Department of
Environmental Protection

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BUREAU OF
AIR REGULATION

DIVISION OF AIR RESOURCES MANAGEMENT

APPLICATION FOR AIR PERMIT - LONG FORM

See Instructions for Form No. 62-210.900(1)

I. APPLICATION INFORMATION

This section of the Application for Air Permit form identifies the facility and provides general information on the scope and purpose of this application. This section also includes information on the owner or authorized representative of the facility (or the responsible official in the case of a Title V source) and the necessary statements for the applicant and professional engineer, where required, to sign and date for formal submittal of the Application for Air Permit to the Department. If the application form is submitted to the Department using ELSA, this section of the Application for Air Permit must also be submitted in hard-copy.

Identification of Facility Addressed in This Application

Enter the name of the corporation, business, governmental entity, or individual that has ownership or control of the facility; the facility site name, if any; and the facility's physical location. If known, also enter the facility identification number.

1. Facility Owner/Company Name: **Piney Point Phosphates, Inc.**

2. Site Name: **Piney Point**

3. Facility Identification Number: **0810002** [ ] Unknown

4. Facility Location:
Street Address or Other Locator: **US 41 N at Piney Point**
City: **Palmetto** County: **Manatee** Zip Code: **34221**

5. Relocatable Facility?
[ ] Yes [**X**] No

6. Existing Permitted Facility?
[**X**] Yes [ ] No

Application Processing Information (DEP Use)

1. Date of Receipt of Application:	Oct 31, 1997
2. Permit Number:	0810002-004-AC
3. PSD Number (if applicable):	PSD-FL-242
4. Siting Number (if applicable):	

Owner/Authorized Representative or Responsible Official

1. Name and Title of Owner/Authorized Representative or Responsible Official:
Robert Stewart, Sr. Vice President, Operations & Administration

2. Owner/Authorized Representative or Responsible Official Mailing Address:

Organization/Firm: **Piney Point Phosphates, Inc.**
Street Address: **13300 US Highway 41 North**
City: **Palmetto** State: **FL** Zip Code: **34221**

3. Owner/Authorized Representative or Responsible Official Telephone Numbers:
Telephone: **(813) 722-4555** Fax: ( )

4. Owner/Authorized Representative or Responsible Official Statement:

I, the undersigned, am the owner or authorized representative of the non-Title V source addressed in this Application for Air Permit or the responsible official, as defined in Rule 62-210.200, F.A.C., 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.*

Robert C Stewart 10-27-97
Signature Date

* Attach letter of authorization if not currently on file.

Scope of Application

This Application for Air Permit addresses the following emissions unit(s) at the facility. An Emissions Unit Information Section (a Section III of the form) must be included for each emissions unit listed.

Emissions Unit ID	Description of Emissions Unit	Permit Type
001	Sulfuric Acid Plant	AC1A
002	Molten Sulfur Storage & Handling Facility	AC1A

Purpose of Application and Category

Check one (except as otherwise indicated):

Category I: All Air Operation Permit Applications Subject to Processing Under Chapter 62-213, F.A.C.

This Application for Air Permit is submitted to obtain:

[ ] Initial air operation permit under Chapter 62-213, F.A.C., for an existing facility which is classified as a Title V source.

[ ] Initial air operation permit under Chapter 62-213, F.A.C., for a facility which, upon start up of one or more newly constructed or modified emissions units addressed in this application, would become classified as a Title V source.

Current construction permit number:

[ ] Air operation permit renewal under Chapter 62-213, F.A.C., for a Title V source.

Operation permit to be renewed:

[ ] Air operation permit revision for a Title V source to address one or more newly constructed or modified emissions units addressed in this application.

Current construction permit number:

Operation permit to be revised:

[ ] Air operation permit revision or administrative correction for a Title V source to address one or more proposed new or modified emissions units and to be processed concurrently with the air construction permit application. Also check Category III.

Operation permit to be revised/corrected:

[ ] Air operation permit revision for a Title V source for reasons other than construction or modification of an emissions unit. Give reason for the revision; e.g., to comply with a new applicable requirement or to request approval of an "Early Reductions" proposal.

Operation permit to be revised:

Reason for revision:

Category II: All Air Operation Permit Applications Subject to Processing Under Rule 62-210.300(2)(b), F.A.C.

This Application for Air Permit is submitted to obtain:

☐ Initial air operation permit under Rule 62-210.300(2)(b), F.A.C., for an existing facility seeking classification as a synthetic non-Title V source.

Current operation/construction permit number(s): ____________________

☐ Renewal air operation permit under Rule 62-210.300(2)(b), F.A.C., for a synthetic non-Title V source.

Operation permit to be renewed: ____________________

☐ Air operation permit revision for a synthetic non-Title V source. Give reason for revision; e.g., to address one or more newly constructed or modified emissions units.

Operation permit to be revised: ____________________

Reason for revision: ____________________

____

Category III: All Air Construction Permit Applications for All Facilities and Emissions Units

This Application for Air Permit is submitted to obtain:

☒ Air construction permit to construct or modify one or more emissions units within a facility (including any facility classified as a Title V source).

Current operation permit number(s), if any: **AO41-206854 & AO41-197112**

☐ Air construction permit to make federally enforceable an assumed restriction on the potential emissions of one or more existing, permitted emissions units.

Current operation permit number(s): ____________________

☐ Air construction permit for one or more existing, but unpermitted, emissions units.

Application Processing Fee

Check one:

[X] Attached - Amount: $ 7,500.00 [ ] Not Applicable.

Construction/Modification Information

1. Description of Proposed Project or Alterations: **The proposed project consists of repair activities to start up the existing sulfuric acid plant and molten sulfur storage & handling system.**
2. Projected or Actual Date of Commencement of Construction: **December 1, 1997**
3. Projected Date of Completion of Construction: **December 1, 1999**

Professional Engineer Certification

1. Professional Engineer Name: : **John B. Koogler, Ph.D., P.E.** Registration Number: **12925**
2. Professional Engineer Mailing Address: Organization/Firm: **Koogler & Associates** Street Address: **4014 NW 13th Street** City: **Gainesville** State: **FL** Zip Code: **32609**
3. Professional Engineer Telephone Numbers: Telephone: **(352) 377 - 5822** Fax: **(352) 377 - 7158**

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 [ ] 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 [X] 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.

Signature

(seal)

10/17/97
Date

Application Contact

1. Name and Title of Application Contact: **Pradeep Raval**	
2. Application Contact Mailing Address: Organization/Firm: **Koogler & Associates** Street Address: **4014 NW 13th Street** City: **Gainesville** State: **FL** Zip Code: **32609**	
3. Application Contact Telephone Numbers: Telephone: (**352**) **377 - 5822**	Fax: (**352**) **377 - 7158**

Application Comment

NA

II. FACILITY INFORMATION

A. GENERAL FACILITY INFORMATION

Facility Location and Type

1. Facility UTM Coordinates:
Zone: **17** East (km): **348.5** North (km): **3057.3**

2. Facility Latitude/Longitude:
Latitude (DD/MM/SS): **29/23/00** Longitude (DD/MM/SS): **82/20/00**

3. Governmental Facility Code: **0**	4. Facility Status Code: **A**	5. Facility Major Group SIC Code: **28**	6. Facility SIC(s): **2874**

7. Facility Comment (limit to 500 characters):

Phosphate Fertilizer

Facility Contact

1. Name and Title of Facility Contact: **Ivan Nance, Corporate Environmental Manager**

2. Facility Contact Mailing Address:
Organization/Firm: **Piney Point Phosphates, Inc.**
Street Address: **13300 US Highway 41 North**
City: **Palmetto** State: **FL** Zip Code: **34221**

3. Facility Contact Telephone Numbers:
Telephone: **(813) 722-4555** Fax: ( )

Facility Regulatory Classifications

1. Small Business Stationary Source?
[ ] Yes [X] No [ ] Unknown

2. Title V Source?
[X] Yes [ ] No

3. Synthetic Non-Title V Source?
[ ] Yes [X] No

4. Major Source of Pollutants Other than Hazardous Air Pollutants (HAPs)?
[X] Yes [ ] No

5. Synthetic Minor Source of Pollutants Other than HAPs?
[ ] Yes [X] No

6. Major Source of Hazardous Air Pollutants (HAPs)?
[ ] Yes [X] No

7. Synthetic Minor Source of HAPs?
[ ] Yes [X] No

8. One or More Emissions Units Subject to NSPS?
[X] Yes [ ] No

9. One or More Emission Units Subject to NESHAP?
[ ] Yes [X] No

10. Title V Source by EPA Designation?
[ ] Yes [X] No

11. Facility Regulatory Classifications Comment (limit to 200 characters):

B. FACILITY REGULATIONS

Rule Applicability Analysis (Required for Category II applications and Category III applications involving non Title-V sources. See Instructions.)

N/A

List of Applicable Regulations (Required for Category I applications and Category III applications involving Title-V sources. See Instructions.)

DEP Core List	
FS 120, 403	
FAC 62-4, 204, 210, 212, 213, 214, 252, 256, 257, 281, 296, 297	
40 CFR 52, 55, 60, 61, 63, 82	

C. FACILITY POLLUTANTS

Facility Pollutant Information

1. Pollutant Emitted	2. Pollutant Classification
PM/PM10	**A**
SO2	**A**
NOX	**A**
CO	**A**
FL	**B**

D. FACILITY POLLUTANT DETAIL INFORMATION NA

Facility Pollutant Detail Information: Pollutant ______ of ______

1. Pollutant Emitted:		
2. Requested Emissions Cap:	(lb/hour)	(tons/year)
3. Basis for Emissions Cap Code:		
4. Facility Pollutant Comment (limit to 400 characters):		

Facility Pollutant Detail Information: Pollutant ______ of ______

1. Pollutant Emitted:		
2. Requested Emissions Cap:	(lb/hour)	(tons/year)
3. Basis for Emissions Cap Code:		
4. Facility Pollutant Comment (limit to 400 characters):		

E. FACILITY SUPPLEMENTAL INFORMATION

Supplemental Requirements for All Applications

1. Area Map Showing Facility Location:
[X] Attached, Document ID: **REPORT** [ ] Not Applicable [ ] Waiver Requested

2. Facility Plot Plan:
[X] Attached, Document ID: **REPORT** [ ] Not Applicable [X] Waiver Requested

3. Process Flow Diagram(s):
[ ] Attached, Document ID:________ [ ] Not Applicable [X] Waiver Requested
Department has on file

4. Precautions to Prevent Emissions of Unconfined Particulate Matter:
[ ] Attached, Document ID:________ [ ] Not Applicable [X] Waiver Requested
Department has on file

5. Fugitive Emissions Identification:
[ ] Attached, Document ID:________ [ ] Not Applicable [X] Waiver Requested
Department has on file

6. Supplemental Information for Construction Permit Application:
[X] Attached, Document ID: **PSD REPORT** [ ] Not Applicable

Additional Supplemental Requirements for Category I Applications Only

7. List of Proposed Exempt Activities:
[ ] Attached, Document ID:________ [X] Not Applicable

8. List of Equipment/Activities Regulated under Title VI:

[ ] Attached, Document ID:________

[ ] Equipment/Activities On site but Not Required to be Individually Listed

[X] Not Applicable

9. Alternative Methods of Operation:
[ ] Attached, Document ID:________ [X] Not Applicable

10. Alternative Modes of Operation (Emissions Trading):
[ ] Attached, Document ID:________ [X] Not Applicable

11. Identification of Additional Applicable Requirements:
[ ] Attached, Document ID:________ [X] Not Applicable

12. Compliance Assurance Monitoring Plan:
[ ] Attached, Document ID:________ [X] Not Applicable

13. Risk Management Plan Verification:

[ ] Plan Submitted to Implementing Agency - Verification Attached,
Document ID:________

[ ] Plan to be Submitted to Implementing Agency by Required Date

[X] Not Applicable

14. Compliance Report and Plan:
[ ] Attached, Document ID:________ [X] Not Applicable

15. Compliance Certification (Hard-copy Required):
[ ] Attached, Document ID:________ [X] Not Applicable

III. EMISSIONS UNIT INFORMATION

A separate Emissions Unit Information Section (including subsections A through L as required) must be completed for each emissions unit addressed in this Application for Air Permit. If submitting the application form in hard copy, indicate, in the space provided at the top of each page, the number of this Emissions Unit Information Section and the total number of Emissions Unit Information Sections submitted as part of this application. Some of the subsections comprising the Emissions Unit Information Section of the form are intended for regulated emissions units only. Others are intended for both regulated and unregulated emissions units. Each subsection is appropriately marked.

A. TYPE OF EMISSIONS UNIT
(Regulated and Unregulated Emissions Units)

Type of Emissions Unit Addressed in This Section

1. Regulated or Unregulated Emissions Unit? Check one:

[X] The emissions unit addressed in this Emissions Unit Information Section is a regulated emissions unit.

[ ] The emissions unit addressed in this Emissions Unit Information Section is an unregulated emissions unit.

2. Single Process, Group of Processes, or Fugitive Only? Check one:

[X] This Emissions Unit Information Section addresses, as a single emissions unit, a single process or production unit, or activity, which produces one or more air pollutants and which has at least one definable emission point (stack or vent).

[ ] This Emissions Unit Information Section addresses, as a single emissions unit, a group of process or production units and activities which has at least one definable emission point (stack or vent) but may also produce fugitive emissions.

[ ] This Emissions Unit Information Section addresses, as a single emissions unit, one or more process or production units and activities which produce fugitive emissions only.

B. GENERAL EMISSIONS UNIT INFORMATION
(Regulated and Unregulated Emissions Units)

Emissions Unit Description and Status

1. Description of Emissions Unit Addressed in This Section (limit to 60 characters): **Sulfuric Acid Plant**		
2. Emissions Unit Identification Number: **001** [ ] No Corresponding ID [ ] Unknown		
3. Emissions Unit Status Code: **A**	4. Acid Rain Unit? [ ] Yes [**X**] No	5. Emissions Unit Major Group SIC Code: **28**
6. Emissions Unit Comment (limit to 500 characters):		

Emissions Unit Control Equipment

A.

1. Description (limit to 200 characters): **Double Absorption**
2. Control Device or Method Code: **044**

B.

1. Description (limit to 200 characters): **Demisters**
2. Control Device or Method Code: **014**

C.

1. Description (limit to 200 characters):
2. Control Device or Method Code:

C. EMISSIONS UNIT DETAIL INFORMATION
(Regulated Emissions Units Only)

Emissions Unit Details

1. Initial Startup Date: **N/A**		
2. Long-term Reserve Shutdown Date: **N/A**		
3. Package Unit: **N/A** Manufacturer:	Model Number:	
4. Generator Nameplate Rating: **N/A**	MW	
5. Incinerator Information: **N/A** Dwell Temperature: Dwell Time: Incinerator Afterburner Temperature:		 °F seconds °F

Emissions Unit Operating Capacity

1. Maximum Heat Input Rate: **N/A**		mmBtu/hr
2. Maximum Incineration Rate: **N/A**	lb/hr	tons/day
3. Maximum Process or Throughput Rate:		
4. Maximum Production Rate: **2000 tons per day 100% H2SO4**		
5. Operating Capacity Comment (limit to 200 characters):		

Emissions Unit Operating Schedule

Requested Maximum Operating Schedule:	
24 hours/day	**7** days/week
52 weeks/year	**8760** hours/year

D. EMISSIONS UNIT REGULATIONS
(Regulated Emissions Units Only)

Rule Applicability Analysis (Required for Category II applications and Category III applications involving non Title-V sources. See Instructions.)

N/A

Emissions Unit Information Section (__1__of__2__): **Sulfuric Acid Plant**

List of Applicable Regulations (Required for Category I applications and Category III applications involving Title-V sources. See Instructions.)

See Page 12.	

E. EMISSION POINT (STACK/VENT) INFORMATION
(Regulated Emissions Units Only)

Emission Point Description and Type

1. Identification of Point on Plot Plan or Flow Diagram:

2. Emission Point Type Code:
[**X**] 1 [ ] 2 [ ] 3 [ ] 4

3. Descriptions of Emissions Points Comprising this Emissions Unit for VE Tracking (limit to 100 characters per point):

4. ID Numbers or Descriptions of Emission Units with this Emission Point in Common:

N/A

5. Discharge Type Code:
[ ] D [ ] F [ ] H [ ] P
[ ] R [**X**] V [ ] W

6. Stack Height: **200** feet

7. Exit Diameter: **7.8** feet

8. Exit Temperature: **147** °F

9. Actual Volumetric Flow Rate:	**86,000** acfm
10. Percent Water Vapor :	%
11. Maximum Dry Standard Flow Rate:	dscfm
12. Nonstack Emission Point Height:	feet
13. Emission Point UTM Coordinates: Zone: East (km): North (km):	
14. Emission Point Comment (limit to 200 characters):	

F. SEGMENT (PROCESS/FUEL) INFORMATION
(Regulated and Unregulated Emissions Units)

Segment Description and Rate: Segment __1__of__1__

1. Segment Description (Process/Fuel Type and Associated Operating Method/Mode) (limit to 500 characters): **Sulfuric Acid Production**	
2. Source Classification Code (SCC): **3-01-023-04**	
3. SCC Units: **Tons 100% H2SO4**	
4. Maximum Hourly Rate: **83.3**	5. Maximum Annual Rate : **730,000**
6. Estimated Annual Activity Factor: **N/A**	
7. Maximum Percent Sulfur: **N/A**	8. Maximum Percent Ash: **N/A**
9. Million Btu per SCC Unit: **N/A**	
10. Segment Comment (limit to 200 characters): **Maximum annual rate = 2000 tpd x 365 days/yr = 730,000 tpy 100% H2SO4**	

G. EMISSIONS UNIT POLLUTANTS
(Regulated and Unregulated Emissions Units)

1. Pollutant Emitted	2. Primary Control Device Code	3. Secondary Control Device Code	4. Pollutant Regulatory Code
SO2	**044**	**014**	**EL**
SAM	**014**	**000**	**EL**
NOx	**000**	**000**	**EL**

H. EMISSIONS UNIT POLLUTANT DETAIL INFORMATION
(Regulated Emissions Units Only - Emissions Limited Pollutants Only)

Pollutant Detail Information:

1. Pollutant Emitted: **SO2**

2. Total Percent Efficiency of Control: **99.7 %**

3. Potential Emissions: **333.3** lb/hour **1460** tons/year

4. Synthetically Limited?
[ ] Yes [X] No

5. Range of Estimated Fugitive/Other Emissions:
[ ] 1 [ ] 2 [ ] 3 _______ to _______ tons/year

6. Emission Factor: **4 LB/TON 100% ACID**
Reference: **Permit**

7. Emissions Method Code:
[X] 0 [ ] 1 [ ] 2 [ ] 3 [ ] 4 [ ] 5

8. Calculation of Emissions (limit to 600 characters):

SO2 = 2000 tpd/24 hrs/day x 4 lb/ton = 333.3 lb/hr
X 8760 hrs/yr X ton/2000 lbs = 1460 tpy

9. Pollutant Potential/Estimated Emissions Comment (limit to 200 characters):

Allowable Emissions (Pollutant identified on front of page)

A.

1. Basis for Allowable Emissions Code: **RULE**
2. Future Effective Date of Allowable Emissions: **N/A**
3. Requested Allowable Emissions and Units: **4.0 lb/ton 100% ACID**
4. Equivalent Allowable Emissions: **333.3** lb/hour **1460** tons/year
5. Method of Compliance (limit to 60 characters): **EPA METHOD 8**
6. Pollutant Allowable Emissions Comment (Desc. of Related Operating Method/Mode) (limit to 200 characters): **40 CFR 60, SUBPART H.**

B.

1. Basis for Allowable Emissions Code:
2. Future Effective Date of Allowable Emissions:
3. Requested Allowable Emissions and Units:
4. Equivalent Allowable Emissions: lb/hr tons/year
5. Method of Compliance (limit to 60 characters):
6. Pollutant Allowable Emissions Comment (Desc. of Related Operating Method/Mode) (limit to 200 characters):

H. EMISSIONS UNIT POLLUTANT DETAIL INFORMATION
(Regulated Emissions Units Only - Emissions Limited Pollutants Only)

Pollutant Detail Information:

1. Pollutant Emitted: **SAM**

2. Total Percent Efficiency of Control: **99** %

3. Potential Emissions: **12.5** lb/hour **54.8** tons/year

4. Synthetically Limited?
[ ] Yes [**X**] No

5. Range of Estimated Fugitive/Other Emissions: **N/A**
[ ] 1 [ ] 2 [ ] 3 ______ to ______ tons/year

6. Emission Factor: **12.5 LB/HR**
Reference: **PERMIT**

7. Emissions Method Code:
[**X**] 0 [ ] 1 [ ] 2 [ ] 3 [ ] 4 [ ] 5

8. Calculation of Emissions (limit to 600 characters):

SAM = 12.5 LB/HR X 8760 HRS/YR X TON/2000 LBS = 54.8 TPY

9. Pollutant Potential/Estimated Emissions Comment (limit to 200 characters):

Allowable Emissions (Pollutant identified on front of page)

A.

1. Basis for Allowable Emissions Code: **RULE**
2. Future Effective Date of Allowable Emissions:**NA**
3. Requested Allowable Emissions and Units: **0.15 lb/ton 100% ACID**
4. Equivalent Allowable Emissions: **12.5** lb/hour **54.8** Tons/year
5. Method of Compliance (limit to 60 characters): **EPA METHOD 8**
6. Pollutant Allowable Emissions Comment (Desc. of Related Operating Method/Mode) (limit to 200 characters): **40 CFR 60, SUBPART H.**

B.

1. Basis for Allowable Emissions Code:
2. Future Effective Date of Allowable Emissions:
3. Requested Allowable Emissions and Units:
4. Equivalent Allowable Emissions: lb/hr tons/year
5. Method of Compliance (limit to 60 characters):
6. Pollutant Allowable Emissions Comment (Desc. of Related Operating Method/Mode) (limit to 200 characters):

H. EMISSIONS UNIT POLLUTANT DETAIL INFORMATION
(Regulated Emissions Units Only - Emissions Limited Pollutants Only)

Pollutant Detail Information:

1. Pollutant Emitted: **NOX**

2. Total Percent Efficiency of Control: %

3. Potential Emissions: **10** lb/hour **43.8** tons/year

4. Synthetically Limited?
[ ] Yes [X] No

5. Range of Estimated Fugitive/Other Emissions: **N/A**
[ ] 1 [ ] 2 [ ] 3 _______ to _______ tons/year

6. Emission Factor: **0.12 lb/ton**
Reference: **Similar Permit**

7. Emissions Method Code:
[X] 0 [ ] 1 [ ] 2 [ ] 3 [ ] 4 [ ] 5

8. Calculation of Emissions (limit to 600 characters):

NOX = 2000 tpd/24 hrs/day x 0.12 lb/ton = 10 lb/hr
X 8760 hrs/yr X ton/2000 lbs = 43.8 tpy

9. Pollutant Potential/Estimated Emissions Comment (limit to 200 characters):

Emission factor based on permits issued to similar sulfuric acid plants.

Emissions Unit Information Section (_1_of_2_): Sulfuric Acid Plant

Allowable Emissions (Pollutant identified on front of page)

A.

1. Basis for Allowable Emissions Code: **RULE**
2. Future Effective Date of Allowable Emissions:**NA**
3. Requested Allowable Emissions and Units: **0.12 lb/ton 100% ACID**
4. Equivalent Allowable Emissions: **10** lb/hour **43.8** Tons/year
5. Method of Compliance (limit to 60 characters): **EPA METHOD 7E**
6. Pollutant Allowable Emissions Comment (Desc. of Related Operating Method/Mode) (limit to 200 characters): **BACT**

B.

1. Basis for Allowable Emissions Code:
2. Future Effective Date of Allowable Emissions:
3. Requested Allowable Emissions and Units:
4. Equivalent Allowable Emissions: lb/hr tons/year
5. Method of Compliance (limit to 60 characters):
6. Pollutant Allowable Emissions Comment (Desc. of Related Operating Method/Mode) (limit to 200 characters):

I. VISIBLE EMISSIONS INFORMATION
(Regulated Emissions Units Only)

Visible Emissions Limitation: Visible Emissions Limitation _1_ of _1_

1. Visible Emissions Subtype: **VE10**

2. Basis for Allowable Opacity: [X] Rule [ ] Other

3. Requested Allowable Opacity:
Normal Conditions: **10%** Exceptional Conditions: %
Maximum Period of Excess Opacity Allowed: min/hour

4. Method of Compliance: EPA METHOD 9

5. Visible Emissions Comment (limit to 200 characters): **40 CFR 60, SUBPART H.**

Visible Emissions Limitation: Visible Emissions Limitation ______ of ______

1. Visible Emissions Subtype:

2. Basis for Allowable Opacity: [ ] Rule [ ] Other

3. Requested Allowable Opacity:
Normal Conditions: % Exceptional Conditions: %
Maximum Period of Excess Opacity Allowed: min/hour

4. Method of Compliance:

5. Visible Emissions Comment (limit to 200 characters):

J. CONTINUOUS MONITOR INFORMATION
(Regulated Emissions Units Only)

Continuous Monitoring System: Continuous Monitor _1_of_1_

1. Parameter Code: **EM**	2. Pollutant(s): **SO2**
3. CMS Requirement:	[X] Rule [ ] Other
4. Monitor Information: Manufacturer: Model Number:	Serial Number:
5. Installation Date:	
6. Performance Specification Test Date:	
7. Continuous Monitor Comment (limit to 200 characters):	

Continuous Monitoring System: Continuous Monitor _____ of _____

1. Parameter Code:	2. Pollutant(s):
3. CMS Requirement:	[ ] Rule [ ] Other
4. Monitor Information: Manufacturer: Model Number:	Serial Number:
5. Installation Date:	
6. Performance Specification Test Date:	
7. Continuous Monitor Comment (limit to 200 characters):	

K. PREVENTION OF SIGNIFICANT DETERIORATION (PSD) INCREMENT TRACKING INFORMATION

(Regulated and Unregulated Emissions Units)

PSD Increment Consumption Determination

1. Increment Consuming for Particulate Matter or Sulfur Dioxide?

If the emissions unit addressed in this section emits particulate matter or sulfur dioxide, answer the following series of questions to make a preliminary determination as to whether or not the emissions unit consumes PSD increment for particulate matter or sulfur dioxide. Check the first statement, if any, that applies and skip remaining statements.

[**X**] The emissions unit is undergoing PSD review as part of this application, or has undergone PSD review previously, for particulate matter or sulfur dioxide. If so, emissions unit consumes increment.

[ ] The facility addressed in this application is classified as an EPA major source pursuant to paragraph (c) of the definition of "major source of air pollution" in Chapter 62-213, F.A.C., and the emissions unit addressed in this section commenced (or will commence) construction after January 6, 1975. If so, baseline emissions are zero, and emissions unit consumes increment.

[ ] The facility addressed in this application is classified as an EPA major source, and the emissions unit began initial operation after January 6, 1975, but before December 27, 1977. If so, baseline emissions are zero, and emissions unit consumes increment.

[ ] For any facility, the emissions unit began (or will begin) initial operation after December 27, 1977. If so, baseline emissions are zero, and emissions unit consumes increment.

[ ] None of the above apply. If so, the baseline emissions of the emissions unit are nonzero. In such case, additional analysis, beyond the scope of this application, is needed to determine whether changes in emissions have occurred (or will occur) after the baseline date that may consume or expand increment.

2. Increment Consuming for Nitrogen Dioxide?

If the emissions unit addressed in this section emits nitrogen oxides, answer the following series of questions to make a preliminary determination as to whether or not the emissions unit consumes PSD increment for nitrogen dioxide. Check first statement, if any, that applies and skip remaining statements.

☒ The emissions unit addressed in this section is undergoing PSD review as part of this application, or has undergone PSD review previously, for nitrogen dioxide. If so, emissions unit consumes increment.

☐ The facility addressed in this application is classified as an EPA major source pursuant to paragraph (c) of the definition of "major source of air pollution" in Chapter 62-213, F.A.C., and the emissions unit addressed in this section commenced (or will commence) construction after February 8, 1988. If so, baseline emissions are zero, and emissions unit consumes increment.

☐ The facility addressed in this application is classified as an EPA major source, and the emissions unit began initial operation after February 8, 1988, but before March 28, 1988. If so, baseline emissions are zero, and emissions unit consumes increment.

☐ For any facility, the emissions unit began (or will begin) initial operation after March 28, 1988. If so, baseline emissions are zero, and emissions unit consumes increment.

☐ None of the above apply. If so, the baseline emissions of the emissions unit are nonzero. In such case, additional analysis, beyond the scope of this application, is needed to determine whether changes in emissions have occurred (or will occur) after the baseline date that may consume or expand increment.

3. Increment Consuming/Expanding Code:			
PM	☐ C	☐ E	☐ Unknown
SO2	☐ C	☐ E	☐ Unknown
NO2	☐ C	☐ E	☐ Unknown
4. Baseline Emissions:			
PM		lb/hour	tons/year
SO2		lb/hour	tons/year
NO2			tons/year
5. PSD Comment (limit to 200 characters):			

L. EMISSIONS UNIT SUPPLEMENTAL INFORMATION
(Regulated Emissions Units Only)

Supplemental Requirements for All Applications

1. Process Flow Diagram
[X] Attached, Document ID: **REPORT** [ ] Not Applicable [ ] Waiver Requested

2. Fuel Analysis or Specification
[ ] Attached, Document ID:________ [X] Not Applicable [ ] Waiver Requested

3. Detailed Description of Control Equipment
[ ] Attached, Document ID:________ [ ] Not Applicable [X] Waiver Requested
Department has on file

4. Description of Stack Sampling Facilities
[ ] Attached, Document ID:________ [ ] Not Applicable [X] Waiver Requested
Department has on file

5. Compliance Test Report
[ ] Attached, Document ID:________

[ ] Previously submitted, Date:_______________

[X] Not Applicable

6. Procedures for Startup and Shutdown
[ ] Attached, Document ID:________ [ ] Not Applicable [X] Waiver Requested
Department has on file

7. Operation and Maintenance Plan
[ ] Attached, Document ID:________ [X] Not Applicable

8. Supplemental Information for Construction Permit Application
[ ] Attached, Document ID:________ [X] Not Applicable

9. Other Information Required by Rule or Statute
[ ] Attached, Document ID:________ [X] Not Applicable

Additional Supplemental Requirements for Category I Applications Only

10. Alternative Methods of Operation

[ ] Attached, Document ID:_______ [**X**] Not Applicable

11. Alternative Modes of Operation (Emissions Trading)

[ ] Attached, Document ID:_______ [**X**] Not Applicable

12. Identification of Additional Applicable Requirements

[ ] Attached, Document ID:_______ [**X**] Not Applicable

13. Compliance Assurance Monitoring Plan

[ ] Attached, Document ID:_______ [**X**] Not Applicable

14. Acid Rain Application (Hard-copy Required)

[ ] Acid Rain Part - Phase II (Form No. 62-210.900(1)(a))
Attached, Document ID:_______

[ ] Repowering Extension Plan (Form No. 62-210.900(1)(a)1.)
Attached, Document ID:_______

[ ] New Unit Exemption (Form No. 62-210.900(1)(a)2.)
Attached, Document ID:_______

[ ] Retired Unit Exemption (Form No. 62-210.900(1)(a)3.)
Attached, Document ID:_______

[**X**] Not Applicable

III. EMISSIONS UNIT INFORMATION

A separate Emissions Unit Information Section (including subsections A through L as required) must be completed for each emissions unit addressed in this Application for Air Permit. If submitting the application form in hard copy, indicate, in the space provided at the top of each page, the number of this Emissions Unit Information Section and the total number of Emissions Unit Information Sections submitted as part of this application. Some of the subsections comprising the Emissions Unit Information Section of the form are intended for regulated emissions units only. Others are intended for both regulated and unregulated emissions units. Each subsection is appropriately marked.

A. TYPE OF EMISSIONS UNIT
(Regulated and Unregulated Emissions Units)

Type of Emissions Unit Addressed in This Section

1. Regulated or Unregulated Emissions Unit? Check one:

[X] The emissions unit addressed in this Emissions Unit Information Section is a regulated emissions unit.

[ ] The emissions unit addressed in this Emissions Unit Information Section is an unregulated emissions unit.

2. Single Process, Group of Processes, or Fugitive Only? Check one:

[ ] This Emissions Unit Information Section addresses, as a single emissions unit, a single process or production unit, or activity, which produces one or more air pollutants and which has at least one definable emission point (stack or vent).

[X] This Emissions Unit Information Section addresses, as a single emissions unit, a group of process or production units and activities which has at least one definable emission point (stack or vent) but may also produce fugitive emissions.

[ ] This Emissions Unit Information Section addresses, as a single emissions unit, one or more process or production units and activities which produce fugitive emissions only.

B. GENERAL EMISSIONS UNIT INFORMATION
(Regulated and Unregulated Emissions Units)

Emissions Unit Description and Status

1. Description of Emissions Unit Addressed in This Section (limit to 60 characters):

Molten Sulfur Storage & Handling System

2. Emissions Unit Identification Number: **002** [ ] No Corresponding ID [ ] Unknown

3. Emissions Unit Status Code: **A**	4. Acid Rain Unit? [ ] Yes [**X**] No	5. Emissions Unit Major Group SIC Code: **28**

6. Emissions Unit Comment (limit to 500 characters):

This unit includes the rail and truck sulfur unloading; receiving pit; storage tank; pumps and piping.

For emission iventory and PSD purposes, the estimated maximum emissions from the sources in this emissions unit are:

PM/PM10 = 0.61 tpy
SO_2 = 1.2 tpy
H_2S = 0.28 tpy
TRS = 0.79 tpy

Emissions Unit Control Equipment

A.

1. Description (limit to 200 characters): **NA**

2. Control Device or Method Code:

B.

1. Description (limit to 200 characters):
2. Control Device or Method Code:

C.

1. Description (limit to 200 characters):
2. Control Device or Method Code:

C. EMISSIONS UNIT DETAIL INFORMATION
(Regulated Emissions Units Only)

Emissions Unit Details

1. Initial Startup Date: **N/A**	
2. Long-term Reserve Shutdown Date: **N/A**	
3. Package Unit: **N/A** Manufacturer:	Model Number:
4. Generator Nameplate Rating: **N/A**	MW
5. Incinerator Information: **N/A** Dwell Temperature: Dwell Time: Incinerator Afterburner Temperature:	 °F seconds °F

Emissions Unit Operating Capacity

1. Maximum Heat Input Rate: **N/A**		mmBtu/hr
2. Maximum Incineration Rate: **N/A**	lb/hr	tons/day
3. Maximum Process or Throughput Rate: **747 tpd**		
4. Maximum Production Rate: NA		
5. Operating Capacity Comment (limit to 200 characters):		

Emissions Unit Operating Schedule

Requested Maximum Operating Schedule:	
24 hours/day	**7** days/week
52 weeks/year	**8760** hours/year

D. EMISSIONS UNIT REGULATIONS
(Regulated Emissions Units Only)

Rule Applicability Analysis (Required for Category II applications and Category III applications involving non Title-V sources. See Instructions.)

N/A

List of Applicable Regulations (Required for Category I applications and Category III applications involving Title-V sources. See Instructions.)

See Page 12.	

E. EMISSION POINT (STACK/VENT) INFORMATION
(Regulated Emissions Units Only)

Emission Point Description and Type

1. Identification of Point on Plot Plan or Flow Diagram:	
2. Emission Point Type Code: [**X**] 1 [ ] 2 [ ] 3 [ ] 4	
3. Descriptions of Emissions Points Comprising this Emissions Unit for VE Tracking (limit to 100 characters per point):	
4. ID Numbers or Descriptions of Emission Units with this Emission Point in Common: **N/A**	
5. Discharge Type Code: [ ] D [ ] F [ ] H [ ] P [ ] R [ ] V [**X**] W	
6. Stack Height:	**NA** feet
7. Exit Diameter:	**NA** feet
8. Exit Temperature:	**200** °F

9. Actual Volumetric Flow Rate:	acfm
10. Percent Water Vapor :	%
11. Maximum Dry Standard Flow Rate:	**NA** dscfm
12. Nonstack Emission Point Height:	**24** feet

13. Emission Point UTM Coordinates:
Zone: East (km): North (km):

14. Emission Point Comment (limit to 200 characters):

Tank vent.

F. SEGMENT (PROCESS/FUEL) INFORMATION
(Regulated and Unregulated Emissions Units)

Segment Description and Rate: Segment 1 of 1

1. Segment Description (Process/Fuel Type and Associated Operating Method/Mode) (limit to 500 characters): **Molten Sulfur Storage & Handling**	
2. Source Classification Code (SCC): **03-01-023-99**	
3. SCC Units: **Tons Processed**	
4. Maximum Hourly Rate: **31 (avg.)**	5. Maximum Annual Rate : **272,655**
6. Estimated Annual Activity Factor: **N/A**	
7. Maximum Percent Sulfur: **N/A**	8. Maximum Percent Ash: **N/A**
9. Million Btu per SCC Unit: **N/A**	
10. Segment Comment (limit to 200 characters):	

G. EMISSIONS UNIT POLLUTANTS
(Regulated and Unregulated Emissions Units)

1. Pollutant Emitted	2. Primary Control Device Code	3. Secondary Control Device Code	4. Pollutant Regulatory Code
PM	**000**	**000**	**NS**
SO2	**000**	**000**	**NS**
H2S	**000**	**000**	**NS**
VOC	**000**	**000**	**NS**

H. EMISSIONS UNIT POLLUTANT DETAIL INFORMATION
(Regulated Emissions Units Only - Emissions Limited Pollutants Only)

Pollutant Detail Information:

1. Pollutant Emitted: **NA**

2. Total Percent Efficiency of Control: %

3. Potential Emissions: lb/hour tons/year

4. Synthetically Limited?
[ ] Yes [ ] No

5. Range of Estimated Fugitive/Other Emissions:
[ ] 1 [ ] 2 [ ] 3 _______ to _______ tons/year

6. Emission Factor:
Reference:

7. Emissions Method Code:
[ ] 0 [ ] 1 [ ] 2 [ ] 3 [ ] 4 [ ] 5

8. Calculation of Emissions (limit to 600 characters):

9. Pollutant Potential/Estimated Emissions Comment (limit to 200 characters):

Allowable Emissions (Pollutant identified on front of page)

A.

1. Basis for Allowable Emissions Code: **NA**		
2. Future Effective Date of Allowable Emissions:		
3. Requested Allowable Emissions and Units:		
4. Equivalent Allowable Emissions:	lb/hour	Tons/year
5. Method of Compliance (limit to 60 characters):		
6. Pollutant Allowable Emissions Comment (Desc. of Related Operating Method/Mode) (limit to 200 characters):		

B.

1. Basis for Allowable Emissions Code:		
2. Future Effective Date of Allowable Emissions:		
3. Requested Allowable Emissions and Units:		
4. Equivalent Allowable Emissions:	lb/hr	tons/year
5. Method of Compliance (limit to 60 characters):		
6. Pollutant Allowable Emissions Comment (Desc. of Related Operating Method/Mode) (limit to 200 characters):		

I. VISIBLE EMISSIONS INFORMATION
(Regulated Emissions Units Only)

Visible Emissions Limitation: Visible Emissions Limitation 1 of 1

1. Visible Emissions Subtype: **VE20**	
2. Basis for Allowable Opacity: [X] Rule	[ ] Other
3. Requested Allowable Opacity: Normal Conditions: **20** % Maximum Period of Excess Opacity Allowed:	Exceptional Conditions: % min/hour
4. Method of Compliance: **EPA METHOD 9**	
5. Visible Emissions Comment (limit to 200 characters): **MOLTEN SULFUR RULE, 62-296.11 FAC.**	

Visible Emissions Limitation: Visible Emissions Limitation ______ of ______

1. Visible Emissions Subtype:	
2. Basis for Allowable Opacity: [ ] Rule	[ ] Other
3. Requested Allowable Opacity: Normal Conditions: % Maximum Period of Excess Opacity Allowed:	Exceptional Conditions: % min/hour
4. Method of Compliance:	
5. Visible Emissions Comment (limit to 200 characters):	

J. CONTINUOUS MONITOR INFORMATION
(Regulated Emissions Units Only)

Continuous Monitoring System: Continuous Monitor _____ of _____

1. Parameter Code:	2. Pollutant(s):
3. CMS Requirement:	[ ] Rule [ ] Other
4. Monitor Information: Manufacturer: Model Number:	Serial Number:
5. Installation Date:	
6. Performance Specification Test Date:	
7. Continuous Monitor Comment (limit to 200 characters):	

Continuous Monitoring System: Continuous Monitor _____ of _____

1. Parameter Code:	2. Pollutant(s):
3. CMS Requirement:	[ ] Rule [ ] Other
4. Monitor Information: Manufacturer: Model Number:	Serial Number:
5. Installation Date:	
6. Performance Specification Test Date:	
7. Continuous Monitor Comment (limit to 200 characters):	

K. PREVENTION OF SIGNIFICANT DETERIORATION (PSD) INCREMENT TRACKING INFORMATION

(Regulated and Unregulated Emissions Units)

PSD Increment Consumption Determination

1. Increment Consuming for Particulate Matter or Sulfur Dioxide?

If the emissions unit addressed in this section emits particulate matter or sulfur dioxide, answer the following series of questions to make a preliminary determination as to whether or not the emissions unit consumes PSD increment for particulate matter or sulfur dioxide. Check the first statement, if any, that applies and skip remaining statements.

[**X**] The emissions unit is undergoing PSD review as part of this application, or has undergone PSD review previously, for particulate matter or sulfur dioxide. If so, emissions unit consumes increment.

[ ] The facility addressed in this application is classified as an EPA major source pursuant to paragraph (c) of the definition of "major source of air pollution" in Chapter 62-213, F.A.C., and the emissions unit addressed in this section commenced (or will commence) construction after January 6, 1975. If so, baseline emissions are zero, and emissions unit consumes increment.

[ ] The facility addressed in this application is classified as an EPA major source, and the emissions unit began initial operation after January 6, 1975, but before December 27, 1977. If so, baseline emissions are zero, and emissions unit consumes increment.

[ ] For any facility, the emissions unit began (or will begin) initial operation after December 27, 1977. If so, baseline emissions are zero, and emissions unit consumes increment.

[ ] None of the above apply. If so, the baseline emissions of the emissions unit are nonzero. In such case, additional analysis, beyond the scope of this application, is needed to determine whether changes in emissions have occurred (or will occur) after the baseline date that may consume or expand increment.

2. Increment Consuming for Nitrogen Dioxide?

If the emissions unit addressed in this section emits nitrogen oxides, answer the following series of questions to make a preliminary determination as to whether or not the emissions unit consumes PSD increment for nitrogen dioxide. Check first statement, if any, that applies and skip remaining statements.

[X] The emissions unit addressed in this section is undergoing PSD review as part of this application, or has undergone PSD review previously, for nitrogen dioxide. If so, emissions unit consumes increment.

[ ] The facility addressed in this application is classified as an EPA major source pursuant to paragraph (c) of the definition of "major source of air pollution" in Chapter 62-213, F.A.C., and the emissions unit addressed in this section commenced (or will commence) construction after February 8, 1988. If so, baseline emissions are zero, and emissions unit consumes increment.

[ ] The facility addressed in this application is classified as an EPA major source, and the emissions unit began initial operation after February 8, 1988, but before March 28, 1988. If so, baseline emissions are zero, and emissions unit consumes increment.

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[ ] None of the above apply. If so, the baseline emissions of the emissions unit are nonzero. In such case, additional analysis, beyond the scope of this application, is needed to determine whether changes in emissions have occurred (or will occur) after the baseline date that may consume or expand increment.

3. Increment Consuming/Expanding Code:

PM	[ ] C	[ ] E	[ ] Unknown
SO2	[ ] C	[ ] E	[ ] Unknown
NO2	[ ] C	[ ] E	[ ] Unknown

4. Baseline Emissions:

PM	lb/hour	tons/year
SO2	lb/hour	tons/year
NO2		tons/year

5. PSD Comment (limit to 200 characters):

L. EMISSIONS UNIT SUPPLEMENTAL INFORMATION
(Regulated Emissions Units Only)

Supplemental Requirements for All Applications

1. Process Flow Diagram
   [ ] Attached, Document ID:________ [ ] Not Applicable [X] Waiver Requested
   Department has on file

2. Fuel Analysis or Specification
   [ ] Attached, Document ID:________ [X] Not Applicable [ ] Waiver Requested

3. Detailed Description of Control Equipment
   [ ] Attached, Document ID:________ [X] Not Applicable [ ] Waiver Requested

4. Description of Stack Sampling Facilities
   [ ] Attached, Document ID:________ [X] Not Applicable [ ] Waiver Requested

5. Compliance Test Report
   [ ] Attached, Document ID:________

   [ ] Previously submitted, Date:______________

   [X] Not Applicable

6. Procedures for Startup and Shutdown
   [ ] Attached, Document ID:________ [X] Not Applicable

7. Operation and Maintenance Plan
   [ ] Attached, Document ID:________ [X] Not Applicable

9. Other Information Required by Rule or Statute
   [ ] Attached, Document ID:________ [X] Not Applicable

Additional Supplemental Requirements for Category I Applications Only

10. Alternative Methods of Operation
[ ] Attached, Document ID:________ [X] Not Applicable

11. Alternative Modes of Operation (Emissions Trading)
[ ] Attached, Document ID:________ [X] Not Applicable

12. Identification of Additional Applicable Requirements
[ ] Attached, Document ID:________ [X] Not Applicable

13. Compliance Assurance Monitoring Plan
[ ] Attached, Document ID:________ [X] Not Applicable

14. Acid Rain Application (Hard-copy Required)

[ ] Acid Rain Part - Phase II (Form No. 62-210.900(1)(a))
Attached, Document ID:________

[ ] Repowering Extension Plan (Form No. 62-210.900(1)(a)1.)
Attached, Document ID:________

[ ] New Unit Exemption (Form No. 62-210.900(1)(a)2.)
Attached, Document ID:________

[ ] Retired Unit Exemption (Form No. 62-210.900(1)(a)3.)
Attached, Document ID:________

[X] Not Applicable

REPORT IN SUPPORT OF
A PSD PERMIT APPLICATION

PREPARED FOR:

PINEY POINT PHOSPHATES, INC.
MANATEE COUNTY, FLORIDA

OCTOBER 1997

PREPARED BY:

KOOGLER & ASSOCIATES
4014 N.W. 13TH STREET
GAINESVILLE, FLORIDA 32609
(352) 377-5822

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APPENDICES

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1.0 SYNOPSIS OF APPLICATION

1.1 APPLICANT

Piney Point Phosphates, Inc.
13300 US Hwy 41 North
Palmetto, Florida 34221-8662

1.2 FACILITY LOCATION

Piney Point Phosphates, Inc. (previously Royster Phosphates) operates a fertilizer plant located approximately nine miles north of Palmetto on US Highway 41 in Manatee County, Florida (see Figures 1-1 and 1-2). The UTM coordinates of the facility are Zone 17, 348.5 km east and 3057.3 km north.

1.3 PROJECT OVERVIEW

Piney Point Phosphates, Inc. (PPP) proposes to start up the existing permitted sulfuric acid plant. The sulfuric acid plant has not been in operation since 1992. The molten sulfur storage & handling system will also be activated to pump molten sulfur to the sulfuric acid plant. PPP does not propose to increase the production rate or pollutant emissions from the plant. Some repair work is proposed prior to plant start up.

The proposed plant repairs (see Appendix A), are no different than those required at other existing sulfuric acid plants over a period of time, on a routine basis. However, the Florida Department of Environmental Protection (FDEP) has indicated that the proposed scope of repairs at PPP is non-routine in nature and would constitute a modification pursuant to Rule 62-212, Florida Administrative Code (FAC).

PPP is not in agreement with FDEP's opinion regarding the rule interpretation. However, in an effort to expedite the sulfuric acid plant start up, this application is being prepared to address the rule requirements applicable to a modification. Based on this approach, the proposed repair project will result in a significant net increase (in accordance with Rule 62-212, Florida Administrative Code), in the emission rates of sulfur dioxide (SO_2), nitrogen oxides (NOx) and sulfuric acid mist (SAM).

PPP is submitting this report in support of the application to bring the existing permitted sulfuric acid plant and molten sulfur system back on-line. The report includes a description of the existing chemical complex and the sulfuric acid plant, a review of Best Available Control Technology, an ambient air quality analysis and an evaluation of the impact of the proposed project on soils, vegetation and visibility.

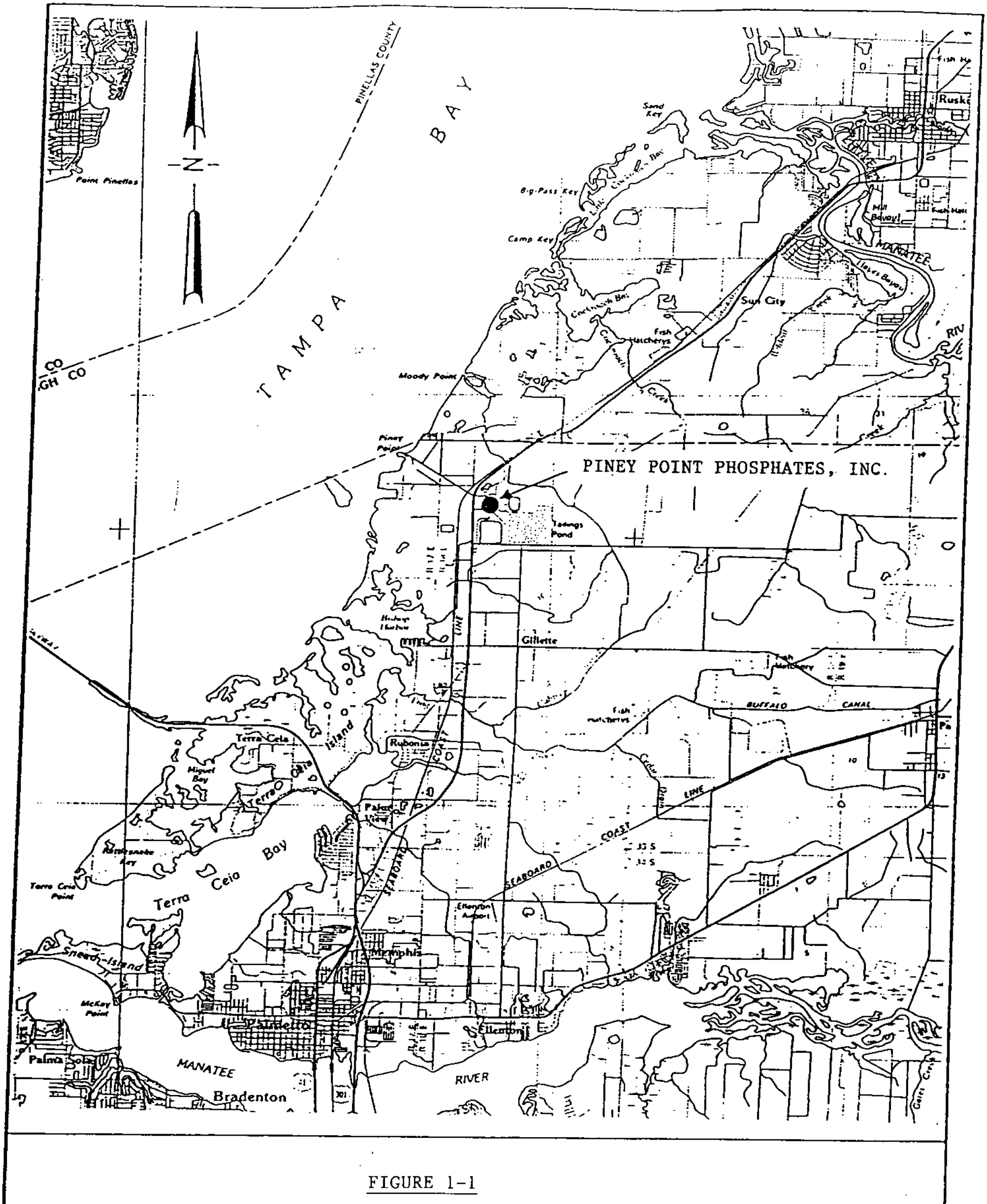

FIGURE 1-1

SITE LOCATION

PINEY POINT PHOSPHATES, INC.

KOOGLER & ASSOCIATES

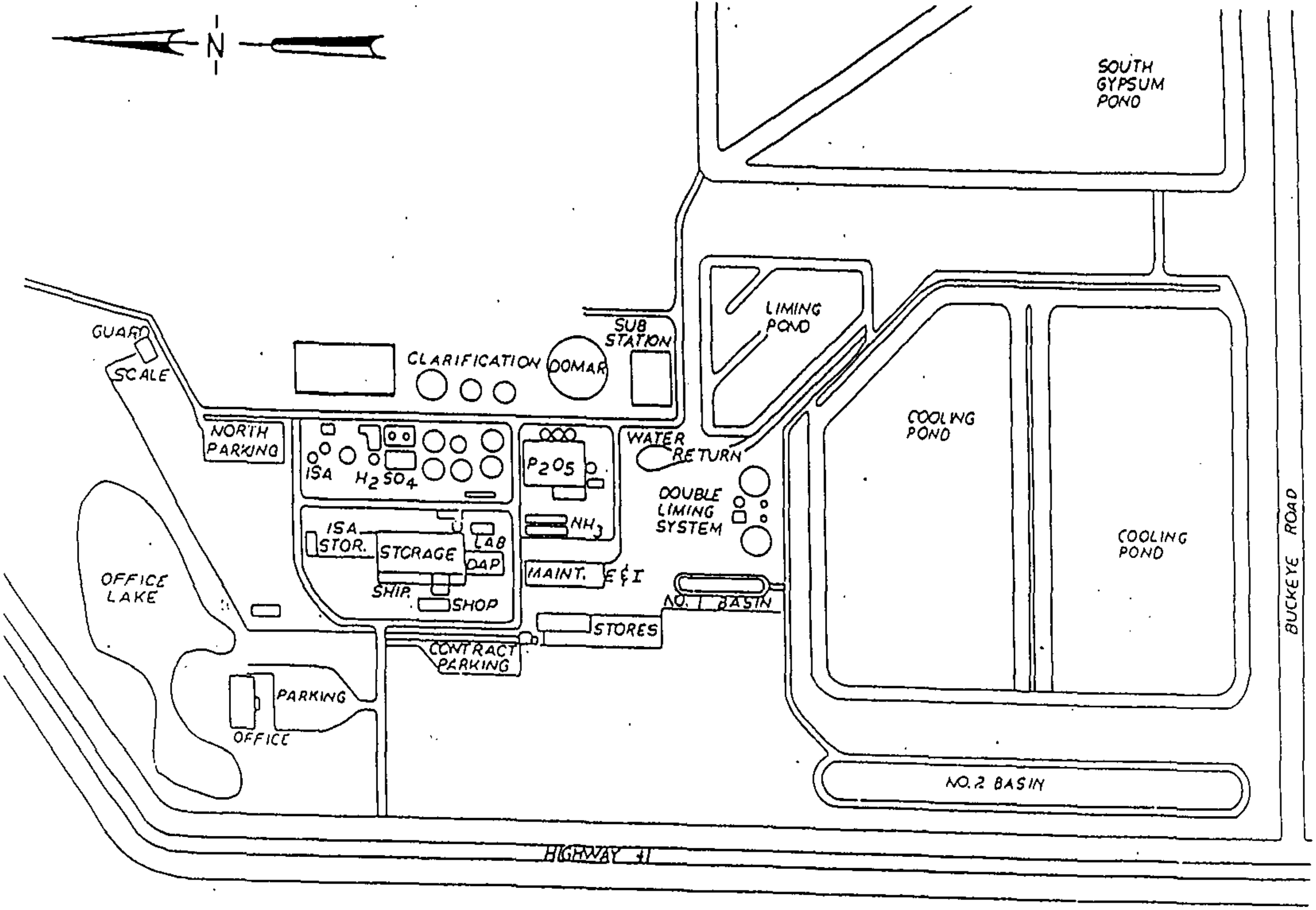

FIGURE 1-2

FACILITY PLOT PLAN

PINEY POINT PHOSPHATES, INC.

KOOGLER & ASSOCIATES

2.0 FACILITY DESCRIPTION

The existing fertilizer complex consists of an auxiliary steam boiler, one sulfuric acid plant, one phosphoric acid plant, one diammonium phosphate plant, storage and handling facilities for molten sulfur, phosphate rock and fertilizer products and a water management system.

2.1 PROCESS DESCRIPTION

The existing sulfuric acid plant is presently permitted for continuous operation at a production rate of 2000 tons per day of 100 percent H_2SO_4. The plant is subject to Federal New Source Performance Standards as set forth in 40 CFR 60, Subpart H.

Molten sulfur is received by truck and rail, unloaded into molten sulfur pits, and pumped to molten sulfur storage tanks for storage. The sulfuric acid plant utilizes the double absorption process which produces sulfuric acid by burning sulfur to produce sulfur dioxide, converting the sulfur dioxide to sulfur trioxide using a catalyst, and then contacting the sulfur trioxide with sulfuric acid in primary and secondary absorption towers. A process flow diagram is presented in Figure 2-1.

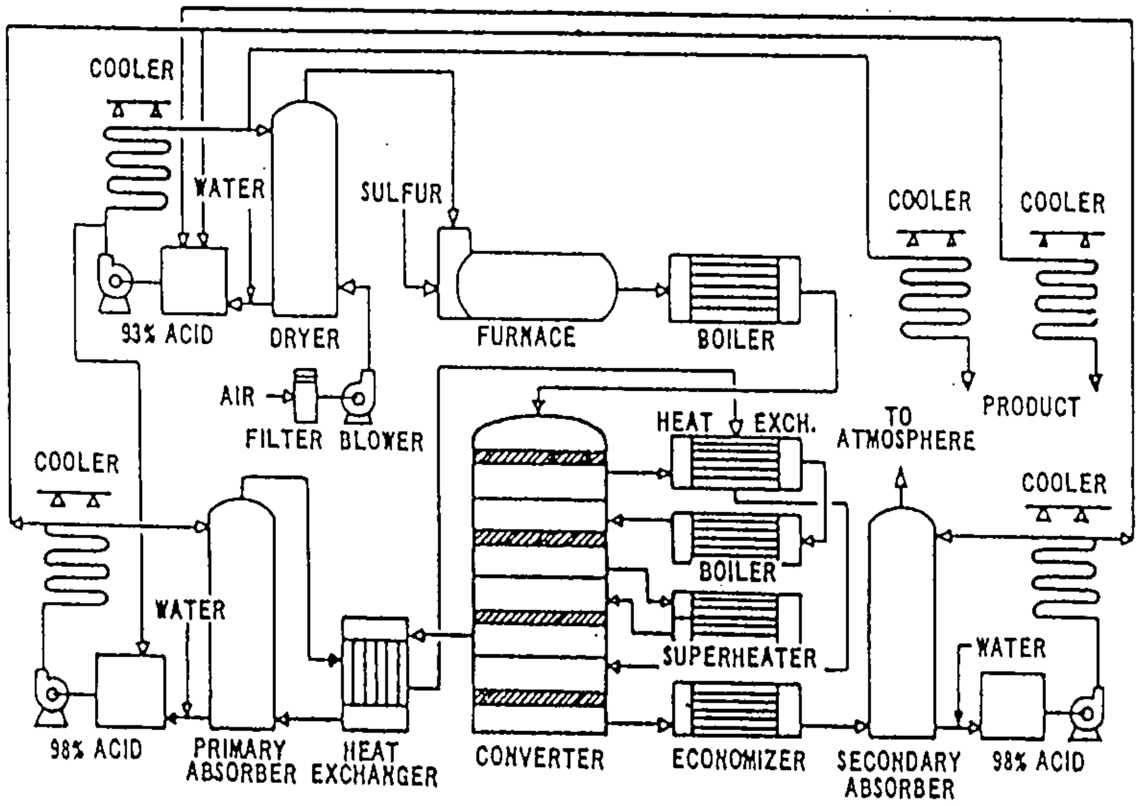

FIGURE 2-1
TYPICAL SULFURIC ACID
DOUBLE ABSORPTION PLANT
PROCESS FLOW DIAGRAM

$S + O_2 \rightarrow SO_2$ (BURNER)

$SO_2 + \frac{1}{2} O_2 \rightleftharpoons SO_3$ (CONVERTER)

$SO_3 + H_2O \rightarrow H_2SO_4$ (ABSORBER)

3.0 PROPOSED PROJECT

PPP proposes to repair and start up the existing sulfuric acid plant and molten sulfur system. Appendix A contains a detailed list of the proposed repair work.

The repair work will not affect the existing process in any way. Any equipment changes will be like-kind replacements, as previously explained to FDEP. As a result, there will be no change in material flows, production rate or emission rates from the existing plant.

The current FDEP air permit numbers for the sulfuric acid plant and the molten sulfur system are as follows:

UNIT	Air Permit No.	Expiration Date
SAP	A041-197112	07-05-96*
Molten Sulfur	A041-206854	02-07-97*

* Extended by Title V provisions.

3.1 AIR EMISSIONS

The sulfuric acid plant is expected to emit sulfur dioxide (SO_2), sulfuric acid mist (SAM) and nitrogen oxides (NOx). The molten sulfur system is expected to emit very small quantities of sulfur particulate (PM), reduced sulfur compounds like hydrogen sulfide (H_2S), volatile organic compounds (VOCs) and SO_2.

The air emissions from the sulfuric acid plant are inherently controlled by the double absorption process and mist eliminators. The air emissions from the molten sulfur system are minimized by work practices.

The emission limits for the sulfuric acid plant are based on the Federal New Source Performance Standards under 40 CFR 60, Subpart H, and the corresponding state rule, which limit SO_2 and SAM emissions to 4.0 and 0.15 pounds per ton of 100 percent sulfuric acid, respectively. Visible emissions are limited to 10 percent opacity.

Visible emissions from the molten sulfur system are limited under the state rule to 20 percent opacity. There are no mass emission standards for the molten sulfur system.

A summary of the permitted, actual and proposed operating characteristics of the sulfuric acid plant and the molten sulfur system is presented in Table 3-1. The emission changes as a result of the proposed project are presented in Table 3-2. As indicated in Table 3-2, there will be a significant net increase, as defined in Rule 62-212, FAC, in the emissions of SO_2, NOx and SAM.

There are fugitive emissions from process operations and vehicular traffic on paved roads at the facility, as acknowledged by existing FDEP permits. Changes in fugitive emissions as a result of the proposed project are expected to be negligible and do not affect the rule applicability for the project.

Emission calculations for the existing plant and molten sulfur system are provided in Appendix B.

3.2 RULE REVIEW

The following are the state and federal air regulatory requirements that apply to new or modified sources subject to a Prevention of Significant Deterioration (PSD) review.

In accordance with EPA and State of Florida PSD review requirements, all major new or modified sources of air pollutants regulated under the Clean Air Act (CAA) are subject to preconstruction review. Florida's State Implementation Plan (SIP), approved by the EPA, authorizes the Florida Department of Environmental Protection (FDEP) to manage the air pollution program in Florida.

The PSD review determines whether or not significant air quality deterioration will result from a new or modified facility. Federal PSD regulations are contained in 40CFR52.21, Prevention of Significant Deterioration of Air Quality. The State of Florida has adopted PSD regulations which are essentially identical to the federal regulations and are contained in Chapter 62-212 of the Florida Administration Code (FAC).

All new major facilities and major modifications to existing facilities are subject to control technology review, source impact analysis, air quality analysis and additional impact analyses for each pollutant subject to a PSD review. A facility must also comply with the Good Engineering Practice (GEP) stack height rule.

A major facility is defined in the PSD rules as any one of the 28 specific source categories (see Table 3-3) which has the potential to emit 100 tons per year (tpy) or more, or any other stationary facility which has the potential to emit 250 tpy or more, of any pollutant regulated under the Clean Air Act. A major modification is defined in the PSD rules as a change at an existing major facility which increases the actual emissions by greater than significant amounts (see Table 3-4).

3.2.1 Ambient Air Quality Standards

The EPA and the state of Florida have developed/adopted ambient air quality standards, AAQS (see Table 3-5). Primary AAQS protect the public health while the secondary AAQS protect the public welfare from adverse effects of air pollution. Areas of the country have been designated as attainment or nonattainment for specific pollutants. Areas not meeting the AAQS for a given pollutant are designated as nonattainment areas for that pollutant. Any new source or expansion of existing sources in or near these nonattainment areas are usually subject to more stringent air permitting requirements. Projects proposed in attainment areas are subject to air permit requirements which would ensure continued attainment status.

3.2.2 PSD Increments

In promulgating the CAA Amendments, Congress quantified concentration increases above an air quality baseline concentration levels for sulfur dioxide (SO_2) and particulate matter less than 10 microns (PM10) which would constitute significant deterioration. The size of the allowable increment depends on the classification of the area in which the source would be located or have an impact. Class I areas include specific national parks, wilderness areas and memorial parks. Class II areas are all areas not designated as Class I areas and Class III areas are industrial areas in which greater deterioration than Class II areas would be allowed. There are no designated Class III areas in Florida.

In 1988, EPA promulgated PSD regulations for nitrogen oxides (NOx) and PSD increments for nitrogen dioxide (NO_2) concentrations. FDEP adopted the NO_2 increments in July 1990 (see Table 3-6 for PSD increments).

In the PSD regulations, baseline concentration is defined as the ambient concentration level for a given pollutant which exists in the baseline area at the time of the applicable baseline date and includes the actual emissions representative of facilities in existence on the applicable baseline date, and the allowable emissions of major stationary facilities which commenced construction before January 6, 1975, but were not in operation by the applicable baseline date.

The emissions not included in the baseline concentration and, therefore, affecting PSD increment consumption are the actual emissions from any major stationary facility on which construction commenced after January 6, 1975, for SO_2 and PM10, and February 8, 1988, for NO_2 and the actual emission increases and decreases at any stationary facility occurring after the baseline date.

3.2.3 Control Technology Evaluation

The PSD control technology review requires that all applicable federal and state emission limiting standards be met and that Best Available Control Technology (BACT) be applied to the source. The BACT requirements are applicable to all regulated pollutants subject to a PSD review.

BACT is defined in Chapter 62-210, FAC as an emission limitation, including a visible emission standard, based on the maximum degree of reduction of each pollutant emitted which the Department, on a case-by-case basis, taking into account energy, environmental, and economic impacts, and other costs, determines is achievable through application of production processes and available methods, systems, and techniques (including fuel cleaning or treatment or innovative fuel combustion techniques) for control of such pollutant. If the Department determines that technological or economic limitations on the application of measurement methodology to a particular part of a source or facility would make the imposition of an emission standard infeasible, a design, equipment, work practice, operational standard or combination thereof, may be prescribed instead, to satisfy the requirement for the application of BACT. Such standard shall, to the degree possible, set forth the emissions reductions achievable by implementation of such design, equipment, work practice or operation. Each BACT determination shall include applicable test methods or shall provide for determining compliance with the standard(s) by means which achieve equivalent results.

The reason for evaluating the BACT is to minimize as much as possible the consumption of PSD increments and to allow future growth without significantly degrading air quality. The BACT review also analyzes if the most current control systems are incorporated in the design of a proposed facility. The BACT, as a minimum, has to comply with the applicable New Source Performance Standard for the source. The BACT analysis requires the evaluation of the available air pollution control methods including a cost-benefit analysis of the alternatives. The cost-benefit analysis includes consideration of materials, energy, and economic penalties associated with the control systems, as well as environmental benefits derived from the alternatives.

EPA recently determined that the bottom-up approach (starting at NSPS and working up to BACT) was not providing the level of BACT originally intended. As a result, in December 1987, EPA strongly suggested changes in the implementation of the PSD program including the "top-down" approach to BACT. The top-down approach requires an application to start with the most stringent control alternative, often Lowest Achievable Emission Rate (LAER), and justify its rejection or acceptance as BACT. Rejection of control alternatives may be based on technical or economical infeasibility, physical differences, locational differences, and environmental or energy impact differences when comparing a proposed project with a project previously subject to that BACT.

3.2.4 Air Quality Monitoring

An application for a PSD permit requires an analysis of ambient air quality in the area affected by the proposed facility or major modification. For a new major facility, the affected pollutants are those that the facility would potentially emit in significant amounts. For a major modification, the pollutants are those for which the net emissions increase exceeds the significant emission rate.

Ambient air monitoring for a period of up to one year, but no less than four months, is required. Existing ambient air data for a location in the vicinity of the proposed project is acceptable if the data meet FDEP quality assurance requirements. If not, additional data would need to be gathered. There are guidelines available for designing a PSD air monitoring network in EPA's "Ambient Monitoring Guidelines for Prevention of Significant Deterioration."

FDEP may exempt a proposed major stationary facility or major modification from the monitoring requirements with respect to a particular pollutant if the emissions increase of the pollutant from the facility or modification would cause air quality impacts less than the de minimis levels (see Table 3-4).

3.2.5 Ambient Impact Analysis

A source impact analysis is required for a proposed major source subject to PSD for each pollutant for which the increase in emissions exceeds the significant emission rate. Specific atmospheric dispersion models are required in performing the impact analysis. The analysis should demonstrate the project's compliance with AAQS and allowable PSD increments. The impact analysis for criteria pollutants may be limited to only the new or modified source if the net increase in impacts due to the new or modified source is below significant impact levels.

Typically, a five-year period is used for the evaluation of the highest, second-highest short-term concentrations for comparison to AAQS or PSD increments. The term "highest, second-highest" refers to the highest of the second-highest concentrations at all receptors. The second-highest concentration is considered because short-term AAQS specify that the standard should not be exceeded at any location more than once a year. If less than five years of meteorological data are used in the modeling analysis, the highest concentration at each receptor is normally used.

3.2.6 Additional Impact Analysis

The PSD rules also require analyses of the impairment to visibility and the impact on soils and vegetation that would occur as a result of the project. A visibility impairment analysis must be conducted for PSD Class I areas along with an air quality related values (AQRV) analysis. Impacts due to commercial, residential, industrial, and other growth associated with the source must be addressed.

3.2.7 Good Engineering Practice Stack Height

In accordance with Rule 62-210, FAC, the degree of emission limitation required for control of any pollutant should not be affected by a stack height that exceeds GEP, or any other dispersion technique. GEP stack height is defined as the highest of:

1. 65 meters (m), or
2. A height established by applying the formula:
   $Hg = H + 1.5 L$
   Where:
   Hg - GEP stack height,
   H - Height of the structure or nearby structure, and
   L - Lesser dimension, height or projected width of nearby structure(s)
3. A height demonstrated by a model or field study.

The GEP stack height regulations require that the stack height used in modeling for determining compliance with AAQS and PSD increments not exceed the GEP stack height. The actual stack height may be higher or lower.

3.3 RULE APPLICABILITY

The proposed repair project, to bring the sulfuric acid plant and molten sulfur storage & handling system back on-line, has been classified as a major modification to a major facility subject to both state and federal regulations as set forth in Chapter 62-212, FAC, by FDEP. PPP does not agree with this determination, but is submitting the permit application to expedite the startup of the plant.

The facility is located in an area classified as attainment for each of the regulated air pollutants.

The proposed repair activities to bring the sulfuric acid plant and molten storage & handling system back on-line will result in significant increases in SO_2, NOx and SAM emissions as defined by Rule 62-212, FAC, and will therefore be subject to PSD preconstruction review requirements. This will include a determination of Best Available Control Technology (BACT), an air quality review, Good Engineering Practice stack height analysis and an evaluation of impacts on soils, vegetation and visibility.

TABLE 3-1

CHANGES IN PRODUCTION AND EMISSION RATES

PINEY POINT PHOSPHATES, INC.
MANATEE COUNTY, FLORIDA

	Sulfuric Acid Plant	Molten Sulfur System
Permit Allowable Conditions : Based on Current Permits		
Rate (TPD)	2000	747
SO_2 (lb/hr)	333.3	NA
(TPY)	1460	NA
Mist (lb/hr)	12.5	NA
(TPY)	54.8	NA
Annual Operating Hours	8760	8760
Actual Conditions : Based on most recent 2-year data (FDEP files)		
Rate (TPD)	0	0
SO_2 (lb/hr)	0	0
(TPY)	0	0
Mist (lb/hr)	0	0
(TPY)	0	0
NOx (lb/hr)	0	0
(TPY)	0	0
Annual Operating Hours	0	0
Proposed Conditions		
Rate (TPD)	2000	747
SO_2 (lb/hr)	333.3	NA
(TPY)	1460	NA
Mist (lb/hr)	12.5	NA
(TPY)	54.8	NA
NOx (lb/hr)	10.0	NA
(TPY)	43.8	NA
Annual Operating Hours	8760	8760

NOTE: (1) The plant has not operated in the last two years.
(2) There are no mass emission limits for the sulfur system.

TABLE 3-2

NET EMISSION INCREASES (1)

PINEY POINT PHOSPHATES, INC.
MANATEE COUNTY, FLORIDA

Pollutant	Emissions (tons/yr) Sulfuric Acid Plant	Emissions (tons/yr) Molten Sulfur System
SO_2		
Present (actual)	0	0
Proposed	1460	1.2
Change	1460	1.2
Contemporaneous Changes	0	
Total Increase	1461.2	
Significant Increase (2)	40	
PSD Review ?	YES	
MIST		
Present (actual)	0	
Proposed	54.8	
Change	54.8	
Contemporaneous Changes	0	
Total Increase	54.8	
Significant Increase (2)	7	
PSD Review ?	YES	
NOx		
Present (actual)	0	
Proposed	43.8	
Change	43.8	
Contemporaneous Changes	0	
Total Increase	43.8	
Significant Increase (2)	40	
PSD Review ?	YES	

(1) See Appendix B for emission calculations.
(2) Significant levels are listed in Rule 62-212, FAC.

Regarding the NSPS for sulfuric acid mist, EPA concluded:

> "Making the acid mist standard more stringent is not believed to be practical at this time because of the need to provide a margin of safety due to in-plant operating fluctuations, which introduce variable quantities of moisture into the sulfuric acid production line."

There has been no change in EPA philosophy related to sulfuric acid plants since the 1985 review.

A review of BACT/LAER determinations published in the EPA Clearinghouse indicates that no new control alternatives have been applied to the double absorption sulfuric acid plants as of 1997 that would result in a consistent reduction in sulfur dioxide emission below 4.0 pounds per ton of acid nor would result in a consistent reduction of sulfuric acid mist emissions below 0.15 pounds per ton of acid. No control technologies for nitrogen oxides are discussed in either the NSPS review or in BACT/LAER determinations as there is typically no control of NOx from the double absorption sulfuric acid plants.

4.2 CONTROL TECHNOLOGIES

The control of sulfur dioxide and sulfuric acid mist emissions from sulfuric acid plants can be achieved by various processes. The process of choice for sulfur dioxide control has been double absorption and the process of choice for controlling sulfuric acid mist emission has been one of the various types of fiber mist eliminators. These processes have been selected based on cost, product recovery, the formation of no undesirable by-products and the fact that neither introduces operating processes that are foreign to plant personnel.

In EPA's review of NSPS for sulfuric acid plants in March 1985 (EPA-450/3-85-012), 46 sulfuric acid plants built between 1971 and 1985 were reviewed. Of these 46 plants, 40 used the double absorption process for sulfur dioxide control with the remaining six using some type of acid gas scrubbing. All 46 plants used the high efficiency mist eliminators for acid mist control. The control of nitrogen oxides in sulfuric acid plants has not been addressed to date because the low concentration of nitrogen oxides in the tail gases of sulfuric acid plants (10-20 parts per million) does not lend itself to cost effective controls.

Also in the 1985 EPA review, several potential control technologies that had been used to control sulfur dioxide and sulfuric acid mist emissions from sulfuric acid plants were addressed. The alternatives included the double absorption process, ammonia scrubbing, sodium sulfite-bisulfite scrubbing, and molecular sieves for sulfur dioxide control and filter type mist eliminators and electrostatic precipitators for sulfuric acid mist control. A review of the EPA BACT/LAER Clearinghouse information indicated that no other control alternatives have been considered for sulfuric acid plants prior to or since the 1985 NSPS review and no emission limits have been set that are more stringent than 4.0 pounds per hour for sulfur dioxide and 0.15 pounds per ton for acid mist. No control alternatives were addressed for nitrogen oxides control in either the 1985 EPA NSPS review or in the BACT/LAER Clearinghouse covering determinations made since the 1985 EPA review.

4.2.1 Sulfur Dioxide Control

The control alternatives for sulfur dioxide have been summarized based upon information compiled by EPA in the 1985 NSPS review for sulfuric acid plants, information recently submitted to FDEP by companies with similar sulfuric acid plants during review of production increase requests (refer to PSD-FL-225, 229, 235 and 238) and on data developed specifically for PPP.

4.2.1.1 Double Absorption Process Including Frequency of Turnaround

The second absorber tower on double absorption sulfuric acid plants is sulfur dioxide control technology. The second absorption tower adds about 20 percent to the cost of a plant and it increases operating costs by reducing the amount of high pressure steam that can be recovered and by increasing the pressure drop across the plant. The second absorption stage, in reducing sulfur dioxide emissions, results in the recovery of about 25-26 pounds of sulfur dioxide per ton of acid produced. This sulfur dioxide is converted to sulfuric acid, resulting in about a two percent increase in acid production. The cost of this additional acid is about $69 per ton compared with a current market price for sulfuric acid of about $35 per ton. From the analysis, it is quite apparent that the second absorption stage is added for sulfur dioxide control, not increased acid production.

As a sulfur dioxide control system, the double absorption process has become the system of choice within the sulfuric acid industry since the promulgation of NSPS in 1971. Of the 46 new sulfuric acid plants constructed between 1971 and 1985, 40 employed this process for sulfur dioxide control. Several single absorption plants have also been converted to double absorption plants in order to comply with sulfur dioxide emission standards. The PPP plant, for example, was built as a single absorption plant and was converted to a double absorption plant in about 1975.

The double absorption process offers the following advantages over other SO_2 control technologies:

1. 99.7 percent of the sulfur is converted to sulfuric acid compared with about 97.7 percent conversion with a single absorption plant;
2. there are no by-products produced;
3. there are no new operating processes that plant personnel must become familiar with;
4. the process permits higher inlet sulfur dioxide concentrations resulting in a reduction in equipment size;
5. there is no reduction in overall plant operating time or efficiency; and
6. there is no increase in manpower requirements.

The double absorption plant is capable of operating at a sulfur dioxide emission rate of 4.0 pounds per ton of acid or less as required by New Source Performance Standards (NSPS). However, in an effort to optimize plant performance, most plants in the fertilizer industry tend to run at sulfur dioxide emission levels close to the permitted rate.

It should be noted that when EPA adopted the NSPS for sulfuric acid plants in 1971, it was recognized that double absorption plants could operate with a sulfur dioxide emission rate in the range of 2-4 pounds per ton of acid. The sulfur dioxide emission limit, however, was set at 4.0 pounds per ton of acid to account for fluctuations that invariably occur in operating plants.

Since the adoption of the NSPS, there have been design and operating changes in sulfur burning sulfuric acid plants as well as changes and improvements in catalyst technology. At the time the NSPS were adopted, the SO_2 concentration in the gas stream leaving the sulfur burner was in the range of 9.0-9.5 percent. In recent years, changes in plant design have increased the sulfur dioxide concentration at the burner exit to 11.5-11.7 percent (see Appendix C).

It should be noted that sulfuric acid plants operating in conjunction with smelters or spent acid regeneration plants still operate with a feed gas sulfur dioxide concentration in the range of 7-9 percent. Because of this difference in the concentration of sulfur dioxide in the feed gas, it is not possible to compare the performance of a sulfur burning sulfuric acid plant as operated in Florida with a sulfuric acid plant operating at a smelter or a spent acid recovery plant. If the PPP sulfuric acid plant were to operate with a sulfur dioxide strength in the range of 7-9%, so as to be comparable to a plant operating at a smelter, the acid production rate would have to be reduced to less than 1400 tons per day.

The second improvement in sulfuric acid plant technology has been in catalyst performance. Changes have occurred in the composition of the vanadium/sodium/potassium catalyst and in the physical shape of the catalyst; from a pellet (4 and 6 millimeters in diameter by 8-15 millimeters long) to a ring-type structure (see Appendix C). The change in the composition of the catalyst plus the change in the catalyst shape has resulted in a catalyst with a higher activity and a much lower pressure drop. These changes coupled with the increase in the sulfur dioxide concentration of the feed gas have allowed sulfur burning sulfuric acid plants to operate much more efficiently and still operate in compliance with the NSPS limit for sulfur dioxide of 4.0 pounds per ton of acid.

As in 1971, plants can still operate with sulfur dioxide emissions somewhat below 4.0 pounds per ton of acid but fluctuations do occur which result in sulfur dioxide emissions that approach the NSPS limit. It was the intent of EPA when the NSPS limits were adopted in 1971 and reviewed in 1985 that the sulfur dioxide emission limit should be set with a margin of safety that will allow for these slight fluctuations in plant operation without the occurrence of a reportable violation.

Another factor that determines the sulfur dioxide emission rate from a double absorption sulfur burning sulfuric acid plant is the specific design of the plant. If maximum sulfuric acid production is the motive of the operator, as will be the case with PPP, the blower of the sulfuric acid plant will be set to operate at the maximum sustainable rate. The sulfur feed rate to the sulfur burner will then be increased until either the sulfuric acid production rate limited by permit is reached or the sulfur dioxide emission rate limited by permit is reached. Data are presented in Appendix D to illustrate the relationship between sulfur dioxide emissions and acid production at one plant.

With the sulfur dioxide emission rate set at or near the emission limit of 4.0 pounds per ton of acid, the plant will operate at a production rate that is maximum for the plant immediately after a turnaround (catalyst screening and partial replacement plus other necessary repairs). As the plant continues to operate, the pressure drop across the catalyst builds; effectively reducing the output of the blower. As this happens and as sulfur dioxide emissions are already at the limits established by NSPS, the sulfur feed rate to the plant has to be cut back resulting in a reduction in sulfuric acid production. The pressure drop across the plant continues to build and the sulfuric acid production rate continues to decline until the loss in production can no longer be tolerated. At this point, the plant is shutdown for a turnaround including catalyst screening and partial replacement and other necessary preventive maintenance to the plant. Typically, the time between turnarounds in double absorption sulfur burning sulfuric acid plants in Florida is in the range of 18-24 months.

Suggestions have been made that if the time between turnarounds is reduced to approximately nine months, the activity of the catalyst will be upgraded more frequently resulting in lower sulfur dioxide emissions. While catalyst activity will be improved as a result of screening and partial replacement, the plant production rate will also be increased. The primary factor driving the plant turnaround schedule is the pressure drop across the plant and more specifically, the sulfuric acid production rate of the plant. In many cases, sulfur dioxide emissions are not significantly reduced during the period of time immediately following a turnaround. Sulfur dioxide emission data and sulfuric acid production data presented both as Figure 4-1 and in Appendix D illustrate this point.

These data show (see Figure 4-1 and Appendix D) that immediately after turnaround the sulfur dioxide emissions are in the range of 3.25 pounds per ton of acid produced and approach 4.0 pounds per ton of acid (daily average) within approximately two months after turnaround. At the same time, it will be noted that immediately following turnaround the production rate is about 1650 tons per day. The production rate drops off at more or less a uniform rate until it reaches a rate in the range of 1400 tons per day prior to the next turnaround.

The effect of increasing the frequency of sulfuric acid plant turnaround at PPP from once every 18 months to once every nine months is forecasted in Appendix D. These data show that total sulfur dioxide emissions over an 18-month period with a turnaround once every 18 months will be in the range of 1566 tons (per 18-month period). With a turnaround once every nine months, the total sulfur dioxide emissions over a similar 18-month period (two successive 9-month periods) will be 1528 tons. The reduction is about 38 tons over an 18-month period, or about 25 tons per year.

Associated with the slight reduction in sulfur dioxide emissions is the cost of the interim turnaround (the 9-month turnaround). This cost is in the range of $600,000 (Table 4-1). The downtime with such a turnaround will be between 7-10 days. For purposes of this analysis, a downtime of 8.5 days was selected. The cost associated with catalyst replacement and disposal, catalyst screening, supplies, contract labor and payroll were developed from data provided by PPP. The steam cost and water treatment cost are the costs associated with operating an auxiliary boiler to provide steam to run the remainder of the PPP fertilizer complex normally provided by the sulfuric acid plant. The sulfuric acid cost is for the sulfuric acid that PPP would have to purchase to continue operating the phosphoric acid plant and granular fertilizer plant during the 8.5 day shutdown. The cost used is the differential cost between what PPP would pay for sulfuric acid on the open market if the acid was available and the cost of production. It should be noted that at the present time, it is very difficult to purchase sulfuric acid in Florida. The fuel cost for reheating is the fuel necessary to reheat the sulfuric acid plant during startup and the sulfur and sulfuric acid lost are quantities of these materials wasted as a result of the shutdown.

In summary, an extra turnaround of the PPP sulfuric acid plant during the ninth month of a normal 18-month turnaround cycle will cost approximately $600,000 and will result in a decrease in sulfur dioxide emissions of approximately 25 tons per year. The cost of sulfur dioxide control is $25,972 per ton. More frequent catalyst changes are therefore rejected from BACT consideration.

4.2.1.2 Addition of Another Catalyst Bed to a Double Absorption Sulfuric Acid Plant

Most double absorption sulfur burning sulfuric acid plants consist of a sulfur burner, three catalyst beds to convert SO_2 to SO_3, an intermediate absorption tower, a fourth catalyst bed, a final absorption tower, acid mist control and a heat recovery system. These plants are referred to as 3 by 1 (three catalyst beds followed by one catalyst bed) plants. The predominance of this type of plant is dictated by the fact that this arrangement has been determined to be the most cost effective design. The PPP sulfuric acid plant is a 4 by 1 plant as a result of the initial design and subsequent modifications that were made in about 1975.

The conversion of sulfur dioxide produced in the sulfur burner to sulfur trioxide in the catalyst bed and the subsequent absorption of the sulfur trioxide determines the conversion efficiency of a plant (conversion of sulfur to sulfuric acid). As the only release of unconverted sulfur is sulfur dioxide (and a small amount of acid mist) in the stack gas, the conversion efficiency also determines the emissions from the plant.

The conversion from sulfur dioxide to sulfur trioxide is a complex reaction (Appendix C). The equilibrium concentrations of this reaction are determined in part by temperature, the oxygen:sulfur dioxide ratio and the sulfur trioxide concentration. The approach to this equilibrium is a function of temperature, reaction time and the activity of the catalyst.

Lower temperatures promote a higher conversion of sulfur dioxide to sulfur trioxide; however, lower temperatures reduce the reaction rate. Increasing the contact time to compensate for a reduced reaction rate at lower temperatures requires more catalyst (greater contact time). The overall conversion process is a complex balance between these and possibly other factors in a temperature range between approximately 770°F and 1150°F and in a time period of approximately 1.5 seconds.

The lower temperature limit is determined by the activation temperature of the catalyst. Conventional catalysts have a minimum activation temperature of approximately 770°F (a practical operating minimum of 790°F). The upper temperature limit of the catalyst is about 1150°F.

In a typical double absorption plant (a 3 by 1 plant), approximately 90-94 percent of the sulfur dioxide is converted to sulfur trioxide in the first three catalyst beds. The gas stream then passes through an intermediate absorption tower where the sulfur trioxide is absorbed resulting in a shift in the equilibrium curve favoring further conversion of sulfur dioxide to sulfur trioxide. In the fourth catalyst bed, conversion from 90-94 percent to the final overall conversion of 99.7 percent occurs. This overall conversion results in a sulfur dioxide emission rate of 4.0 pounds per ton of acid produced.

The addition of one or more catalyst beds following the final bed (without the addition of a third absorption tower) will theoretically result in a fractional increase in conversion efficiency. The increase is limited by the slope of the equilibrium curve as 100 percent conversion is approached (see Appendix C) and by the fact that the temperature required to reach the higher conversion approaches the lower activation limits of the catalyst.

In practice, however, it has been observed that there is no measurable improvement in conversion between a 3 by 1 plant and a 3 by 2 plant (The same would apply between a 4 by 1 plant and a 4 by 2 plant). The cost to add an additional catalyst bed to an existing 2000 ton per day sulfuric acid plant is estimated to be in the range $1.5-2.0 million. Operational costs will also increase because of the increased pressure drop across the plant and maintenance costs will increase. This expenditure might theoretically result in an additional 10 to 15 percent conversion (from 99.7 to 99.73 or 99.75 percent) but in practice will result in no observable conversion increase. The cost estimated to add a third absorption tower followed by an additional catalyst bed is in the range of $6.6 million. It is for these reasons that the addition of more catalyst beds to double absorption plants has been determined to be impractical.

4.2.1.3 Ammonia Scrubbing

Five sulfuric acid plants constructed between 1971 and 1985 use ammonia scrubbing for sulfur dioxide control. None of these plants were double absorption plants. The process can be effective for reducing sulfur dioxide emissions to below 4.0 pounds per ton and also for controlling sulfuric acid mist emissions. The major disadvantages of ammonia scrubbing are:

1. a waste by-product is produced;
2. the scrubbing system is a high maintenance item and requires additional manpower for operation; and
3. no sulfuric acid production increase benefits are achieved with the scrubbing system; and
4. the environmental liabilities of introducing a potential Hazardous Air Pollutant release point at another location in the plant.

Ammonia scrubbing uses anhydrous ammonia and water in a scrubbing system to convert sulfur dioxide to ammonium sulfite/bisulfite and eventually to ammonium sulfate. The ammonium sulfate can be crystallized and sold as a market commodity, it can be blended back into the fertilizer plant or it can be disposed of as a waste. One plant that operates ammonia scrubbers on sulfuric acid plants had an ammonium sulfate crystallizer but abandoned it because of the volatility of the market.

There are several factors that must be considered when determining whether or not ammonium sulfate can be blended back into a fertilizer plant; particularly back into an existing plant. The ammonium sulfate would be added back as about a 20% solution. The options for adding it back include adding it to the attack tank of the phosphoric acid plant or, in the case of PPP, adding it to the reactor of the DAP plant.

Adding the ammonium sulfate solution to the phosphoric plant has three major drawbacks. First, the additional sulfate affects the sulfate balance in the reaction between the sulfuric acid and phosphate rock creating problems with the gypsum crystal growth; the heart of phosphoric acid production. Secondly, and related to gypsum crystal formation, the added sulfate will affect the filterability of the phosphoric acid resulting in a greater P_2O_5 loss. The third major drawback is that the water added along with the ammonium sulfate will increase the load on the evaporators of the phosphoric acid plant. In an existing plant, the added load on the evaporators will result in a reduction in phosphoric acid production.

When added to the DAP plant, the ammonium sulfate solution has other drawbacks. First, the addition water in the ammonium sulfate solution will add to the evaporative load of the DAP dryer; resulting in greater fuel use and the associated emission increases. Secondly, the additional sulfate interferes with the granulation process making an acceptable grade of granulative product more difficult to produce. Thirdly, and perhaps most critical, the additional sulfate will "dilute" the nitrogen and P_2O_5 contents of DAP. DAP typically has a nitrogen content of 18% and a P_2O_5 content of 46%. This grade is necessary for the product to be competitive on the international market. The added sulfate will reduce the nitrogen and P_2O_5 contents resulting in a product that may not be marketable.

PPP has determined that with all factors considered, the ammonium sulfate scrubbing liquor cannot be incorporated into the DAP plant. Thus, at PPP, the ammonium sulfate must be considered a waste and counted as a cost in the ammonia scrubbing cost analysis.

The cost of an ammonia scrubber on the existing PPP sulfuric acid plant was based on a sulfuric acid production rate of 2000 tons per day and the reduction of sulfur dioxide emissions to 2.0 pounds per ton of acid. The cost of an ammonia scrubber was estimated to be $3.5 million. This cost and other cost factors are summarized in Table 4-2. The total annual cost for recovering capital and operating an ammonia scrubber is approximately $2.23 million. The sulfur dioxide emission reduction (from 4.0 to 2.0 pounds per ton of acid) will be approximately 730 tons per year. The cost of sulfur dioxide removal will be approximately $3,053 per ton. This cost, coupled with the reduced reliability factor that will be introduced by the add-on scrubber system, makes ammonia scrubbing not cost effective as BACT.

It should also be noted that ammonia scrubbers have not been added to any double absorption sulfuric acid plant in Florida nor to any double absorption sulfuric acid plant anywhere as far as could be determined.

This fact confirms the conclusion reached herein regarding the cost effectiveness of ammonia scrubbers as add-on control for double absorption plants.

4.2.1.4 Other Scrubbing Technologies

Between 1971 and 1985, two sulfuric acid plants were constructed employing sodium sulfite-bisulfite scrubbing to control sulfur dioxide emissions. One of the plants was subsequently converted to ammonia scrubbing and the second plant has never been used. As a result, sodium sulfite-bisulfite scrubbing is not considered a demonstrated sulfur dioxide control alternative.

Other scrubbing liquors that have a potential for reducing sulfur dioxide emissions include caustic, sodium carbonate, calcium oxide and hydrogen peroxide. Without going through a detailed cost analysis to evaluate these scrubbing technologies, it can be stated that the capital investment cost and many of the direct and indirect annual costs will be very similar to the costs incurred with ammonia scrubbing (Table 4-2). Because of higher chemical costs and/or waste disposal costs, these other technologies are expected to be more costly than ammonia scrubbing. For this reason, these technologies would not be considered the scrubbing technology choice.

4.2.1.5 Molecular Sieves

A molecular sieve was installed at one sulfuric acid plant in Florida for sulfur dioxide control. The system was effective for controlling sulfur dioxide; however, extensive operating problems were experienced as the molecular sieve also absorbed nitrogen oxides. The regeneration of sieves resulted in the formation of nitric acid within the sulfuric acid plant. The nitric acid/sulfuric acid mixture resulted in severe corrosion problems which caused the molecular sieve system to be abandoned. As a result, molecular sieves are not considered a viable alternative for sulfur dioxide control in sulfuric acid plants.

4.2.1.6 Catalyst Selection

The two papers in Appendix C reference changes in catalyst composition and shape that have occurred since NSPS for sulfuric acid plants were adopted in the early 1970s. The first major change was a change in catalyst shape. The catalyst went from pellets that were 4.0 millimeters and 6.0 millimeters in diameter by 8-15 millimeters long to a ring-type catalyst. The major effect of this shape change was to reduce the pressure drop through the sulfuric plants both initially and over time. The results of this improvement were to extend the time between plant turnarounds from approximately nine months to 18 months or more and to reduce blower operating costs.

A change in catalyst composition, beyond changes in the vanadium content of the catalyst, has been the reintroduction of the "cesium catalyst". The cesium catalyst is a 6-8 percent vanadium catalyst with a portion of the potassium promoter replaced by cesium. The introduction of cesium reduces the activation temperature of the catalyst by approximately 20°F (from about 770°F to 750°F). At temperatures above approximately 770°F, the performance of the cesium catalyst and the conventional catalyst are about the same.

The advantage of the cesium catalyst is that it allows the startup of a sulfuric acid plant at a lower entrance gas temperature. This is a distinct advantage for sulfuric acid plants operating at smelters and spent acid recovery plants where there are frequent plant startups and shutdowns. In sulfuric acid plants that are operating at a steady-state, the potential advantage of using a cesium catalyst is that the temperature (normally of the last catalyst bed) can be reduced about 20°F.

The shift to a lower temperature also has a disadvantage; i.e.,reducing the reaction rate which slows the approach to equilibrium. In existing plants, physical constraints limit the amount of catalyst that can be used, thus limiting how much the contact (reaction) time can be increased to offset the reduced reaction rate. The reduction in reaction rate therefore could offset the more favorable conversion resulting in no appreciable overall improvement in plant conversion efficiency.

Cesium catalyst has not been used in any sulfur burning double absorption plant in the U.S. as far as could be determined. The Monsanto paper in Appendix C cites five examples of the utilization of cesium catalyst; two in double absorption spent acid plants, one in a single absorption spent acid plant and two in single absorption sulfur burning plants. Four of the five plants were operating with feed gas sulfur dioxide concentrations in the range of 7-9 percent (compared with 11.5-11.75 percent in Florida plants). Performance data from these plants therefore cannot be extrapolated to Florida plants. The fifth example was a double absorption spent acid plant with a "12 percent SO_2 gas strength." The paper says nothing about the oxygen:sulfur ratio of this plant and further says nothing about sulfur dioxide emissions other than they were "low".

It was also pointed out (Appendix C) that cesium catalyst has rarely been used in sulfur burning plants but that it has some advantages in spent acid and metallurgical sulfuric acid plants. The advantages are related to plant startup at lower gas temperatures. Both papers in Appendix C discuss potential problems with pressure buildup when using cesium catalyst and the Monsanto paper discusses the compatibility of the heat exchange systems in existing plants with cesium catalyst. Another disadvantage of the cesium catalyst is that the cesium catalyst cost is 2.5-3.0 times the cost of conventional catalyst.

Although cesium catalyst has the potential for reducing sulfur dioxide emissions, the results have not been demonstrated in sulfur burning double absorption plants as operated in Florida. The potential improvement in conversion efficiency is the result of operating a catalyst bed at a lower temperature. This shift in temperature also has the effect of reducing the sulfur dioxide to sulfur trioxide reaction rate. In existing plants where plant geometry is fixed, the amount of catalyst that can be used (and hence, the contact time or reaction time) is fixed. As a result, the approach to equilibrium is rate limited.

Thus, the improved conversion efficiency must be balanced against the reduced reaction rate and the heat exchange capacity of existing plants. Other unknowns or disadvantages of using cesium catalyst in sulfur burning double absorption plants include the potential for pressure drop buildup which will increase plant turnaround frequency and the costs associated therewith, and the premium costs of cesium catalysts.

As a result of weighing the potential advantage of cesium catalyst (improved performance as a result of operating at a lower temperature and not the result of a higher catalyst activity) against the potential disadvantages of the catalyst (slower reaction rate, potential for pressure drop buildup, heat exchange compatibility and cost), cesium catalyst has not been used in sulfur burning double absorption plants and hence, is not a demonstrated technology.

4.2.1.7 Monsanto Heat Recovery System

The Monsanto Heat Recovery System (HRS) is not a sulfur dioxide control option. It was developed, as the name implies, to improve heat recovery in sulfuric acid plants. The system is mentioned here only to clarify this point.

The HRS is described in Appendix E. Although the paper addresses reduced sulfur dioxide emissions from the plant where the heat recovery system (HRS) was installed, the primary focus of the paper was on the more efficient recovery of the heat generated in sulfuric acid plants.

The plant on which the HRS was installed was a single absorption 1350 ton per day sulfuric acid plant with a feed gas SO_2 concentration of 7.8 percent. The sulfur dioxide to sulfur trioxide conversion prior to the installation of the HRS was 97.7 percent; a conversion typical of single absorption sulfuric acid plants. It was guaranteed that following the installation of the HRS, the plant could operate with an 8.3 percent sulfur dioxide feed gas, the acid production of the plant would remain at 1350 tons per day and the sulfur dioxide to sulfur trioxide conversion would increase to 99.6 percent.

In actuality, the HRS converted the single absorption plant to a double absorption plant by introducing an intermediate absorption tower followed by a fourth catalyst bed. The actual production of the plant increased to 1430-1440 tons per day and the sulfur dioxide to sulfur trioxide conversion improved to 99.85-99.90 percent. Neither the increased production nor the conversion efficiency is surprising. The production increase resulted from the improvement in conversion and from the planned increase in the SO_2 concentration of the feed gas stream from 7.8 percent to 8.3 percent.[1] The higher than guaranteed conversion efficiency is strictly a function of the effect of the high oxygen:sulfur dioxide ratio on the sulfur dioxide:sulfur trioxide conversion equilibrium.

4.2.2 Sulfuric Acid Mist Control

Control alternatives that were reviewed by EPA in the 1985 New Source Performance Standards review are summarized in the following sections.

4.2.2.1 Fiber Mist Eliminators

The 46 new sulfuric acid plants constructed between 1971 and 1985, all used the fiber-type mist eliminators for sulfuric acid mist control. Operations demonstrated that these types of mist eliminators can control sulfuric acid mist emissions to 0.15 pounds per ton of sulfuric acid or less.

The mist eliminators are the choice of control for sulfuric acid mist within the sulfuric acid industry because they require very little operation and maintenance attention and because of the small space requirement associated with these devices. The disadvantage of this type of mist eliminator is that the pressure drop across the elements varies

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[1] <u>Note</u>: Pre-conversion production of 1350 tpd x (8.3/7.8), ratio of pre- and post-conversion SO_2 feed concentrations x (99.85/97.7), ratio of conversion efficiencies = Expected post-conversion production; 1468 tpd.

from five to 15 inches of water; resulting in an increase in operating utility costs.

4.2.2.2 Electrostatic Precipitators

Electrostatic precipitators (ESPs) have the potential for controlling sulfuric acid mist emissions from sulfuric acid plants; however, there is no demonstrated application of ESPs. The disadvantages associated with ESPs and hence, the reason they have not been used, include the initial cost, size requirements, operating and maintenance requirements and the potential for corrosion.

4.2.3 Nitrogen Oxides Control

The combustion of sulfur in a sulfur burning sulfuric acid plant is a relatively low temperature process at oxygen levels that are, out of necessity, relatively high. The gas temperature exiting a sulfur furnace is in the range of 2000°F with an oxygen concentration in the range of 9.2 percent. If the oxygen concentration is decreased (and the sulfur dioxide concentration correspondingly increased), the catalyst in sulfuric acid plants becomes ineffective and sulfur dioxide to sulfur trioxide conversion efficiency drops off markedly. The temperature of the exit gas is strictly a function of the heat of combustion of sulfur at the air flow rate necessary to provide approximately 9.2 percent oxygen and 11.7 percent sulfur dioxide in the furnace exit gas.

Compared to a fossil fuel fired combustion source, the temperature of a sulfur furnace is generally lower and the oxygen content of the combustion gas is generally higher. As a result of the relatively low combustion temperature, the nitrogen oxides concentration in the gas stream leaving the sulfur furnace is inherently quite low; in the range of 20 parts per million (v/v). This compares with NOx concentrations of several hundred parts per million in stack gases from typical fossil fuel combustion sources. As a result, there has historically not been any emphasis placed on controlling NOx emissions from the sulfuric acid plants. For purposes of this analysis, control technologies for NOx will be briefly reviewed as they might apply to sulfur burning sulfuric acid plants.

Flue gas recirculation and low-NOx burners are not applicable. Flue gas recirculation would not be practical as reducing oxygen levels below 9.2 percent will be counterproductive as previously discussed. The low-NOx burner is not applicable for the reason that combustion temperatures are already relatively low and further refinements to the combustion process will not be productive in further reducing the NOx concentration in the furnace exit gas. Furthermore, low-NOx burners for sulfur furnaces do not exist.

Add-on control devices include selective catalytic and non-catalytic NOx reduction. Both involve the introduction of ammonia to the stack gas. If introduced, the ammonia would first react with any sulfuric acid mist that is present, producing an ammonium sulfite/bisulfite/sulfate aerosol. These aerosols will plug the mist eliminator normally used in sulfuric acid plants if the NOx control system is installed prior to the mist eliminator. If installed after the mist eliminator, the aerosols will be extremely difficult to remove from the gas stream and will result in a very visible plume from the sulfuric acid plant.

Another consideration related to the use of catalytic and non-catalytic NOx reduction is the operating temperatures of the systems. The catalytic reduction system requires a temperature in the range of 600-750°F while the non-catalytic reduction system requires a temperature between 1500-2200°F. The temperature of the gas stream exiting a sulfuric acid plant is normally in the range of 170°F. The energy to heat the gas stream to a temperature range of even 600-750°F would be about 50 MMBtu per hour. The NOx generated by the production of this heat (by fossil fuel combustion) would be about 7.5 pounds per hour. This compares to a total NOx emission rate from the PPP sulfuric acid plant of 10.0 pounds per hour.

This brief analysis of NOX control alternatives demonstrates that none are applicable to sulfur burning sulfuric acid plants.

4.3 BACT CONCLUSION

All recent FDEP and EPA BACT determinations for sulfur burning double absorption sulfuric acid plants have concluded that the double absorption process for sulfur dioxide control and the fiber mist eliminators for sulfuric acid mist control represent BACT. No control has been imposed for NOx emissions. These determinations were based on case-by-case analyses taking into account environmental, energy and economic impacts, the degree of emission reduction and the demonstrated availability of the control technology. The BACT determinations placed no restrictions on plant operating practices nor were they specific regarding component parts of the plant.

The BACT review conducted for PPP has reviewed the basic double absorption system, modifications to this system, changes in normal sulfuric acid plant operating practices, changes in catalyst type and various add-on control systems for sulfur dioxide control. For sulfuric acid mist control, the PPP BACT analysis included the fiber-type high efficiency mist eliminators and electrostatic precipitators. For NOx control, the analysis included sulfur furnace modifications and add-on control systems.

From the results of this BACT analysis, it can be concluded that for sulfur dioxide:

1. Increasing the frequency of plant turnarounds for catalyst screening and partial replacement could result in a slight decrease in sulfur dioxide emissions. The cost of sulfur dioxide control with this alternative however is in the range of $26,000 per ton (Table 4-1).

2. The addition of catalyst beds to a double absorption sulfuric acid plant theoretically could slightly reduce emissions but practically will have no measurable effect on emissions. The capital cost of one additional catalyst bed is in the range of $1.5-2.0 million. The operating and maintenance costs will also be increased.

3. The use of an add-on ammonia scrubber to control emissions from a double absorption sulfuric acid plant could be effective. The cost of sulfur dioxide control using an ammonia scrubber is in the range of $3,100 per ton (Table 4-2). In addition to this cost, the operating factor of a sulfuric acid plant will be reduced because of the additional downtime associated with the ammonia scrubber.

4. Other scrubbing technologies will have the same approximate capital and operating costs as an ammonia scrubber. However, chemical and/or waste disposal costs will be higher. As a result, other scrubbing technologies were excluded for further consideration.

5. Molecular sieves are not a control alternative because of severe corrosion problems inherent to these systems.

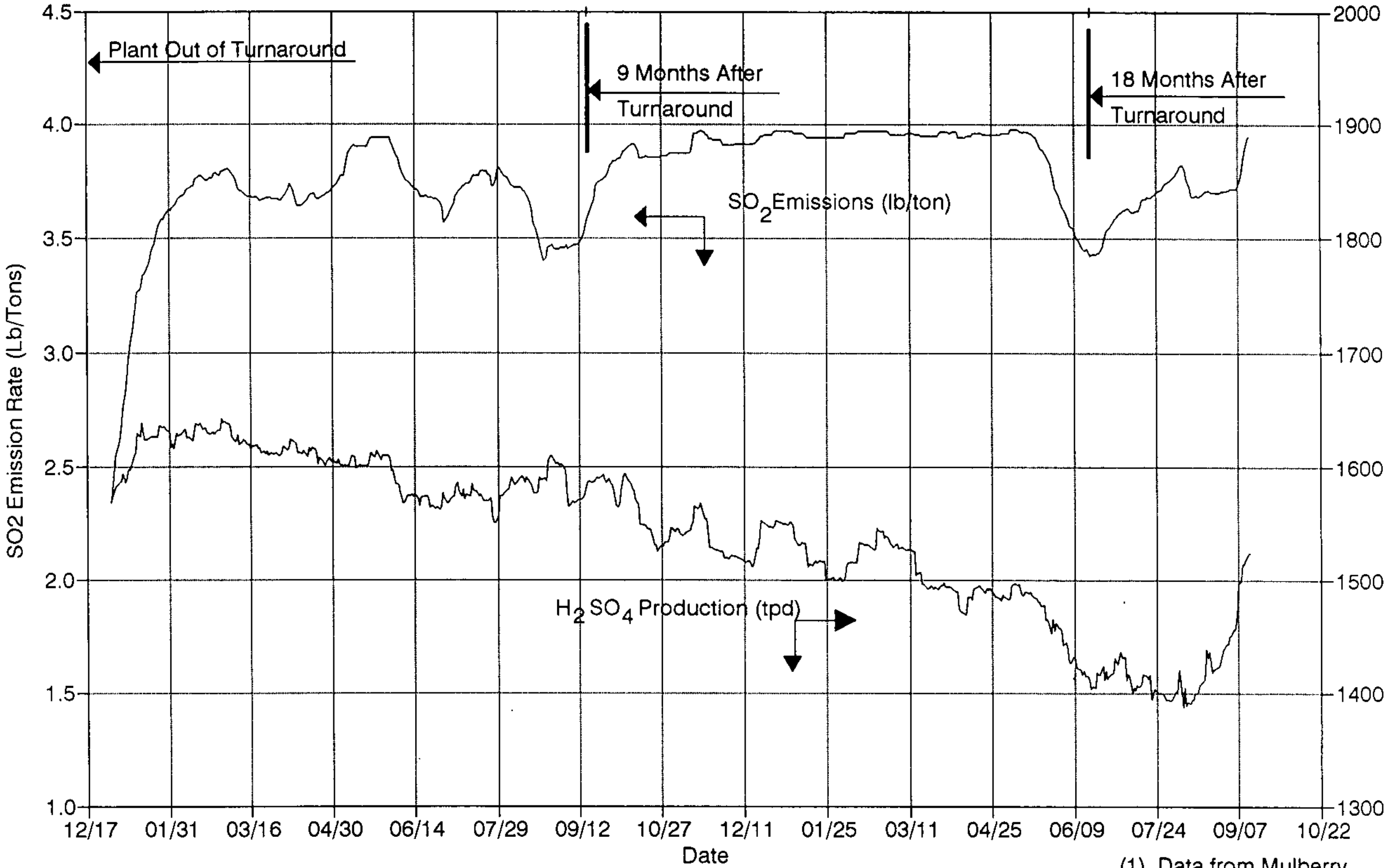
6. The use of a cesium catalyst is not demonstrated technology when applied to sulfur burning double absorption sulfuric acid plants as operated in Florida. There are potential advantages and potential disadvantages to the use of cesium catalyst in sulfur burning double absorption plants. The net effect of the advantages and disadvantages could be that there is no reduction in sulfur dioxide emissions. The technology is not proven.

7. The Monsanto Heat Recovery System (HRS) is a heat recovery system; not a sulfur dioxide control system. Sulfur dioxide emissions might be reduced by the HRS; but as the result of another absorption tower and another catalyst bed that are integral parts of the HRS.

For sulfuric acid mist control, this analysis considered fiber mist eliminators and electrostatic precipitators. Mist eliminators were determined to be the choice of control for sulfuric acid mist throughout the industry.

The review of control technologies for NOx emissions demonstrated that sulfur furnace modifications were not applicable for reducing the NOx generated during the sulfur combustion process. The analysis also demonstrated that selective catalytic and non-catalytic reduction for NOx control was not feasible for sulfuric acid plants because of temperature incompatibilities.

Considering all of these factors, PPP will continue to use the double absorption system for sulfur dioxide control with no restrictions on operating practices or on catalyst type. For sulfuric acid mist control, PPP will continue to use fiber mist eliminators and for NOx emissions, no control is proposed. This determination is based on a top-down BACT analysis and the conclusions are consistent with the 1985 EPA NSPS review for sulfuric acid plants and with BACT determinations that have been made since that time; both in Florida and elsewhere in the U.S.



(1) Data from Mulberry Phosphates, Inc Mulberry, Florida

Figure 4-1
Sulfur Dioxide Emission Rate (lb/ton of acid) and Production Rate (tons/day of acid) as a Function of Time After Plant Turnaround (1)
Piney Point Phosphates, Manatee County, Florida

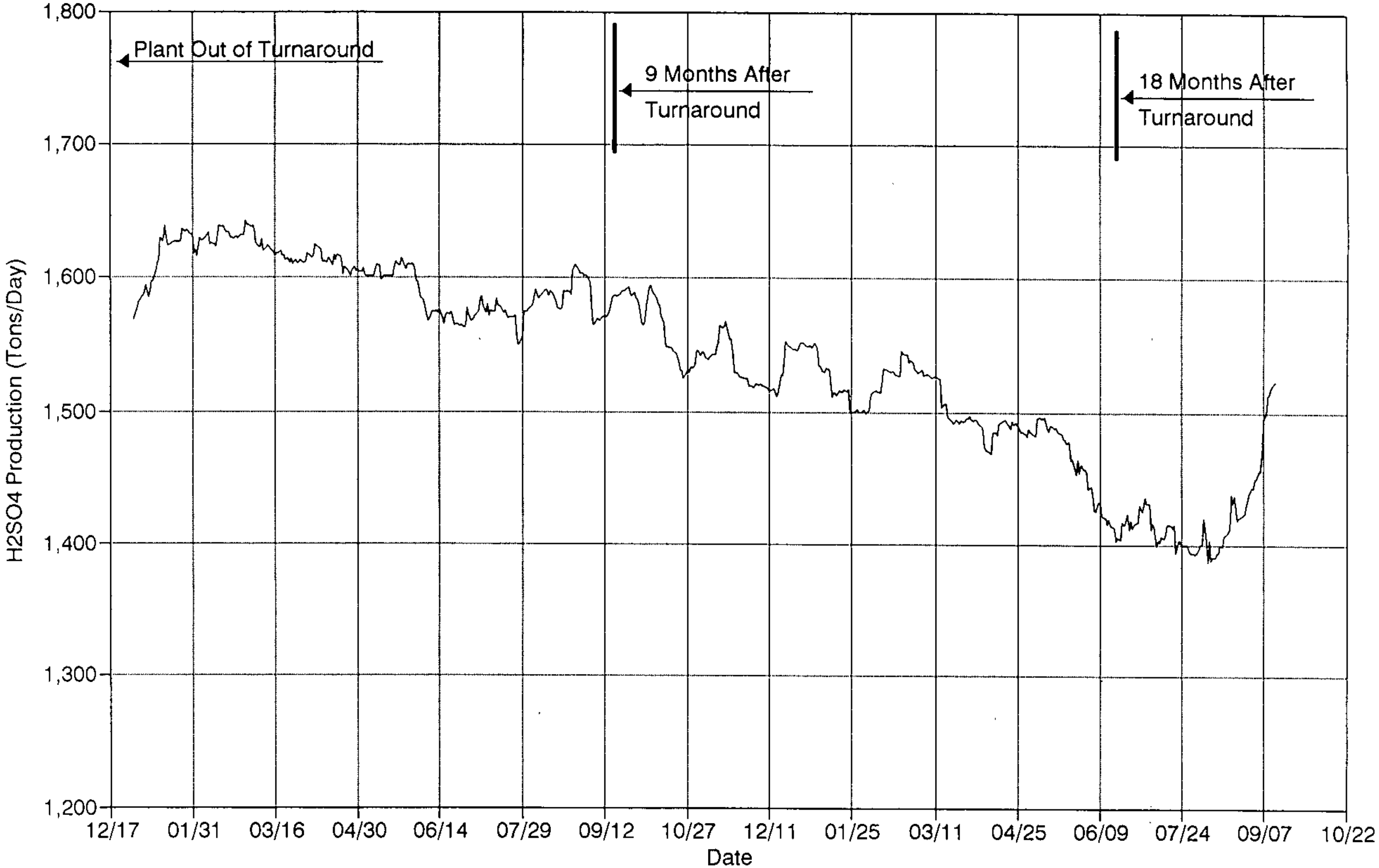


Figure 4-2
Sulfuric Acid Production Rate as a Function of Time After Plant Turnaround (1)
Piney Point Phosphates, Manatee County, Florida

(1) Data from Mulberry Phosphates, Inc. Mulberry, Florida

TABLE 4-1

COST ANALYSIS OF AN INTERIM SULFURIC ACID PLANT TURNAROUND FOR CATALYST SCREENING AND PARTIAL REPLACEMENT(1)

PINEY POINT PHOSPHATES, INC.
MANATEE COUNTY, FLORIDA

Average Downtime for Catalyst Screening - 8.5 days

Catalyst Replacement (includes disposal)	$ 49,900
Screening (Contract)	39,600
Supplies/Equipment/Contract Labor	48,500
Warehouse Issued Materials	14,300
Payroll	12,800
	$ 165,100
Steam Cost by Auxiliary Boiler (2) Fuel @ 1350 gal/hr x $0.70/gal x (24 x 8.5) hr	$ 192,800
Water Treatment for Boiler (2)	10,000
H_2SO_4 Cost Differential (3) 2000 tpd x 8.5 day x ($35-20)/ton(4)	255,000
Fuel to Reheat	9,600
Sulfur Lost(5)	3,000
H_2SO_4 Lost(5)	13,800
TOTAL COST OF TURNAROUND	$ 649,300

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(1) Determined from records of actual turnaround costs at Mulberry Phosphates, Inc.

(2) Steam produced by plant auxiliary boiler to run fertilizer complex while sulfuric acid plant is down.

(3) Differential cost (market cost minus cost that would have been incurred by PPP) to provide 2000 tpd H_2SO_4 to run fertilizer complex while sulfuric acid plant is down.

(4) Sulfuric acid prices fluctuate between $28-42 per ton.

(5) Material wasted because of shutdown.

TABLE 3-3

MAJOR FACILITY CATEGORIES

PINEY POINT PHOSPHATES, INC.
MANATEE COUNTY, FLORIDA

Fossil fuel fired steam electric plants, more than 250 MMBTU/hr heat input
Coal cleaning plants (with thermal dryers)
Kraft pulp mills
Portland cement plants
Primary zinc smelters
Iron and steel mill plants
Primary aluminum ore reduction plants
Primary copper smelters
Municipal incinerators capable of charging more than 250 tons of refuse per day
Hydrofluoric acid plants
Sulfuric acid plants
Nitric acid plants
Petroleum refineries
Lime plants
Phosphate rock processing plants
Coke oven batteries
Sulfur recovery plants
Carbon black plants (furnace process)
Primary lead smelters
Fuel conversion plants
Sintering plants
Secondary metal production plants
Chemical process plants
Fossil fuel boilers (or combinations thereof) totaling more than 250 million BTU/hr heat input
Petroleum storage and transfer units with total storage capacity exceeding 300,000 barrels
Taconite ore processing plants
Glass fiber processing plants
Charcoal production plants

TABLE 3-4

REGULATED AIR POLLUTANTS - SIGNIFICANT EMISSION RATES

PINEY POINT PHOSPHATES, INC.
MANATEE COUNTY, FLORIDA

Pollutant	Significant Emission Rate tons/yr	De Minimis Ambient Impacts ug/m3
CO	100	575 (8-hour)
NOx	40	14 (NO2, Annual)
SO_2	40	13 (24-hour)
Ozone	40 (VOC)	-
PM	25	10 (24-hour)
PM10	15	10 (24-hour)
TRS (including H2S)	10	0.2 (1-hour)
H2SO4 mist	7	-
Fluorides	3	0.25 (24-hour)
Vinyl Chloride	1	15 (24-hour)
	pounds/yr	
Lead	1200	0.1 (Quarterly avg)
Mercury	200	0.25 (24-hour)
Asbestos	14	-
Beryllium	0.8	0.001 (24-hour)

TABLE 3-5

AMBIENT AIR QUALITY STANDARDS

PINEY POINT PHOSPHATES, INC.
MANATEE COUNTY, FLORIDA

	FDEP (State)		USEPA (National)			
			Primary		Secondary	
Pollutant	ug/m3	PPM	ug/m3	PPM	ug/m3	PPM
SO_2, 3-hour	1,300	0.5	-	-	1300	0.5
24-hour	260	0.1	365	0.14	-	-
Annual	60	0.02	80	0.03	-	-
PM10, 24-hour	150	-	150	-	150	-
Annual	50	-	50	-	50	-
CO, 1-hour	40,000	35	40,000	35	-	-
8-hour	10,000	9	10,000	9	-	-
Ozone, 1-hour	235	0.12	235	0.12	235	0.12
NO_2, Annual	100	0.053	100	-	100	-
Lead, Quarterly	1.5	-	1.5	-	1.5	-

TABLE 3-6

PSD INCREMENTS

PINEY POINT PHOSPHATES, INC.
MANATEE COUNTY, FLORIDA

Pollutant		Allowable PSD Increments (State/National) Class I ug/m3	Class II ug/m3	Class III ug/m3
PM10,	Annual	4	17	34
	24-hour	8	30	60
SO_2,	Annual	2	20	40
	24-hour	5	91	182
	3-hour	25	512	700
NO_2,	Annual	2.5	25	50

4.0 BEST AVAILABLE CONTROL TECHNOLOGY

Best Available Control Technology (BACT) is required to control air pollutants emitted from newly constructed major sources or from modification to the major emitting facilities if the modification results in significant increase in the emission rate of regulated pollutants (see Table 3-4 for significant emission levels).

The emission rates from the repaired plant have been summarized in Table 3-2. The SO_2, SAM and NOx emissions increases from the proposed project were determined to represent a significant increase by FDEP.

The SO_2, SAM and NOx are present in the tail gas from all contact process sulfuric acid plants. In a typical plant with a single absorption system, the sulfur dioxide in the tail gas is approximately 30 pounds per ton of acid produced and the acid mist is approximately 4 pounds per ton of acid produced. In a typical plant with a double absorption system, the sulfur dioxide in the tail gas is approximately 4 pounds per ton of acid produced and the acid mist is approximately 0.15 pounds per ton of acid produced. The nitrogen oxides that are present in the tail gas are formed in the sulfur burners as a result of the fixation of atmospheric nitrogen. Recent measurements have indicated that the concentration of nitrogen oxides in the tail gas from a sulfuric acid plant can be around 0.12 pound per ton of acid produced.

4.1 EMISSION STANDARDS FOR SULFURIC ACID PLANTS

Federal New Source Performance Standards (NSPS) for sulfuric acid plants became effective on August 17, 1971. These standards are codified in 40 CFR 60, Subpart H and require sulfur dioxide emissions to be limited to no more than 4.0 pounds per ton of 100 percent acid produced and require that sulfuric acid mist emissions be limited to no more than 0.15 pounds per ton of 100 percent acid produced. Additionally, the standards limit the opacity of the emissions from new or modified sulfuric acid plants to less than 10 percent. There are no emission standards under NSPS for nitrogen oxides from sulfuric acid plants.

EPA's most recent review of the New Source Performance Standards for sulfuric acid plants in 1985 (EPA-450/3-85-012), concluded that because of variations in sulfur dioxide emissions as a function of catalyst age:

> "... the level of SO_2 emissions as specified in the current NSPS (should) not be changed ...."

TABLE 4-2
COST ANALYSIS OF AMMONIA SCRUBBING TO REDUCE SO_2 EMISSIONS FROM A 2000 TPD SULFURIC ACID PLANT

PINEY POINT PHOSPHATES, INC.
MANATEE COUNTY, FLORIDA

CAPITAL COST FACTORS		
Total Direct Cost (DC)		$ 3,500,000
Indirect Costs (IC)		
Total (0.31 x DC)		$ 1,085,000
Total Capital Investment (TCI)		
DC + IC		$ 4,585,000
ANNUAL COST FACTORS		
Direct Annual Costs (DAC)		
Operating Labor [2 hr/day x 360 d/yr x $20.00/hr] x 1.15	=	$ 16,600
Maintenance Labor plus Materials 3% of TCI	=	$ 137,600
Chemicals	=	$ 155,100
Water Treatment for Scrubber Make-up Water	=	$ 52,300
Waste Disposal	=	$ 451,800
Utilities	=	$ 247,200
Cost of 2 days per year H2SO4 Plant downtime because of scrubber	=	$ 122,700
TOTAL DIRECT ANNUAL COST (DAC)		$ 1,173,300
Indirect Annual Costs (IAC)		
Overhead (60 % of Operating & Maintenance)	=	$ 92,500
Admin/Tax/Ins (0.04 x TCI)	=	$ 183,400
Capital Recovery (10 years at 11%) (0.170 x TCI)		$ 779,500
TOTAL INDIRECT ANNUAL COST (IAC)		$ 1,055,400
Total Annual Cost		
DAC + IAC		$ 2,228,700

5.0 AIR QUALITY REVIEW

The air quality review for the proposed project included emission increases associated with the sulfuric acid plant and the molten sulfur system. The modeling associated with this review demonstrated that the maximum predicted air impacts of SO_2, SAM and NOx emission increases are less than significant.

5.1 AIR QUALITY MODELING

A preliminary modeling analysis was conducted to determine the ambient air impacts resulting from SO_2, SAM and NOx emissions as a result of the proposed project. The allowable pollutant emission levels associated with the existing sulfuric acid plant and the molten sulfur system were considered in the preliminary modeling analysis. As acknowledged by FDEP and suggested by EPA modeling guidance, the allowable emissions of the existing plant were included in the modeling as these emissions are from a permitted source and have been carried forward in the sulfur dioxide emissions inventories for all PSD projects in the area.

5.1.1 Significant Impact Analysis

The Significant Impact Analysis (SIA) modeling was conducted using the Industrial Source Complex-Short Term air quality model, Version 96113 (ISC3), in accordance with guidelines established by EPA and published in the document, *Guideline for Air Quality Modeling*, (Revised), July 1986.

The SO_2 emissions modeled for the SIA were the emissions associated with the existing sulfuric acid plant, the repaired sulfuric acid plant and molten sulfur system. The currently permitted SO_2 emissions were represented as negative inputs while the proposed (identical) SO_2 emissions from the repaired plant and molten sulfur system were represented as positive inputs to the model. The plant was modeled at annual hours of operation of 8760. Modeling inputs are presented in Table 5-1.

A SIA was also conducted for the nearest Class I area, Chassahowitzka National Wildlife Refuge, located about 115 kilometers north of the plant. Although the ISC3 model is not generally recommended for impact analyses beyond 50 kilometers from a source, it has been accepted by FDEP, EPA and the NPS as a preliminary "screening" model to determine the potential impacts of a proposed project on areas beyond 50 kilometers. From a practical standpoint, the regulatory agency has accepted ISC3 modeling analyses in these types of circumstances mainly because (a) the impacts predicted by the ISC model over such long distances are far greater (more conservative) than impacts predicted by the EPA recommended MESOPUFF (long range transport) model; and, (b) effort intensive MESOPUFF modeling could potentially be avoided by favorable ISC3 results.

The Class I area SIA modeling included 13 discrete receptors previously determined by FDEP to be representative of the Chassahowitzka National Wildlife Refuge boundary.

The meteorological data used for the modeling were for Tampa, Florida, and represented the five consecutive year period of 1987-1991.

The modeling results, summarized in Table 5-2, indicate less than significant ambient air impacts in both Class I and Class II PSD areas as a result of the proposed project. Therefore, additional refined modeling was not necessary.

TABLE 5-1

AIR QUALITY MODELING PARAMETERS

PINEY POINT PHOSPHATES, INC.
MANATEE COUNTY, FLORIDA

Emission Unit	Stack Ht (m)	Stack Dia (m)	Stack Gas Vel (mps)	Stack Gas Temp (°K)	Emission Rates SO_2 (g/s)	Emission Rates SAM (g/s)	Emission Rates NOx (g/s)
Sulfuric Acid Plant							
Exist.	60.98	2.38	8.75	338	42.0	1.6	1.3
Prop.	60.98	2.38	8.75	338	42.0	1.6	1.3
Molten Sulfur							
Exist.	7.3	1.21	0.1	366	0.03	NA	NA
Prop.	7.3	1.21	0.1	366	0.03	NA	NA

NOTES:

1. The molten sulfur system stack corresponds to the large storage tank vent.

2. Building downwash effects were included in the modeling.

TABLE 5-2

SUMMARY OF SULFUR DIOXIDE, NITROGEN OXIDES AND SULFURIC ACID MIST SIGNIFICANT IMPACT ANALYSIS

PINEY POINT PHOSPHATES, INC.
MANATEE COUNTY, FLORIDA

MAXIMUM PREDICTED CLASS I/II IMPACTS (ug/m^3) (1)(2)(3)

MET DATA	SULFUR DIOXIDE 3-hr	24-hr	Annual	NITROGEN OXIDES Annual	SULFURIC ACID MIST Annual
1987	0	0	0	0	0
1988	0	0	0	0	0
1989	0	0	0	0	0
1990	0	0	0	0	0
1991	0	0	0	0	0

NOTE:

(1) The maximum predicted impacts represent the highest-high impacts, as requested by FDEP.

(2) Class I and Class II area impacts; impacts in both areas are zero.

(3) The predicted impacts, being zero, are less than significant.

6.0 GOOD ENGINEERING PRACTICE STACK HEIGHT

The criteria for good engineering practice stack height in Rule 62-210, FAC, states that the height of a stack should not exceed the greater of 65 meters (213) feet or the height of nearby structures plus the lesser of 1.5 times the height or cross-wind width of the nearby structure. This stack height policy is designed to prevent achieving ambient air quality goals solely through the use of excessive stack heights and air dispersion.

Based on this policy, the limiting height for the sulfuric acid plant stacks is 213 feet. The sulfuric acid plant stack is less than 213 feet in height above-grade, and therefore, in compliance with GEP stack height criteria.

7.0 IMPACTS ON SOILS, VEGETATION AND VISIBILITY

The U. S. Environmental Protection Agency was directed by Congress to develop primary and secondary ambient air quality standards. The primary standards were to protect human health and the secondary standards were to:

> "... protect the public welfare from any known or anticipated adverse effects of a pollutant."

The public welfare was to include soils, vegetation and visibility.

As a basis for promulgating the air quality standards, EPA undertook studies related to the effects of all major air pollutants and published criteria documents summarizing the results of the studies. The studies included in the criteria documents were related to both acute and chronic effects of air pollutants. Based on the results of these studies, the criteria documents recommended air pollutant concentration limits for various periods of time that would protect against both chronic and acute effects of air pollutants with a reasonable margin of safety.

The preliminary air quality modeling for the proposed project demonstrated that the maximum predicted impacts will be less than significant. Consequently, it is reasonable to conclude that there will be no adverse effect to the soils, vegetation or visibility of the area. Also, the proposed project is not expected to have any growth related impacts associated with the plant start up.

8.0 CLASS I AREA AQRV ANALYSIS

In the previous section, the impact of the air emission increases on air quality related values in the vicinity of the proposed project was addressed. The analysis addressed in this section extends the review of the impact of increased emissions on air quality related values to the Chassahowitzka Class I PSD area; an area in excess of 115 kilometers northwest of the proposed project.

As preliminary air quality modeling for the proposed project demonstrated that the maximum predicted Class I area impacts will be less than significant, it is reasonable to conclude that there will be no adverse impact on the Class I area air quality related values from the proposed project.

9.0 CONCLUSION

It can be concluded from the information in this report that the proposed project, consisting of repair and start up of the existing PPP sulfuric acid plant and molten sulfur system, as described in this report will not cause or contribute to a violation of any air quality standard, PSD increment, or any other provision of Chapter 62, FAC.

APPENDICES

APPENDIX A

LIST OF PROPOSED REPAIRS

EXTENT OF WORK

1. Sulfur Burner (Existing)

The existing sulfur burner will be retained with minor repairs. The air inlet windbox requires castable and metal repairs. The air inlet damper (BV-1) will be replaced. A new rain shield will be installed over the outlet gas duct and tied into the existing rain shields over the unit.

2. BFW Heater(Deaerator) (New)

The existing boiler feedwater heater/deaerator and associated piping, valves, and instrumentation will be demolished. A new unit, sized in accordance with MEC design standards, will be installed on the existing foundation and steel. New piping, valves and instrumentation are provided for the unit. The new unit has the capacity to heat and deaerate 220,000 lb/hr (normal) and 255,000 lb/hr (design) of boiler feedwater at 55°F.

3. Waste Heater Boilers (Existing)

The two existing boilers shall be maintained and re-rated as required by the manufacturer to meet the acid plant capacity requirements as defined in Section 1, Design Basis. The boilers shall be re-rated and certified as required for 350 psig design pressure and a 300 psig operating pressure.

The tube (process gas) side will be mechanically cleaned and inspected. The hot end ferrules and castable will be removed and replaced.

The shell (water/steam) sides of both boilers and common steam drum will be inspected and hydro tested at 350 psig, or in accordance with the manufacturer's recommendations. Any necessary repairs will be identified. The pressure relief valves will be removed, shop inspected, certified, and re-installed. Any necessary repairs to the pressure relief valves will be identified. The hand-hold inspection plates will be replaced.

All repairs identified from inspections, including manufacturer's evaluations, recommended or required repairs, shall be undertaken.

4. Economizer (New)

The existing economizer and associated piping, valves and instruments are to be demolished. A new economizer will be installed on the existing foundation and new piping, valves and instruments will be provided. The water side will be designed and stamped per ASME code. The new economizer is designed to cool the gases to 350°F prior to entering the interpass tower. The heat transfer area is approximately 28,000 ft.

5. Main Compressor (Existing)

The main air compressor is an Elliott centrifugal compressor which is driven by a 275/40 psig steam turbine. The compressor, steam turbine and steam control valve are to be disassembled, cleaned as necessary, and each sent to a qualified repair facility for inspection and for any repairs that are identified.

The compressor and turbine shall be re-rated as required by the manufacturer to meet the acid plant capacity requirements.

Repairs identified from these inspections required to achieve the acid plant capacity shall be undertaken.

The compressor, steam turbine and steam control valve will be returned to the plant site for reinstallation. This includes reinstallation of all piping, valves, instrumentation, and controls, proper alignment of the system, cleaning and refilling of the lube oil system, and checking out and test-running the unit.

The vibration monitor (and its wiring) will be replaced with a new unit.

6. No. 1 Converter (Existing)

The existing 35'-3" diameter No. 1 converter will be retained. All of the catalyst and quartz will be removed and screened. The pass 1 shell and roof, catalyst support grates, and the grate support steel will be replaced. The pass 1 shell and roof will be ASTM 516 Grade 70 and metallized. The pass 1 6" support grates and posts will be HS Meehanite. The pass 1 division plate will be replaced. The catalyst and quartz will be reinstalled. All of the external insulation will be removed and replaced. All of the floor and wall insulating brick will be removed and replaced. The converter loadings will be as follows:

Catalyst loading at 2000 STPD:

Pass No.	Liters	Type
1	51,000	MEC Existing T-210 and New LP-120
2	55,600	MEC Existing T-210 and New LP-120
3	48,000	MEC Existing T-11 and New LP-110
4	56,000	MEC Existing T-11 and New LP-110

After catalyst make-up needs have been determined, the purchase and delivery of the make-up will be undertaken. The catalyst screening losses will be removed and disposed of at an approved facility by MEC.

7. No. 2 Converter (Existing)

The existing 42" diameter No. 2 converter will be retained. All of the catalyst and quartz will be removed and disposed of at an approved facility by MEC. New MEC LP-110 catalyst will be provided. The catalyst and quartz will be reinstalled. All of the external insulation will be removed and replaced. The converter floor will be inspected, and needed repairs identified. Any required repairs will be undertaken. The converter loading will be as follows:

Pass No.	Liters	Type
5	117,000	New MEC LP-1120

8. Drying Tower (New)

The new drying tower is 18'-0" diameter IDB by approximately 35 ft tall. It is a vertical, dished bottom, acid-brick-lined carbon steel vessel. The packed section contains 8 ft of 3" ceramic saddles capped by an 8" layer of 2" ceramic saddles as a spray catcher zone. The distribution system is comprised of Mondi header pipes, SX troughs and 310M stainless steel downcomers. The mist eliminators are set at the top of the vessel on a 326L tubesheet within the 14 ft diameter carbon steel housing. The new drying tower will be relocated to a new foundation and away from the top of the control room for safety reasons.

The gas inlet and outlet nozzles are 66" diameter carbon steel. The external piping is Mondi with Lewmet butterfly valves for control.

Interpass Tower (New)

The new interpass tower is 18'-0" diameter IDB by approximately 55 ft tall. It is a vertical, dished bottom, acid-brick-lined carbon steel vessel. The packed section contains 8 ft of 3" ceramic saddles capped by an 8" layer of 2" ceramic saddles as a spray catcher zone. The distribution system is comprised of Mondi header pipes, SX troughs and 310M stainless steel downcomers. The mist eliminators are set at the top of the vessel on a 316L tubesheet within the 19 ft diameter carbon steel housing. The new interpass tower will be relocated to a new foundation and away from the top of the control room for safety reasons.

The gas inlet and outlet nozzles are 66" diameter carbon steel. The external piping is Mondi with Lewmet butterfly valves for control.

Final Tower (New)

The new interpass tower is 18'-0" diameter IDB by approximately 45 ft tall. It is a vertical, dished bottom, acid-brick-lined carbon steel vessel. The packed section contains 8 ft of 3" ceramic saddles capped by an 8" layer of 2" ceramic saddles as a spray catcher zone. The distribution system is comprised of Mondi header pipes, SX troughs and 310M stainless steel downcomers. The mist eliminators are set at the top of the vessel on a 316L tubesheet within the 14 ft diameter carbon steel housing. The new final tower will be placed on the original support of the existing tower.

The gas inlet and outlet nozzles are 66" diameter carbon steel. The external piping is Mondi with Lewmet butterfly valves for control.

9. Drying Tower Mist Eliminators (New)

Six (6) Monsanto Enviro-Chem CS-IP Co-Knit mist eliminators, plus an additional blank for a future element, will be installed in an approximate 14 ft diameter "dog house" atop of the new drying tower. These elements provide excellent collection efficiency of a wide range of mist particle sizes.

Interpass Tower Mist Eliminators (New)

Thirty-six (36) Monsanto Enviro-Chem ES mist eliminators, plus an additional 4 blanks for future elements, will be installed in an approximate 21 ft diameter "dog house" atop of the new interpass tower. These elements provide excellent collection efficiency of a wide range of mist particle sizes.

Final Tower Mist Eliminators (New)

Ten (10) Monsanto Enviro-Chem CSII-P mist eliminators, plus an additional blank for future element, will be installed in an approximate 14 ft diameter "dog house" atop of the new final tower. These elements provide excellent collection efficiency of a wide range of mist particle sizes.

10. Cold Interpass Heat Exchanger (Cold Shell) (New)

The existing Cold IP heat exchanger (cold shell) will be demolished. A new heat exchanger will be installed on new grillage on the existing foundation. The new exchanger has a heat transfer area of approximately 14,000 ft^2. The unit will be shop pressure tested before shipping.

Cold Interpass Heat Exchanger (Hot Shell) (Existing)

The existing Cold IP heat exchanger (hot shell) will be retained. The exchanger will be cleaned on both the tube side and shall side where accessible. The exchanger will be inspected and the tubes tested for leaks with low pressure air.

Hot Interpass Head Exchanger (Existing)

The existing Hot IP heat exchanger will be retained. The exchanger will be cleaned on both the tube side and shell side where accessible. The exchanger will be inspected and the tubes tested for leaks with low pressure air.

Any repairs identified from the inspections or tests will be undertaken.

11. No. 1 Superheater (Existing)

The existing superheater will be retained. The tubes will be cleaned both internally and externally. The tubes will be hydro tested at 350 psig.

Any repair needs identified during the testing will be undertaken.

12. Condensate Storage Tank (New)

The existing condensate storage tank at the phosphoric acid plant and associated pump, piping, valves, electrical and instrumentation will be demolished. A new 14 ft diameter by 16 ft tall 304 SS tank complete with piping, valves, electrical and instrumentation will be installed. The tank will have the capacity for 18,000 gallons of condensate.

13. Cooling Tower (New)

The new cooling tower will be installed within the area occupied by the previous unit. A new pump pit will be provided. Fire and lightning protection will be provided. The capacity of the tower will be 13,500 gpm of water from 113°F to 89°F.

14. Combination Acid Coolers (New)

The existing cooling coils along with all associated pumps, piping, valves, electrical and instrumentation will be demolished. Prior to the demolition of any acid containing equipment, the residual acid will be neutralized. Two new MEC shell and tube exchangers will be installed in the existing cooling pit along with the necessary piping, valves, electrical and instrumentation. The coolers will be sized in accordance with the design standards, plus an additional 10% of excess area for fouling. The two coolers are identical in duty, and are approximately 40 in. diameter by 30 ft. Tube length with approximately 4,400 ft^2 each of heat transfer area.

Product Acid Cooler (New)

The existing cooling coils along with all associated pumps, piping, valves, electrical and instrumentation will be demolished. Prior to the demolition of any acid containing equipment, the residual acid will be neutralized. One new MEC shell and tube exchanger will be installed in the existing cooling pit along with the necessary piping, valves, electrical and instrumentation. The cooler will be sized in accordance with MEC design standards, plus an additional 10% of excess area for fouling. The cooler is approximately 15 in. diameter by 32 ft tube length with approximately 1,100 ft^2 of heat transfer area.

15. Acid Pump Tank (New)

The bottom 10 ft of the interpass tower serves as the pump boot for the acid system. The drying and final towers drain back to the boot, and the dilution water is added with the drying tower return acid. The outlet of the interpass tower feeds the common acid circulating pump. The interpass tower will contain a packing chip internal strainer manufactured of SX at the tower acid outlet line to the common acid pump.

16. Sulfuric Acid Storage Tanks (Existing)

Repair of these tanks will be by PPPI, and will involve cleaning and neutralizing the tanks, inspection and thickness tests, repairs to welds, catwalks, grating and stairs, and sandblasting/painting tanks.

17. Plant Stack (Existing)

Repair of the existing 7'-9" minimum diameter stack will be by PPPI. The soft waster system in the bottom of the stack will be replaced with three new softeners and water pumps; piping and hoses will be required/replaced, and the well water line will be replaced. The catwalks, ladders and grating on the stack will be repaired and it will be repainted.

18. Sulfur Pumps (New)

The three sulfur pumps are vertical, centrifugal submerged, Lewis pumps to be installed in the existing sulfur pit. The capacity of each pump will be 68 gpm of molten sulfur at approximately 275 ft TDH. Two of the pumps will be motor driven and one will be steam turbine driven. One of the motor driven pumps is an installed spare. The pumps discharge into a common header for sulfur feed to either the sulfur burner or the sulfur storage tank.

Common Acid Circulating Pump (New)

The one acid circulating pump is a vertical, centrifugal external Lewis pump to be installed on the interpass tower outlet line. The pump has a capacity of 8,200 gpm at 85 ft TDH. The pump will be motor driven and provides the required acid flow to/around the common acid coolers to all three acid towers.

Acid Drain Pump (New)

The acid drain pump is a horizontal, centrifugal Alloy 20 pump to be installed on a pad near the acid coolers. The pump will have a capacity of 1250 gpm at 100 ft TDH. The pump will be piped to allow complete drainage of the interpass tower pump boot and the acid coolers.

Cooling Water Pumps (New)

The two cooling water pumps are vertical, centrifugal pumps to be installed in a new cooling water pit. The capacity of each pump is approximately 13,500 gpm at 100 ft TDH. One pump will be motor driven, and the other will be steam turbine driven. The motor driven pump is an installed spare. The wetted pump parts shall not contain any copper-bearing alloys.

Condensate Transfer Pump (New)

The condensate transfer pump is a horizontal, centrifugal pump to be installed on a pad next to the new condensate tank at the Phosphoric acid plant. The capacity of the pump will be 300 gpm at 250 ft TDH. The pump will be motor driven.

19. Gas Ducts (New)

The following gas ducts will be replaced (all of the new ducts are carbon steel, except Pass 1 outlet, which is 304 S.S. Metallized ducts are denoted by an "M"):

Compressor inlet duct, inlet screen, and silencer (as required) to meet OSHA-established noise levels)
Compressor outlet duct to the drying tower
Drying tower to the sulfur furnace with new manually-controlled BV-1 damper, new control-room-operated GV-1 isolation valve, and repaired (by change order) secondary air damper.
Pass 1 outlet to the No. 2 WHB
New heat-up duct from pass 1 inlet to No. 2 converter, with manually operated BV53-A gas valve and gas-tight blank - M
Pass 2 outlet to hot IP heat exchanger - M
Hot IP heat exchanger to pass 3 - M
Pass 3 to the superheater - M
Superheater to pass 4 - M
Pass 4 to the economizer - M
Economizer to the interpass tower
Interpass tower to the first Cold IP heat exchanger (sloped)
Cold IP heat exchanger to the final tower
Final tower to the stack

20. Strong Acid Piping (New)

All of the existing acid circulation system piping along with the associated pumps, valves, electrical and instrumentation will be demolished. Prior to the demolition of any acid containing equipment, the residual acid will be neutralized. Mondi piping will be supplied and installed for the three acid towers, the three acid coolers, and the acid drain pump for tie-in to the storage tanks.

The existing acid return line, which originates from the north acid storage tank pump, shall be re-routed to the interpass tower pump tank (tower bottom). New piping shall be 4" minimum.

Miscellaneous Piping

The existing steam piping will be inspected (as per API 574) and hydro tested, and any necessary repairs will be undertaken. The BFW piping at the new economizer will be replaced. New cooling water piping will be provided to/from the cooling tower pump pit to the acid coolers. New piping will be provided at the condensate storage tank and pumped to the softened water storage tank.

Valves

All of the existing acid valves will be replaced. All of the existing BFW and steam system pressure relief valves will be removed, shop-certified, and re-installed. All of the existing BFW and steam control valves will be hydro tested in-line. Any repairs will be undertaken. New BFW valves will be provided at the deaerator and the economizer. New cooling water valves will be provided at the cooling tower pump pit and acid coolers. Coordinated inlet/dump valves are provided at the condensate tank inlet as well as isolation valves at the condensate transfer pump. The No. 1 boiler by-pass valve BV-3 will be removed and the spare will be fully reinstalled in its place, checked out, and tested. The No. 2 boiler by-pass valve (BV-4) will be inspected. Any repair needs identified for BV-4 will be undertaken. Operators will be provided for BV-3 and BV-4 and controlled remotely from the control room.

21. So$_2$ Monitor (Existing)

The existing S0$_2$ monitor will be retrofitted with new solid state parts. This work will be undertaken by PPPI.

22. Offices (Existing)

A generator and air compressor will be removed and a new office will be constructed from the existing room. Also, the existing control room walls will be repaired/rebuilt as necessary. This work will be undertaken by PPPI.

23. Structural Steel

The existing structural steel within the Sulfuric Acid Plant battery limits (to include the portion of main pipe rack where utilities connect to the plant adjacent to the Cooling Water Tower and along SAP battery limits to the Sulfur Furnace) will be sandblasted and inspected as part of MEC scope. Modification of grillage steel at the Cold IP Heat Exchanger (X-51), and at the Cooling Tower pipe rack (to facilitate removal of steel, piping and equipment to allow installation of a new pump pit) is included. Grating, handrail, stairs and ladders will be repaired or replaced at the following existing equipment/access areas: Sulfuric Acid Storage, Deaerator, Waste Heat Boiler, Sulfur Furnace burner access platform, and both Converters. Any repairs/replacement beyond this scope such as existing pipe racks, Main Compressor enclosure, etc. will undertaken.

New access/platform steel will be provided at the Acid Towers at the following locations: Platform with stair access to Tower/Pump support level, Platform with ladder access at distributor pipe inlet, tubesheet and roof (Mist Eliminator Access) levels, Platform with ladder access to damper GV-1 at Drying Tower. New steel is provided for pipe and duct support.

Insulation

All new equipment, duct, piping and associated tie-ins will be insulated per MEC specifications. Existing insulation will be removed and replaced at both the 4-pass and single 5th Pass converters and the duct run between the WHB-2 tube bundle and the 2nd Pass of the 4-pass converter. Repair of damaged insulation will be performed upon the WHB steam drum and both tube bundles. The duct from the Interpass Tower to the Cold IP Heat Exchanger X-51 will be insulated. If additional insulation replacement such as sulfur, steam, and utility piping, Heat Exchangers (X52/X53) and interconnecting duct is required it will be undertaken.

Painting

All new equipment, vessels, steel, piping and ductwork will be painted per MEC specifications. All existing support and access steel will be painted per MEC specifications.

Electrical

A fusible disconnect will be installed at the existing main substation with a 4160 volt feeder in aluminum cable tray run to a new MVC located in the existing Control Building. PPPI will provide space in existing building to accommodate the new MVC equipment. New 5 kV starters will be vacuum type. The existing 480 volt MCC will be modified to accommodate additional electrical requirements per MEC scope. Modifications will include the re-use of existing starters or installation of new combination starters with fusible disconnects, installation of fusible switches for auxiliary transformers and panels and the addition of a 5 KVA uninterruptible power supply for new electronic instrumentation.

New lighting will be metal halide fixtures.

Aluminum tray, aluminum conduit and copper tray cable will be provided for new power, control and instrumentation wiring per MEC design standards. No electrical heat tracing is provided. Demolition of the existing electrical system will be limited to that required to allow for installation of the new electrical system.

Piling/Foundation

New piling is provided for the Drying and Interpass Acid Towers, new Compressor Inlet duct support structure and pipe rack addition between the new Acid Coolers and IPA/Final Acid Towers. One test pile is included.

New foundations are provided for the Drying and Interpass towers, Compressor Inlet Duct support structure, new pipe rack, and pipe/duct support. Existing foundations will be modified for the Acid Coolers and Drain pump, Cooling Tower pump pit, Final tower, and Condensate Storage Tank.

24. Instrumentation

MEC will provide new electronic instrumentation and a control panel in the existing Control Room. New instrumentation will be provided for the Acid Circulation, Acid Cooling, Transfer and Drain system, Cooling Tower and Cooling Water system, Dilution water system, Deaerator/Economizer and interconnecting BFW system, Sulfur Storage and Pump system and Condensate Storage Collection/Transfer system at the Phosphoric Acid Area. Moore controllers are preferred by PPPI. The existing panel added during MEN 2014 (IPA conversion) project will be demolished to make room for the new control panel. Only the stack analyzer recorder will be relocated to the new panel with all other instrumentation demolished in place. No additional modification of the existing control panel is included in MEC scope.

MEC will quote Moore DCS system as an alternate to the electronic instruments (base case). Subject to PPPI's selection, the incremental cost of the DCS system will be undertaken.

25. Molten Sulfur Storage Tank (Existing)

The bottom part of the existing 800 ton sulfur storage tank will be cut away and replaced. New piping, steam coils, electrical tie-ins, access stairs, and platforms will be provided for the tank.

Sulfur Pit (Existing)

The existing sulfur pit contains some sulfur which will be removed. The pit walls will be inspected and any necessary repairs will be undertaken. The steam coils, piping and traps will be replaced with new ones. The new coils will be removable without requiring that the pit be drained. The pit cover will be replaced, with structural support steel external to the pit.

26. Auxiliary Boiler (New)

A new 150,000 lb/hr 300 psig packaged boiler is to be supplied and installed by PPPI to replace the existing 75,000 lb/hr boiler. Note: PPPI is already permitted for this boiler (Permit No. AC41-232096).

27. Miscellaneous

This includes many incidental and support items such as asbestos removal, replacement of insulation and miscellaneous pumps and motors, etc. Also includes allowances for change orders and contingencies.

APPENDIX B

EMISSION RATE CALCULATIONS

EMISSION RATE CALCULATIONS

1.0 PERMITTED EMISSION RATES

1.1 SULFURIC ACID PLANT

SO_2 = 333.3 lbs/hr
x 8760 hrs/yr x ton/2000 lbs
= 1460 TPY

SAM = 12.5 lbs/hr
x 8760 hrs/yr x ton/2000 lbs
= 54.8 TPY

1.2 MOLTEN SULFUR SYSTEM

PM/PM10 = 0.61 TPY
SO_2 = 1.2 TPY
H2S = 0.28 TPY
VOC = 0.79 TPY

NOTE: Pollutant emissions associated with the molten sulfur storage & handling system are provided for emission inventory and PSD purposes only and are not considered allowable emission rates.

2.0 ACTUAL EMISSION RATE CALCULATIONS

The following actual emission rates for the sulfuric acid plant are based on compliance test results and annual operation hours previously submitted to FDEP.

OPERATION YEAR	ANNUAL OPERATING HOURS
1988	3982
1989	7762
1990	7875
1991	6881
1992	3410
1993	0
1994	0
1995	0
1996	0

NOTES: (1) Data based on annual operation reports submitted to FDEP.

The sulfuric acid plant and molten sulfur system were not operated during the most recent two years. Therefore, for purposes of this PSD application actual pollutant emissions are assumed to be zero. It should be noted that FDEP's assessment of actual emissions for the existing plant, documented in the Technical Evaluation and Preliminary Determination dated September 8, 1995, reflect annual emissions for SO_2, NOx and SAM of 820.5 tpy, 19.7 tpy and 17.4 tpy, respectively. The Department may utilize these emissions as actual emissions. However, the following analysis is based on an assumption of zero actual emissions to provide a conservative analysis.

3.0 PROPOSED EMISSION RATES

3.1 SULFURIC ACID PLANT

SO_2 = 83.3 tph x 4 lb/ton
= 333.3 lbs/hr
x 8760 hrs/yr x ton/2000 lbs
= 1460 TPY

SAM = 83.3 tph x 0.15 lb/ton
= 12.5 lbs/hr
x 8760 hrs/yr x ton/2000 lbs
= 54.8 TPY

NOx = 83.3 tph x 0.12 lb/ton
= 10.0 lbs/hr
x 8760 hrs/yr x ton/2000 lbs
= 43.8 tpy

3.2 MOLTEN SULFUR SYSTEM

PM/PM10 = 0.61 TPY

SO_2 = 1.2 TPY

H2S = 0.28 TPY

VOC = 0.79 TPY

NOTE: Pollutant emissions associated with the molten sulfur storage & handling system are provided for emission inventory and PSD purposes only and are not to be considered allowable emission rates.

4.0 NET EMISSIONS INCREASE

The net emissions increase from the proposed project are as follows:

SO_2 = (1460 - 0) tpy + (1.2 - 0) tpy
= 1461.2 tpy

SAM = (54.8 - 0) tpy
= 54.8 tpy

NOx = (43.8 - 0) tpy
= 43.8 tpy

Please note that there are no contemporaneous increases or decreases associated with the proposed project. The above increases exceed the PSD significant emissions levels, under Rule 62-212, FAC, of 40 tpy, 7 tpy and 40 tpy for SO_2, SAM and NOx, respectively.

APPENDIX C

REFERENCES ON SULFURIC ACID PLANTS

Comparison of Sulfuric Acid Plant Catalysts

by

Leonard J. Friedman

Acid Engineering & Consulting, Inc.
Lakeland, Florida

Comparison of Sulfuric Acid Plant Catalysts

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Introduction

The contact process for the production of sulfuric acid is based on the oxidation of sulfur dioxide to sulfur trioxide in the presence of a vanadium catalyst. From its beginnings in 1831 when Phillips of Bristol, England patented the oxidation of SO2 to SO3 over a platinum catalyst to the modern plants of today using high activity, low pressure drop, ribbed rings of vanadium catalyst, the contact process and the catalyst it is based on have undergone significant (but subtle) changes, with the vast majority of developments in the last thirty years.

This paper will review the basic principals of the catalytic sulfuric acid process, and using a summary of operating data compare the three catalysts normally used in North America in the areas of conversion efficiency, activity, ignition temperature, loss in activity over time and screening losses. The paper will also review the advantages and problems with extensive plant converter testing using gas chromatography, Reich or other test methods.

Background

Before 1900, essentially all sulfuric acid was produced by the "Chamber" process, where nitrogen oxides were used to catalyze the oxidation of sulfur dioxide to sulfur trioxide. Plant size was small, unusually less than 50 STPD, and product acid strength limited to 65% to 75% sulfuric acid. The development of the chemical (dye) industry and the need for gun powder in the late 1800's necessitated a process to produce high strength sulfuric acid and Oleum. Early work (1870's - 1910) based on platinum as a solid catalyst, usually as platinum impregnated asbestos gauze, was the first technical and economic application of the "Contact" process. The high cost of platinum and its susceptibility to poisoning by many materials (notably arsenic present in the roaster gas streams of the day), led to the development of vanadium pentoxide based catalysts using alkali metal prompters on a porous silica carrier in the early 1900's (BASF patent of 1913). This is essentially the vanadium based catalyst used today. The following table shows the transition from the Chamber to Contact process:

Transition to the Contact Process

	1910	1930	1950	1960	1980
Contact Process %	20	27	75	85	100
Chamber Process %	80	73	25	15	0

Vanadium Catalyst

Vanadium catalyst usually contains 6% - 9% vanadium pentoxide with alkali metal promoters. The promoters are potassium sulfate with an atomic ratio of potassium to vanadium of 2 - 4 and a small amount of sodium sulfate to adjust (lower) the eutectic melt temperature of the mixture. The active components are supported on a highly porous silica base (diatomaceous earth).

In 1948 Topsoe & Nielsen demonstrated catalyst at operating temperatures exists as a melt within the pores of the silica support. The melt consists of vanadium sulfur complexes dissolved in pyrosulfates. In other words, the oxidation of sulfur dioxide to sulfur trioxide is a homogeneous reaction in the liquid film covering the surfaces of the support and not the heterogeneous reaction it would appear to be. The activity of the catalyst is from active species of vanadium pentoxide (V2O5), with the mechanism involving changes in the valence of vanadium.

The reaction rate is the result of many factors, including; the solubility of SO2, SO3 and oxygen in the melt, mass transfer limitations, the concentration of the active catalyst components and their solubility's in the melt, the porosity and pore size distribution of the silica support, as well as other less obvious factors (manufacturing process, etc.). The effect and interaction of each variable is not completely defined, so changes leading to improvements are more by trial and error than science. The difference between conversion predicted by rate equations and conversion actually obtained is accounted for by adding a so called "catalyst effectiveness factor" or fudge factor to the rate equation. The reaction rate can be described by the following relationship:

$$r = k\,[p(SO2)^{l}\,p(O2)^{m}\,p(SO3)^{-n}]\ K\,act\ \ K\,eff$$

r = reaction rate - g mole SO2/g catalyst, sec
k = rate constant - function on catalyst properties
$p()^{x}$ = partial pressure of components
K act = adjustment factor for catalyst activity
K eff = adjustment factor for system unknowns

The acknowledgment of the reaction taking place in the liquid melt leads to an understanding of catalyst ignition temperature as the temperature at which the melt first forms. The decrease in activity at low temperature is explained by the precipitation of some of the vanadium compounds reducing the concentration of the vanadium in the melt. The loss in catalyst activity at high temperature is attributed to the melt exceeding the capacity of the catalyst pores, with the liquid melt forming large inactive globules. The "old wives tale" of catalyst having a memory - once operated at high temperature, it must always be operated at high temperature - is explained by the loss in activity from melt components flowing out of the catalyst.

Sulfur dioxide to sulfur trioxide equilibrium is determined by the following equation:

$$Kp = \frac{p(SO3)}{p(SO2)\,p(O2)^{.5}}$$

A typical equilibrium curve showing operating lines for a four bed single or double absorption system is shown in Figure 1. The figure shows the change in the equilibrium curve resulting from the removal of SO3 in the interstage absorber (upper equilibrium line), and the reason the double absorption process increases conversion of SO2 to SO3 from 98.5% to 99.7%.

A review of the equilibrium equation indicates increasing pressure will increase equilibrium conversion. Figure 2 shows the effect of increasing pressure. In the example shown, increasing pressure from 1.3 bar (3.8 psi) to 10 bar (127 psi) will increase equilibrium conversion in a first catalyst stage from 63% to 75%. In the late 1960's, I did extensive work developing and evaluating a pressure process for sulfuric acid production - looking at single absorption at pressure versus double absorption. The conclusion of that work indicated double absorption could not be avoided at reasonable pressures to meet 99.7% conversion, eliminating the pressure process from economic consideration. In the mid 1970's, Krebs built a plant at PCUK in France based on the pressure process. The plant was a double absorption unit operating at 70 psi. Analysis indicated capital cost savings compared to the conventional double absorption route to be small (< 10%), with the plant experiencing extremely high corrosion and low energy efficiency.

Another route to increased conversion is to increase the oxygen concentration in the converter gas by using enriched air or pure oxygen. Analysis indicates improved conversion efficiency, but not enough to eliminate double absorption. A process using pure oxygen was evaluated in the late 1960's as an alternate to double absorption. The system was not economically sound due to the continuing cost of oxygen. No plants based on pure oxygen have been built. A number of spent acid regeneration plants use enriched air to overcome capacity limitations in the gas cleaning sections of the plant, and oxygen use to enrich the gas in the contact section is being used in a few places. The cost is a balance of the need for additional capacity versus the continuing cost of oxygen.

Catalyst Shape and Composition

In the 1960's and early 1970's catalyst was in the form of pellets, usually 1/4" and 5/32" diameter by 0.3" to 0.6" long (6 mm & 4 mm diameter by 8 mm - 15 mm long). The catalyst normally contained 6% to 8% V2O5, and was sold in North America by many vendors:

Stauffer	Allied
Cyanamid	Monsanto
BASF	Topsoe
Catalyst & Chemicals	Imperial Smelting

In the mid to late 1970's lower pressure drop through the catalyst bed was achieved by the use of a larger diameter pellet, 8 mm in diameter or 5/16" rather than 6 mm diameter. This size pellet was heavily promoted by Monsanto as 516 catalyst. At about the same time Topsoe introduced the ring shape catalyst to the North American market. Topsoe claimed significantly lower pressure drop and greater dust holding capacity. Initial installations used ring catalyst to top off the pellets in the first catalyst bed. Data showed lower initial pressure drop, and lower rate of pressure drop build-up (greater dust holding capacity). Complete first beds of ring catalyst showed acceptable activity and conversion while maintaining the low pressure drop and pressure drop build-up. Ring catalyst allowed an increase in operating time between turnarounds from 12 months to 18 - 24 months. It took a number of years for ring catalyst to be accepted and used in the entire converter. Now the three principal catalyst suppliers to North America (Topsoe, BASF, Monsanto) all offer ring shaped catalyst - with pellet and 516 catalyst essentially obsolete. The most recent change in catalyst shape has been the ribbed ring, offered by Topsoe as "Daisy" and BASF as "Star" rings, providing about 20% lower pressure drop than the normal 10 mm rings.

In addition to catalyst shape changes, in the last twenty years catalyst composition changes have provided improved performance permitting 99.7% conversion in a double absorption plant with increasing SO2 gas strengths (9.5% - 10% in the 1970's to 11.5% - 11.75% today). A catalyst with 6% - 8% V2O5 is used in the first and second beds of the converter to attain resistance to activity loss at high temperature and maintain high temperature strength (reduced screening loss). The lower vanadium content - lower activity is offset by the higher average operating temperature of the upper beds, resulting in a high reaction rate and acceptable catalyst loading and approach to equilibrium. A catalyst with 7% to 9% V2O5 is used in the third and fourth catalyst beds to provide higher activity, lower ignition temperature and high reaction rate at the lower average operating temperature. The higher vanadium, lower bed catalyst has 10% to 20% greater activity than the 6% - 8% V2O5 upper bed catalyst.

The most recent catalyst development (re-invention of a 1948 discovery) is the so called "Cesium Catalyst". Cesium catalyst is really a 6% - 8% V2O5 catalyst with the formulation adjusted by substituting cesium for a portion of the potassium promoter. The use of cesium doubles the activity of the catalyst in the low temperature region, permitting continuous operation at bed inlet temperatures in the 720 F - 730 F region. The high cost of cesium promoted catalyst (about 2.5 times standard catalyst) limits its use to special applications.

The various catalyst shapes are shown in Figures 3 and 4. The following tables compare catalyst size and composition.

Shape

		Pellet	Pellet	Ring	Ribbed Ring
Diameter	mm	6	8	10	12
Length	mm	8	12 - 15	9 - 14	10
Pressure Drop	"H2O	1.0	0.9 - 0.95	0.5	0.4

Composition

	V2O5 Content	**Comments**
Upper Bed Catalyst	6% to 8%	High Temperature Operation Hardness & Temperature Resistance
Lower Bed Catalyst	7% to 9%	Low Temperature Operation High Activity - Softer Catalyst
Cesium Catalyst	6% to 8%	High Activity at Low Temperature (720 F) Can be Sticky at High Temperature

Catalyst Operation Analysis

Over the last ten years Acid Engineering & Consulting, Inc. has been involved with the operation of over one-hundred sulfuric acid plants around the world. In many cases data collected included information on various catalysts, including conversion efficiency, ignition temperature, loss in activity, screening loss, pressure drop and pressure drop build-up. A statistical analysis was performed on the data and the resulting observations are presented below. The analysis was made for the three main North America catalyst suppliers, Topsoe, BASF, and Monsanto, identified and supplier "A", "B", and "C". Note: If the analysis is on target, acid plant operators should be able to connect the supplier with their performance data.

Conversion Efficiency - The data suggests little significant difference in overall conversion efficiency between the three suppliers. Conversion efficiency analysis was complicated by many operating plants with more than one manufacturers catalyst in the converter, and many with two or three suppliers catalyst in a particular bed. Although there was some statistical difference, one could not use the conversion efficiency difference to tell which catalyst was in a particular converter.

Loss in Activity - The reduction in activity of a particular catalyst over time was determined by a review of catalyst suppliers activity test results and operating data showing changes in bed inlet and exit temperatures and conversions over time. The results were based on plants operating with high converter inlet SO2 concentrations resulting in bed 1 exit temperatures of 1140 F to 1160 F. The table below summarizes the activity loss over an 18 month to 24 month period for ring catalyst.

Loss in Activity (18 - 24 Months)

	Supplier "A"	Supplier "B"	Supplier "C"
Bed 1	20% - 35%	9% - 12%	9% - 13%
Bed 2	8% - 12%	5% - 8%	5% - 8%
Bed 3	< 5%	< 5%	< 5%
Bed 4	< 5%	< 5%	< 5%

The data indicates supplier "A" upper bed catalyst looses activity at a significantly higher rate than the others, about 2 to 3 times the activity loss between turnarounds. This would suggest a formulation problem resulting in the melt solution leaving the pores of the catalyst when operating at high temperature. The data is consistent over many years, eliminating the possibility of a bad batch or run of catalyst causing the results. In fact, for many years this supplier recommended limiting first bed exit temperature to less than 1125 F.

Screening Loss - Data for screening loss was based on ring catalyst, vacuum screened per suppliers instructions, usually by the same two commercial catalyst screening companies. The wide variation in the data for a particular supplier is attributed to operating time at high temperature, screening rate and the amount of broken pieces returned to the converter.

Screening Loss (% of Bed)

	Supplier "A"	Supplier "B"	Supplier "C"
Bed 1	25% - 40%	10% - 15%	11% - 16%
Bed 2	20% - 30%	9% - 15%	10% - 15%
Bed 3	15% - 20%	8% - 14%	8% - 14%
Bed 4	12% - 17%	8% - 12%	8% - 12%

The data is consistent, indicating a problem with supplier "A" catalyst, especially in the high temperature area, suggesting a formulation problem (high screening loss and loss in activity). The data is from many plants over a number of years with more data points for beds 1 and 2, and limited data for beds 3 and 4.

Pressure Drop Build-up - Data for sulfur burning plants was analyzed to determine differences in the rate of pressure drop build-up over an 18 month operating period between turnarounds. The analysis was complicated by unknown variations in the ash content of the sulfur and the amount of broken pieces returned to the converter after screening. After some adjustment for bed area, gas velocity, etc., the data indicated no significant difference in the rate of pressure drop build-up between the three catalysts.

Comparison Summary

Overall the catalyst comparison indicates supplier "A" has a problem with its upper bed ring catalyst when operated at high gas strength - high temperature (exit temperatures above 1130 F), resulting in excessive loss of activity over time and screening losses two to three times the others. In fact, the high screening loss and subsequent make-up with fresh catalyst obscures the activity loss problem, so overall plant conversion efficiency is maintained. Based on the analysis, supplier "B" and "C" catalyst are close in all aspects studied, with supplier "A" upper bed catalyst of lower overall performance.

Cesium Promoted Catalyst

Cesium promoted catalyst is offered by the three North American suppliers. The high cost, about 2.5 - 3 times conventional catalyst, has limited use to special situations. Cesium catalyst is rarely used in sulfur burning plants, but has found some advantages in spent acid regeneration and metallurgical plants. The catalyst has been used as a top layer of the first catalyst bed to provide operation at 720 F - 730 F, reducing gas heat exchanger requirements, while allowing restart of the plant when the catalyst bed is at 600 F.

Early installations of cesium promoted catalyst experienced severe pressure drop build-up. Pressure drop in some plants increased 30" to 60" H2O in a few months. Investigation indicated the plants experiencing the problem were operating at first bed inlet temperature of 780 F to 820 F, while plants without problems operated at 720 F to 740 F. The operating data indicates the cesium catalyst becomes very sticky at elevated temperatures. Recently, Topsoe has reformulated their cesium catalyst so it can be operated at low or high temperature without the pressure drop build-up problem. The other suppliers are expected to produce an adjusted formulation in the near future.

Converter Testing

Traditionally catalyst performance evaluations are made by reviewing bed inlet temperatures and temperature rise, inlet SO2 gas strength and overall conversion efficiency. Changes in these operating variables, although small from day to day, are good indicators of catalyst bed performance over time. Recently, one catalyst supplier has offered portable gas chromatograph testing of converter systems. The tests provide the composition of gas into and out of each catalyst bed. Comparing actual bed conversion with calculated conversion and equilibrium would be a superior way of determining catalyst activity - performance.

Acid Engineering & Consulting, Inc. has reviewed the results of a number of gas chromatograph tests of converter systems. In most cases, the test data was consistent with evaluations based on traditional methods, and was a useful tool in determining catalyst activity - replacement requirements for an upcoming turnaround. In a number of cases, the test results were obviously incorrect and the interpretation of the results flawed and self-serving. Objectivity comes into question when the one doing the testing is selling catalyst or testing his own catalyst to show how good it is, or how bad a competitors is. In one case, the test data indicated 7% to 8% conversion of SO2 to SO3 in the sulfur furnace - well above equilibrium. This was coupled with extremely low conversion in the first catalyst bed, indicating low catalyst activity and the need for additional replacement catalyst. In another case, a spent acid regeneration plant was experiencing conversion efficiency problems (very low first bed temperature rise) after a major plant modification. The catalyst in the first bed was changed, but the same problem persisted. Gas chromatograph tests (purchased with the replacement bed of catalyst) were run at various O2/SO2 ratios (0.72 to 0.92) and SO2 gas strengths (9.4% - 10.7%). Note: Most sulfur burning plants operate at O2/SO2 ratios of 0.75 to 0.77 and SO2 gas strengths of 11.5% - 11.75%. The test results are summarized below:

Plant Test Data

	Run 1	Run 2	Run 3
O2/SO2 Ratio	0.72	0.86	0.92
Overall Conversion	90.8%	94.2%	95.4%
Bed 1 Catalyst Activity	104%	83%	82%

Note: Catalyst activity dropped 22% between test runs 1 and 3. This was reported as "catalyst activities are in the normal range".

The conclusion presented by the testing company - catalyst supplier was the plant design at 0.75 O2/SO2 ratio and 97% conversion in a single absorption plant was not possible with the catalyst type, volume and O2/SO2 ratio. However, the catalyst supplier - testing company would be happy to study ways to achieve plant conversion and capacity, although they stated "there are no clear cut, low cost ways to do this". Note: Acid Engineering & Consulting, Inc. adjusted plant operating conditions and in four hours the plant was able to meet design capacity at an O2/SO2 ratio of 0.75 with conversion exceeding 98%. In this case, knowledge and experience was able to do what blind or self-serving testing could not do - get the plant operating at or above design without additional catalyst or costly modifications.

Conclusion

This work was intended to provide an understanding of sulfuric acid plant catalysts and to present a comparison of the three catalysts used in North America. Data from many plants over a number of years was reviewed, adjusted and evaluated to obtain comparative catalyst performance. The data indicated suppliers "B" and "C" catalyst to be about equal in each of the areas examined, with supplier "A" catalyst of lower performance (activity loss over time and high screening loss).

If some have a better understanding of sulfuric acid plant converter operation and catalysts, and supplier "A" is encouraged to improve their catalyst, the time and effort spent on this work will have been justified.

Figure 1

Converter Equilibrium

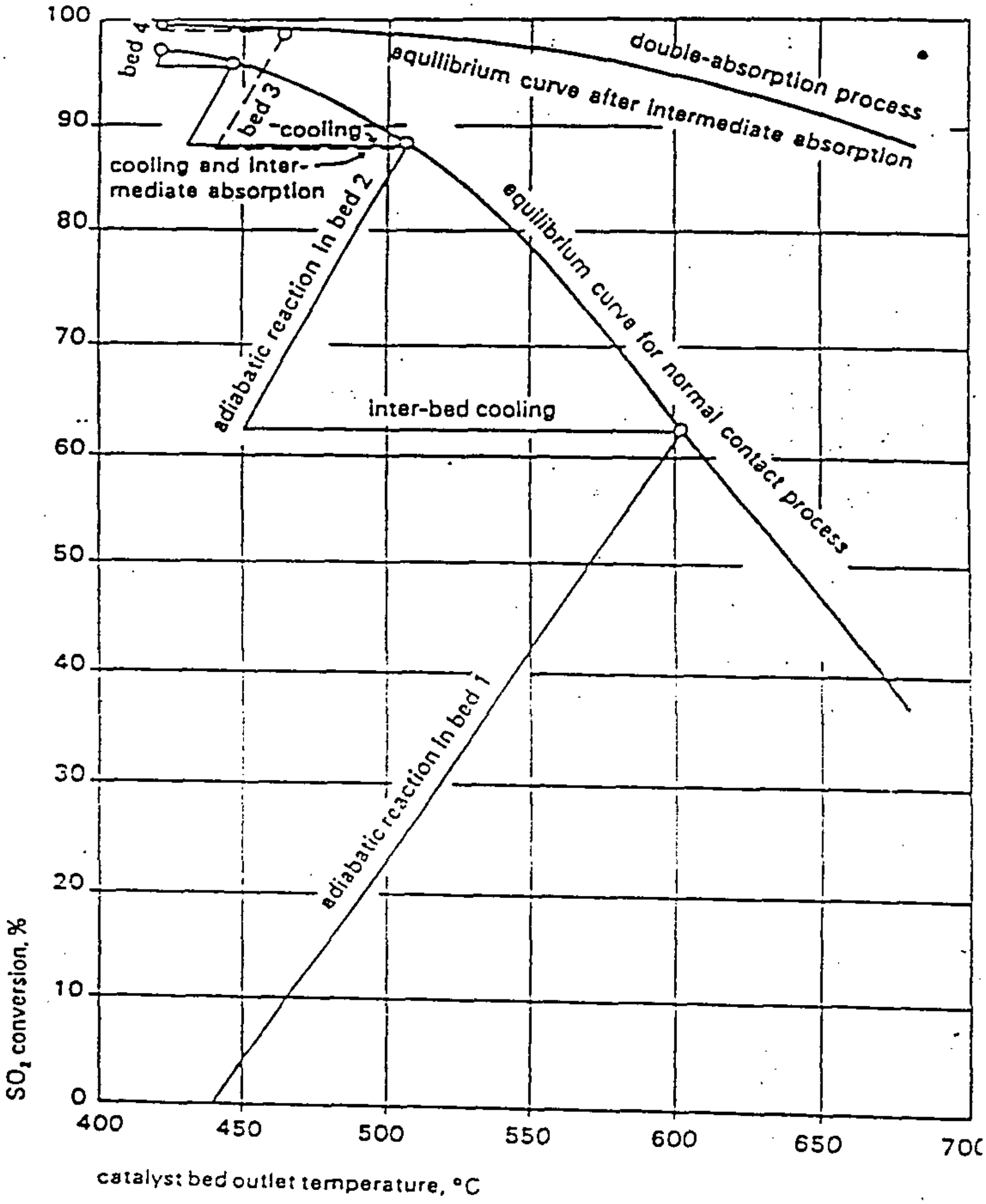


Figure 2

Pressure Effect on Equilibrium

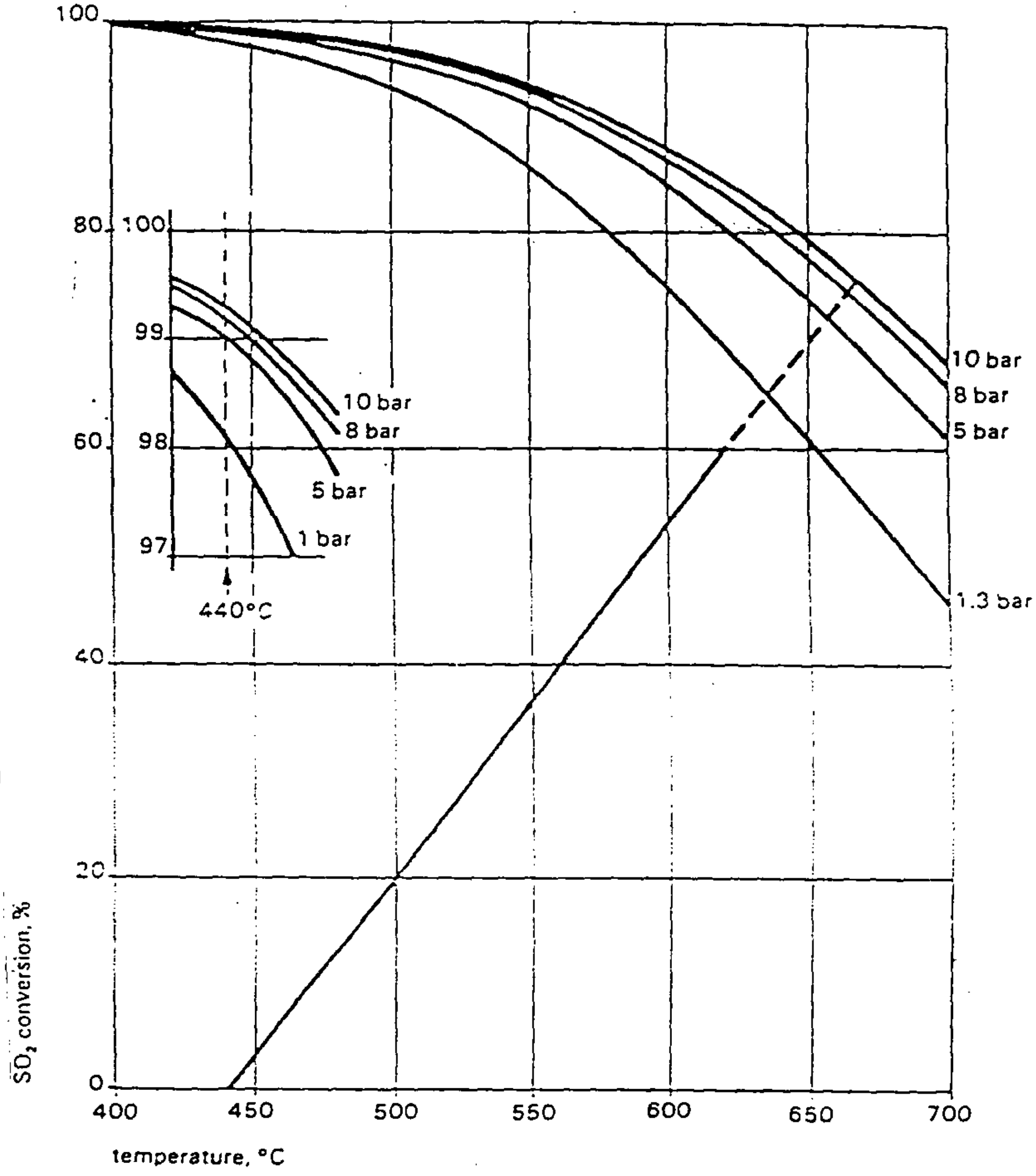


Figure 3

Catalyst Shapes & Sizes

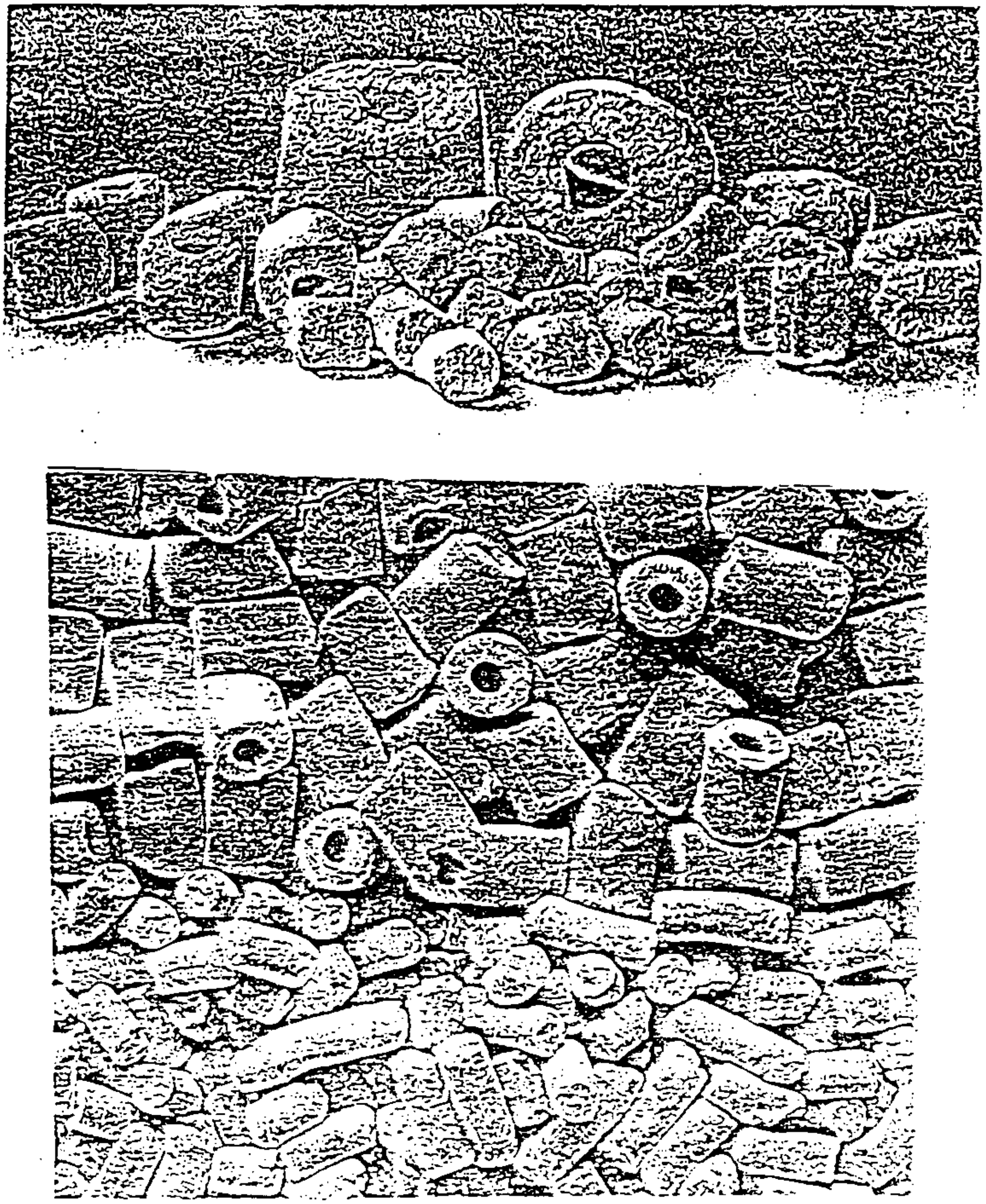
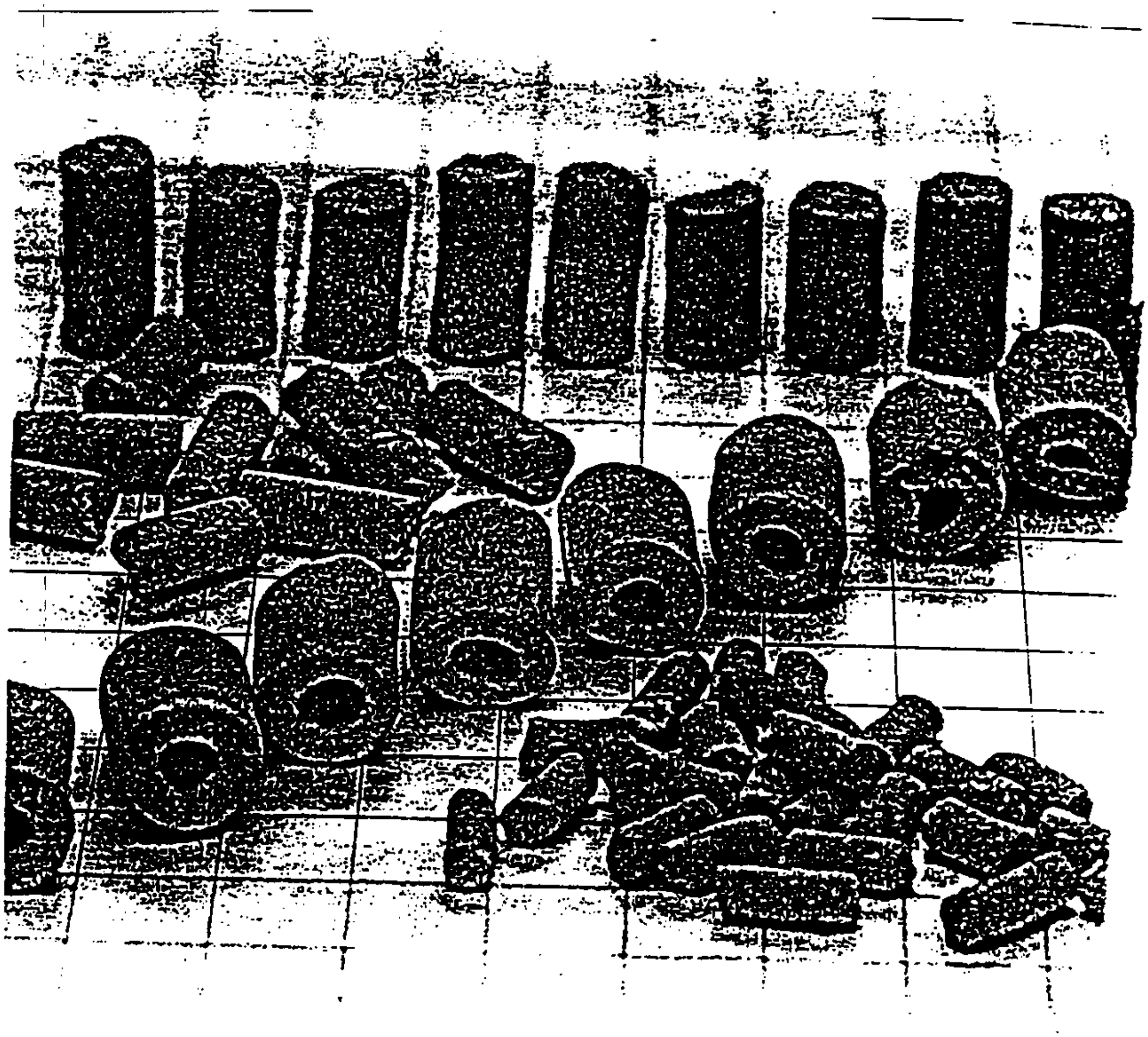


Figure 4

Catalyst Shapes & Sizes



SO_2 EMISSIONS REDUCTIONS IN SULFURIC ACID PLANTS

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ABSTRACT

The current trend in the sulfuric acid industry is to reduce the emission of sulfur dioxide (SO_2) to the atmosphere while maintaining or increasing acid production. Utilizing Monsanto cesium-modified catalysts, a number of sulfuric acid producers have effectively reduced their SO_2 emissions in both single absorption and double absorption cases. This paper will present the realized possibilities for the reduction in emissions using Monsanto Cesium Catalyst and the optimization of plant operations utilizing the Monsanto Portable Gas Analysis System (PeGASyS). The portable gas analyzer has served as an invaluable tool to optimize plant operations and demonstrate the advantages of the cesium catalyst in reducing emissions. The utilization of both the Monsanto Cesium Catalyst and the Portable Gas Analysis System in many plant applications will set the new standard for sulfuric converter performance.

INTRODUCTION

The trends in sulfuric acid plant design have changed dramatically over the last several decades. The demand for operations with minimal SO_2 emissions has required the development of the double absorption contact process for SO_2 oxidation which is capable of generating greater than 99.7 % conversion of the sulfur dioxide fed to the plant. Pollution reduction commitments by many major corporations as well as government regulatory requirements are responsible for the continuing trend to develop new and cost effective technologies to further reduce the SO_2 emission levels from sulfuric acid plants.

There are still a large number of sulfuric acid plants in the world which operate in the single absorption mode with SO_2 conversion levels near 98 %. Although these plants are operating within authorized conversion limits, many companies are striving to reduce the SO_2 emissions as much as is technically and economically feasible. Until recently, the technologies to accomplish this goal were limited. Plant operations were "optimized" using crude chemical techniques and often inaccurate temperature measurements, resulting in less than ideal performance in the plants. Over the years, conventional sulfuric acid catalyst improvements have enhanced the plant performance significantly, but further advances were limited by thermodynamic and kinetic barriers.

This paper presents the results of implementing two new technologies in the sulfuric acid industry. Monsanto Enviro-Chem has developed a low temperature cesium-promoted catalyst which eases some of the aforementioned limitations and improves the overall conversion in both single and double absorption plants, resulting in significantly less SO_2 emissions to the stack. A discussion of some case histories of cesium (Cs) catalyst installations and the potential applications of the technology are presented. The second technology developed by Monsanto Enviro-Chem is the Portable Gas Analysis System (PeGASyS) which is used to measure and optimize sulfuric acid plant converter/heat exchanger performance. Using this state-of-the-art instrumentation, plant problems are quickly and easily identified and resolved. Catalyst performance can be quickly determined and optimum operation conditions can be determined based on the catalyst quality and desired conversion results. Examples of the applications of the PeGASyS technology are presented in this paper. When utilized together, the cesium catalyst technology and the PeGASyS system can generate the optimum performance from any sulfuric acid plant and lead to lower SO_2 emissions.

CATALYST DEVELOPMENT AND APPLICATIONS

In the contact sulfuric acid process, there is often an interest in lowering the inlet temperatures to the various adiabatic catalyst beds in order to provide more favorable equilibrium conditions. The addition of cesium (Cs) to the conventional alkali-vanadium sulfuric acid catalyst has long been known to enhance the low temperature properties of the catalyst (1). The cesium salt promoter stabilizes the vanadium +5 oxidation state at temperatures below 420°C (790°F) and keeps the vanadium species solubilized in the melt and available for reaction. In the conventional K-V catalyst, vanadium compounds precipitate out of the molten salt at lower temperatures, causing loss of catalyst activity (2,3). The stabilizing effects of the cesium appear at relatively low Cs concentrations. A qualitative display of this effect is shown in Figure 1. At high temperatures (> 430°C/806°F), the activity of the conventional catalyst and the cesium-promoted catalysts are fairly similar. However, near 410°C (770°F), the reaction rate of the conventional catalyst drops off dramatically due to the precipitation of vanadium compounds (curve breakpoint # 1). As the temperature is further lowered (moving to the right on the graph), the cesium-promoted catalyst maintains a higher reaction rate until the temperature drops well below 400°C (750°F) when its activity finally begins to decline due to vanadium salt precipitation (curve breakpoint # 2). Although the reaction rate of the cesium-promoted catalyst drops off at relatively low temperatures, it is still sufficiently high to generate good conversion at acceptable catalyst loadings. Over the last several years, Monsanto Enviro-Chem has utilized its strong base in cesium catalyst studies (4-7) to develop an optimized and affordable cesium promoted catalyst (Cs-120 and Cs-110). These products contain the optimum levels of alkali metal salts (potassium and cesium) to provide excellent *low* and *high* temperature performance in the converter. Following extensive lab development and field testing, the products were commercialized in 1989 and have been installed in over 20 sulfuric acid plants worldwide.

There are many applications for the cesium-promoted catalyst in sulfuric acid plants. The smaller 9.5 mm (3/8 in.) Cs-110 rings can be loaded into the lower beds and allow for lower bed inlet temperatures and higher overall conversion. Figure 2 shows a graphical display of the advantage of using the Cs-110 catalyst in the 4th pass of a single absorption plant. The lower inlet temperature with Cs-110 catalyst opens a larger thermodynamic "window" which permits greater overall conversion. This higher level of conversion is not possible with the conventional catalyst at the lower inlet temperature as the catalyst loadings would have to be extremely high, creating excessive pressure drop. A similar scenario can be devised for the lower beds of double absorption plants, resulting in lower stack emissions.

Another cesium-promoted catalyst application involves installing a 33-50 % cap of Cs-120 rings in the first pass of a sulfuric acid plant. This catalyst configuration will dramatically lower the required inlet temperature for good conversion in this bed. Figure 3 shows that the conversion versus bed depth profile for a capped Cs-120 bed with an inlet temperature of 380°C (715°F). A full bed of conventional catalyst will produce very little conversion with this low inlet temperature at any reasonable catalyst loading. A full first bed of Cs-120 rings is not required in this application as the outlet temperature from the cesium catalyst portion of the bed is high enough to ignite the remaining conventional catalyst layer. The lower first pass inlet temperature is advantageous for plants with very high inlet SO_2 strength. In this case, the lower inlet temperature will lead to a lower outlet temperature, therefore extending the life of the first pass exit posts and grids. Furthermore, the overall conversion in the first pass will also be increased over that possible with conventional catalyst. The use of the Cs-120 rings in Pass 1 will also reduce or eliminate the need for startup gas pre-heating in spent acid and metallurgical plants following short shutdowns.

The cesium-promoted catalyst can also be utilized in situations where heat exchanger deficiencies (undersized or plugged) limit the inlet temperatures to lower passes. The Cs-110 rings can effectively operate at the reduced temperatures and hence maintain the needed conversion in the lower beds. Also, the Cs-120 first pass caps and the full beds of Cs-110 in the lower passes can greatly reduce the time required to startup the sulfuric acid plant. The cesium catalyst beds will ignite at much lower temperatures than conventional catalyst beds and hence require less pre-heating. Also, due to the high activity at low temperatures, the cesium catalyst beds help to minimize the stack SO_2 emissions during plant startup operations. Examples of many of these cesium catalyst applications are presented in subsequent sections.

Cs-110/Cs-120 CATALYST APPLICATIONS

The applications of the Cs-110 and Cs-120 catalysts in reducing SO_2 emissions will be presented as a series of case histories. Although the applications vary from plant to plant, the common threads in each case are lower stack emissions and improved operating versatility. The following are five examples of Monsanto cesium promoted catalyst performance: (Note: STPD = Short Tons acid produced Per Day)

Case 1: *Single Absorption Spent Acid Plant*

Pre-Cs Data:

(1) Conventional catalyst in Pass 4.
(2) Pass 4 operating at 430°C (806°F) inlet temperature.
(3) Conversion at 98.0 % with 9 % SO_2 feed gas.
(4) Stack SO_2 emissions were over 25 lbs./STPD.

Post-Cs Information:

(1) Installed full bed of Cs-110 ring in Pass 4.
(2) Pass 4 inlet temperature optimized at 410°C (770°F).
(3) Conversion measured at 98.5 % with 9 % SO_2 fed.
(4) Stack SO_2 emissions at 19 lbs./STPD (24 % reduction).

Case 2: *Single Absorption Sulfur Burning Plant*

Pre-Cs Data:

(1) Aging, conventional catalyst in all beds.
(2) Pass 4 operating at 427°C (800°F) inlet temperature.
(3) Conversion at 97.5 % with 8 % SO_2 feed gas.
(4) Stack SO_2 emissions at 33 lbs./STPD.

Post-Cs Information:

(1) Screened all beds; full fourth pass of Cs-110.
(2) Pass 4 operating at 395-405°C (743-760°F).
(3) Conversion measured at 98.4 % with 8 % SO_2 fed.
(4) Stack SO_2 emissions at 21 lbs./STPD (36 % reduction).

Case 3: *Single Absorption Sulfur Burning Plant*

Pre-Cs Data:

(1) Used conventional catalyst in all five passes.
(2) Pass 5 operating near 430°C (806°F) inlet temp.
(3) Conversion at 98 % (air dilution plant).
(4) Stack SO_2 emissions at 26 lbs./STPD.

Post-Cs Information:

(1) Fresh catalyst in all beds; Cs-110 in Passes 4 and 5.
(2) Passes 4 and 5 operating at 410°C (770°F) inlet temp.
(3) Conversion reaches *99.1 %* with 8 % SO_2 fed.
(4) Stack SO_2 emissions at 12 lbs./STPD (*50 % reduction*).

Case 4: *Double Absorption Spent Acid Plant*

Pre-Cs Data:

(1) Standard catalyst in all beds; 12 % SO_2 gas strength.
(2) Pass 1 at 405°C (760°F); Pass 3 at 400°C (750°F).
(3) Heat exchanger pluggage limited Pass 3 inlet temp.
(4) Pre-heater required, especially after short shutdowns.
(5) Rate reduced to stay with SO_2 stack requirements.

Post-Cs Information:

(1) Cs-120 cap in Pass 1; full 3rd bed of Cs-110 rings.
(2) Pass 1 inlet at 360°C (680°F); outlet at 600°C (1110°F).
(3) Pass 3 operating well at 400°C (750°F).
(4) Need for pre-heater virtually eliminated.
(5) Rate dramatically increased with low SO_2 emissions.

Case 5: *Double Absorption Spent Acid Plant*

Pre-Cs Data:

(1) Used conventional catalyst in all beds; 7 % SO_2 fed.
(2) Pass 3 inlet at 410°C (770°F); heat exchange limits.
(3) Pass 4 inlet at 390°C (735°F) due to low 3rd pass temp.
(4) Emissions high (especially at startup);rate limited.

Post-Cs Information:

(1) Installed full bed of Cs-110 rings in Pass 3.
(2) Pass 3 operating very well at 410°C (770°F) inlet.
(3) Pass 4 operating very well at 425°C (800°F) inlet.
(4) Very low startup emissions; production rate increased;
no gas pre-heating required after short shutdown.

Several other applications for the cesium promoted catalyst are under consideration. Scenarios have been developed for increasing the acid production rates for double absorption plants and yet maintaining the same permitted hourly SO_2 emissions. Using Cs-110 rings in the bottom pass of double absorption plants, it is possible to reduce the lbs. SO_2 per ton of acid and hence allowing for greater production at the same SO_2 ppm level in the stack.

In order to take advantage of the benefits of the cesium-promoted Cs-120 and Cs-110 catalysts, there are some considerations that need to be evaluated prior to installation. Firstly, the heat exchange capacity in the plant must be evaluated in order to insure the feasibility of reaching the lower inlet temperatures required for the cesium catalyst beds. Secondly, there may be a greater tendency for pressure drop buildup in first passes equipped with cesium catalyst caps if the incoming gas stream is very dust-laden or contains acid mist. The highly active cesium-promoted catalyst has a more mobile molten salt than that of the conventional catalyst, which has a slightly greater tendency for accumulating incoming converter dust. The larger Cs-120 rings (12.5 mm, 1/2 in.) were developed to minimize the potential pressure drop buildup and yet maintain the required performance. The low temperature benefits of the Cs-120 rings in the first pass must be weighed against the slight possibility of higher pressure drop. Cs-110 applications in all other passes have been in operation for over two years without any indication of pressure drop buildup and/or loss of activity.

Overall, the use of the cesium-promoted catalyst in sulfuric acid converters has contributed to the significant reduction in SO_2 emissions and improved operability of the acid plants.

PORTABLE GAS ANALYSIS SYSTEM *(PeGASyS)*

The Monsanto Enviro-Chem Portable Gas Analysis System was developed several years ago to provide sulfuric acid producers with the means to fully characterize their plant operations. The PeGASyS system consists of a highly specialized gas sampling system and the state-of-the-art gas analyzer. Figure 4 shows a photograph of a portion of the gas analyzer system, including the specially design gas syringe. The analyzer is generally set up near a control room or laboratory and occupies a desk-sized space. A gas sample is taken from a slip stream of gas at the converter, heat exchanger, or absorbing tower pressure tap (or any available sampling port). The gas sample is then injected into the analyzer (state-of-the-art gas chromatograph) which accurately determines the SO_2 and O_2 levels. The PeGASyS method for characterizing the sulfuric acid plant operations is much more reliable and accurate than the standard wet chemical Reich test method. A typical sulfur burning plant can be completely analyzed in only a few hours with the PeGASyS system.

The results obtained with the PeGASyS system consist of an analysis report of the SO_2 and O_2 levels in each sample and a conversion calculation for each specific converter sample based on the inlet gas to the first bed. Figure 5 shows a typical Converter Performance Summary for a sulfur burning double absorption plant. The custom PeGASyS software also calculates gas flow rates based on the given production rates. Utilizing the PeGASyS data, the converter performance can be effectively simulated using the Monsanto Enviro-Chem proprietary modeling software. This information can then be used to optimize the plant operations, adjusting bed inlet temperatures, upgrading catalyst charges to maximize conversion and minimize SO_2 emissions.

Another important application of the PeGASyS system is in gas-gas heat exchanger leak detection. The exchanger must have shell side and tube side gas streams which contain different SO_2 levelsin order for the analysis to be effective. Figure 6 shows the typical output for a heat exchanger analysis. Often, leaking heat exchangers contribute to high SO_2 emissions by bleeding high SO_2 gas directly to the stack or flooding lower pass catalyst beds with SO_2-rich gas. Once the leaking exchanger is identified, it can be repaired, leading to a direct reduction in the stack emissions.

The following are case histories of typical applications of the PeGASyS service to reducing stack emissions:

Case 1: *Spent Acid Double Absorption Plant*

Issue: SO_2 emissions higher than expected.

Result: PeGASyS analysis indicated that the aging first pass was operating at a reduced efficiency. Replacement of the first pass resulted in significant reduction in stack emissions.

Case 2: *Sulfur Burning Double Absorption Plant*

Issue: SO_2 emissions were approaching permitted limit.

Result: PeGASyS analysis indicated a severe leak in the cold heat exchanger. Following exchanger repair, SO_2 emissions decreased from 3.9 lbs./STPD to 2.0 lbs./STPD.

Case 3: *Sulfur Burning Single Absorption Plant*

Issue: Emissions extremely high; poor conversion.

Result: PeGASyS analysis determined that Passes 2 and 3 were performing very poorly. It was determined that low bed inlet temperatures were responsible. Raising the temperatures led to a dramatic reduction in SO_2 emissions. The results also indicated that a 4th pass Cs-110 application was justified. With a full 4th pass of Cs-110 rings, this plant now has extremely low SO_2 emissions.

Case 4: *Spent Acid Double Absorption Plant*

Issue: SO_2 emissions approaching allowed limit.

Result: PeGASyS analysis of the cold heat exchanger identified a minute leak which was allowing some first pass feed gas to bypass directly to the final tower. This leak added over 200 ppm SO_2 to the stack. Repairs to this exchanger resolved the problem.

As can be seen from these examples, the Portable Gas Analysis System is an extremely effective tool for optimizing sulfuric plant operations and reducing stack SO_2 emissions. In a number of cases, the PeGASyS results have led to the installation of Monsanto cesium-promoted catalyst which resulted in the best overall conversion and the lowest level of sulfur dioxide escaping to the atmosphere.

CONCLUSIONS

The effectiveness of the Monsanto Enviro-Chem cesium-promoted catalysts (Cs-120 and Cs-110 rings) in improving sulfur dioxide conversion and reducing stack emissions has been demonstrated in a number of applications. The cesium catalyst can be applied in a variety of situations which can reduce emissions as well as enhance the versatility of the plant operations. In many situations, the catalyst can be used to reduce the impact of heat exchanger limitations. Cesium catalyst effectiveness in both single absorption and double absorption plants has been demonstrated and novel applications are still under development.

The Monsanto Enviro-Chem Portable Gas Analysis System (PeGASyS) has effectively been used in a variety of plants to optimize converter performance and identify problem areas. The results of the gas analyses are often used to identify the most effective applications of the Monsanto Cesium Catalyst in order to minimize SO_2 emissions and maximize converter performance. The use of these products and services allows for not only a positive impact on the environment but also improved performance and profitability for the sulfuric acid producer.

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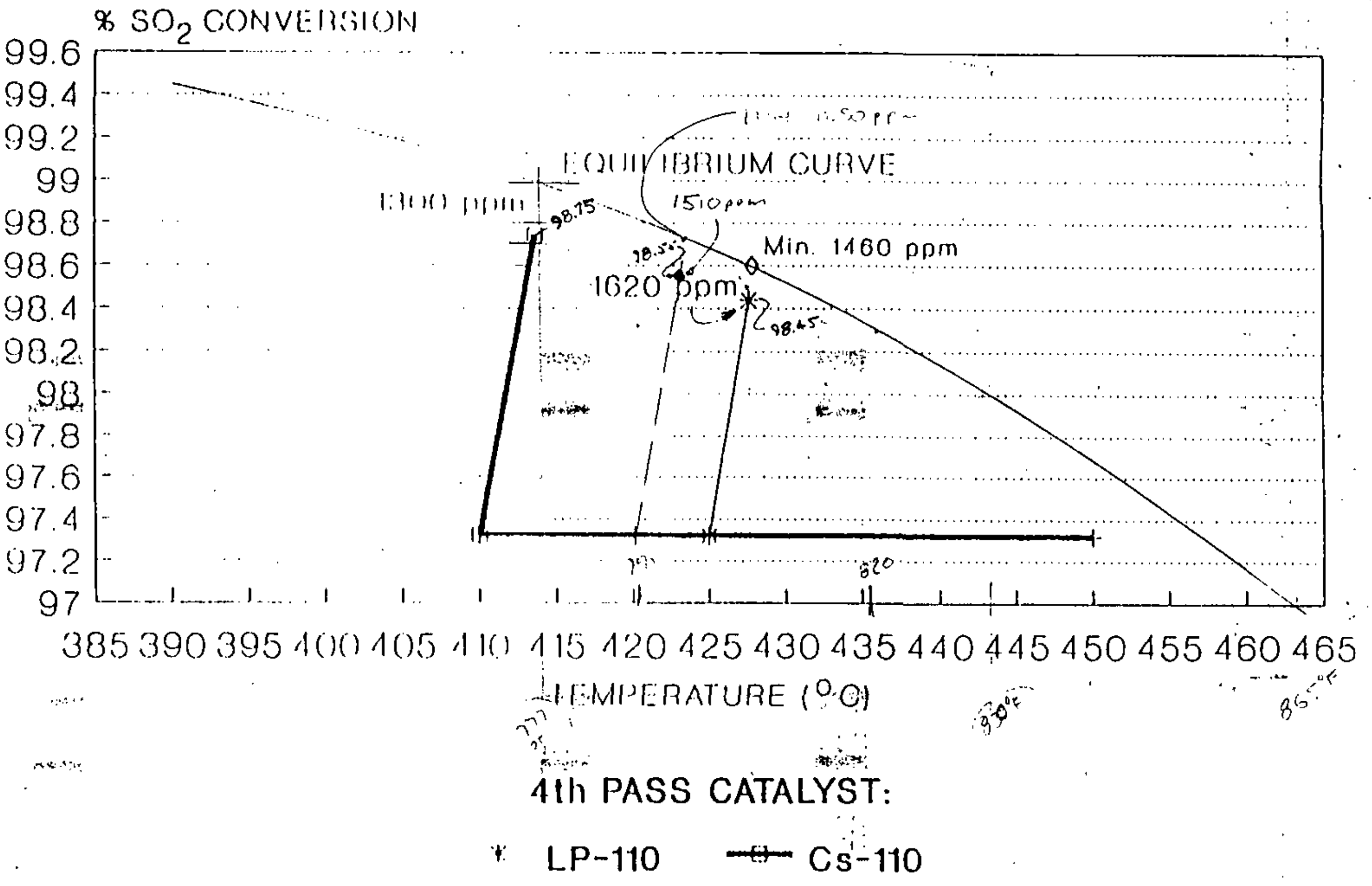
Figure 2

SINGLE ABSORPTION: Cs ADVANTAGE



FEED GAS = 9 % SO_2, 11.9 % O_2
410°C = 770°F; 425°C = 797°F

Figure 1

SO$_2$ OXIDATION RATE VERSUS TEMPERATURE

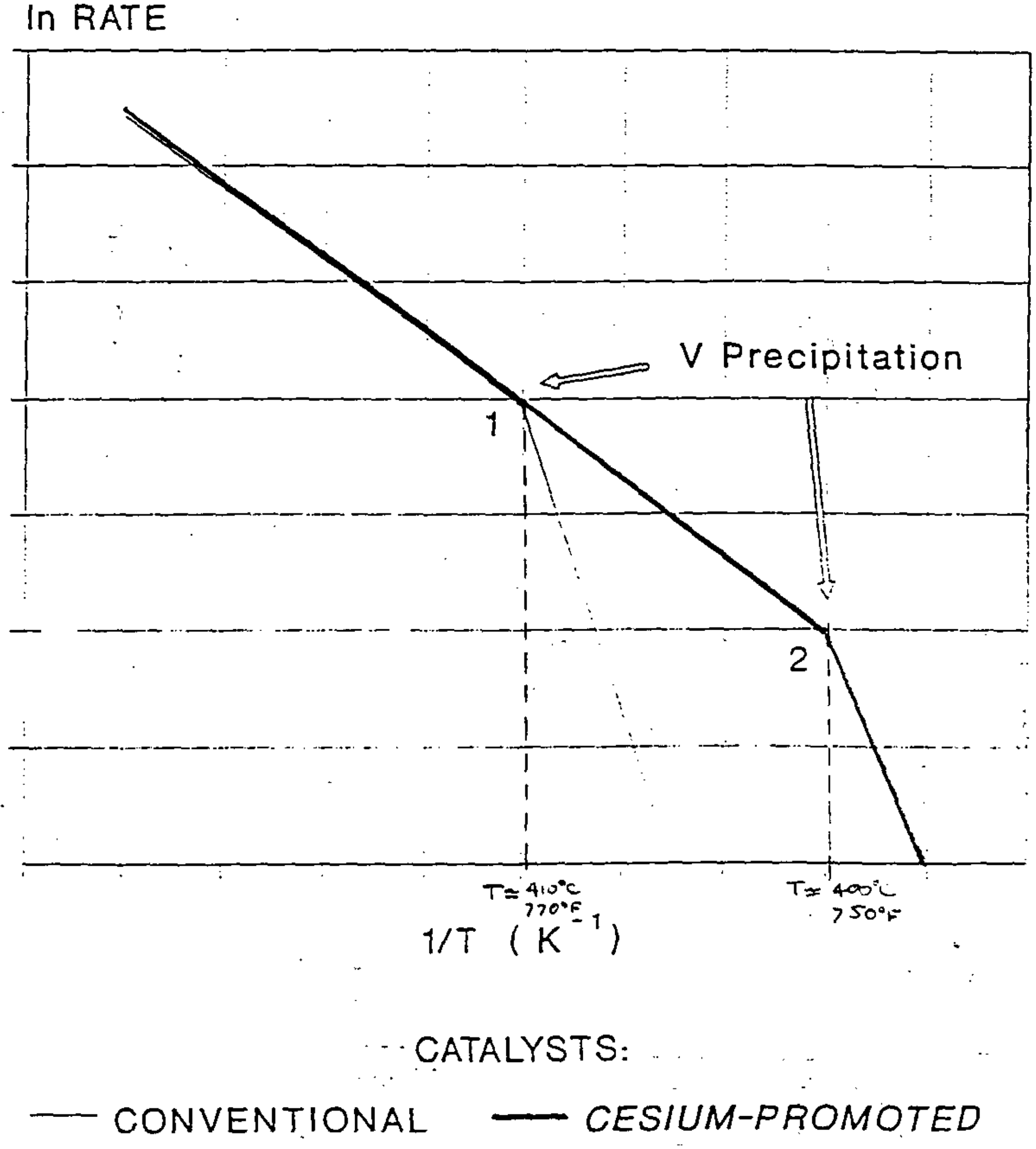
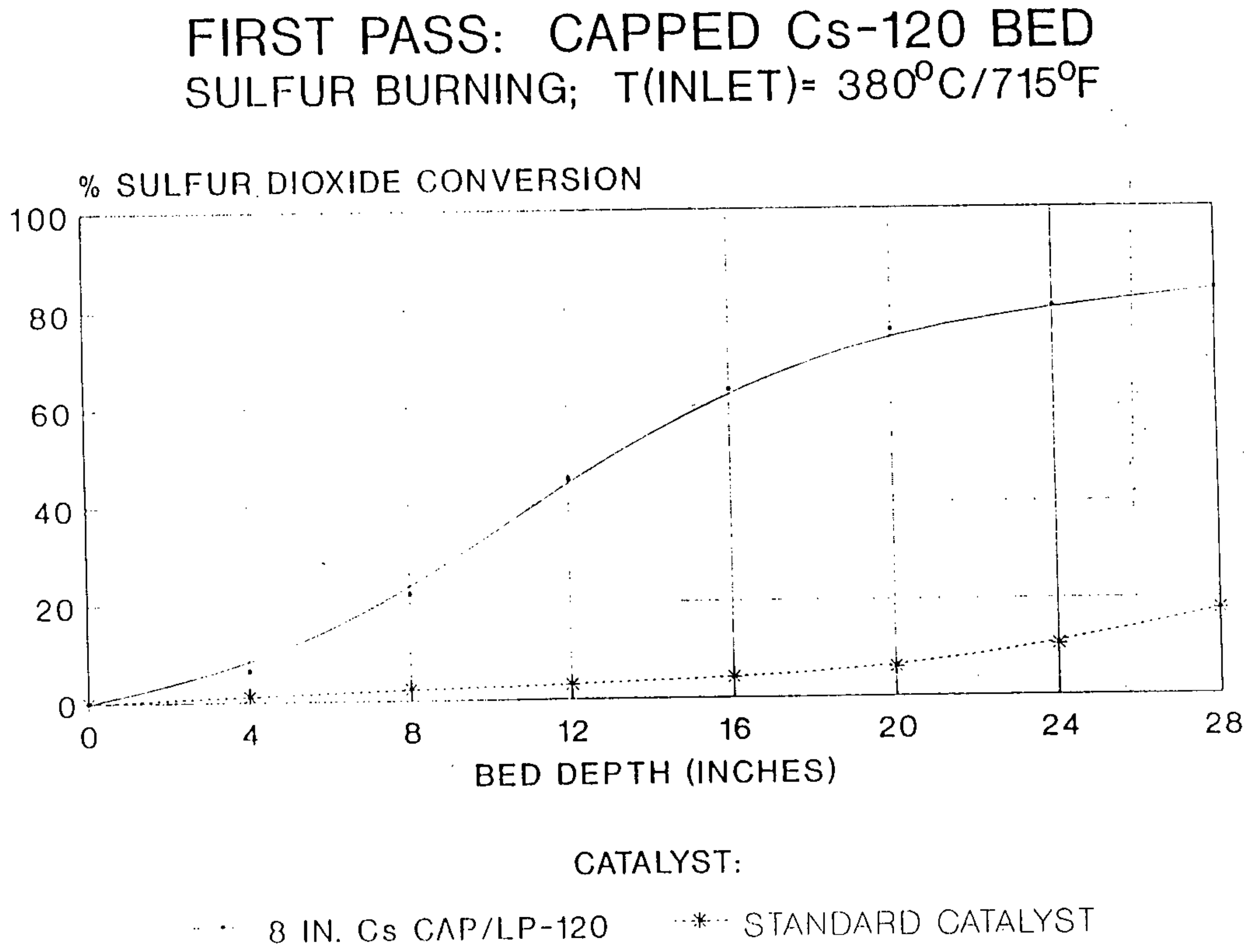


Figure 3

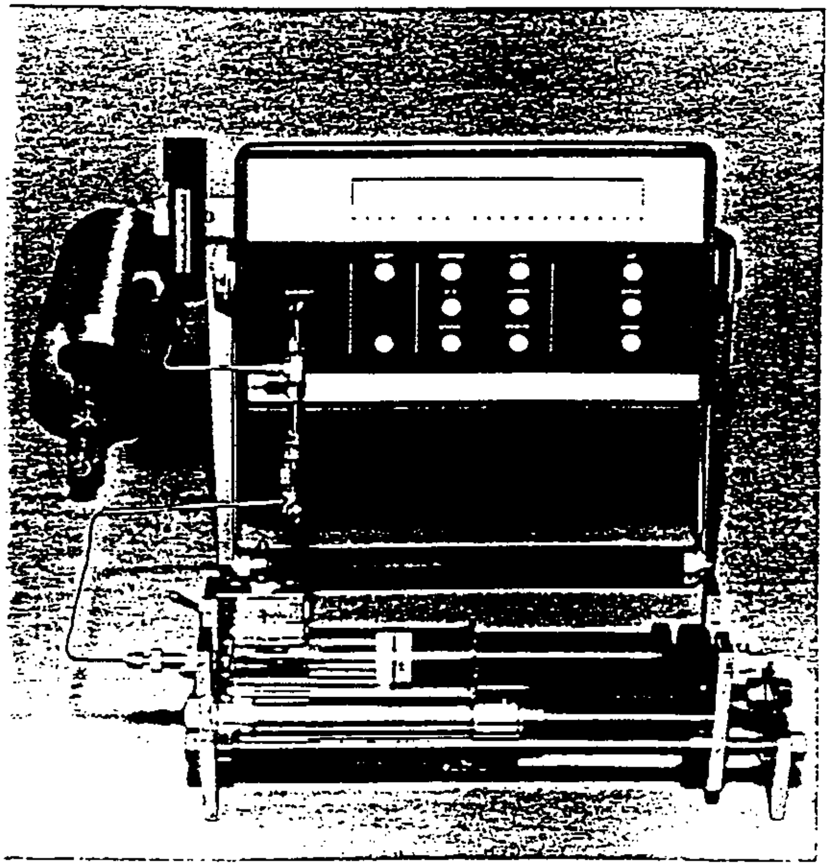


8 IN. Cs-120 CAP ON LP-120 RINGS

Figure 4

PeGASyS

Portable Gas Analysis System



Monsanto Enviro-Chem Systems, Inc.

Figure 5

MONSANTO ENVIRO-CHEM SYSTEMS, INC.

CONVERTER PERFORMANCE SUMMARY

CUSTOMER NAME: EXAMPLE 3 DATA FILE: XXX003.SAM

PLANT LOCATION: U. S. A.

PLANT NUMBER: 3

PLANT TYPE: SULFUR BURNER DOUBLE ABSORPTION

SAMPLE NO.	SAMPLE IDENTIFICATION	DATE / TIME OF SAMPLE		% SO_2	% O_2	% CONV.
5	SULFUR BURNER OUTLET	4-1-91	1600	11.209	9.506	1.563
4	FIRST PASS OUTLET	4-1-91	1600	5.135	6.998	59.394
3	SECOND PASS OUTLET	4-1-91	1600	2.088	5.638	84.269
2	THIRD PASS OUTLET	4-1-91	1600	0.911	5.144	93.257
1	FOURTH PASS OUTLET	4-1-91	1600	0.035	4.771	99.744
		SULFUR BURNER GAS		11.366	9.580	

SAMPLE NO.	SAMPLING POINT
1	OUTLET OF FINAL TOWER ABOVE MIST ELIM.
2	PASS 4 INLET AT CONVERTER TAP
3	PASS 3 INLET AT CONVERTER TAP
4	PASS 2 INLET AT CONVERTER TAP
5	PASS 1 INLET AT CONVERTER TAP

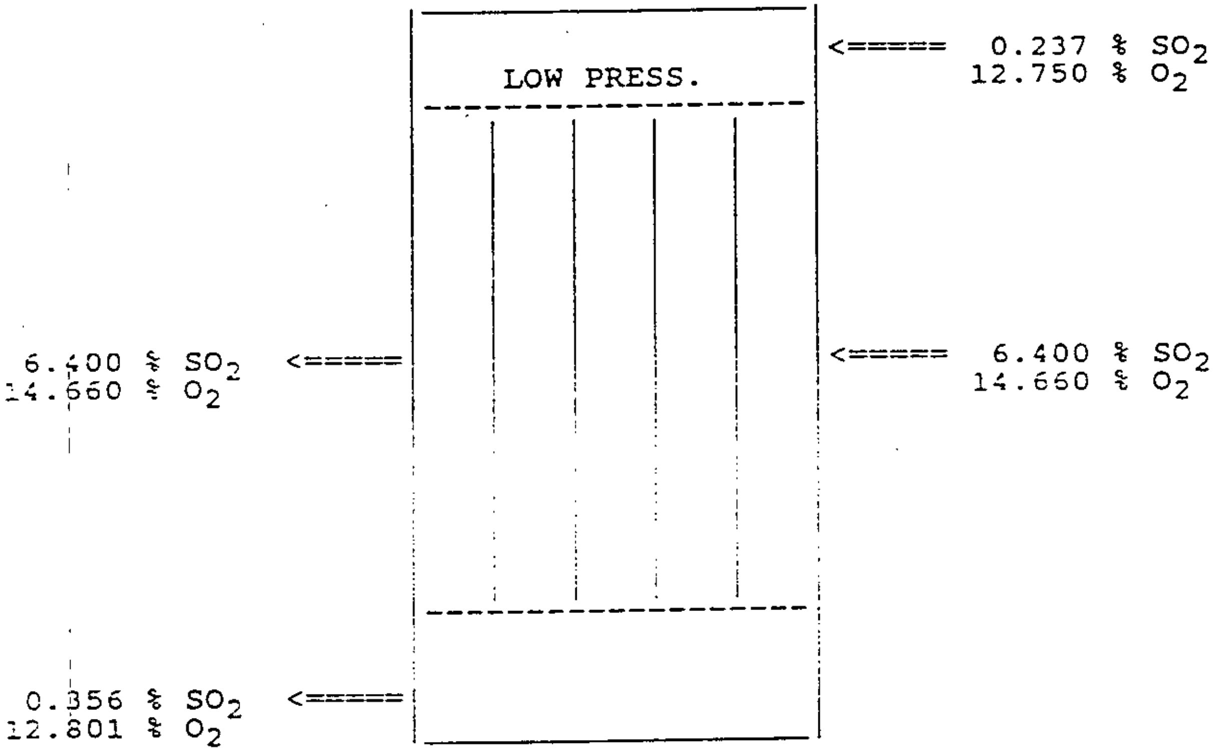
```
X X X X X X X X X X X X X X X X X X X X X X X X X X X X X X X X X X X X X X X X
X                                                        X                           X
X                            KG/HR.        LBS./HR.      X        CATALYST BED       X
X                         ----------------------         X        TEMPERATURES       X
X                                                        X        ------------       X
X   SULFUR FEED RATE        26054.80       57441.31      X                           X
X   SO2 EMISSIONS             133.04         293.30      X L/STPD  BED     OF   OC   X
X                                                        X ------  ---     -    -    X
X   LBS.SO2/TON =    3.35   KG SO2/TON =    1.67         X         1 IN    779  415  X
X                                                        X  31.5   1 OUT  1130  610  X
X                           NM3/HR          SCFM         X          RISE   351  195  X
X                         ----------------------         X         2 IN    824  440  X
X                                                        X  33.0   2 OUT   988  531  X
X   AIR TO SULFUR BURNER   160139.22      94243.89       X          RISE   164   91  X
X   CONVERTER INLET GAS    160139.22      94243.89       X         3 IN    831  444  X
X   CONVERTER OUTLET GAS   132907.50      78217.69       X  38.5   3 OUT   891  477  X
X   DILUTION AIR                0.00          0.00       X          RISE    60   33  X
X   TOTAL GAS TO PLANT     160139.22      94243.89       X         4 IN    795  424  X
X                                                        X  50.5   4 OUT   844  451  X
X   PRODUCTION RATE = 2100.00 SHORT TONS PER DAY         X          RISE    49   27  X
X                                                        X         5 IN              X
X                                                        X         5 OUT             X
X   NOTE: ALL GAS VOLUMES ARE BASED ON                   X          RISE             X
X         DRY, SO3-FREE GAS.                             X                           X
X                                                        X        TOTAL R  624  346  X
X                                                        X                           X
X X X X X X X X X X X X X X X X X X X X X X X X X X X X X X X X X X X X X X X X
```

Figure 6

MONSANTO ENVIRO-CHEM SYSTEMS, INC.

HEAT EXCHANGER EVALUATION

DATE / TIME:	4-1-91 / 1500	FILE: INTHEX.HEX
CUSTOMER:	EXAMPLE	
PLANT LOCATION:	U. S. A.	
PLANT NUMBER:	1	
PLANT TYPE:	METALLURGICAL; SINGLE ABSORPTION	
HEAT EXCHANGER:	INTERMEDIATE HEX	



2.0 % OF SHELL SIDE GAS IS LEAKING INTO TUBE SIDE

TUBE SIDE INLET GAS WAS SAMPLED AT:
INLET TO INTERMEDIATE HEX

TUBE SIDE OUTLET GAS WAS SAMPLED AT:
PASS 4 INLET AT CONVERTER

APPENDIX D

SO_2 EMISSION RATES AND H_2SO_4 PRODUCTION RATES FOR MULBERRY PHOSPHATES, INC. SULFURIC ACID PLANT FOR 21 MONTHS FOLLOWING A TURNAROUND

12/95-9/97

MULBERRY PHOSPHATES, INC.
MULBERRY, FLORIDA

Appendix D

	SO_2 Emission Rate		H_2SO_4 Production		SO_2 Emissions	
Date	Daily Average (lb/ton)	Monthly Average (lb/ton)	Production (ton/day)	Monthly Average (ton/day)	(ton/day)	Monthly Average (ton/day)
12/20/95	1.45		1539		1.116	
12/21/95	1.54		1553		1.196	
12/22/95	1.43		1545		1.105	
12/23/95	1.47		1571		1.155	
12/24/95	1.42		1573		1.117	
12/25/95	1.41		1545		1.089	
12/26/95	1.43		1564		1.118	
12/27/95	1.46		1542		1.126	
12/28/95	1.45		1493		1.082	
12/29/95	1.55		1703		1.320	
12/30/95	1.69		1424		1.203	
12/31/95	2.11	1.53	1493	1,545	1.575	1.183
01/01/96	2.02		1593		1.609	
01/02/96	1.97		1146		1.129	
01/03/96	Plant Down					
01/04/96	3.33		1729		2.879	
01/05/96	3.23		1317		2.127	
01/06/96	2.71		1666		2.257	
01/07/96	2.95		1633		2.409	
01/08/96	3.13		1692		2.648	
01/09/96	3.14		1631		2.561	
01/10/96	3.12		1642		2.562	
01/11/96	2.98		1653		2.463	
01/12/96	3.08		1655		2.549	
01/13/96	3.15		1662		2.618	
01/14/96	3.06		1669		2.554	
01/15/96	2.96		1408		2.084	
01/16/96	3.09		1644		2.540	
01/17/96	3.21		1649		2.647	
01/18/96	3.23		1652		2.668	
01/19/96	3.46		1651		2.856	
01/20/96	3.42		1678		2.869	
01/21/96	3.41		1700		2.899	
01/22/96	3.41		1620		2.762	
01/23/96	3.54		1721		3.046	
01/24/96	3.27		1329		2.173	
01/25/96	3.32		1660		2.756	
01/26/96	3.49		1702		2.970	
01/27/96	3.53		1705		3.009	
01/28/96	3.63		1654		3.002	
01/29/96	3.52		1636		2.879	
01/30/96	3.47		1662		2.884	
01/31/96	3.57	3.18	1619	1,613	2.890	2.577
02/01/96	3.69		1640		3.026	
02/02/96	3.84		1649		3.166	
02/03/96	3.87		1447		2.800	
02/04/96	3.16		1435		2.267	
02/05/96	3.68		1710		3.146	
02/06/96	3.77		1663		3.135	
02/07/96	3.86		1671		3.225	
02/08/96	3.89		1659		3.227	
02/09/96	3.92		1657		3.248	
02/10/96	3.94		1657		3.264	
02/11/96	3.91		1671		3.267	
02/12/96	3.73		1691		3.154	
02/13/96	3.67		1565		2.872	
02/14/96	3.16		1699		2.684	
02/15/96	3.61		1609		2.904	

Appendix D

	SO2 Emission Rate		H2SO4 Production		SO2 Emissions	
Date	Daily Average (lb/ton)	Monthly Average (lb/ton)	Production (ton/day)	Monthly Average (ton/day)	(ton/day)	Monthly Average (ton/day)
02/16/96	3.84		1599		3.070	
02/17/96	3.84		1654		3.176	
02/18/96	3.29		1307		2.150	
02/19/96	3.78		1713		3.238	
02/20/96	3.66		1587		2.904	
02/21/96	3.69		1713		3.160	
02/22/96	3.79		1593		3.019	
02/23/96	3.75		1724		3.233	
02/24/96	3.74		1711		3.200	
02/25/96	3.70		1749		3.236	
02/26/96	3.69		1692		3.122	
02/27/96	3.89		1419		2.760	
02/28/96	3.78		1651		3.120	
02/29/96	3.89	3.73	1595	1,625	3.102	3.030
03/01/96	3.96		1600		3.168	
03/02/96	3.95		1647		3.253	
03/03/96	3.95		1668		3.294	
03/04/96	3.91		1677		3.279	
03/05/96	3.91		1700		3.324	
03/06/96	3.87		1585		3.067	
03/07/96	3.87		1606		3.108	
03/08/96	3.49		1673		2.919	
03/09/96	3.83		1544		2.957	
03/10/96	3.99		1661		3.314	
03/11/96	3.90		1658		3.233	
03/12/96	3.67		1630		2.991	
03/13/96	3.71		1642		3.046	
03/14/96	3.70		1669		3.088	
03/15/96	3.76		1630		3.064	
03/16/96	3.71		1647		3.055	
03/17/96	3.69		1610		2.970	
03/18/96	3.76		1616		3.038	
03/19/96	3.88		1602		3.108	
03/20/96	3.80		1663		3.160	
03/21/96	3.78		1603		3.030	
03/22/96	3.66		1640		3.001	
03/23/96	3.43		1452		2.490	
03/24/96	3.16		1662		2.626	
03/25/96	3.17		1698		2.691	
03/26/96	3.31		1579		2.613	
03/27/96	3.23		1391		2.246	
03/28/96	3.76		1657		3.115	
03/29/96	3.76		1652		3.106	
03/30/96	3.78		1636		3.092	
03/31/96	3.81	3.71	1593	1,622	3.035	3.016
04/01/96	3.88		1632		3.166	
04/02/96	3.82		1627		3.108	
04/03/96	3.82		1633		3.119	
04/04/96	3.78		1605		3.033	
04/05/96	3.69		1718		3.170	
04/06/96	3.64		1428		2.599	
04/07/96	3.72		1707		3.175	
04/08/96	3.76		1536		2.888	
04/09/96	3.85		1655		3.186	
04/10/96	3.84		1573		3.020	
04/11/96	3.77		1743		3.286	
04/12/96	3.76		1533		2.882	
04/13/96	3.65		1710		3.121	

Appendix D

	SO2 Emission Rate		H2SO4 Production		SO2 Emissions	
Date	Daily Average (lb/ton)	Monthly Average (lb/ton)	Production (ton/day)	Monthly Average (ton/day)	(ton/day)	Monthly Average (ton/day)
04/14/96	3.63		1574		2.857	
04/15/96	3.72		1616		3.006	
04/16/96	3.88		1647		3.195	
04/17/96	3.74		1597		2.986	
04/18/96	3.67		1606		2.947	
04/19/96	3.68		1668		3.069	
04/20/96	3.68		1638		3.014	
04/21/96	3.70		1585		2.932	
04/22/96	3.58		1687		3.020	
04/23/96	3.54		1608		2.846	
04/24/96	3.90		1620		3.159	
04/25/96	Plant Down					
04/26/96	2.99		1624		2.428	
04/27/96	3.08		1603		2.469	
04/28/96	3.11		1614		2.510	
04/29/96	3.25		1362		2.213	
04/30/96	3.83	3.65	1624	1,613	3.110	2.949
05/01/96	3.84		1604		3.080	
05/02/96	3.96		1734		3.433	
05/03/96	3.97		1552		3.081	
05/04/96	3.99		1617		3.226	
05/05/96	3.95		1631		3.221	
05/06/96	3.96		1615		3.198	
05/07/96	3.95		1639		3.237	
05/08/96	3.97		1632		3.240	
05/09/96	3.24		1483		2.402	
05/10/96	3.62		1442		2.610	
05/11/96	3.86		1698		3.277	
05/12/96	3.88		1641		3.184	
05/13/96	3.83		1454		2.784	
05/14/96	3.91		1706		3.335	
05/15/96	3.93		1731		3.401	
05/16/96	3.95		1524		3.010	
05/17/96	3.93		1647		3.236	
05/18/96	3.96		1603		3.174	
05/19/96	3.97		1624		3.224	
05/20/96	3.97		1670		3.315	
05/21/96	3.98		1553		3.090	
05/22/96	3.97		1598		3.172	
05/23/96	3.98		1621		3.226	
05/24/96	3.95		1602		3.164	
05/25/96	3.95		1616		3.192	
05/26/96	3.96		1616		3.200	
05/27/96	3.95		1605		3.170	
05/28/96	3.98		1586		3.156	
05/29/96	3.97		1602		3.180	
05/30/96	3.73		1443		2.691	
05/31/96	3.98	3.90	1623	1,604	3.230	3.134
06/01/96	3.97		1635		3.245	
06/02/96	3.97		1624		3.224	
06/03/96	3.97		1624		3.224	
06/04/96	3.95		1628		3.215	
06/05/96	3.95		1603		3.166	
06/06/96	3.98		1672		3.327	
06/07/96	3.97		1588		3.152	
06/08/96	3.88		1623		3.149	
06/09/96	3.88		1629		3.160	
06/10/96	3.84		1615		3.101	

Appendix D

	SO2 Emission Rate		H2SO4 Production		SO2 Emissions	
Date	Daily Average (lb/ton)	Monthly Average (lb/ton)	Production (ton/day)	Monthly Average (ton/day)	(ton/day)	Monthly Average (ton/day)
06/11/96	3.93		1630		3.203	
06/12/96	3.96		1571		3.111	
06/13/96	3.97		1637		3.249	
06/14/96	3.97		1649		3.273	
06/15/96	3.97		1590		3.156	
06/16/96	3.96		1628		3.223	
06/17/96	3.88		1588		3.081	
06/18/96	3.44		1268		2.181	
06/19/96	3.66		1615		2.955	
06/20/96	3.02		1268		1.915	
06/21/96	3.59		1589		2.852	
06/22/96	3.49		1596		2.785	
06/23/96	3.07		1440		2.210	
06/24/96	3.06		1327		2.030	
06/25/96	3.52		1609		2.832	
06/26/96	3.65		1680		3.066	
06/27/96	3.68		1541		2.835	
06/28/96	3.69		1621		2.991	
06/29/96	3.63		1669		3.029	
06/30/96	3.76	3.74	1552	1,577	2.918	2.962
07/01/96	3.82		1706		3.258	
07/02/96	3.77		1512		2.850	
07/03/96	3.65		1420		2.592	
07/04/96	Reduced Rate					
07/05/96	3.52		1850		3.256	
07/06/96	3.94		1631		3.213	
07/07/96	3.92		1610		3.156	
07/08/96	3.97		1681		3.337	
07/09/96	3.54		1531		2.710	
07/10/96	3.91		1423		2.782	
07/11/96	3.98		1603		3.190	
07/12/96	3.89		1600		3.112	
07/13/96	3.95		1629		3.217	
07/14/96	3.90		1615		3.149	
07/15/96	3.60		1571		2.828	
07/16/96	3.53		1650		2.912	
07/17/96	3.01		1628		2.450	
07/18/96	1.84		1474		1.356	
07/19/96	3.55		1146		2.034	
07/20/96	3.97		1616		3.208	
07/21/96	3.98		1657		3.297	
07/22/96	3.99		1539		3.070	
07/23/96	3.98		1584		3.152	
07/24/96	3.97		1676		3.327	
07/25/96	3.97		1448		2.874	
07/26/96	3.97		1414		2.807	
07/27/96	3.95		1812		3.579	
07/28/96	3.71		1414		2.623	
07/29/96	3.96		1679		3.324	
07/30/96	3.94		1682		3.314	
07/31/96	3.93	3.75	1514	1,577	2.975	2.965
08/01/96	3.97		1693		3.361	
08/02/96	3.96		1695		3.356	
08/03/96	3.97		1609		3.194	
08/04/96	3.96		1540		3.049	
08/05/96	3.96		1608		3.184	
08/06/96	3.97		1594		3.164	

Appendix D

	SO2 Emission Rate		H2SO4 Production		SO2 Emissions	
Date	Daily Average (lb/ton)	Monthly Average (lb/ton)	Production (ton/day)	Monthly Average (ton/day)	(ton/day)	Monthly Average (ton/day)
08/07/96	3.98		1255		2.497	
08/08/96	Plant Down					
08/09/96	Plant Down					
08/10/96	Plant Down					
08/11/96	3.91		1630		3.187	
08/12/96	3.96		1590		3.148	
08/13/96	3.58		1639		2.934	
08/14/96	3.65		1655		3.020	
08/15/96	2.40		1146		1.375	
08/16/96	3.46		1468		2.540	
08/17/96	3.57		1648		2.942	
08/18/96	3.57		1633		2.915	
08/19/96	3.56		1644		2.926	
08/20/96	3.64		1616		2.941	
08/21/96	3.68		1648		3.032	
08/22/96	3.64		1621		2.950	
08/23/96	3.79		1633		3.095	
08/24/96	3.70		1719		3.180	
08/25/96	3.70		1625		3.006	
08/26/96	3.65		1538		2.807	
08/27/96	3.62		1625		2.941	
08/28/96	3.60		1614		2.905	
08/29/96	3.71		1654		3.068	
08/30/96	3.70		1567		2.899	
08/31/96	3.62	3.70	1617	1,590	2.927	2.948
09/01/96	3.42		1620		2.770	
09/02/96	3.42		1608		2.750	
09/03/96	3.30		1560		2.574	
09/04/96	2.17		1393		1.511	
09/05/96	3.24		1578		2.556	
09/06/96	3.30		1626		2.683	
09/07/96	3.31		1614		2.671	
09/08/96	2.93		1592		2.332	
09/09/96	2.40		1618		1.942	
09/10/96	Plant Down					
09/11/96	3.74		1620		3.029	
09/12/96	3.70		1610		2.979	
09/13/96	3.70		1643		3.040	
09/14/96	3.74		1595		2.983	
09/15/96	3.74		1599		2.990	
09/16/96	3.24		1560		2.527	
09/17/96	3.27		1571		2.569	
09/18/96	3.72		1612		2.998	
09/19/96	3.69		1600		2.952	
NOTE: 9 MONTHS AFTER TURNAROUND						
09/20/96	3.74		1637		3.061	
09/21/96	3.77		1608		3.031	
09/22/96	3.81		1584		3.018	
09/23/96	3.92		1124		2.203	
09/24/96	Plant Down					
09/25/96	3.19		1171		1.868	
09/26/96	3.81		1637		3.118	
09/27/96	3.80		1741		3.308	
09/28/96	3.78		1580		2.986	
09/29/96	3.76		1644		3.091	
09/30/96	3.85	3.48	1656	1,571	3.188	2.740
10/01/96	3.81		1603		3.054	
10/02/96	3.77		1646		3.103	

Appendix D

	SO2 Emission Rate		H2SO4 Production		SO2 Emissions	
Date	Daily Average (lb/ton)	Monthly Average (lb/ton)	Production (ton/day)	Monthly Average (ton/day)	(ton/day)	Monthly Average (ton/day)
10/03/96	3.81		1641		3.126	
10/04/96	3.76		1667		3.134	
10/05/96	3.79		1629		3.087	
10/06/96	3.78		1634		3.088	
10/07/96	3.87		1597		3.090	
10/08/96	3.97		1628		3.232	
10/09/96	3.98		1666		3.315	
10/10/96	3.96		1653		3.273	
10/11/96	3.95		1595		3.150	
10/12/96	3.94		1738		3.424	
10/13/96	3.96		1456		2.883	
10/14/96	3.86		1534		2.961	
10/15/96	3.98		1646		3.276	
10/16/96	Plant Down					
10/17/96	Plant Down					
10/18/96	3.96		1466		2.903	
10/19/96	3.96		1566		3.101	
10/20/96	3.94		1482		2.920	
10/21/96	3.81		1254		2.389	
10/22/96	3.97		1572		3.120	
10/23/96	3.94		1642		3.235	
10/24/96	3.97		1482		2.942	
10/25/96	3.95		1551		3.063	
10/26/96	3.98		1657		3.297	
10/27/96	3.97		1643		3.261	
10/28/96	3.98		1520		3.025	
10/29/96	3.97		1547		3.071	
10/30/96	3.97		1529		3.035	
10/31/96	3.97	3.91	1573	1,580	3.122	3.092
11/01/96	3.76		1432		2.692	
11/02/96	2.90		1509		2.188	
11/03/96	2.78		1179		1.639	
11/04/96	3.95		1589		3.138	
11/05/96	3.93		1591		3.126	
11/06/96	3.83		1549		2.966	
11/07/96	3.90		1615		3.149	
11/08/96	3.95		1456		2.876	
11/09/96	3.97		1495		2.968	
11/10/96	3.95		1587		3.134	
11/11/96	3.98		1582		3.148	
11/12/96	3.99		1576		3.144	
11/13/96	3.98		1582		3.148	
11/14/96	3.98		1591		3.166	
11/15/96	3.98		1566		3.116	
11/16/96	3.98		1570		3.124	
11/17/96	3.99		1573		3.138	
11/18/96	3.98		1515		3.015	
11/19/96	3.97		1589		3.154	
11/20/96	3.97		1537		3.051	
11/21/96	3.97		1557		3.091	
11/22/96	3.97		1543		3.063	
11/23/96	3.97		1554		3.085	
11/24/96	3.98		1598		3.180	
11/25/96	3.96		1550		3.069	
11/26/96	3.98		1574		3.132	
11/27/96	3.97		1562		3.101	
11/28/96	3.98		1586		3.156	
11/29/96	3.98		1587		3.158	
11/30/96	3.97	3.88	1591	1,546	3.158	3.009

Appendix D

	SO2 Emission Rate		H2SO4 Production		SO2 Emissions	
Date	Daily Average (lb/ton)	Monthly Average (lb/ton)	Production (ton/day)	Monthly Average (ton/day)	(ton/day)	Monthly Average (ton/day)
12/01/96	3.96		1550		3.069	
12/02/96	3.97		1533		3.043	
12/03/96	3.98		1620		3.224	
12/04/96	3.97		1645		3.265	
12/05/96	3.99		1492		2.977	
12/06/96	3.78		1189		2.247	
12/07/96	3.68		1522		2.800	
12/08/96	3.83		1252		2.398	
12/09/96	3.51		1207		2.118	
12/10/96	3.98		1570		3.124	
12/11/96	3.94		1545		3.044	
12/12/96	3.95		1562		3.085	
12/13/96	3.98		1549		3.083	
12/14/96	3.97		1559		3.095	
12/15/96	3.98		1564		3.112	
12/16/96	3.66		1509		2.761	
12/17/96	3.72		1426		2.652	
12/18/96	3.95		1540		3.042	
12/19/96	3.98		1543		3.071	
12/20/96	3.97		1597		3.170	
12/21/96	3.98		1583		3.150	
12/22/96	3.98		1554		3.092	
12/23/96	3.98		1572		3.128	
12/24/96	3.98		1524		3.033	
12/25/96	3.98		1567		3.118	
12/26/96	3.96		1550		3.069	
12/27/96	3.99		1569		3.130	
12/28/96	3.96		1538		3.045	
12/29/96	3.96		1574		3.117	
12/30/96	3.97		1565		3.107	
12/31/96	3.98	3.92	1538	1,520	3.061	2.982
01/01/97	3.98		1562		3.108	
01/02/97	3.98		1565		3.114	
01/03/97	3.97		1590		3.156	
01/04/97	3.98		1491		2.967	
01/05/97	3.98		1560		3.104	
01/06/97	3.98		1609		3.202	
01/07/97	3.97		1500		2.978	
01/08/97	3.97		1511		2.999	
01/09/97	3.96		1522		3.014	
01/10/97	3.98		1541		3.067	
01/11/97	3.98		1550		3.085	
01/12/97	3.98		1538		3.061	
01/13/97	3.97		1553		3.083	
01/14/97	3.98		1554		3.092	
01/15/97	3.95		1526		3.014	
01/16/97	3.98		1523		3.031	
01/17/97	3.98		1573		3.130	
01/18/97	3.99		1549		3.090	
01/19/97	3.99		1570		3.132	
01/20/97	3.98		1541		3.067	
01/21/97	3.99		1565		3.122	
01/22/97	3.98		1621		3.226	
01/23/97	3.94		1441		2.839	
01/24/97	3.60		1215		2.187	
01/25/97	3.94		1506		2.967	
01/26/97	3.95		1494		2.951	
01/27/97	3.97		1548		3.073	

Appendix D

	SO2 Emission Rate		H2SO4 Production		SO2 Emissions	
Date	Daily Average (lb/ton)	Monthly Average (lb/ton)	Production (ton/day)	Monthly Average (ton/day)	(ton/day)	Monthly Average (ton/day)
01/28/97	3.99		1605		3.202	
01/29/97	3.94		1540		3.034	
01/30/97	3.97		1552		3.081	
01/31/97	3.60	3.95	1026	1,517	1.847	3.001
02/01/97	3.95		1558		3.077	
02/02/97	3.96		1561		3.091	
02/03/97	3.97		1551		3.079	
02/04/97	3.98		1627		3.238	
02/05/97	3.98		1467		2.919	
02/06/97	3.97		1541		3.059	
02/07/97	3.97		1586		3.148	
02/08/97	3.98		1510		3.005	
02/09/97	3.99		1569		3.130	
02/10/97	4.95		1064		2.633	
02/11/97	3.98		1551		3.086	
02/12/97	3.98		1557		3.098	
02/13/97	3.98		1534		3.053	
02/14/97	3.98		1617		3.218	
02/15/97	3.97		1466		2.910	
02/16/97	3.98		1586		3.156	
02/17/97	3.98		1570		3.124	
02/18/97	3.99		1584		3.160	
02/19/97	3.99		1525		3.042	
02/20/97	3.98		1518		3.021	
02/21/97	3.99		1515		3.022	
02/22/97	3.98		1590		3.164	
02/23/97	3.98		1500		2.985	
02/24/97	3.98		1584		3.152	
02/25/97	3.98		1576		3.136	
02/26/97	3.98		1546		3.077	
02/27/97	3.91		1530		2.991	
02/28/97	3.95	4.01	1538	1,533	3.038	3.065
03/01/97	3.96		1540		3.049	
03/02/97	3.97		1545		3.067	
03/03/97	3.96		1536		3.041	
03/04/97	3.98		1609		3.202	
03/05/97	3.99		1475		2.943	
03/06/97	3.97		1512		3.001	
03/07/97	3.98		1549		3.083	
03/08/97	3.98		1464		2.913	
03/09/97	3.98		1580		3.144	
03/10/97	3.98		1579		3.142	
03/11/97	3.98		1500		2.985	
03/12/97	3.97		1529		3.035	
03/13/97	3.98		1539		3.063	
03/14/97	3.97		1454		2.886	
03/15/97	3.99		1519		3.030	
03/16/97	3.98		1534		3.053	
03/17/97	3.52		1428		2.513	
03/18/97	3.98		1547		3.079	
03/19/97	3.98		1472		2.929	
03/20/97	3.98		1586		3.156	
03/21/97	3.99		1527		3.046	
03/22/97	3.99		1467		2.927	
03/23/97	3.97		1520		3.017	
03/24/97	3.97		1600		3.176	
03/25/97	3.96		1530		3.029	
03/26/97	3.97		1530		3.037	

Appendix D

	SO2 Emission Rate		H2SO4 Production		SO2 Emissions	
Date	Daily Average (lb/ton)	Monthly Average (lb/ton)	Production (ton/day)	Monthly Average (ton/day)	(ton/day)	Monthly Average (ton/day)
03/27/97	3.99		1526		3.044	
03/28/97	3.97		1569		3.114	
03/29/97	3.97		1512		3.001	
03/30/97	3.97		1520		3.017	
03/31/97	3.97	3.96	1524	1,527	3.025	3.024
04/01/97	3.83		1014		1.942	
04/02/97	3.98		1545		3.075	
04/03/97	3.99		1527		3.046	
04/04/97	3.77		1252		2.360	
04/05/97	3.97		1454		2.886	
04/06/97	3.97		1521		3.019	
04/07/97	3.98		1509		3.003	
04/08/97	3.97		1542		3.061	
04/09/97	3.99		1593		3.178	
04/10/97	3.98		1432		2.850	
04/11/97	3.99		1522		3.036	
04/12/97	3.99		1505		3.002	
04/13/97	3.98		1506		2.997	
04/14/97	3.98		1515		3.015	
04/15/97	3.99		1547		3.086	
04/16/97	Reduced Rate					
04/17/97	3.98		1525		3.035	
04/18/97	3.98		1502		2.989	
04/19/97	3.97		1517		3.011	
04/20/97	3.97		1477		2.932	
04/21/97	3.97		1493		2.964	
04/22/97	3.98		1557		3.098	
04/23/97	3.98		1475		2.935	
04/24/97	3.98		1507		2.999	
04/25/97	3.44		1106		1.902	
04/26/97	3.98		1507		2.999	
04/27/97	3.98		1485		2.955	
04/28/97	3.97		1493		2.964	
04/29/97	3.98		1489		2.963	
04/30/97	3.94	3.95	1472	1,469	2.900	2.904
05/01/97	3.98		1553		3.090	
05/02/97	3.99		1449		2.891	
05/03/97	3.99		1503		2.998	
05/04/97	3.97		1527		3.031	
05/05/97	3.99		1549		3.090	
05/06/97	3.97		1457		2.892	
05/07/97	3.96		1491		2.952	
05/08/97	3.97		1504		2.985	
05/09/97	3.98		1578		3.140	
05/10/97	3.99		1444		2.881	
05/11/97	3.97		1562		3.101	
05/12/97	3.99		1432		2.857	
05/13/97	3.99		1463		2.919	
05/14/97	3.98		1450		2.886	
05/15/97	3.99		1545		3.082	
05/16/97	3.98		1466		2.917	
05/17/97	3.98		1452		2.889	
05/18/97	3.99		1638		3.268	
05/19/97	3.98		1432		2.850	
05/20/97	3.98		1512		3.009	
05/21/97	3.97		1458		2.894	
05/22/97	3.98		1512		3.009	
05/23/97	3.97		1454		2.886	

Appendix D

	SO2 Emission Rate		H2SO4 Production		SO2 Emissions	
Date	Daily Average (lb/ton)	Monthly Average (lb/ton)	Production (ton/day)	Monthly Average (ton/day)	(ton/day)	Monthly Average (ton/day)
05/24/97	3.97		1541		3.059	
05/25/97	3.97		1460		2.898	
05/26/97	3.97		1475		2.928	
05/27/97	3.99		1525		3.042	
05/28/97	3.66		1222		2.236	
05/29/97	3.95		1490		2.943	
05/30/97	3.98		1559		3.102	
05/31/97	3.97	3.97	1502	1,490	2.981	2.958
06/01/97	3.94		1495		2.945	
06/02/97	3.98		1575		3.134	
06/03/97	3.95		1371		2.708	
06/04/97	3.78		1467		2.773	
06/05/97	3.58		1455		2.604	
06/06/97	3.59		1486		2.667	
06/07/97	3.58		1447		2.590	
06/08/97	3.58		1467		2.626	
06/09/97	3.64		1465		2.666	
06/10/97	3.70		1070		1.980	
06/11/97	3.59		1469		2.637	
06/12/97	3.72		1452		2.701	
06/13/97	3.10		1236		1.916	
06/14/97	3.00		1785		2.678	
06/15/97	2.99		1342		2.006	
06/16/97	3.09		1626		2.512	
06/17/97	3.38		1389		2.347	
06/18/97	3.37		1456		2.453	
06/19/97	3.40		1452		2.468	
06/20/97	3.41		1102		1.879	
06/21/97	3.43		1594		2.734	
NOTE: 18 MONTHS AFTER TURNAROUND						
06/22/97	3.39		1310		2.220	
06/23/97	3.51		1140		2.001	
06/24/97	3.42		1491		2.550	
06/25/97	3.34		1413		2.360	
06/26/97	3.54		1455		2.575	
06/27/97	3.39		1315		2.229	
06/28/97	3.57		1468		2.620	
06/29/97	3.57		1477		2.636	
06/30/97	3.46	3.50	1444	1,424	2.498	2.490
07/01/97	3.63		1468		2.664	
07/02/97	3.61		1344		2.426	
07/03/97	3.69		1433		2.644	
07/04/97	3.14		1407		2.209	
07/05/97	3.31		1207		1.998	
07/06/97	3.64		1543		2.808	
07/07/97	3.76		1416		2.662	
07/08/97	3.72		1470		2.734	
07/09/97	3.67		1401		2.571	
07/10/97	3.75		1450		2.719	
07/11/97	3.73		1467		2.736	
07/12/97	3.74		1434		2.682	
07/13/97	3.67		1556		2.855	
07/14/97	3.76		1439		2.705	
07/15/97	3.72		1502		2.794	
07/16/97	3.65		1468		2.679	
07/17/97	3.73		1479		2.758	
07/18/97	3.72		1453		2.703	
07/19/97	3.73		1457		2.717	

Appendix D

	SO2 Emission Rate		H2SO4 Production		SO2 Emissions	
Date	Daily Average (lb/ton)	Monthly Average (lb/ton)	Production (ton/day)	Monthly Average (ton/day)	(ton/day)	Monthly Average (ton/day)
07/20/97	3.74		1463		2.736	
07/21/97	3.63		1303		2.365	
07/22/97	3.64		1340		2.439	
07/23/97	3.66		1434		2.624	
07/24/97	Plant Down					
07/25/97	3.56		884		1.574	
07/26/97	3.54		1466		2.595	
07/27/97	3.50		1413		2.473	
07/28/97	3.21		1040		1.669	
07/29/97	3.47		1570		2.724	
07/30/97	3.58		1408		2.520	
07/31/97	3.70	3.62	1495	1,407	2.766	2.552
08/01/97	3.70		1380		2.553	
08/02/97	3.90		1482		2.890	
08/03/97	3.90		1425		2.779	
08/04/97	3.72		1537		2.859	
08/05/97	3.90		1405		2.740	
08/06/97	3.92		1403		2.750	
08/07/97	3.62		1478		2.675	
08/08/97	3.76		851		1.600	
08/09/97	3.96		1734		3.433	
08/10/97	3.93		1386		2.723	
08/11/97	3.94		1503		2.961	
08/12/97	3.96		1438		2.847	
08/13/97	3.96		1461		2.893	
08/14/97	3.97		1399		2.777	
08/15/97	3.93		1418		2.786	
08/16/97	3.94		1444		2.845	
08/17/97	Reduced Rate					
08/18/97	3.87		1446		2.798	
08/19/97	3.86		1483		2.862	
08/20/97	3.90		1367		2.666	
08/21/97	3.91		1475		2.884	
08/22/97	3.95		1414		2.793	
08/23/97	3.94		1449		2.855	
08/24/97	3.94		1211		2.386	
08/25/97	Plant Down					
08/26/97	Plant Down					
08/27/97	3.75		723		1.356	
08/28/97	2.89		1519		2.195	
08/29/97	2.90		1139		1.652	
08/30/97	2.68		1489		1.995	
08/31/97	2.72	3.73	1482	1,391	2.016	2.592
09/01/97	2.75		1461		2.009	
09/02/97	3.75		1488		2.790	
09/03/97	3.94		1593		3.138	
09/04/97	3.83		1519		2.909	
09/05/97	3.79		1603		3.038	
09/06/97	3.96		1482		2.934	
09/07/97	3.97		1574		3.124	
09/08/97	3.98		1570		3.124	
09/09/97	3.98		1534		3.053	
09/10/97	3.97		1551		3.079	
09/11/97	Reduced Rate					
09/12/97	3.97		1497		2.972	
09/13/97	3.97		1564		3.105	
09/14/97	3.98		1549		3.083	
09/15/97	3.97		1541		3.059	

Appendix D

	SO2 Emission Rate		H2SO4 Production		SO2 Emissions	
Date	Daily Average (lb/ton)	Monthly Average (lb/ton)	Production (ton/day)	Monthly Average (ton/day)	(ton/day)	Monthly Average (ton/day)
09/16/97	3.98		1582		3.148	
09/17/97	3.96		1578		3.124	
09/18/97	3.95		1483		2.929	
09/19/97	3.97		1547		3.071	
09/20/97	3.97		1484		2.946	
09/21/97	3.97		1572		3.120	
09/22/97	3.98		1461		2.907	
09/23/97	3.98		1557		3.098	
09/24/97	3.97		1492		2.962	
09/25/97	3.97		1619		3.214	
09/26/97	3.98		1517		3.019	
09/27/97	3.98		1509		3.003	
09/28/97	3.98		1611		3.206	
09/29/97	3.99		1571		3.134	
09/30/97	3.98	3.91	1519	1,539	3.023	3.011

18-Month		551	Days		78.7	Weeks	18.18	Months				
12/20/95	to	06/21/97	Average				Average			Total		
			3.73	lb/ton			1,558	ton/day		1566.49	ton for the	
											550 day Period	
9-Month		275	Days		39.3	Weeks	9.07	Months				
12/20/95	to	09/19/96	Average				Average			Total		
			3.55	lb/ton			1,599	ton/day		763.72	ton for the	
											275 day Period	
										Total		
									763.72	x 2 =	1527.43	tons
										for two 275 day Period		

APPENDIX E

MONSANTO ENVIRO-SYSTEMS, INC. HEAT RECOVERY SYSTEMS FOR SULFURIC ACID PLANTS

Monsanto Enviro-Chem

SULFURIC ACID HEAT RECOVERY SYSTEM (HRS) OPERATIONS AT NAMHAE CHEMICAL CORPORATION, KOREA

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Presented at "Sulphur 88" - Vienna, Austria
November, 1988

ABSTRACT

Monsanto Enviro-Chem's (MEC) patented new Heat Recovery System (HRS) recovers most of the heat from sulfuric acid plant absorbers at up to 10 bars pressure. HRS was proven in pilot plant operation from 1983 to 1985. The first commercial unit was started up very successfully on Namhae Chemical Corporation's (NCC) 1350 t/d plant in November, 1987. With almost a year of operating experience, HRS has proven easy to operate, met all design criteria and has operated with a high on-stream time. HRS has been sold to several other customers and many others are evaluating the economics in their plants.

The following comment was made by K.P. Chae, Managing Director of Engineering and Projects and former Plant Manager of Namhae's Yeosu site:

> "Without challenging spirit, you can't get much. We are proud of being the first case of commercial application of Monsanto Enviro-Chem's HRS technology.
>
> After many sleepless nights during the initial start-up and then following eight months' uninterrupted operation, now I can comfortably say that Namhae has made the right decision to go ahead with HRS, which has been tremendously profitable for Namhae Chemical Corporation by killing 'three birds with one stone': Energy saving, production increase and lowering emission."

TECHNICAL BACKGROUND

The production of sulfuric acid in sulfur burning acid plants generates large quantities of heat from the combustion of sulfur to sulfur dioxide; the catalytic oxidation of sulfur dioxide to sulfur trioxide; and the heat of formation of acid as SO_3 is absorbed in sulfuric acid.

The heat of sulfur combustion and oxidation of sulfur dioxide have been utilized for years to generate steam. Until the mid-1970's, energy recovery from acid plants was about 55%. Then, as fuel prices increased, acid plants were optimized to generate more steam. Low gas-temperature economizers, low pressure drop catalyst, suction drying towers, increased SO_2 gas concentration and preheating boiler feedwater with acid became commonplace and energy recovery from acid plants increased to 70%. However, 30% of the heat was still lost. This heat loss was primarily in the acid formation and cooling process.

Monsanto Enviro-Chem initiated a major research effort in the late 1970's to recover more of this lost energy. The research progressed through studies and laboratory tests until 1983 when a pilot tower was installed in a 550 t/d acid plant to demonstrate the now patented Heat Recovery System (HRS).

The basis of the HRS is that sulfuric acid in the 99% range has low corrosivity toward certain commercially available alloys at temperatures up to 220°C and higher. The high acid temperature provides the driving force to economically generate steam while the acid still readily absorbs SO_3 gas.

The HRS becomes commercially viable when it is located before existing absorption towers or is used as the interpass absorption tower in a new plant. Figure 1 is a process diagram showing the major equipment items. The sulfur trioxide ladened gas flows to the Heat Recovery Tower (HRT) where the sulfur trioxide is absorbed in sulfuric acid. The absorption of the sulfur trioxide increases the temperature and concentration of the sulfuric acid. Concentrated, hot sulfuric acid leaves the tower at Point B. The acid is cooled by generating steam in a boiler and leaves the boiler at Point C. After the product is removed, the remaining acid is diluted with water and recirculated to the tower at Point A.

The process is shown on the HRS operating cycle diagram in Figure 2. The curves on the left are isocorrosion lines for 310 stainless steel. The right hand line defines the limiting conditions for the absorption of sulfur trioxide. The points on the triangle correspond to the process conditions identified in the Figure 1 process diagram. Acid near 100% concentration leaves the tower at 200°C (Point B). The acid is cooled in the boiler to approximately 160°C (Point C). The acid is diluted to 99% with a temperature rise due to heat of dilution (Point A). Finally, sulfur trioxide is absorbed in the tower, raising the acid concentration and temperature to complete the cycle.

This example is a 3.5 bar (50 psig) steam system but steam can be generated at up to 10 bar (150 psig). HRS can boost energy recovery to 90% to 95% of the total energy generated in a sulfur burning plant.

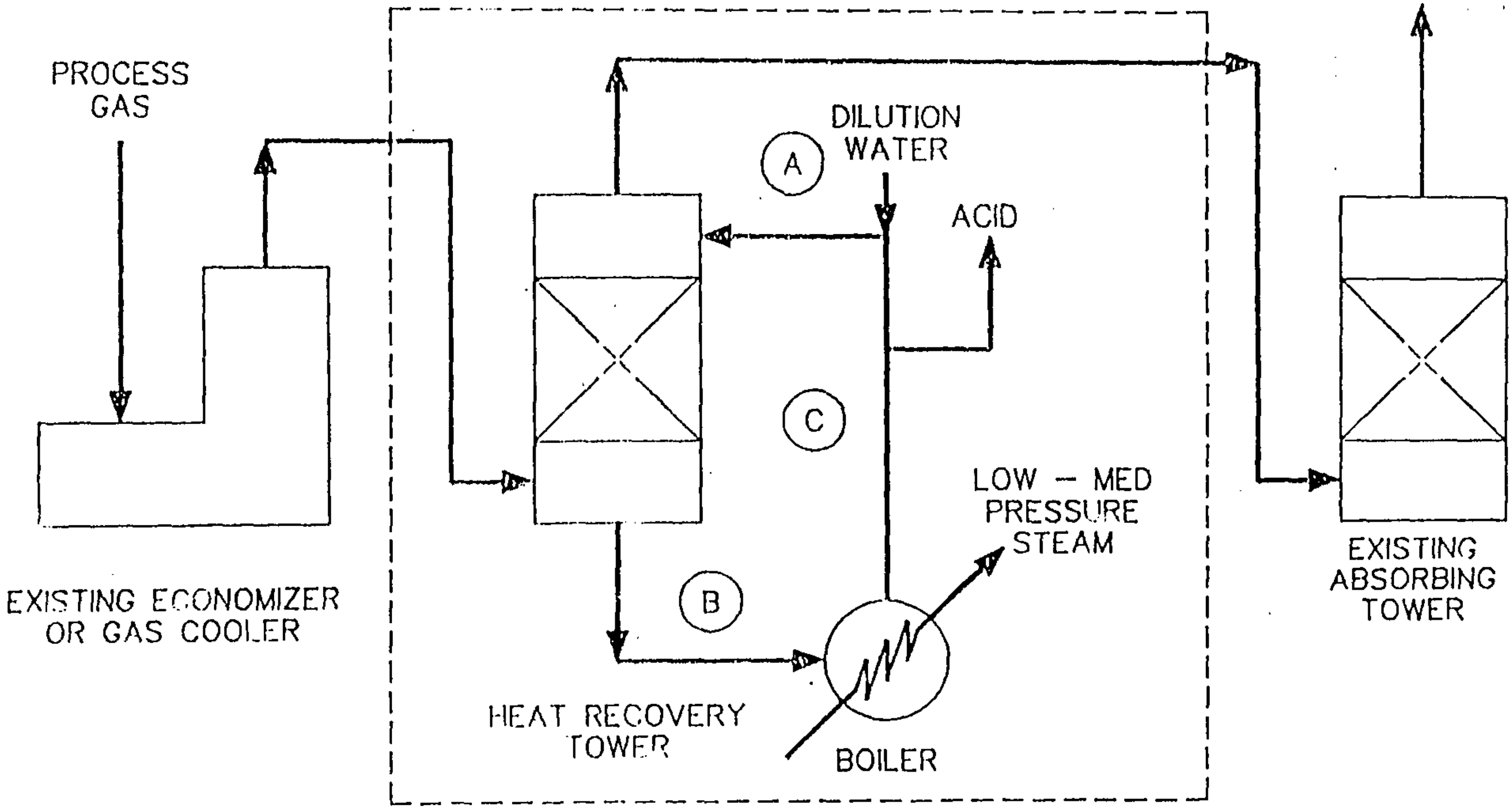

FIGURE 1 – HEAT RECOVERY SYSTEM

Monsanto Enviro-Chem

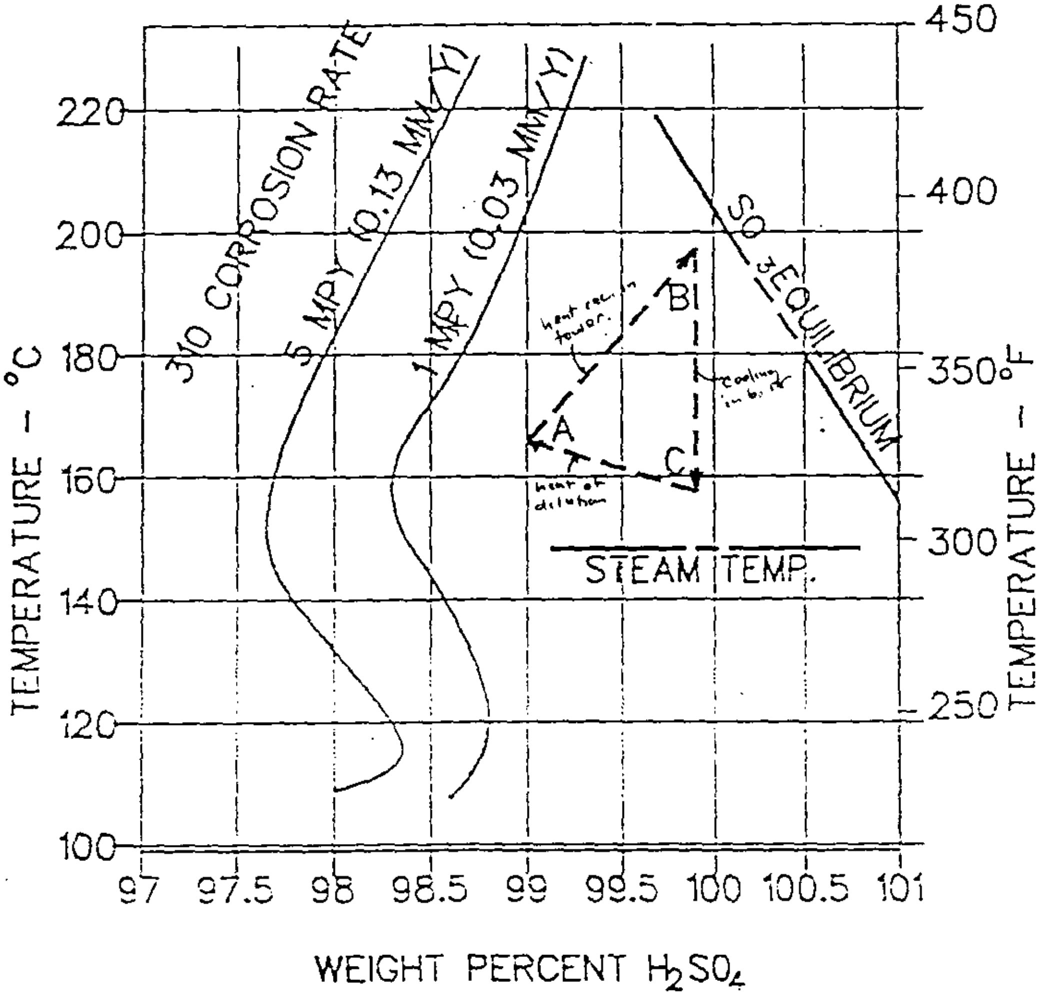

FIGURE 2 — HRS OPERATING CYCLE

NAMHAE HRS PROJECT

Namhae of Yeosu, South Korea is a billion dollar a year producer of fertilizer chemicals. Namhae is committed to supply competitively priced quality products to their worldwide clients through efficient operations and best available up-to-date plant technology.

In 1986, Namhae initiated a project to reduce the SO_2 emissions from their two existing, ten year old, single absorption sulfur burning sulfuric acid plants. Monsanto Enviro-Chem of St. Louis, Missouri, U.S.A., made several proposals for Namhae's consideration:

- Add tail gas ammonia scrubbing tower to the plants.
- Convert the plants to double absorption plants with an interpass tower and acid cooler addition.
- Convert the plants to double absorption using the new Heat Recovery System (HRS) as the interpass tower.

Although Monsanto Enviro-Chem had extensive pilot plant experience and data, there were no commercial Heat Recovery Systems in existence at that time. However, Namhae's commitment to cost effective operations and confidence in Monsanto Enviro-Chem's 55 years of reliable acid plant design experience convinced K. P. Chae, Namhae's Managing Director of Engineering and Projects, to select the new Heat Recovery System for Namhae's sulfuric acid plants.

In October, 1986, Namhae awarded Monsanto Enviro-Chem the contract to modify the plants. The project goals were to:

- Increase SO_2 to SO_3 conversion from 97.7% to 99.6%.
- Maintain each plant capacity at 1350 t/d. The original 1050 t/d plants were debottlenecked using Monsanto LP catalyst, increasing gas strength to 8.3% from 7.8% and adding low-temperature economics.
- Increase steam production by adding HRS and adding a new turbine generator dedicated to HRS steam.
- Maximize use of existing plant equipment.

The final design included:

- The Monsanto Enviro-Chem Heat Recovery System as the interpass absorption tower to remove SO_3 and a 150 psig heat recovery boiler to remove the heat of acid formation.
- A final separate one-pass stainless steel converter for the after interpass absorption conversion of SO_2 to SO_3. Monsanto Enviro-Chem LP catalyst was used here and in some passes in the existing converter to lower pressure drop and ensure required conversion was met.

- Cold interpass and hot interpass heat exchangers to heat gas going from the HRS interpass absorption tower to the final catalyst pass.
- Additional economizers and superheaters to recover more heat in the form of high pressure steam than in the form of low pressure steam.
- Much existing equipment was reused without modifications (blower, boiler, economizers and superheaters).

The gas flow diagram in Figure 3 shows the modifications.

In addition, a 9000 kWh turbogenerator was installed to convert the 130,000 lbs/hr of 150 psig steam from HRS to electricity.

Namhae's Project Manager, M. K. Oh, committed to a fast 14 month schedule. The first plant came on-line 13 months after the contract award and both plants and the turbogenerator were demonstrated in an excellent 14-1/2 months.

NAMHAE HEAT RECOVERY SYSTEM

The HRS operates very similar to a sulfuric acid plant absorbing tower. The main difference is higher acid temperatures; the acid is cooled in a boiler rather than an acid cooler; and the tower is stainless steel rather than bricklined steel. The flow diagram for HRS is shown in Figure 4.

The main equipment items in an HRS are:

1. Heat Recovery Tower

   This is a two stage 310 stainless steel tower with ceramic Intalox packing and Monsanto Enviro-Chem ES mist eliminators.

2. HRS Acid Circulation Pump

   This is a vertical submerged stainless steel pump manufactured by the Lewis Pump Co. The pump design is very similar to the proven design of the many vertical sulfuric acid pumps now in service.

3. HRS Boiler and Heaters

   This is a "kettle" type boiler with acid flow through stainless steel tubes. The water side of the boiler is operated and controlled similar to other firetube boilers.

   The HRS water heaters are similar to shell and tube acid coolers but without anodic protection. Their function is to cool product acid by heating the boiler feedwater coming to the HRS boiler.

4. The diluter is where hot dilution water is mixed and absorbed by the hot acid in a turbulent reaction.

5. Instrumention

HRS includes flow, temperature and pressure measurement and control instruments that are normally used in acid plants, but there are also three special instruments that we want to tell you more about.

A. Concentration Control

The acid concentration to the tower must be controlled above 98.5% acid to minimize corrosion. Modern electrodeless torroidal conductivity analyzers were used to provide the reliable and accurate concentration measurement that is needed. These improved analyzers will rapidly become the standard of the industry in all drying and absorbing towers as well as in HRS.

B. Corrosion Monitor

The corrosion monitor measures the current generated by the corrosion reaction of the stainless steel probes in the acid circuit. The monitor, located in the control room, indicates the corrosion rate of the stainless steel and alarms if the rate exceeds set limits for any reason.

C. Acoustic Leak Monitor (ALM)

The acoustic leak monitor was especially developed several years ago by Monsanto and the manufacturer to detect boiler or heat exchanger leaks using acoustic (sound) emissions. The acoustic (sound) wave is transformed into an electric signal and is monitored in the control room.

Boiler or heat exchanger leaks cause an increase in the acoustic emission which sounds the alarm so the plant can be shutdown safely for repairs. There have been no leaks at Namhae.

The other materials in an HRS such as pipe, valves, thermowells and etc. are made of stainless steels compatible with high temperature sulfuric acid.

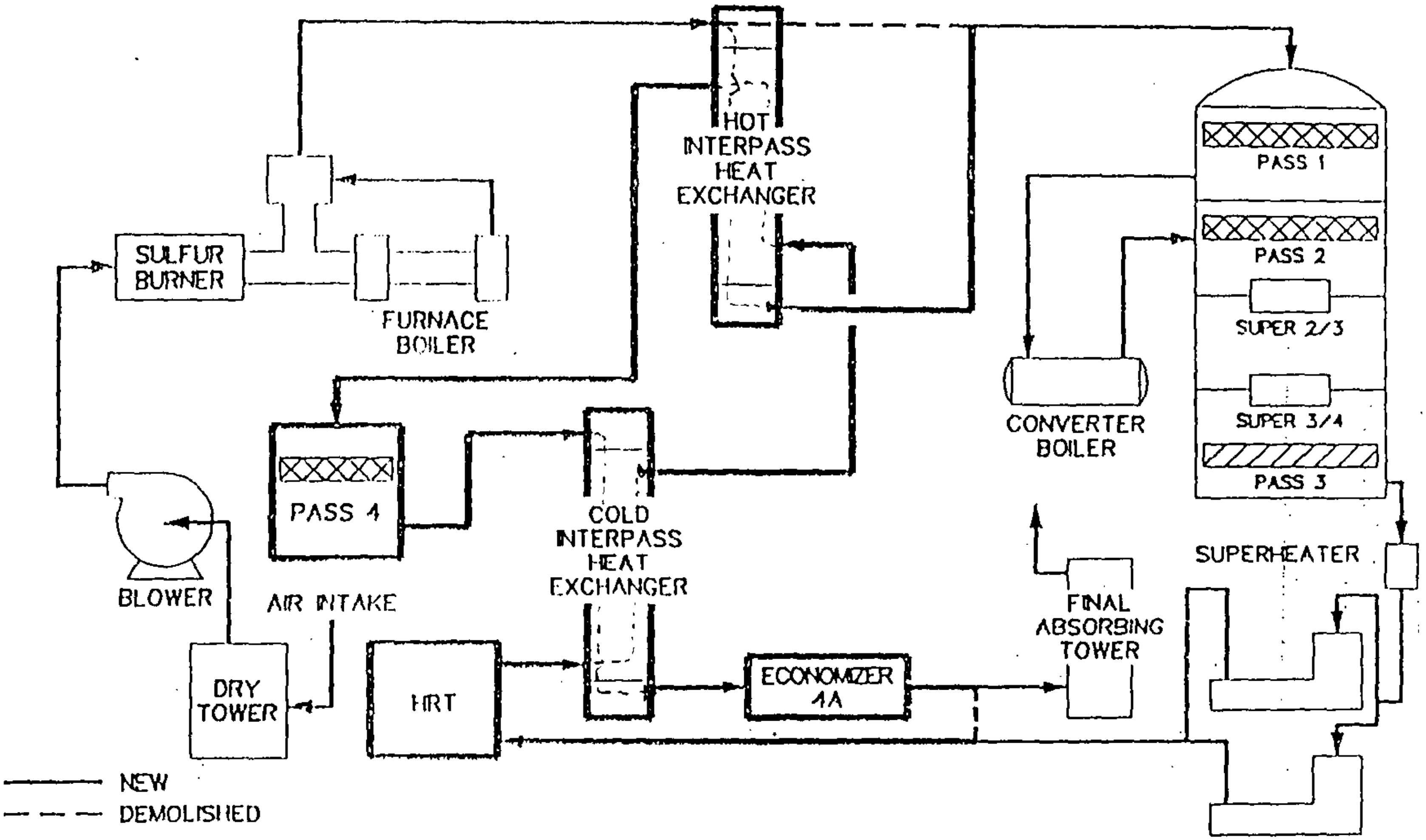

FIGURE 3 – GAS FLOW DIAGRAM

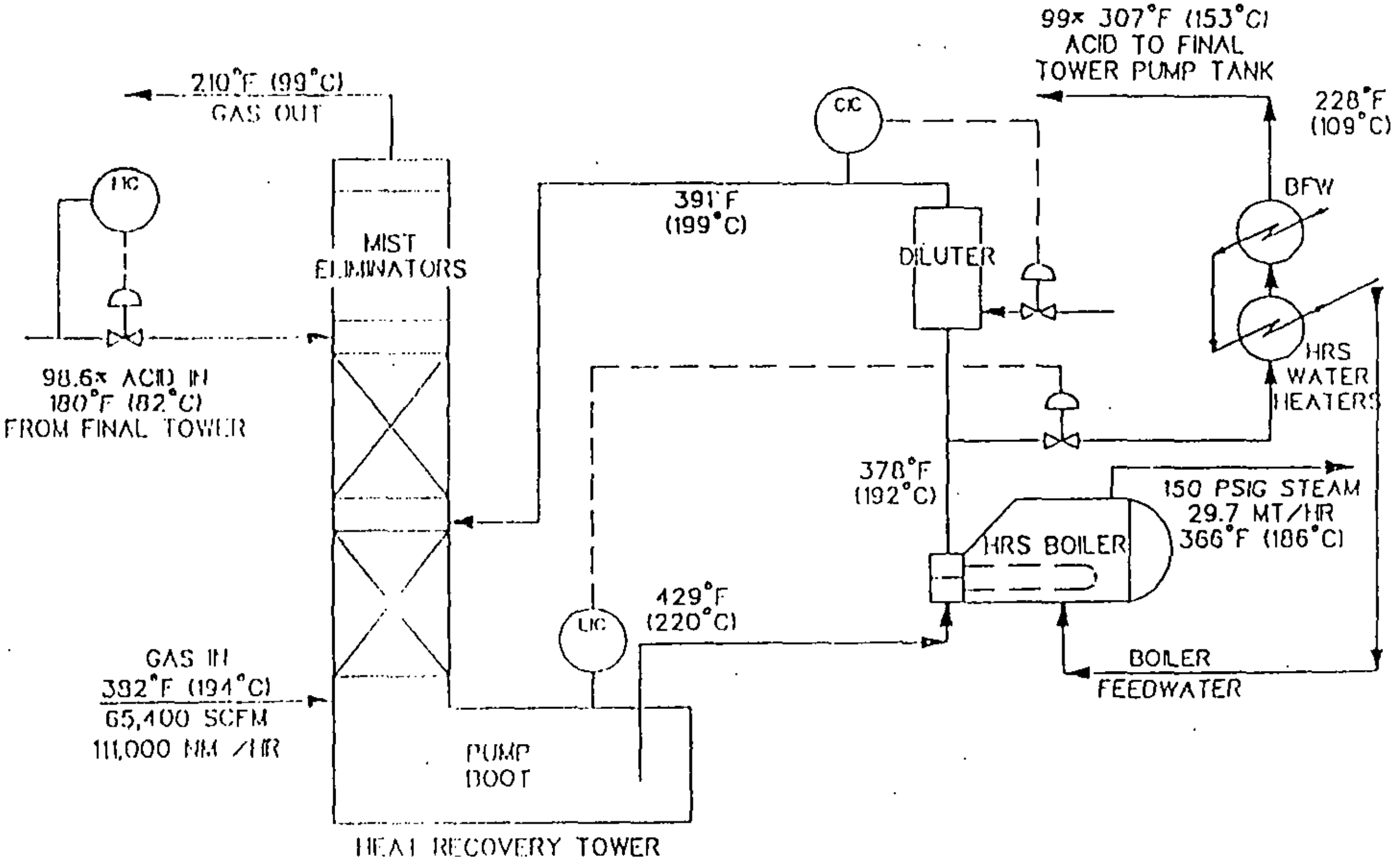

FIGURE 4 — HEAT RECOVERY SYSTEM

HRS START-UP (NOVEMBER AND DECEMBER, 1987)

The plant and HRS start-ups went extremely well. The first plant started up November 19, 1987, and all guarantees were demonstrated within 2-1/2 weeks. The second plant and the turbogenerator power guarantees were demonstrated 1 week after the Plant No. 2 start-up December 23, 1987.

All project guarantees and expectations were readily achieved. The conversion of SO_2 to SO_3 was much better than expected. In fact, the conversion analysis was double and triple checked before it was accepted.

HRS DEMONSTRATION RESULTS

	Guarantee	Expected	Plant #1	Plant #2
Production, t/d	1350	1350	1442	1430
SO_2 Emission, ppm	500	370	208	152
Steam Production, t/hr	27.9	29.7	33.2	30.6
Tons/Ton Acid	.50	.53	.55	.51
Conversion	99.6	99.7	99.85	99.9
T/G Electrical Power kWh	8760		8772 for both plants	

There were a few minor problems during the start-up. In fact, loss of control of acid strength, which is the major concern of many customers, occurred a few hours after start-up. When acid concentration was first put on automatic control, acid strength was rapidly dropped to 94% because the control action was reversed. It took a few hours to get the acid strenth into control and the plant was exposed to 200°C and 94% concentration. Inspection of the plant showed that the only damage was excessive corrosion on the acid pump impeller and wear parts where velocity is highest. However, the pump was still serviceable and was put back into operation. After examination of the pump, Lewis and Monsanto metallurgists concluded that damage was related completely to the low acid strength. However, Namhae had some concerns so some parts of alternate materials were installed for testing in one pump.

A second problem was excessive vibrations transmitted from the diluter to the platform walkway. The mixing of hot water and hot acid produces a turbulent reaction. The diluter requires a solid structural support to grade. The original diluter was supported from horizontal steel beams that support the walkway. The support was redesigned on heavier steel beams that extend down to grade. Excessive walkway vibrations were eliminated.

A third problem was collapse of some teflon lined pipe that was used between the diluter and the tower as a precaution against incomplete mixing which would cause higher than expected localized corrosion rates. Part of the pipe liner collapsed during the start-up period when the plant was shutdown and the acid was drained from the diluter causing a vacuum in the line. Some of the liner was removed as not being necessary and a vacuum breaker will be installed to further protect the remaining liner.

Typical start-up instrument adjustment difficulties were experienced on the Plant No. 1 start-up for the acoustic leak detector and the corrater. However, the Plant No. 2 instrument adjustment was minimal after Namhae's Instrument Section assumed responsibility from the construction contractor.

OPERATION - (JANUARY TO AUGUST, 1988)

Following the demonstration in December, both HRS units continued to operate according to the design and there were no significant operating or equipment problems.

In April, Namhae and Enviro-Chem showed the plant to 40 potential customers from all over the world. During the discussion a customer asked Namhae how many acid plant shutdowns had been caused by HRS equipment. After checking the record, Namhae stated there had only been one 4 hour shutdown to inspect the acid pump on the No. 1 plant. The pump was inspected in March and showed little additional corrosion since exposure to 94% acid during the initial start-up. The No. 2 acid plant continued to run well and was not even inspected until August.

Corrosion coupons that were installed in the acid system were checked occasionally. All showed the expected low corrosion rate except the one located directly after the diluter which showed 20 mils per year. This showed the need for improved mixing of the acid and water in the diluter. These modifications were delayed until the diluter supports were strengthened during the August turnaround because of the possibility that vibration would increase. It was not considered urgent because piping after the dilutor was teflon and no damage was being done.

During normal operation 0.5 to 1.0 liters per shift of drip acid was drained ahead of the cold interpass heat exchanger. This was considered to be condensation particularly on the dome of the tower which was not insulated and did not cause much concern. We have increased our attention to this matter since some duct leaks developed prior to the August turnaround. Improvements are being implemented which are expected to stop the drip acid.

The HRS performed well, consistently producing steam to generate over 9 MW of electrical power. HRS equipment performed as expected. Acid quality is significantly improved with the elimination of iron sulfates, cast iron slag, brick mortar particles and etc. as compared to bricklined acid towers.

The annual gross savings for both plants is 6600 tons of sulfur saved based on a 2.1% conversion improvement and a 350 day per year operating schedule at design rate. Also, 74,000 MWh of electrical power is generated under these conditions. The savings in U.S. dollars would be $0.9 million for sulfur, based on a $130/t delivered price, and $4.6 million for electrical power, based on $0.062/kWh costs, for a total yearly savings of $5.5 million. These cost figures are used for illustration only and are not necessarily those used by Namhae.

TURNAROUND INSPECTION - (AUGUST, 1988)

Plant No. 2 was shutdown for scheduled maintenance on August 20 after eight (8) months of operation. Plant No. 1 was shutdown on September 3 after nine (9) months of service. Both HRS units and sulfuric plants were inspected carefully to determine if any problems were developing.

Overall, both HRS units were in excellent condition. The corrosion rates were as expected.

The corrosion rates were determined by exact weight losses of metal coupons placed throughout the system and numerous metal thickness measurements of pipe and tower walls. Excluding the first start-up days, the corrosion rate of the tower and piping system was less than 2 mils per year (0.050 mm/yr) in all areas. The corrosion rate of the acid pipe from the tower to the boiler was about 1.5 mils per year (0.037 mm/yr) and less than 0.5 mil per year (0.012 mm/yr) after the boiler.

The corrosion rate of the coupons in the teflon lined pipe between the diluter and the tower was between 20 and 30 mils per year (.5 and .75 mm/yr). This higher than expected rate was attributed to inadequate mixing of the acid and water in the diluter. Inspection showed only normal corrosion on the tower as is discussed below. However, the diluter is being modified to improve acid and water mixing.

In addition to the corrosion coupons, the HRS units were checked by taking thickness readings with an ultrasonic thickness gauge ("D" meter) and micrometer. The ultrasonic thickness gauge uses sound waves to measure the thickness of equipment when it is impractical to reach both sides of a plate or pipe wall. The actual measured corrosion rates of HRS plate and pipe supported the data of the corrosion coupons.

The No. 2 plant HRS acid pump was pulled for the first time and inspected. The visual inspection of the pump showed it to be in good condition. Corrosion was no more than that experienced on other absorbing tower circulation pumps. The replaceable static wear rings were replaced to assure reliable service until the next turnaround and the pump was placed back in service. Although replaced, most of the wear rings were still within specification. We have concluded that the original materials of construction specification for the HRS pump was the proper choice for long-term life.

The HRS boiler was in excellent condition on both the acid and water side. The corrosion rate on the acid side was less than 2 mils per year.

All HRS equipment was inspected and found to be in good condition. The HRS tower shell, packing, packing supports and mist eliminators checked out in fine condition. Acid distributor header orifices showed some corrosion which could result from the poor mixing in the diluter or it could have occurred at the time the 94% acid corroded the acid pump.

The gas duct from the HRS tower to the cold interpass heat exchanger and the shell side inlet to the exchanger were inspected since drip acid had been routinely drained from the duct. There was significant iron sulfate in the bottom of the duct and on the exchanger tubesheet. There were a few leaking tubes which were repaired by driving a smaller tube inside. During the turnaround the top of the tower was insulated and the acid drain system ahead of the heat exchanger was modified to improve drainage and keep acid from getting into the exchanger. Drains will be monitored and gas sampling is planned to see that the problem has been solved.

The design, construction and successful demonstration of the first two commercial Heat Recovery Systems, complete with dedicated turbogenerator, is considered an outstanding success by Namhae Chemical Corporation and Monsanto Enviro-Chem Systems, Inc.

Many sulfuric acid plant operators from around the world have visited the Namhae acid plant. Visitors are quite impressed with the Namhae's HRS installation, clean and orderly facilities and Namhae's courage and dedication to install the first HRS.

SUMMARY

Namhae Chemical Corporation has proven that the HRS is a successful commercial process.

The initial concerns have been laid to rest and most of the minor problems have been solved. And, as a customer who visited the plant during the recent turnaround said, "The few remaining problems can be readily solved and I am not afraid of the Heat Recovery System".

Namhae and Monsanto Enviro-Chem will continue to review the HRS operations for good performance and maintenance. As with all new technology, improvements in design and HRS products are expected as experience is gained.

Three new HRS units are now being designed for clients who have visited the Namhae facilities. HRS projects are under consideration by other clients.

The attraction of using the HRS as an interpass absorption tower to reduce SO_2 emissions while producing an additional 0.5 t steam/t acid produced or 3.1 kWh of electrical power per t/d of H_2SO_4 will make the HRS a key component of future sulfuric acid plants.

FALCONBRIDGE, NORWAY

Several people have asked about the Falconbridge HRS start-up status. Falconbridge Nikkelverks of Kristiansand, Norway has a 240 t/d sulfuric acid plant and HRS for their smelter SO_2 offgas. Fenco Engineers of Toronto, Canada designed and constructed the acid plant as well as the SO_2 gas purification system. The acid plant is designed so that the HRS can operate as an interpass tower with normal interpass acid temperatures or as an HRS where steam is generated from cooling the acid.

The acid plant started up in October, 1987, in the conventional acid plant mode without steam generation. The HRS circuit has not operated much of the time because of operating problems in other parts of the acid plant and roasters. However, the HRS was successfully operated several weeks during mid-1988 and tests showed that it is operating in accordance with design. However, Falconbridge has commitments to produce liquid SO_2 which have required that the acid plant be shutdown until the last quarter of 1988.

REFERENCES

McAlister, D. R.; Corey, A. G.; Ewing, L. J.; Ziebold, S.A., "A Major Breakthrough in Sulfuric Acid Heat Recovery", paper presented at the 1986 Annual Meeting of AIChE, New Orleans, Louisiana.

Johnson, C. A.; Smith, R. M., "Reduce P_2O_5 Costs 10% by Recovering 95% of the Energy from Your Sulfuric Plants". Proceedings of the IFA Technical Conference, Port el Kantoui, Tunisia (October, 1986).

Niesse, J. E.; McAlister, D. R., "Stainless Steels for Heat Recovery from High Temperature Sulfuric Acid", Paper No. 22 presented at the March, 1987, "Corrosion 87" Meeting of NACE.

"HRS Fronts Monsanto's Latest Push in Sulphuric Acid Technology". Supplement to <u>Sulphur 189</u> (March-April, 1987).

APPENDIX F

AIR MODELING INFORMATION

KOOGLER & ASSOCIATES

THIS DISK CONTAINS SULFUR DIOXIDE (SO2), NITROGEN DIOXIDE (NOX), SULFURIC ACID MIST (SAM), MODELING FILES FOR THE PINEY POINT PHOSPHATES PLANT IN MANATEE COUNTY, FLORIDA.

THE FOLLOWING FILES CONTAIN ISCST3 MODELING OF:
    SIGNIFICANT IMPACT ANALYSIS (SIA) FOR CLASS 2 AREA
    SIA FOR CHASSAHOWITZKA NWR PSD CLASS I AREA, AND
    BUILDING DOWNWASH, BUILDING PROFILE INPUT PROGRAM (BPIP)
AND ARE IN SELF EXTRACTING ARCHIVE FORMAT.

SO2 ASI ANALYSIS OF CHASSAHOWITZKA NWR PSD CLASS I AND CLASS 2 AREA:
PINY-SO2 EXE 150,006 10-22-97

NOX ASI ANALYSIS OF CHASSAHOWITZKA NWR PSD CLASS I AND CLASS 2 AREA:
PINY-NOX EXE 82,196 10-22-97

SULFURIC ACID MIST (SAM) ANALYSIS OF LOCAL ARES IMPACT:
PINY-SAM EXE 67,022 10-22-97

AND:
PNY-BPIP EXE 20,010 10-22-97 BUILDING DOWNWASH CALCULATIONS

TO UNARCHIVE THESE FILES COPY THEM TO A HARD DISK DRIVE AND TYPE THE FILE NAME. FOR EXAMPLE TO UNARCHIVE THE SO2 ASI CLASS 2 ISCST3 OUTPUT FILES, TYPE "PINY-SO2" AND PRESS ENTER. THE FILES WILL AUTOMATICALLY UNARCHIVE TO THE HARD DISK DRIVE. THESE ARCHIVED FILES CONTAIN THE MODELING AND ANALYSIS FILES IN ASCII FORMAT DESCRIBED AS FOLLOWS;

SO2 MODELING FILES FOR THE CHASSAHOWITZKA NWR PSD CLASS 1, AND CLASS 2 SIGNIFICANT IMPACT ANALYSIS (SIA) ARE PROVIDED:

PNY1ASI0 OUT	57,392	08-28-97	PSD CLASS 1 ASI FOR 1987
PNY1ASI1 OUT	57,377	08-28-97	PSD CLASS 1 ASI FOR 1988
PNY1ASI7 OUT	57,407	08-28-97	PSD CLASS 1 ASI FOR 1989
PNY1ASI8 OUT	57,407	08-28-97	PSD CLASS 1 ASI FOR 1990
PNY1ASI9 OUT	57,392	08-28-97	PSD CLASS 1 ASI FOR 1991

PNY2ASI0 OUT	187,546	08-28-97	PSD CLASS 2 ASI FOR 1987
PNY2ASI1 OUT	187,546	08-28-97	PSD CLASS 2 ASI FOR 1988
PNY2ASI7 OUT	187,546	08-28-97	PSD CLASS 2 ASI FOR 1989
PNY2ASI8 OUT	187,546	08-28-97	PSD CLASS 2 ASI FOR 1990
PNY2ASI9 OUT	187,546	08-28-97	PSD CLASS 2 ASI FOR 1991

NOX MODELING FILES FOR THE CHASSAHOWITZKA NWR PSD CLASS 1, AND CLASS 2 SIGNIFICANT IMPACT ANALYSIS (SIA) ARE PROVIDED:

```
C1NOX87  OUT        31,161 10-22-97   PSD CLASS 1 ASI FOR 1987
C1NOX88  OUT        31,161 10-22-97   PSD CLASS 1 ASI FOR 1988
C1NOX89  OUT        31,161 10-22-97   PSD CLASS 1 ASI FOR 1989
C1NOX90  OUT        31,161 10-22-97   PSD CLASS 1 ASI FOR 1990
C1NOX91  OUT        31,161 10-22-97   PSD CLASS 1 ASI FOR 1991

C2NOX87  OUT        78,776 10-22-97   PSD CLASS 2 ASI FOR 1987
C2NOX88  OUT        78,776 10-22-97   PSD CLASS 2 ASI FOR 1988
C2NOX89  OUT        78,776 10-22-97   PSD CLASS 2 ASI FOR 1989
C2NOX90  OUT        78,776 10-22-97   PSD CLASS 2 ASI FOR 1990
C2NOX91  OUT        78,776 10-22-97   PSD CLASS 2 ASI FOR 1991
```

SULFURIC ACID MIST (SAM) IMPACT ANALYSIS FOR THE PLANT AREA:

```
C2SAM87  OUT       162,305 10-22-97  FOR 1987
C2SAM88  OUT       162,305 10-22-97  FOR 1988
C2SAM89  OUT       162,305 10-22-97  FOR 1989
C2SAM90  OUT       162,305 10-22-97  FOR 1990
C2SAM91  OUT       162,305 10-22-97  FOR 1991
```

THERE ARE RECEPTORS AT 100 METER INTERVALS ALONG THE PROPERTY LINE, DISCRETE POLAR RECEPTORS FROM 700 METERS TO 1100 METERS AND POLAR RECEPTORS AT 1200, 1500, 1750, 2000, 2500, 5000, 7500, AND 10000 METERS. POLAR RECEPTORS ARE CENTERED AT X=315, Y=260 THE APPROXIMATE GEOMETRIC CENTER OF THE FACILITY.

BUILDING INPUT PROFILE PROGRAM (BPIP) FILES USED IN MODELING ARE PROVIDED:

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PNY-BPI  INP         1,373 08-28-97   INPUT FOR SO2  SOURCES
PNY-BPI  OUT         3,898 08-28-97   OUTPUT FOR SO2 SOURCES
PNY-BPI  SUM        56,773 08-28-97   SUMMARY FOR SO2 SOURCES
```

IF I MAY PROVIDE ADDITIONAL FILES, OR CLARIFICATION PLEASE CONTACT ME.

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OCTOBER 22, 1997