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Plant City, Florida 33564-9007
Telephone: 813/782-1591

CF Industries, Inc.
Plant City Phosphate Complex

December 7, 1990

RECEIVED
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DER - BAQM

Mr. C. H. Fancy, P.E., Chief
Bureau of Air Regulation
Florida Department of
Environmental Regulation
2600 Blair Stone Road
Tallahassee, Florida 32399-2400

RE: Sulfur Storage Permit Modification AC29-187327
Sulfuric Acid Plants "C" and "D" Permit
Modification AC29-186931

Dear Mr. Fancy:

In reference to your letter dated October 25, 1990 stating incompleteness of the application for modification of the construction permit, for molten sulfur storage and handling, the following is offered:

1. Please submit the calculation sheet showing the derivation/assumptions of the revised emission estimates for PM/PM_{10}, SO_2, TRS/H_2S and VOC emissions.

   Derivation/assumptions for emissions estimates were supplied in the original permit application dated June 28, 1989. The revised emission calculations are based on the emissions stated in the construction permit number AC29-167204 at specific condition 8. The increase in through-put will result in a 10% increase in the number of trucks being unloaded. Therefore, the expected emissions from the increased trucks should result in a 10% increase in total emissions. The revised table for specific condition 8 was derived by multiplying the expected emissions by a factor of 1.10.

2. Why does this application state that the sulfuric acid production for the facility is increasing from 6900 TPD to 7600 TPD, when the application for permit modifications of sulfuric acid plants "C" and "D" requests a facility increase from 6900 TPD to 7300 TPD?

   Applications for permit modifications for "C" and "D" sulfuric acid plants were submitted to increase the production rate for each plant from 2400 tons/day to 2600 tons/day.

   It is anticipated that applications to increase the production rates for "A" and "B" sulfuric acid plants from 1050 tons/day to 1200 tons/day will be submitted within the next year. The modification to the sulfur handling permit was calculated to allow this increase before the fact, to avoid having to modify the permit again in less than a year's time.

Answers to questions 1 through 6 concerning the "C" and "D" Sulfuric Acid Plant permit modifications are attached, as provided by Dr. John B. Koogler.

A reply to your November 13 letter on SO_2 modeling for these plants will be provided by mid-December.

Should you have additional questions, please call Jim Martin at (813) 782-1591.

Sincerely,

J. E. Parsons
General Manager

JEP/CJM/tjj

Attachment

cc: P.R. Roberts/T.A. Edwards
C.J. Martin/Env. File
C. Fred Deuel
Jerry Campbell (HCEPC)
Harry Kerns (DER SW District)
Phillips

CJM

DETERMINATION OF NO_x CONCENTRATIONS IN SULFURIC ACID PLANT STACK EMISSIONS

Alan A. Pratt
CF Industries, Inc.

NO_x concentrations in "C" and "D" Sulfuric Acid Production plant stack emissions were determined through manual sampling techniques and analyzed using a chemiluminescence detector (NO_x Box) at the University of South Florida, Tampa.

INTRODUCTION

The chemiluminescence detector-based method for trace NO_x in air samples is used and approved by the Environmental Protection Agency.(1)

Concentrations of nitrogen oxides in ambient air are determined by photometrically measuring the light intensity resulting from the chemiluminescent reaction of nitric oxide (NO) with ozone (O_3). NO_2 and NO_3 are also measured by conversion to NO.

Normally, NO_x analyzers are used for continuous operation. Since CF Industries, Inc. does not currently own a chemiluminescence analyzer, consultation of remote sampling techniques was done with Dr. Robert S. Braman of the University of South Florida (USF) and analyses were acquired using their NO_x analyzer.

EXPERIMENTAL

Apparatus. A Thermal Electron Corporation Model 14 B/E Chemiluminescent NO_x analyzer donated to USF by the DER (#17149) was used for the analysis. Inboard flow rate was controlled by a mass flow meter set to approximately 250 mL./min. The output signal was recorded by means of a Linear Instruments, Inc. Model 252A integrating recorder. The apparatus arrangement is shown in figure 1.

Procedure - Sampling. Sampling tubes were constructed of 1/4" glass tubing to which a coating of cobalt oxide (CoO) had been deposited. CoO absorbs NO, NO_2, and NO_3 gas and releases as NO upon heating. Sampling tubes were "blanked" before use by heating with a heating coil while carrier gas was passed through and into the NO_x analyzer. After cooling and capping, the tubes were taken to CFII for sample collection.

Sampling was achieved by purging inlet lines to the continuous SO_2 monitors with a vacuum pump and pulling a

50mL. sample from a "T" through the sample tube with a Hamilton Gastight air syringe. Sampling apparatus is shown in figure 2.

Several ambient air samples were taken for background data in 200 mL. volumes. All sample tubes were capped immediately after sampling for transport to USF for analysis.

Procedure - Analysis. Sample tubes were connected in-line to the NO_x analyzer and heated with a heating coil wrapped around the tube with 40V a/c current. Response times averaged 2 minutes. A typical response is shown in figure 3.

Procedure - Response Calibration. A vanadium oxide packed tube was blanked. Triplicate injections into the cool packed tube of standard KNO_3 solution was done at each of four different volumes. Heating the tube at 15V produced response. A calibration regression was established for sample comparison (figure 4).

RESULTS

Table I lists the results of each analysis. Results were obtained in units of nanograms N per 50 mL. sample and reported as ppm (uL/L) NO. A sample calculation is as follows:

$$\frac{\text{ng. N}}{\text{50 mL.}} \times \frac{\text{1,000 mL.}}{\text{1 L}} \times \frac{\text{1 ug}}{10^3\text{ ng}} \times \frac{\text{30 ug NO/mole}}{\text{14 ug N/mole}} \times \frac{\text{22.4 uL}}{\text{30 ug.}} \times \frac{298}{273} = \text{ul/L}$$

LITERATURE CITED

(1) Federal Register. Vol. 54, No. 211, 1989, 40 CFR Part 60. Method 7E.

Figure 1. Apparatus Arrangement

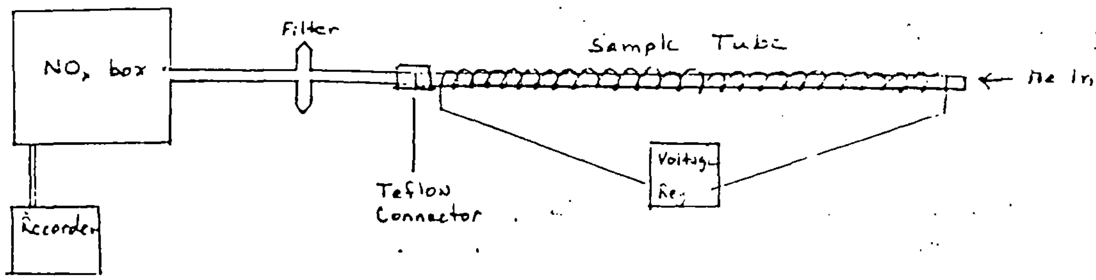

Figure 2. Sampling Apparatus

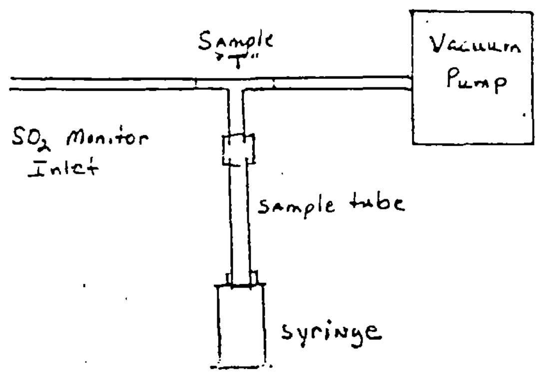

Figure 3. Typical Response of Chemiluminescence Detector

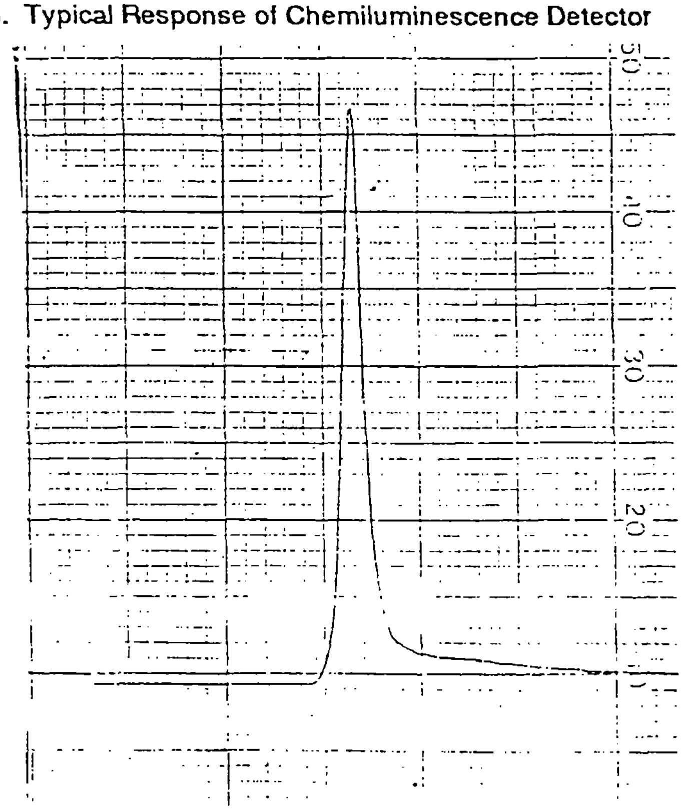

Figure 4. Standard Regression Curve

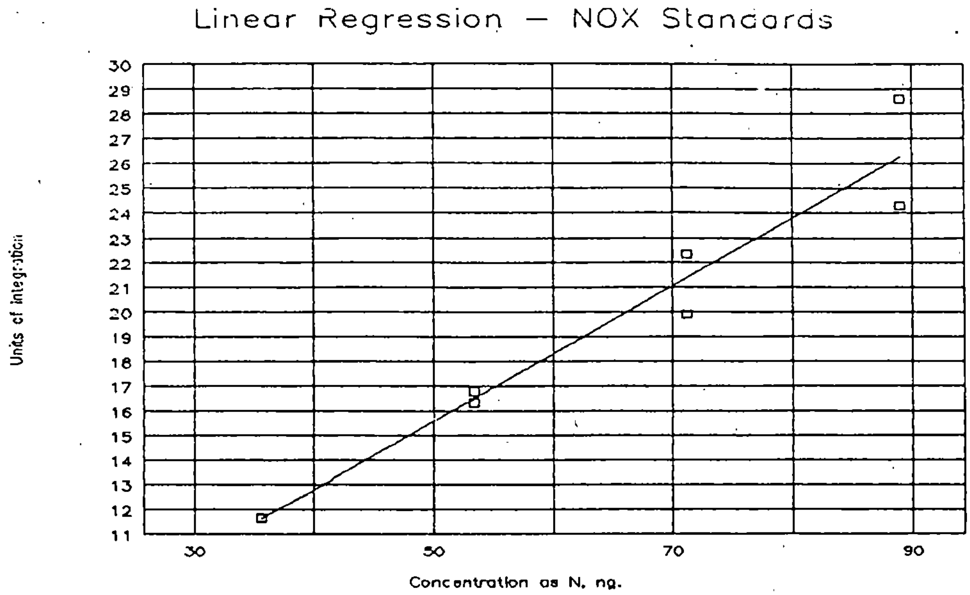

Table I. Concentration of NOX – Results

C SAP

Sample #	Units	N, ng	NO, ppm.
1	39.88	138.50	4.84
2	41.93	145.96	5.10

D SAP

Sample #	Units	N, ng	NO, ppm.
1	43.75	152.58	5.33
2	22.85	76.52	2.67
3	19.09	62.84	2.20

Ambient Air

Sample #	Units	N, ng	NO, ppm.
1	6.29	16.26	0.14

1. Is the 99.7% efficiency (listed on page 5 of the application) of the dual absorption towers based on current test data or is that the proposed efficiency of the towers after they are repacked?

Since the towers have already been repacked (see Question 2, below), this efficiency represents current and proposed operation efficiency. The 99.7 percent efficiency for sulfur dioxide is based on the sulfur recovery necessary to comply with the NSPS emission limit of 4.0 pounds of sulfur dioxide per ton of 100 percent sulfuric acid. The sulfur (M.W. = 32) required to produce 1.0 ton of H_2SO_4 (M.W. = 98) is 653.1 pounds. Sulfur loss in the stack gas is 2.0 pounds per ton (2.0 lbs. sulfur per 4.0 lbs SO_2). The efficiency of sulfur recovery is (653.1-2.0) x 100/(653.1) = 99.7 percent.

2. How are the absorption towers to be repacked? Is the packing material to be a new type?

There is to be no change in the configuration of the absorption towers. The changes that were made pursuant to the 1988 permitting, in concert with a recent maintenance re-packing of the towers, have resulted in greater capacity than anticipated at the time of permitting.

3. The application states that NO_x emissions will be minimized by operating the burners of the sulfuric acid plants within the limits established by the designer. What, specifically, are these limits?

No specific operating parameters are specified by the designer. Operation of the sulfur furnace is based on conditions established by CF and operating practices that are consistent throughout the industry. The sulfur feed rate to the sulfur furnace will be 35.4 tons per hour (corresponding to a production rate of 2,600 tons per day of 100 percent H_2SO_4). The oxygen and SO_2 at the furnace exit will be maintained in the range of 9.2 - 9.4 percent and 11.8 - 11.6 percent, respectively. These operating conditions will result in a furnace temperature of 2000° - 2100°F.

Another factor related to NO_x that also needs updating is the NO_x concentration in the stack gas from the CF sulfuric acid plants. In the original application, a "typical" NO_x concentration of 2.1×10^{-6} lb NO_x per cubic foot (18 ppm NO_x by volume) was used. This concentration was measured at a 2250 ton per day sulfuric acid plant in Polk County by Koogler & Associates personnel in about 1976 (using EPA Method 7) and has been used in several sulfuric acid plant permitting projects since that time. Actual measurements recently made by CF personnel on the subject sulfuric acid plants with a chemiluminescent NO_x analyzer (report attached) showed NO_x concentrations in the stack gas in the range of 5 ppm by volume. Using this site-specific measurement, the predicted NO_x increment is deminimis. The amended application includes these data.

4. Please show the correlation between the gas flow rate of 146,162 dscfm (listed on page 6 of the application) and the gas flow rate of 67,500 dscf/ton of acid (listed on page 7b).

The gas flow of 67,500 dscf/ton of 100 percent acid is a "typical" gas volume for double absorption sulfuric acid plants. The gas flow factor specific to the CF Industries "C" and "D" plants averages 64,500 dscf/ton (based on stack test data). This latter factor should have been used in the calculations referenced on page 7b of the application as should have a NO_x concentration of 5 ppm. Amended sections of the application are attached.

Based on the gas flow rate of 64,500 dscf/ton of acid, the stack gas flow rates on page 6 of the applications have also been changed.

5. The application states that the nitrogen oxide concentration in the tail gas stream of a typical sulfuric acid plant is in the range of 20 parts per million. What is the source of this information?

See response to Department question No. 3.

6. The uncontrolled emissions calculations for acid mist (shown on page 7c) need to be recalculated.

The referenced correction has been made in the attached amended application.

General

The change made by the Department on page 2 of the application is appreciated.

It is presumed from the statement regarding actual emissions that no further action is necessary as the emission increases are significant as calculated.

SECTION III: AIR POLLUTION SOURCES & CONTROL DEVICES (Other than Incinerators)

A. Raw Materials and Chemicals Used in your Process, if applicable:

Description	Contaminants		Utilization Rate - lbs/hr	Relate to Flow Diagram
	Type	% Wt		
Sulfur	Ash	0.005	71,000	1

B. Process Rate, if applicable: (See Section V, Item 1)

1. Total Process Input Rate (lbs/hr): 71,000 as sulfur

2. Product Weight (lbs/hr): 232,975 as 93% H_2SO_4

C. Airborne Contaminants Emitted: (Information in this table must be submitted for each emission point, use additional sheets as necessary)

Name of Contaminant	Emission[1]		Allowed[2] Emission Rate per Rule 17-2	Allowable[3] Emission lbs/hr	Potential[4] Emission		Relate to Flow Diagram
	Maximum lbs/hr	Actual T/yr			lbs/~~yr~~ hr	T/yr	
SO_2	433.3	1898	17-2.600(2)(b)	433.3	433.3	1898	2
NOx	4.2	18.4	17-2.630	4.2(1)	4.2	18.4	2
Acid Mist	16.2	71.2	17-2.600(2)(b)	16.2	270	1183	2
VE	10%	-	17-2.600(2)(b)	10%	-	-	2
(1) Expected emissions; no applicable emission limiting standard.							

[1]See Section V, Item 2.

[2]Reference applicable emission standards and units (e.g. Rule 17-2.600(5)(b)2. Table II, E. (1) - 0.1 pounds per million BTU heat input)

[3]Calculated from operating rate and applicable standard.

[4]Emission, if source operated without control (See Section V, Item 3).

H. Emission Stack Geometry and Flow Characteristics (Provide data for each stack):

Stack Height: 198.5 ft. Stack Diameter: 8.0 ft.

Gas Flow Rate: 140,060 ACFM 116,460 DSCFM Gas Exit Temperature: 175 °F.

Water Vapor Content: 0 % Velocity: 58.3 FPS

SECTION IV: INCINERATOR INFORMATION

NOT APPLICABLE

Type of Waste	Type 0 (Plastics)	Type I (Rubbish)	Type II (Refuse)	Type III (Garbage)	Type IV (Pathological)	Type V (Liq.& Gas By-prod.)	Type VI (Solid By-prod.)
Actual lb/hr Incinerated							
Uncontrolled (lbs/hr)							

Description of Waste ____________________

Total Weight Incinerated (lbs/hr) __________ Design Capacity (lbs/hr) __________

Approximate Number of Hours of Operation per day ______ day/wk ______ wks/yr. __________

Manufacturer ____________________

Date Constructed __________ Model No. __________

	Volume (ft)^3	Heat Release (BTU/hr)	Fuel		Temperature (°F)
			Type	BTU/hr	
Primary Chamber					
Secondary Chamber					

Stack Height: ______ ft. Stack Diamter: __________ Stack Temp. __________

Gas Flow Rate: __________ ACFM __________ DSCFM* Velocity: __________ FPS

*If 50 or more tons per day design capacity, submit the emissions rate in grains per standard cubic foot dry gas corrected to 50% excess air.

Type of pollution control device: [ ] Cyclone [ ] Wet Scrubber [ ] Afterburner

[ ] Other (specify) __________

Proposed: 2600 tons per day 100% acid

SO_2 - 4.0 lb/ton

Mist - 0.15 lb/ton

Operating factor - 1.0

Emission Rates: (Each plant - as permitted and operated)

SO_2: Hourly = 4.0 lb/ton x 2400/24 tons/hr
= 400 lb/hr.

Annual = 400 lb/hr x 8760 hr/yr x 1/2000 lb/ton
= 1752 tpy

MIST: Hourly = 0.15 lb/ton x 2400/24 tons/hr
= 15.0 lb/hr

Annual = 15.0 x 8760/2000
= 65.7 tpy

NOx: Based on 64500 dscf per ton of acid and
0.6×10^{-6} lb NOx per dscf (5 ppm, v/v)

Hourly = 64500 dscf/ton x 2400/24 ton/hr
x (0.6×10^{-6}) lb/ft^3
= 3.9 lb/hr

Annual = 3.9 lb/hr x 8760/2000
= 17.0 tpy

Emission Rates: (Each plant - as proposed)

SO_2: Hourly = 4.0 lb/ton x 2600/24 tons/hr
= 433.3 lb/hr.

Annual = 433.3 lb/hr x 8760 hr/yr x 1/2000 lb/ton
= 1898 tpy

MIST: Hourly = 0.15 lb/ton x 2600/24 tons/hr
= 16.2 lb/hr

Annual = 16.2 x 8760/2000
= 71.2 tpy

NOx: Hourly = 64500 dscf/ton x 2600/24 ton/hr
x (0.6×10^{-6}) lb/ft^3
= 4.2 lb/hr

Annual = 4.2 lb/hr x 8760/2000
= 18.4 tpy

NOTE: No other air pollutants are discharged from the C and D sulfuric acid plants.

3. Uncontrolled Emissions

SO_2 - Controlled and uncontrolled emissions of SO_2 are identical for a double absorption sulfuric acid plant.

Mist - The control efficiency of high efficiency mist eliminators is estimated to be 94 percent based on measurements at similar plants.

Hourly = 16.2 lb/hr controlled/(1-0.94)
= 270 lb/hr

Annual = 270 lb/hr x 8760 hr/yr x 1/2000 lb/ton
= 1183 tons/yr

4. Control System

SO_2 will be controlled by the existing two absorption towers and acid mist will be controlled with the existing high efficiency mist eliminators.

5. Control Efficiency

SO_2 - Sulfur input to plant = 71000 lb/hr (as S)

Efficiency = (71000-216.7)x100/7100
= 99.7%

Mist - High efficiency mist eliminators are estimated to be 94 percent efficient based on measurements made on similar double absorption plants.

6. Flow Diagram - See attached.

7. Location Map - See attached.

8. Site Map - See attached.

ATTACHMENT 1B

ANNUAL AIR POLLUTANT EMISSION CHANGES RESULTING FROM THE PROPOSED SULFURIC ACID PLANT RATE INCREASES (1)

CF INDUSTRIES, INC.
PLANT CITY PHOSPHATE COMPLEX
HILLSBOROUGH COUNTY, FLORIDA

POLLUTANT (Tons/Year)		Sulfuric Acid Plant C	Sulfuric Acid Plant D
SO2			
	Present (actual)	1752	1752
	Proposed	1898	1898
	Annual Change	146	146
	Subtotal	292	
	De minimis Increase (2)	40	
Mist			
	Present (actual)	65.7	65.7
	Proposed	71.2	71.2
	Annual Change	5.5	5.5
	Subtotal	11.0	
	De minimis Increase (2)	7	
NOx			
	Present (actual)	17.0	17.0
	Proposed	18.4	18.4
	Annual Change	1.4	1.4
	Subtotal	2.8 (3)	
	De minimis Increase (2)	40	

(1) Based on differences between present actual/permitted and proposed operating conditions.

(2) Defined in 17-2.500(2)(e)2,FAC.

(3) The emission rate increase of 2.8 tpy, when combined with NOx emission rate increases of 1.6 tpy and 8.3 tpy permitted in 1988 (and based on a stack gas concentration of 5 ppm, volume) is less than the de minimis emission rate increase of 40 tpy for NOx defined in 17-2.500(2)(e)2,FAC.

Revised 11/28/90