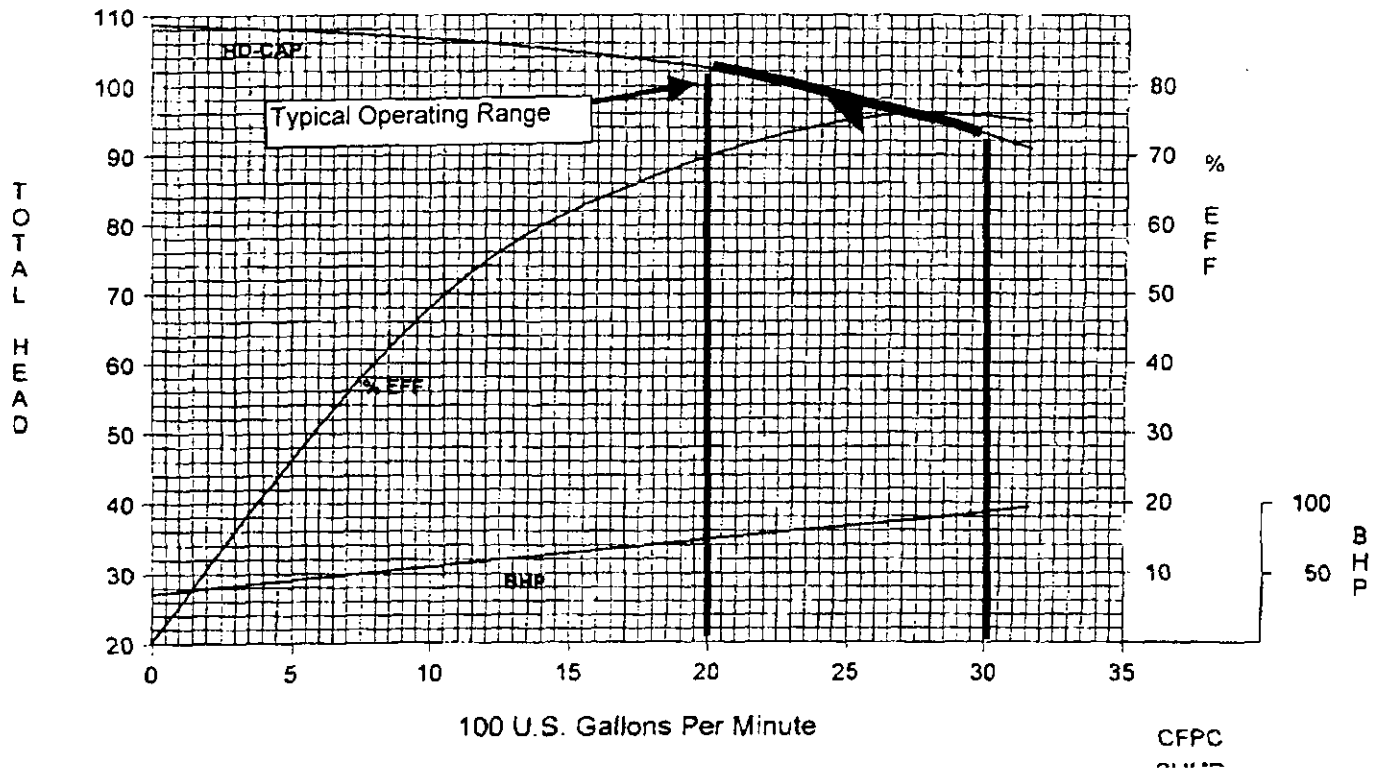


Figure 5

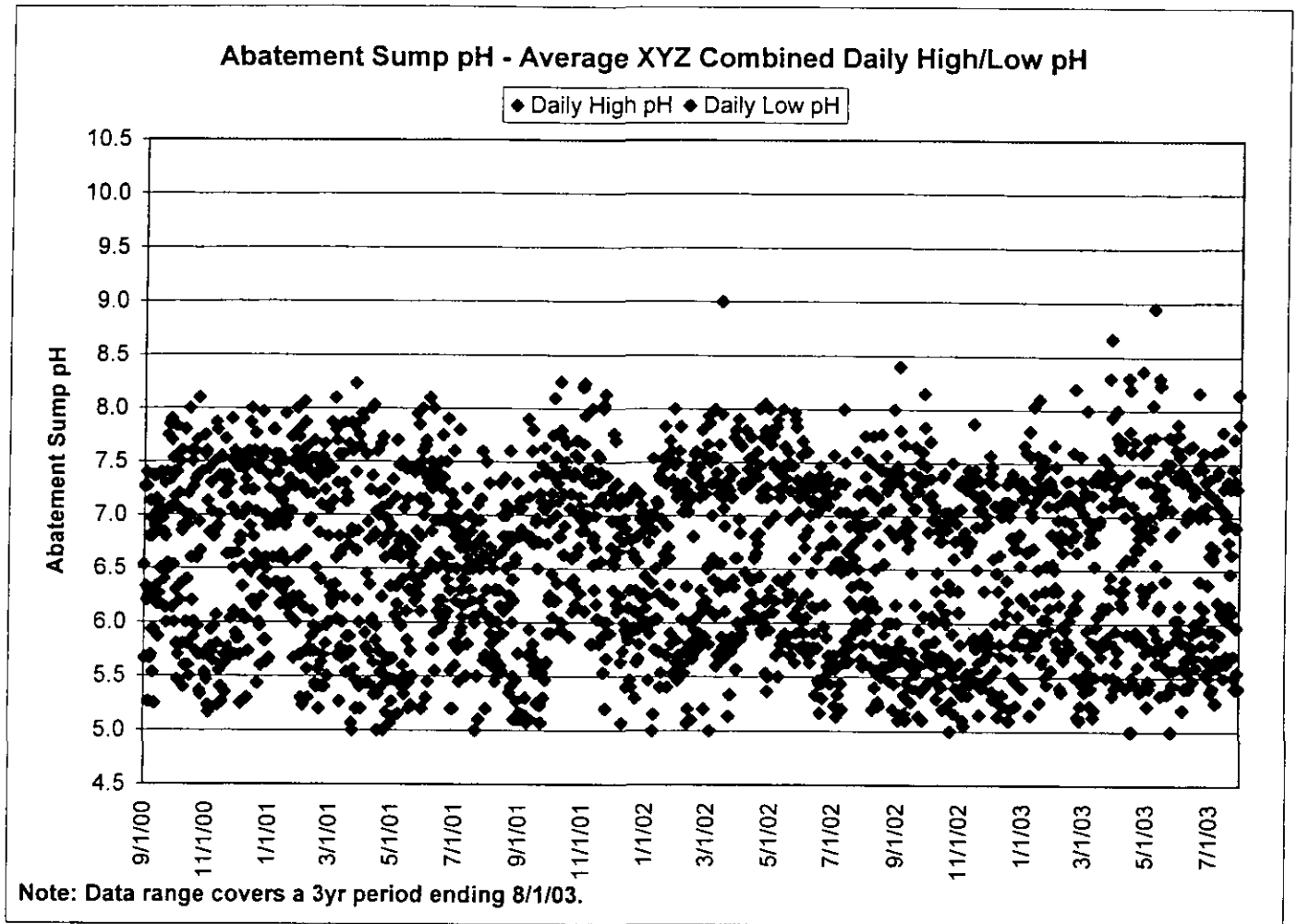
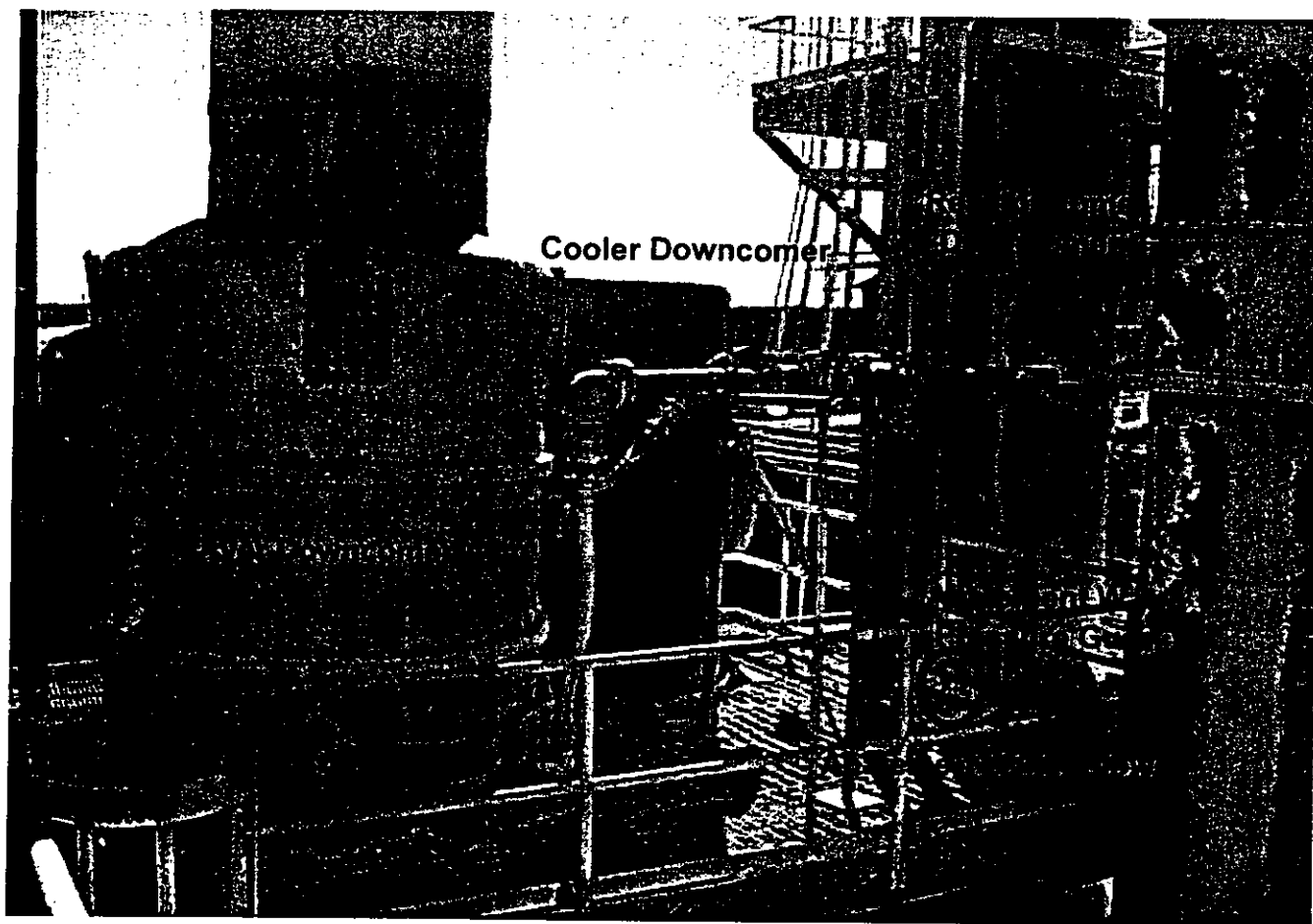
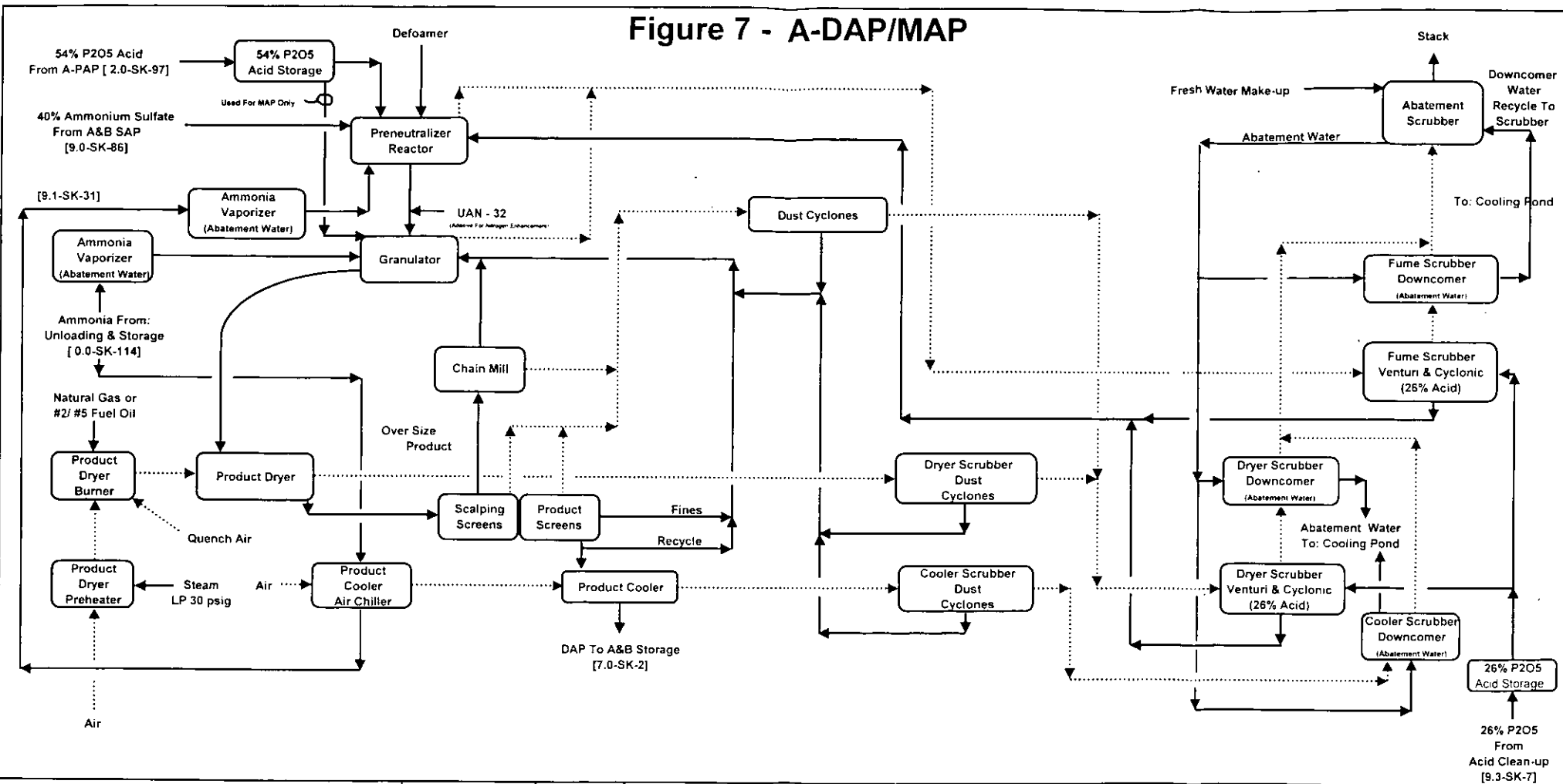


Figure 6 - A-DAP Downcomers



### Figure 7 - A-DAP/MAP



<b>Legend</b>		<b>Revision By</b>	<b>Date</b>		<b>CF Industries, Inc.</b> Plant City Phosphate Complex P.O. Drawer L Plant City, Florida 33564 Phone: (813) 782-1591 Fax: (813) 788-9126	<b>Title</b>	<b>DWR. NO.</b>
..... Fume or Air Duct	_____ Other	Randy Charlot	01/16/04			A-DAP/MAP Process Block Flow Diagram	5.0-SK-101
_____ 25% / 54% P <sub>2</sub> O <sub>5</sub> Acid							
_____ Ammonia							
_____ Granular DAP/MAP							
_____ Abatement Water							

ATTACHMENT 7

CF ALTERNATIVE MONITORING PROPOSAL SUMMARY

MAY 3, 2004

SCRUBBER	LIQUID MONITORING	GAS MONITORING
A-Phosphoric Acid Packed Bed Cross-Flow Scrubber	Liquid Flow, continuous	Pressure Drop, continuous
B- Phosphoric Acid Packed Bed Cross-Flow Scrubber	Liquid Flow, continuous	Pressure Drop, continuous
"A" Granulation Plant:		
Dryer Acid Cyclonic Scrubber		Segment* Pressure Drop, continuous
Dryer Acid Venturi Scrubber		Segment* Pressure Drop, continuous
Reactor Acid Cyclonic Scrubber		Segment* Pressure Drop, continuous
Reactor Acid Venturi Scrubber		Segment* Pressure Drop, continuous
Downcomer Freshwater Fluoride Scrubber	Liquid Flow, continuous**	Segment* Pressure Drop, continuous
Freshwater Fluoride Abatement Scrubber	Liquid Flow** & pH, continuous	***
X, Y, Z Granulation Plants:		
Fume Acid Venturi Scrubbers (3)		Segment* Pressure Drop, continuous
Fume Acid Cyclonic Scrubbers (3)		Segment* Pressure Drop, continuous
Fume Pondwater Cyclonic Scrubbers (3)	Delivery Pressure, 2-hour interval	Segment* Pressure Drop, continuous
Dryer Acid Venturi Scrubbers (3)		Segment* Pressure Drop, continuous
Dryer Acid Cyclonic Scrubbers (3)		Segment* Pressure Drop, continuous
Dryer Pondwater Cyclonic Scrubbers (3)	Delivery Pressure, 2-hour interval	Segment* Pressure Drop, continuous
Cooler Pond Water Cyclonic Scrubbers (3)	Delivery Pressure, 2-hour interval	Segment* Pressure Drop, continuous
Dust Acid Venturi Scrubbers (3)		Segment* Pressure Drop, continuous
Dust Acid Cyclonic Scrubbers (3)		Segment* Pressure Drop, continuous
Freshwater Fluoride Abatement Scrubbers (3)	Liquid Flow, continuous, & pH, continuous	***

\* A segment constitutes a train of scrubbers in series or a single scrubber, excluding the freshwater fluoride abatement scrubber.

\*\* One flow meter in the common header pipe that delivers water to the three downcomer scrubbers and the abatement scrubber.

\*\*\* Gas flow indicated by Segment Pressure Drop.