

TO: R. D. Gamblin

TGG: JCL: FGJ: AC: AJO: RF

XF: 1000

FROM: T. G. Grumbles

DATE: November 15, 1991

SUBJ: 1991 DEPARTMENT ACCOMPLISHMENTS

Interoffice
Communication

VISTA

Below is a summary of the activities and significant accomplishments during FY 1991.

REGULATORY

It was an active year for federal and state regulators in multiple areas. The department provided extensive technical support and advice to the plants, R&D, and S&T on the impact of the revised Clean Air Act, continued implementation of TC and Land Ban regulations, OSHA Process Safety Standards, and multiple DOT regulations including HM-181 and HM-126. Departmental personnel participated or led teams to analyze or develop implementation plans in the DOT and OSHA areas.

Departmental personnel also provided active technical assistance to Aberdeen in negotiating new state air and wastewater permits to Hammond in addressing wastewater permit concerns, to the LCCC in negotiating the NPDES and 304(1) wastewater permits, and to LCLAB in managing the impact of the Boiler and Industrial Furnace Rule.

TRAINING

During the year the department conducted four DOT training sessions and multiple environmental awareness training sessions at Aberdeen and the LCCP. A training program on FDA regulations and how they impact Vista's products was developed and provided to two marketing offices.

AUDITING

Departmental personnel conducted and participated in multiple audits. Two environmental audits and two DOT audits were conducted. Department personnel also participated in three ex-plant audits with S&T and audited nine waste treatment and disposal facilities used by company locations.

ASSESS PURCHASE AGREEMENT ISSUES

Multiple projects were initiated this year that were impacted by various APA retained liability provisions. A major cost sharing agreement was negotiated for the remedial investigation and remediation work that must be done at the LCCC for some 50 solid waste management units. This work will be active over the next 3-5 years.

VVV 000008155

A cost sharing agreement was negotiated with BP to cover remedial investigation and remediation work to be done at the Blane site.

A cost sharing and services reimbursement agreement was negotiated with Conoco to cover work at the Aberdeen plant that will determine the extent of groundwater contamination present, allow for excavation and recovery of 20MM pounds of resin currently buried at the old Pond 2 site, and removal of multiple drums of plasticizer waste buried prior to 1984. These agreements were reached in the absence of a governmental order compelling Conoco to participate with us in these activities.

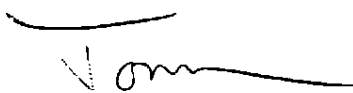
RESPONSIBLE CARE®

Responsible CARE® activities continued as the initial Distribution Code and Process Safety Code, and the second Pollution Prevention and CAER Code self-evaluations were completed.

New activities to support implementation included the development of a Responsible CARE® newsletter and organization of the Responsible CARE® Steering Team.

MISCELLANEOUS

Despite the absence of two professional staff members for four months, the department scored a 9.5 on our Q-Scorecard and moved our natural team rating from a 12 to a 14.



T. G. Grumbles

dlj

VVV 000008156

TO: TGG

FROM: Frank G. Jeanson

DATE: November 13, 1991

SUBJ: ENVIRONMENTAL HIGHLIGHTS - 1991

I. Environmental Audits

A. Plants

1. Austin - Complete audit of all media; air, water, waste, etc.
2. Blane - Complete audit of all media; air, water, waste, etc.

B. Ex-Plant

1. Rhone Poulenc, Sedalia, MO - Audit with S&T toll processor of ethoxylates.
2. Royal Plastics, Toronto, Ontario, Canada - Audit with Conoco potential customer of pond resin.
3. Sun Polymers, St. Gabriel, LA - Audit with Conoco potential processor of pond resin.

C. Disposal Facilities

1. Laidlaw, Crowley, LA - Audit potential handler of haz. waste for LCCP.
2. Calgon, ^{near Calh} Pittsburg, PA - Audit potential recycler of waste for LCVCM.
3. Calgon, Hunnington, WV - Audit potential recycler of waste for LCVCM.
4. Safety Kleen, Louisville, KY - Audit potential handler of haz. waste for LCVCM.
5. CWM, Niagra Falls, NY - Audit disposal facility for Blane haz. waste.
6. Laidlaw, North Andover, MA - Audit haz. waste storage and transport terminal used by Blane.

VVV 000008157

7. Clean Harbors, Braintree, MA - Audit potential haz. waste storage and transport terminal for Blane.

8. Recovery Systems, Foxboro, MA - Audit recycler of waste oil used by Blane.

9. Hawk Plastics, Birmingham, AL - Audit potential recycler of by-product from Aberdeen.

II. Projects

A. Aberdeen Pond 2 Resin Recovery Project - Worked with Aberdeen plant obtaining customer, getting approval from Conoco, getting contracts put together.

B. Aberdeen Superfund Sites - Worked with plant, Conoco, and contractor (DERS) in completing Remedial Investigation, submitting report to the Miss. DEQ, working on follow up sampling program, and planning future work.

C. CMA 313 Reporting - Collected all plants 313 reports and sent in to CMA.

D. 313 Report Analysis - Put all of Vista's 313 report information together in a presentation format.

E. Industrial Toxics Project (33/50) - Attended EPA and CMA meeting, got input from plants on emissions reduction plans, and totaled emission reductions for total company.

F. Aberdeen Buried Drum Removal Project - Put together bid packet, evaluated 6 bids, worked with Conoco choosing contractor, and worked with legal putting together contract.

G. CMA Work Group - Member of RCRA Waste Classification Work Group.

H. Aberdeen Environmental Training - Participated in Environment training of engineering and management personnel.

I. Ex-Plant Audit Questionnaire - Worked with S&T revising their Ex-Plant Environmental Audit questionnaire.

J. CMA Waste Survey - Collected all of the plants completed forms and sent in to CMA. Also put out summary of 1989 vs. 1990 results.

K. CMA Pollution Prevention Code Self Analysis - Collected all of the plants completed forms and sent in to CMA. Also put out summary of 1989 vs. 1990 results.

L. LCCC Financial Assurance - Worked with Treasury, LCCC putting together financial assurance for closure of all TC haz. waste units.

M. Blane Underground Storage Tank Financial Assurance - Worked with Treasury putting together financial assurance documents for the fuel oil UST.

N. Vinyl Institute Initiator Bottle Recycle - Worked on committee to recycle initiator bottles on an industry wide basis. Also evaluated a bottle recycler for this project.

JCL 1991 Highlights

Assisted Hammond in negotiations with the City of Hammond and Rhone-Poulenc regarding the Hammond wastewater permit. Helped convince the City that the Hammond Plant does not need a wastewater permit to discharge to Rhone-Poulenc.

Worked with the Aberdeen plant in negotiations with MSDEQ regarding the appropriate VCM unit risk factor to be used to evaluate fence line risk. Got DEQ to accept a more favorable factor which will avoid the need for emission reductions.

Assisted Aberdeen in negotiations with MSDEQ on a new wastewater discharge permit. Final permit was considerably less burdensome than the proposed version.

Lead a team to develop and submit Vinyl Institute comments on the Louisiana VCM air toxics limit. The Louisiana program was delayed approximately a year and the final limit has not been promulgated.

Participated in negotiations with EPA on the LCCC NPDES permit renewal. The EPA is issuing a compliance order that will allow sufficient time to implement VISION while temporarily not lowering permit limitations.

Did environmental training at Aberdeen on 6/13 and LCCP on 4/4-5.

Obtained Kosher certification for PTAU alcohols and glycerine.

Participated in contractor evaluation and selection for the Blane Phase II and III waste site remediation. Phase II is currently underway. The firm of CH2M-Hill was selected as the contractor.

Participated in negotiations and evaluation of alternatives for the Aberdeen groundwater, drum removal and resin reclaim project.

Analyzed the regulations and advised LCVCM regarding classification of several wastes streams as F024. The plant has installed an interim system to insure that F024 wastes are not sent to the wastewater treatment ponds.

Worked with LCLAB to analyze the impact of the Boiler and Industrial Furnace rule on ASO burning. The plant

VVV 000008160

decided to ship ASO off-site for destruction rather than permit the Hot Oil Heater as a RCRA facility.

Analyzed numerous provisions of the amended Clean Air Act and communicated the implications to plants and management.

Participated in 6 meetings with magazine editors to promote the environmental safety of LAS.

Held FDA training with the Lisle and Saddlebrook sales offices.

Lead the effort to support alcohol sales to Aristech by developing a SARA 313 delisting petition for DNOP. Radian was hired as the contractor and a draft petition has been written.

11/12/91

VVY 000008161

TO: T. G. Grumbles

FROM: A. Clark

DATE: November 13, 1990

SUBJ: 1991 ACCOMPLISHMENTS

Per your request, here the major accomplishments in FY 1990 for the Product Safety Specialist position:

1. AC and AJO revised 5 material safety data sheets (MSDS) on the new form which includes expanded regulatory information. Twenty-four more are currently going through the approval process. Twenty new product MSDS's were generated. Forty-eight MSDS's had corrections made which caused reissue of those MSDS's. Sources for all MSDS data are being defined and documented for product liability concerns.
2. MJH participated in HM-126C Team with members of S&T to assure compliance with the Docket, Emergency Response Communication Standards.
3. AC reorganized HM-181 Team to continue developing compliance procedures for this Docket which will align the U.S. with international hazardous material transportation regulations.
4. AC led the DOT Team in conducting DOT Audits and Training at two plants, and two DOT Training sessions for S&T. Twenty plant personnel and 34 S&T personnel received training. Test scores from pre- to post-tests showed an average increase of 40% for all 4 classes.
5. AC responded to approximately 65 internal and external customer questions regarding MSDS's, TSCA, product constituents, regulatory status, etc.

Anne Clark

AC

VVV 000008162

~~TGE~~: ~~JCL~~: ~~FGJ~~: AC: AJO: RF

XF: None

TO: Distribution

FROM: T. G. Grumbles
DATE: November 18, 1991

VISTA

Interoffice
Communication

SUBJ: EPA HF STUDY - NPRA RESPONSE

Paul Gowan received the attached information from NPRA. This is a draft of the "API Recommended Practice on Hydrofluoric Acid Alkylation Unit Safety".

By copy of this memo, I am asking Paul to forward NPRA HF correspondence he receives to the distribution below.

Tom dy

T. G. Grumbles

dlj
.337

Attachment

Distribution: J. Ware-LCLAB, R. Bryan, T. Huffman, M. Reynolds-
Houston

VVV 000008163

Paul C. Gowan

VISTA

To TGG, THA, JWW

Date 11-14-91

Attached is a copy of the AFT draft program for HF. It has been given to EPA as the refining industry recommended risk management program.

I have told NPRA to put me on the distribution list for HF related developments and that Vista will decide whether to identify ~~ourselves~~ ourselves to EPA as users. NPRA will not "tip our hand" on the issue.

Let me know your thoughts on an appropriate distribution list for future info. from NPRA.

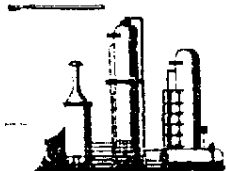


VVV 000008164

7

8

9



NATIONAL PETROLEUM REFINERS ASSOCIATION

Founded 1902

SUITE 1000, 1899 L STREET, N.W., WASHINGTON, D.C. 20036
TELEPHONE (202) 457-0480

DORIS J. DEWTON
Director
Government Relations

October 29, 1991

MEMORANDUM TO THOSE COMPANIES ON ATTACHED LIST

SUBJECT: EPA ACTIVITIES ON STUDY ON HYDROFLUORIC ACID USES

As you have seen in the Washington Bulletin of October 25, NPRA participated in the EPA roundtable held on October 17 on the study on hydrofluoric acid mandated in the Clean Air Act. Section 301 (n)(6) of Title III of the Clean Air Act, the Hazardous Air Pollutant title contains the following language:

"Hydrofluoric Acid. Not later than 2 years after the date of enactment of the Clean Air Act Amendments of 1990, the Administrator shall, for those regions of the country which do not have comprehensive health and safety regulations with respect to [HF], complete a study of the potential hazards of [HF] and the uses of [HF] in industrial and commercial applications to public health and the environment considering a range of events including worst-case accidental releases and shall make recommendations to the Congress for the reduction of such hazards, if appropriate."

The EPA roundtable was designed to solicit input from all interested parties regarding the contents and methodology for the HF study. EPA hopes to complete its "risk analysis" in December 1991, have the draft report completed in February 1992 to issue for peer technical review. In April, they intend to hold a public meeting to review and discuss the findings, and they intend to meet the November 1992 deadline for the report to Congress. This is a very compressed schedule for a complex issue, one that requires some type of risk assessment to be performed by EPA.

Over recent months, a number of refiners have been working through an API task force to develop a new draft "API Recommended Practice on Hydrofluoric Acid Alkylation Unit Safety." API has just received comments back on its latest draft, and intends to finalize it shortly. For those of you who have not already received this draft, we are providing it for your information. This draft has already been provided to EPA as the industry recommended risk management program for HF, and will be reviewed by EPA in making its recommendations to Congress. EPA has also asked for copies of any risk assessments that refiners have made of their HF alkylation units. Please advise us if you have such studies.

Enclosure (to those listed on attached list)

VVV 000008165

LIST OF REFINERS WITH HYDROFLUORIC ACID ALKYLATION UNITS

COMPANIES NOT ON API TASK FORCE
(and receiving enclosed API
draft):

Cenex
Clark
Coastal
Crown
Diamond-Shamrock
Farmland
Flying J (Big West)
Frontier
Giant
Hill
Indiana Farm Bureau
Koch
Mapco
NCRA
Navajo
Placid
Powerine
Shell
Total
Valero
Wyoming

COMPANIES ON API TASK FORCE:

Amoco
Ashland
BP
Champlin
Chevron
Conoco
Exxon
Fina
Kerr-McGee
Marathon
Mobil
Murphy
Phillips
Southwestern (Kerr-McGee)
Sun
Texaco
Ultramar
Unocal
Unoven

7

Hydrofluoric Acid Alkylation Unit Safety
API Recommended Practice XXXX
First Edition, XXXXX 1991

SPECIAL NOTES

1. API PUBLICATIONS NECESSARILY ADDRESS PROBLEMS OF A GENERAL NATURE. WITH RESPECT TO PARTICULAR CIRCUMSTANCES, LOCAL, STATE, AND FEDERAL LAWS AND REGULATIONS SHOULD BE REVIEWED.
2. API IS NOT UNDERTAKING TO MEET THE DUTIES OF EMPLOYERS, MANUFACTURERS, OR SUPPLIERS TO WARN AND PROPERLY TRAIN AND EQUIP THEIR EMPLOYEES, AND OTHERS EXPOSED, CONCERNING HEALTH AND SAFETY RISKS AND PRECAUTIONS, NOR UNDERTAKING THEIR OBLIGATIONS UNDER LOCAL, STATE, OR FEDERAL LAWS.
3. INFORMATION CONCERNING SAFETY AND HEALTH RISKS AND PROPER PRECAUTIONS WITH RESPECT TO PARTICULAR MATERIALS AND CONDITIONS SHOULD BE OBTAINED FROM THE EMPLOYER, THE MANUFACTURER OR SUPPLIER OF THAT MATERIAL, OR THE MATERIAL SAFETY DATA SHEET.
4. NOTHING CONTAINED IN ANY API PUBLICATION IS TO BE CONSTRUED AS GRANTING ANY RIGHT, BY IMPLICATION OR OTHERWISE, FOR THE MANUFACTURE, SALE, OR USE OF ANY METHOD, APPARATUS, OR PRODUCT COVERED BY LETTERS PATENT. NEITHER SHOULD ANYTHING CONTAINED IN THE PUBLICATION BE CONSTRUED AS INSURING ANYONE AGAINST LIABILITY FOR INFRINGEMENT OF LETTERS PATENT.
5. GENERALLY, API STANDARDS ARE REVIEWED AND REVISED, REAFFIRMED, OR WITHDRAWN AT LEAST EVERY FIVE YEARS. SOMETIMES A ONE-TIME EXTENSION OF UP TO TWO YEARS WILL BE ADDED TO THIS REVIEW CYCLE. THIS PUBLICATION WILL NO LONGER BE IN EFFECT FIVE YEARS AFTER ITS PUBLICATION DATE AS AN OPERATIVE API STANDARD OR, WHERE AN EXTENSION HAS BEEN GRANTED, UPON REPUBLICATION. STATUS OF THE PUBLICATION CAN BE ASCERTAINED FROM THE API AUTHORIZING DEPARTMENT [TELEPHONE (202) 682-8000]. A CATALOG OF API PUBLICATIONS AND MATERIALS IS PUBLISHED ANNUALLY AND UPDATED QUARTERLY BY API, 1220 L STREET, N.W., WASHINGTON, D.C. 20005.

Copyright © 1991 American Petroleum Institute

VVV 000008168

FOREWORD

In January 1990, API issued Recommended Practice 750, Management of Process Hazards, which outlines the key elements of a comprehensive program for managing all potentially hazardous processes. In March 1990, API issued a policy statement entitled "The Use of Hydrofluoric Acid in the Petroleum Refining Alkylation Process" that outlines four systems that if properly installed and maintained, would minimize the risks associated with this process.[1] While these documents will have a beneficial impact on HF alkylation safety, a supplemental document, expanding on concerns specific to HF alkylation, can have an even larger effect. This recommended practice, developed by an API committee concerned with further improving the industry's good safety record, is intended to serve that purpose. It is an outline of many of the procedures and practices used effectively in the industry to minimize the process hazards of HF alkylation. Throughout this recommended practice, it is assumed that the reader is familiar with API Recommended Practice 750.

Hydrofluoric acid (HF) alkylation is a widely used refinery process important in producing a significant share of the nation's high-quality motor gasoline. The acid used in these units is a hazardous and corrosive liquid which, if accidentally released, can form a vapor cloud. Contact with HF acid liquid or vapor can produce serious, painful chemical burns, sometimes with delayed onset.

However, with proper alkylation unit design and careful process management, the acid in these units does not present a significant risk to the community or to the environment. This process has been operated for nearly 50 years, with only a small number of incidents affecting the surrounding communities. Moreover, safety improvements in process design and management are continually being made to further reduce the risks to workers and surrounding communities. The petroleum and chemical industries have conducted extensive research on HF safety. The results are being used to prevent incidents and to mitigate the effects of an incident should one occur.

The engineering systems and procedures described herein will, when properly implemented, minimize the potential for an HF release, mitigate the effects of a release in the unlikely event that one occurs, and provide for oversight and audit of the entire process.

API publications may be used by anyone desiring to do so. Every effort has been made by the Institute to assure the accuracy and reliability of the data contained in them; however, the Institute

VVV 000008169

makes no representation, warranty, or guarantee in connection with this publication and hereby expressly disclaims any liability or responsibility for loss or damage resulting from its use or for the violation of any federal, state, or municipal regulation with which this publication may conflict.

Suggested revisions are invited and should be submitted to the director of the Refining Department, American Petroleum Institute, 1220 L Street, N.W., Washington D.C. 20005.

VVV 000008170

CONTENTS

SECTION 1-HAZARDS MANAGEMENT

1.1	Process Hazards Management Plan	00
1.1.1	Process Hazards Analysis	00
1.1.2	Management of Change	00
1.1.3	Emergency Response and Control	00
1.1.4	Audit Programs	00
1.2	Environmental Impact	00
1.2.1	Process Byproduct Materials	00
1.2.2	Vent Gas Scrubbing	00
1.2.3	Leaks	00
1.3	Internal Incident Review	00

SECTION 2-OPERATING PROCEDURES AND WORKER PROTECTION

2.1	General	00
2.2	Health Hazard Information	00
2.3	Operating Manuals	00
2.3.1	Content	00
2.3.2	HF Release Response	00
2.3.3	Temporary Shelter-in-Place Control Rooms	00
2.3.4	Testing Critical Systems	00
2.3.5	Changes in Procedures	00
2.4	Personnel Training	00
2.4.1	Operator Training	00
2.4.2	Non-Operating Personnel	00
2.4.3	Maintenance Training	00
2.4.4	Emergency Response Training	00
2.4.5	Personal Protective Equipment Training	00
2.5	Protective Equipment and Clothing	00
2.5.1	Personal Protective Equipment and Clothing	00
2.5.2	Safety Showers and Eye-Wash Stations	00
2.6	Controlled Access to the HF Alkylation Unit	00
2.6.1	Unit Demarcation	00
2.6.2	Entry by Maintenance Personnel	00
2.6.3	Entry by Visitors	00
2.6.4	Nearby Units	00
2.7	Medical Response to HF Exposure	00
2.7.1	First Aid	00
2.7.2	Followup Medical Treatment	00
2.8	Sampling and Handling of Samples Containing HF Acid	00
2.8.1	Training for Acid Sampling	00
2.8.2	Sample Station Design	00

VVV 000008171

2.8.3	Sample Containers	00
2.8.4	Laboratory Safety	00
SECTION 3—MATERIALS, MAINTENANCE, AND INSPECTION		
3.1	General	00
3.2	Materials and Methods of Construction	00
3.2.1	Materials	00
3.2.2	Pressure-Vessel Welds	00
3.2.3	Piping Specifications	00
3.2.4	Pumps	00
3.2.5	Flanged Joints	00
3.2.6	Heat Exchangers	00
3.2.7	Gauge Glasses	00
3.3	Equipment Maintenance	00
3.3.1	General	00
3.3.2	Temporary Repairs	00
3.3.3	Safety Relief Valves	00
3.3.4	Isolation and Neutralization	00
3.3.5	Material Removed From Unit	00
3.3.6	Lifts	00
3.3.7	Equipment in Service	00
3.4	Inspection of Unit Equipment	00
3.4.1	Inspection Frequency	00
3.4.2	Inspector Qualification	00
3.4.3	Operator Surveillance	00
3.4.4	Storehouse Materials	00
3.5	Record Keeping	00
3.5.1	Inspection Records	00
3.5.2	Equipment Work List	00
3.5.3	Unit Documentation	00
SECTION 4—TRANSPORTATION AND INVENTORY CONTROL		
4.1	Refiner-Shipper Cooperation	00
4.1.1	Shipping Containers	00
4.1.2	Routes	00
4.1.3	Hoses and Valves	00
4.1.4	Personnel and Clothing	00
4.1.5	Training	00
4.1.6	Emergency Procedures	00
4.2	HF Unloading	00
4.3	Inventory Control	00
SECTION 5—RELIEF, UTILITY, AND MITIGATION SYSTEMS		
5.1	Relief and Neutralization Systems	00
5.1.1	General	00

VVV 000008172

5.1.2	Acid-Soluble Oil Neutralization	00
5.1.3	Pressure Relief and Flare Systems	00
5.1.4	Product Treatment	00
5.1.5	Process Drains and Neutralization	00
5.2	Utility Systems	00
5.2.1	General	00
5.2.2	Cooling Water	00
5.2.3	Steam Systems	00
5.2.4	Condensate Systems	00
5.2.5	Nitrogen Systems	00
5.2.6	Breathing Air	00
5.2.7	Electrical Systems	00
5.2.8	Instrument Air Supply Systems	00
5.3	Mitigation Systems	00
5.3.1	General	00
5.3.2	Monitoring and Detection Systems	00
5.3.3	Release Mitigation Systems	00
5.3.4	Water Mitigation Systems	00
5.3.5	Emergency Isolation Valves	00
5.3.6	Acid Deinventory Systems	00
5.3.7	Hazard Analysis	00

SECTION 6—REFERENCES

6.1	Standards, Codes, and Specifications	00
6.2	Books, Articles, and Reports	00

APPENDIX A—ELEMENTS OF A COMPREHENSIVE AUDIT	00
APPENDIX B—EXPOSURE LIMITS FOR HF ACID	00
APPENDIX C—ACID TRUCK UNLOADING PROCEDURES	00
APPENDIX D—EXAMPLES OF TASKS FOR EACH CLOTHING CLASS	00
APPENDIX E—DESIGN FEATURES OF AN ACID TRUCK UNLOADING STATION	00
APPENDIX F—MONITORING AND DETECTION SYSTEMS	00
APPENDIX G—WATER MITIGATION SYSTEMS	00
APPENDIX H—EMERGENCY ISOLATION OF AN HF RELEASE	00
APPENDIX I—BIBLIOGRAPHY	00

Tables

1—Inspection Frequencies for Equipment in HF Alkylation Service	00
B-1—Exposure Limits	00

VVV 000008173

Hydrofluoric Acid Alkylation Unit Safety

SECTION 1—HAZARDS MANAGEMENT

1.1 Process Hazards Management Plan

API Recommended Practice 750, Management of Process Hazards, outlines an eleven-step procedure for managing the hazards found in refining process units. OSHA proposed regulations found in "Process Safety Management of Highly Hazardous Chemicals" will also strongly impact hazards management.[2]

Process Hazards Management (PHM) has excellent application to HF alkylation units. These units handle liquefied petroleum gas (LPG) and hydrofluoric acid (HF) which, if released in quantity, may cause significant fire and toxic hazards. Each operating HF alkylation unit shall have a PHM plan.

PHM plans used for HF alkylation units must comply with any federal, state or local regulations. These regulations may have requirements different from those of Recommended Practice 750.

1.1.1 PROCESS HAZARDS ANALYSIS

1.1.1.1 Priority

A Process Hazards Analysis (PHA) is a logical first step in a PHM program and should be conducted in all HF alkylation facilities. It will help identify and evaluate events that could lead to releases of HF or LPG. Alkylation should be high in the priority list of process units to be analyzed because of the dual hazards represented by HF and LPG. For the same reason, the interval between analyses should be no more than three to five years. Applicable regulations should be reviewed regarding the interval.

1.1.1.2 Methods

A variety of analytic techniques are available to the refiner for evaluating process hazards. Guidelines for Hazard Evaluation Procedures and "Process Safety Management of Highly Hazardous Chemicals" summarize some advantages and disadvantages of hazard analysis systems and provide guidance in selecting appropriate PHA tools.[3] A Hazard and Operability Study (HAZOP) is one method of PHA appropriate to an HF alkylation unit. The final choice of an analytic technique will depend on a number of site-specific criteria. There may be a benefit in varying the technique from one analysis to another.

VVV 000008174

Regardless of the method selected, the following situations should be included in the analysis:

- a. Routine operations, including acid unloading and sampling.
- b. Startup.
- c. Shutdown.
- d. Upset conditions.
- e. Emergencies.

Vapor cloud dispersion modeling in conjunction with PHA can be used to help judge the consequences of a specific hypothetical release scenario.

1.1.2 MANAGEMENT OF CHANGE

In addition to the procedures suggested by API Recommended Practice 750, changes in technology or facilities in an HF alkylation unit should be subject to some form of PHA, paying particular attention to the potential for loss of containment integrity that may be caused by the changes.

1.1.3 EMERGENCY RESPONSE AND CONTROL

1.1.3.1 Content

An emergency response and control plan for the HF alkylation unit should be established. This plan must be in accordance with existing federal, state, and local regulations and industry guidelines. (For example; see 29 Code of Federal Regulations Part 1910.38, "Employee Emergency Plans and Fire Prevention Plans," 29 Code of Federal Regulations Part 1910.120, "Hazardous Waste Operations and Emergency Response," and other OSHA references listed in 6.1.) In addition to the items covered by regulations, the plan should include the following:

- a. The impact of a potential HF release in addition to an LPG release.
- b. The possible need for and sources of additional emergency response equipment and personal protective equipment (PPE) suitable for HF exposure.
- c. The possible need for and location of emergency medical treatment for HF exposure.
- d. The possible contamination of runoff water with HF.
- e. The possible need for outside emergency response personnel who are trained in handling both HF and LPG emergencies.

VVV 000008175

f. The mechanism, when necessary, to communicate to the surrounding community a response appropriate to the situation: for example, evacuate or shelter-in-place.

1.1.3.2 Emergency Response Team

An HF alkylation emergency response team is desirable to help establish on-the-spot control of the emergency. Such a team is normally a part of the refinery's general emergency response organization. The team should be trained in all areas of the emergency response plan, per applicable federal, state and local regulations.

Information gained from real or simulated HF and/or LPG incidents should be reviewed to determine what, if any, improvements need to be made to the HF alkylation unit/refinery emergency response and control plan.

The balance of this recommended practice will primarily address the HF aspects of an alkylation unit.

1.1.4 AUDIT PROGRAMS

1.1.4.1 Frequency

Auditing allows an organization to systematically review its success in satisfying the PHM provisions of API Recommended Practice 750, and to assess compliance with its own internal regulations and practices. In addition, auditing should verify that federal, state, and local requirements are being met. Each operating unit should have a comprehensive audit plan and should be audited at least every three years.

1.1.4.2 Content

The audit plan should cover safety, hazard, and operability aspects of the alkylation unit. The plan should identify, by title, the individuals responsible for carrying out the audit and specify training for them as appropriate. It should provide a checklist specific to the HF unit, including items such as those listed below. Further details are in Appendix A.

Auditors should check a representative sampling of each of the following items, concentrating on the time period since the last audit:

- a. Review HF-related incident reports.
- b. Review various unit records, including operating procedures, logs, checklists, and operator training.

VVV 000008176

- c. Review inspection and maintenance records and training.
- d. Review the mechanical and procedural changes that have been made in the unit.
- e. Review testing and maintenance of detection, monitoring, and automatic control systems used to minimize the risk of an HF incident.
- f. Review testing and maintenance of systems used to mitigate the accidental release of HF to the atmosphere.
- g. Observe and interview unit and plant personnel for evidence of compliance with, and understanding of established procedures.
- h. Review the mechanism for investigating and implementing changes in technology which may permit reduction in risk.

1.2 Environmental Impact

The operation of an HF alkylation unit generates waste material and by-products that, because of their physical or toxicological properties, may require on-site processing prior to final disposition. To achieve this, procedures and facilities should be in place for the safe on- and off-site handling of these materials. Handling methods must be in compliance with applicable environmental regulations.

1.2.1 PROCESS BYPRODUCT MATERIALS

The following are among the process byproduct materials that may require further treatment:

- a. CBM (constant boiling mixture) or HF/water mixtures.
- b. ASO (acid soluble oils), or polymer.
- c. Neutralization pit or caustic regeneration solids.
- d. Defluorination solids.
- e. Acid-area surface water drainage.
- f. KF, KOH, NaF or NaOH drainings from treater operation.
- g. Neutralizing and cleaning chemicals from turnarounds.
- h. Runoff from water mitigation systems.

1.2.2 VENT GAS SCRUBBING

In HF alkylation the main potential air emission is the acid itself. There should be a scrubber to remove HF from acidic vent gas before directing such gas to a flare.

1.2.3 LEAKS

Small acid leaks occasionally develop in alkylation unit equipment and may become large leaks if not handled promptly. A regular monitoring program should help to identify this type of leak

VVV 000008177

so that repairs can be made before a more serious leak develops. Regular operator inspections are recommended to identify very small leaks. (Refer to section 3.4.3 for details.)

1.3 Internal Incident Review

If an HF release is of sufficient quantity, there will be regulatory reporting requirements under the Emergency Planning and Community Right to Know Act (Superfund Amendments and Reauthorization Act, Title III), the Comprehensive Environmental Response, Compensation and Liability Act (CERCLA), and other laws. Moreover, all HF incidents, including releases of less than reportable quantities and potentially serious incidents (near misses), should be investigated. Procedures should clearly specify the level of investigation to be made based on event severity, the format and distribution of the investigation report, and parties responsible for taking corrective action to prevent recurrences.

VVV 000008178

SECTION 2—OPERATING PROCEDURES AND WORKER PROTECTION

2.1 General

API Recommended Practice 750 clearly spells out the need for careful communication of the process-design intent, capability, and limitations of affected process units to personnel working on these units. HF alkylation units need specific written operating procedures which address the toxic and corrosive nature of the acid catalyst. Because HF acid is not usually found in other operating parts of the refinery, some of these procedures may be unique to this unit and special training may be warranted.

2.2 Health Hazard Information

Pure hydrogen fluoride is a clear, colorless, corrosive liquid that boils at 67°F. Depending on release conditions, it can form a vapor cloud if released to the atmosphere. It has a sharp, penetrating odor that human beings can detect at very low concentrations in the air. It is completely soluble in water to form hydrofluoric acid, which in concentrated solutions, fumes when exposed to moist air.

Even brief contact with hydrofluoric acid liquid or vapor can produce serious, painful chemical burns, sometimes with delayed onset. The vapor can be extremely irritating to the eyes, skin, and respiratory tract. Short-term exposure at higher concentrations can cause serious health effects or death due to extensive respiratory damage. There may be chronic health effects, such as fluorosis, from repeated exposures. **FOR ADDITIONAL INFORMATION, CONSULT YOUR EMPLOYER, THE MANUFACTURER OR SUPPLIER OF THE MATERIAL, OR THE MATERIAL SAFETY DATA SHEET.**

Facilities must comply with the requirements of worker protection health standards and regulations applicable to their location. For example, 29 Code of Federal Regulations Part 1910.1000, "Air Contaminants," currently sets workplace exposure limits for HF (as F) at 3 ppm for an eight hour Time Weighted Average. The Short Term Exposure Limit is 6 ppm for a 15 minute time weighted average, set by the same rule. Appendix B contains other sources of exposure guidelines (refer to the latest editions of the applicable sources).

Facilities must also comply with applicable hazard communication (right-to-know) regulations. For example, see 29 Code of Federal Regulations Part 1910.1200, which addresses labeling, material safety data sheets, worker training and record keeping requirements.

VVV 000008179

Consider the applicability of 29 Code of Federal Regulations Part 1910.120 regulations in the light of specific operations and emergency response plans at the site.

2.3 Operating Manuals

2.3.1 CONTENT

Operating manuals should be developed and made available to all assigned operating personnel of an HF alkylation unit. These manuals should be unit- and site-specific, and they should include the descriptive materials called for in Recommended Practice 750 as well as piping and equipment limitations, steps to follow in the event of an HF release, and detailed first-aid procedures. Routine operations that are unique to HF alkylation need very specific procedures. Such operations include acid sampling, unit neutralization and dryout, and unloading of fresh acid shipments. Other procedures will be mentioned in the applicable sections of this practice.

For reference, an example of a procedure for unloading fresh acid is included in this practice as Appendix C.

2.3.2 HF RELEASE RESPONSE

The operating procedures manual should include a section on HF acid release detection and appropriate response procedures. This section should guide the operator in the steps to be taken if an HF release occurs, including the following information:

- a. Accounting for all personnel in the unit.
 - b. Criteria for initiation and operation of the following emergency systems, where available:
 1. Unit evacuation horn or other notification procedures.
 2. Remote-operated isolation valves.
 3. Water mitigation.
 4. Rapid deinventory or emergency acid movements.
 - c. Initiation of emergency response or other contingency plans.
- Refer to section 1.1.3.

2.3.3 TEMPORARY SHELTER-IN-PLACE CONTROL ROOMS

Where control rooms are used for temporary shelter-in-place, written procedures should guide operating and non-operating personnel in entering and securing the rooms against HF intrusion, testing the atmosphere in the rooms and in criteria for leaving such temporary locations.

VVV 000008180

2.3.4 TESTING CRITICAL SYSTEMS:

A written procedure should be in effect for identifying and periodically testing critical alarms and HF detection, isolation, and mitigation devices. This procedure should include valve stroking, isolation and testing of primary elements and controls, testing critical pump auto start/stop systems, testing water-spray equipment, and calibration and testing of shutdown systems.

2.3.5 CHANGES IN PROCEDURES

Written operating procedures should identify the job position responsible for authorizing changes to procedures and for insuring that such changes receive appropriate reviews and documentation, and that appropriate training has taken place.

2.4 Personnel Training

Many standards and regulations are relevant to training requirements in process units. Examples include 29 Code of Federal Regulations Part 1910.1200; API Recommended Practice 750, Section 7; and others. Included below are some matters specific to HF alkylation that should be considered in alkylation unit training programs.

2.4.1 OPERATOR TRAINING

Because of the potential hazards of HF, training of operating personnel in the process and mechanical limitations of the alkylation unit is especially important. The systems installed for prevention, detection, and mitigation of HF releases may be complex and unique to the HF alkylation unit. Training should emphasize the importance and proper operation of these systems.

2.4.2 NON-OPERATING PERSONNEL

Appropriate written procedures for non-operating personnel should be developed and made available to all people who do work on or enter an HF alkylation unit routinely, such as supervisors and technical, maintenance, and contractor personnel. These procedures should address the hazardous nature of HF, appropriate first-aid procedures, the steps to be taken in the event of an acid release, and other information relative to the specific work assignment. A variety of presentation methods may enhance communication to the targeted personnel. Inclusion of these procedures in the operating manual will help unit operators enforce them.

VVV 000008181

2.4.3 MAINTENANCE TRAINING

Employees involved in maintaining the mechanical integrity of the HF alkylation unit equipment should be trained in the mechanical and materials limitations, procedures, and safe work practices applicable to their job tasks, including the hazards of HF.

2.4.4 EMERGENCY RESPONSE TRAINING

The emergency response plan outlined in section 1.1.3 should be included in the training for employees and off-site support personnel who are designated to respond to an emergency in the HF alkylation unit. To aid proficiency, periodic drills and simulations are encouraged.

2.4.5 PERSONAL PROTECTIVE EQUIPMENT TRAINING

Training must be provided for all personnel who work in the HF alkylation unit, or who are designated to respond to emergencies in the unit, in the use of applicable personal protective equipment (PPE) and clothing.

2.5 Protective Equipment and Clothing

2.5.1 PERSONAL PROTECTIVE EQUIPMENT AND CLOTHING

2.5.1.1 Availability and Written Policy

Proper protective equipment shall be available for all personnel who work in or enter an HF alkylation unit for any reason.

Each HF alkylation unit should have a written policy outlining protective equipment and clothing requirements, including the potential health impacts of using protective equipment under extreme ambient conditions. Heating or cooling systems for personnel wearing PPE in extreme working conditions are available.

2.5.1.2 Classes of PPE and Clothing

In selecting PPE a combination of clothing and equipment should be chosen in conformance with applicable regulations and to provide an appropriate level of protection without impairing work performance. As conditions change the level of protection should change as appropriate to the situation.

As a guideline, levels of protection may be divided into four classes denoted as A, B, C, and D, where A is the lowest level of protection and D the highest. This classification system is widely used in the refining industry and is outlined below. Note, however, that EPA and OSHA have a lettering system for PPE classification

VVV 000008182

which is the inverse of the one used in this recommended practice (i.e., A is the highest level of protection, and D is the lowest). The substantive criteria within each letter level may not be completely comparable between the industry and government levels. Therefore, the list below should be used in the context of OSHA regulations on personal protective equipment and respiratory protection. (See 29 Code of Federal Regulations Part 1910.132-136, and, if applicable, Part 1910.120.) Distinctions between the list below and EPA/OSHA levels should be noted in training.

- a. Class A clothing consists of a face shield or eye goggles, acid-resistant gauntlets or gloves, acid-resistant rubbers or boots, and an acid-resistant jacket (optional). This class is used where no physical contact with acid-containing equipment is to be made.
- b. Class B clothing consists of a face shield, eye goggles (optional), acid-resistant gauntlets, acid-resistant rubbers or boots, acid-resistant jacket, and acid-resistant overall pants. This class is used for routine work on acid-containing equipment but when no acid exposure is expected.
- c. Class C clothing consists of positive pressure self-contained breathing apparatus (SCBA) with hood or air-supplied HF acid hood with escape pack, acid-resistant gauntlets, acid-resistant rubbers, acid-resistant jacket, and acid-resistant overall pants. This class is used where minimal, low level HF exposure is anticipated.
- d. Class D clothing consists of a totally enclosed acid-resistant pressurized suit with SCBA or with air supplied via an external air hose. The SCBA for class D clothing should contain a nominal 30-minute air supply. Air-supplied suits should be equipped with escape air supply. These suits should include provisions for remote communications, such as voice activated radios. This class is used where HF vapor exposure is known or where there is potential for HF liquid exposure. Note that direct contact with liquid HF acid may result in premature failure of protective equipment and should be avoided whenever possible.

Appendix D outlines some typical tasks that help define the need for each of the above clothing classes.

2.5.1.3 Backup Personnel

When performing work that requires class C or D equipment and clothing as listed above in 2.4.1.2, at least two persons should be present, dressed in appropriate equipment and clothing (see 29 Code of Federal Regulations Part 1910.134).

VVV 000008183

2.5.1.4 Multiple Storage Areas

Consider providing an inventory of protective clothing for emergency response in more than one location against the possibility that a location becomes inaccessible during an incident. Consider heated storage areas for PPE in cold climates.

2.5.1.5 Care and Cleaning

Designated areas and facilities should be provided for neutralization, cleaning, and storage of all protective clothing.

Protective clothing should be neutralized and cleaned after each use. Since protective clothing is acid-resistant, not acid-proof, it should be washed and neutralized immediately following any contact with HF acid.

Procedures should be established to keep potentially contaminated clothing and equipment away from the clean change area and from the control room.

2.5.1.6 Inspection

All protective equipment, including new clothing, should be inspected prior to use. Procedures for inspection, testing, and replacement of protective clothing and equipment should be developed. Consider testing gloves and boots following each usage.

2.5.2 SAFETY SHOWERS AND EYE-WASH STATIONS

Safety showers and eye-wash stations shall be provided in the HF alkylation unit. These showers should be located so as to provide timely and unrestricted access by personnel from all acid containing locations in the unit. Control room and local alarms should be provided to alert unit operators when a safety shower has been activated. Each shower should be tested at a defined frequency and the results of such tests documented. Consider providing a heated water supply to the showers in cold climates or if supply water is very cold.

2.6 Controlled Access to the HF Alkylation Unit

2.6.1 UNIT DEMARCATION

The HF alkylation unit should be distinctively marked at all points of entry. Such markings should warn people that HF is present, that access is strictly limited, and that protective clothing is required.

VVV 000008184

2.6.2 ENTRY BY MAINTENANCE PERSONNEL

Entry to the unit by maintenance personnel should require approval by the operator in charge of the unit, including a sign-in, sign-out procedure. A work permit system describing the equipment to be worked on and the protective clothing required and affirming that the equipment is properly prepared for work is recommended as a prerequisite for maintenance work on the unit.

2.6.3 ENTRY BY VISITORS

Access into the HF alkylation unit by visitors and other personnel not normally assigned to work in that area should be controlled and documented. A sign-in and sign-out procedure administered by the operator in charge of the unit is recommended. All visitors should be given a safety orientation before entering the alkylation unit and should wear the proper protective clothing. Refer to section 2.4.1.2.

2.6.4 NEARBY UNITS

Consider providing response training for operators in nearby areas to help effect safe shutdown or continued operations of their units in the event of an HF acid release.

2.7 Medical Response to HF Exposure

Written procedures should outline an appropriate response when people are exposed to HF vapor or liquid, including inhalation. Signs and symptoms of exposure should be included. Since speed of response is a primary means of minimizing the impact of HF exposure, proper training in this area is of utmost importance.

Operating procedures and training should help the first-aid provider determine if immediate medical assistance is needed. Procedures should include instructions on transportation to a medical facility and appropriate communication with that facility. A knowledgeable employee should accompany the affected person to the medical facility in emergency cases. This employee can ensure that attending medical personnel are aware of the HF involvement and can supply them with copies of any prearranged treatment plans.

2.7.1 FIRST AID

2.7.1.1 First-Aid Kits

Suitably equipped first-aid kits should be readily available to HF alkylation units. Operating procedures should indicate the number, location, content, and replenishment schedules for first-aid kits.

Refrigerated storage of kits will extend the shelf life of certain of the key components.

2.7.1.2 Portable First-Aid Kits

Consider locating additional portable first-aid kits at the site of work in enclosed or difficult access areas.

2.7.1.3 Trained Personnel

Personnel trained in HF first aid should be available on all shifts.

2.7.2 FOLLOWUP MEDICAL TREATMENT

Each facility should develop a prearranged plan for follow-up examination and treatment, as needed after initial first aid, at one or more nearby medical facilities. The plan should include written protocols for treatment of HF exposures, provision of protective equipment for facility personnel as needed, stocking of supplies for HF treatment, training as appropriate, communication with refinery medical personnel, and admission to the hospital if needed following emergency treatment.

2.8 Sampling and Handling of Samples Containing HF Acid

2.8.1 TRAINING FOR ACID SAMPLING

Sampling of streams containing potentially harmful quantities of acid requires special precautions. Procedures should be established for HF sampling techniques, for design of connections and equipment, and for communication of hazards. Appropriate training should be provided for all operating and laboratory personnel who may collect or handle samples containing HF acid.

2.8.2 SAMPLE STATION DESIGN

2.8.2.1 Location

HF sampling connections should be located at grade or on an unobstructed structure with easy egress for persons in protective clothing.

2.8.2.2 Minimizing Exposure

Sample systems for streams containing HF should be designed to minimize personnel exposure to acid.

VVV 000008186

2.8.2.3 Valves

Sample connections should have two block valves per connection and should be sealed or plugged when not in use.

2.8.2.4 Marking Sample Points

Sample points should be permanently connected and clearly marked as acid sample points.

2.8.3 SAMPLE CONTAINERS

Written standards should be established for HF sample containers. Standards should include materials of construction and procedures for neutralizing, cleaning, storing, and periodically inspecting and testing HF sample containers. Sample containers should be clearly identified as containing HF. Use of these containers should be limited to HF.

2.8.4 LABORATORY SAFETY

"Occupational Exposure to Hazardous Chemicals in Laboratories," 29 Code of Federal Regulations Part 1910.1450, may provide guidance applicable for refinery laboratory safety.

2.8.4.1 Designated Area

Laboratories should provide a designated area for storing, handling, and analyzing HF-containing samples.

2.8.4.2 Fume Hood

Laboratories should be equipped with a fume hood for handling HF. The hood should meet all applicable regulatory requirements for design, construction, and operation.

VVV 000008187

SECTION 3-MATERIALS, MAINTENANCE, AND INSPECTION

3.1 General

Companies that license the HF alkylation process have developed carefully engineered materials and process specifications for HF acid service. These materials specifications are generally adequate when process conditions are kept within the design parameters. Care should be taken to insure that the materials specifications are consistently and fully observed. One of the most important measures in preventing a release of acid is a comprehensive, written inspection procedure and program for maintaining the mechanical integrity of the unit. Each operating alkylation unit should have such written inspection and maintenance procedures.

3.2 Materials and Methods of Construction

In addition to licenser specifications, the following factors should be considered in developing maintenance and inspection procedures.

3.2.1 MATERIALS

The principal materials of construction for HF service are high quality [such as hydrogen induced cracking (HIC) resistant] carbon steel and Monel. Other alloys useful in specific applications are 70/30 cupro-nickel and Hastelloy C or B.

Exposure to HF acid can cause hard steels, welds and weld heat affected zones (HAZ) to stress crack or fracture in a brittle manner or can cause dirty steels to blister from build up of hydrogen in the steel. Both effects can be greatly reduced by carefully controlling the composition and quality of steels used during construction. Cracking can also be reduced by monitoring hardness and post weld heat treating (PWHT) as needed.

Monel stressed by cold work or applied stress can crack when exposed to HF, particularly in the vapor phase. This effect is accelerated by the presence of a trace of oxygen.

Corrosion of carbon steel by HF acid is a function of water content, temperature, velocity, and contaminants, and is too complex to treat adequately in this recommended practice.

Arsenic may play a role in the cracking of carbon steel. The arsenic content of fresh acid should be limited to about 25 ppmw.

VVV 000008188

3.2.2 PRESSURE-VESSEL WELDS

Hardness of pressure vessel welds and HAZ should be controlled by PWHT or by limiting the carbon equivalent (CE) of the steel used to 0.40 maximum. The CE limit of 0.40 is based on the chemical composition as calculated from the following formula:

$$CE = \%C + \frac{\%Mn}{6} + \frac{\%Cr + \%Mo + \%V}{5} + \frac{\%Ni + \%Cu}{15}$$

Where:

- C = percentage of carbon in the steel
- Mn = manganese
- Cr = chromium
- Mo = molybdenum
- V = vanadium
- Ni = nickel
- Cu = copper

The sum of the vanadium and columbium (niobium) contents of the steel should not exceed 0.1 percent for effective PWHT.

Vessel welds should be radiographed and all slag inclusions removed. Welding slag is rapidly attacked by HF acid.

The PWHT procedure given in ASME Code Section VIII, paragraphs UW-40, UW-49, and UCS-56 should be followed except that notes in table UCS-56 do not apply. All vessel welds, regardless of type or size, requiring PWHT for hardness control should be PWHT at a minimum temperature of 1150°F. External attachments or seal-welded threaded connections on ASME Section VIII, P-1 Group 1 and 2 materials do not require PWHT.

Repairs to vessels should be made at least to the specifications of the latest edition of the National Board Inspection Code and other applicable codes, and should be PWHT if needed to control weld and HAZ hardness.

3.2.3 PIPING SPECIFICATIONS

Each operating HF alkylation unit should have a complete written specification for piping systems in HF service. This specification should be kept current, and all deviations from the specification should receive safety and process hazards management review. The specification should include materials of construction, welding details, flange rating, bolting, gasketing, valves, packing, minimum piping size, allowable acid velocities, requirements for PWHT, and minimum wall thickness or corrosion allowance.

VVV 000008189

Monel should be used in areas where high corrosion rates have been experienced or where equipment temperatures in contact with HF may be high. Monel is less corrosion resistant where HF is contaminated with oxygen.

3.2.4 PUMPS

Pumps in HF service should preferably have dual seals or should be of sealless design. If pumps equipped with single seals are used, they should have auxiliary mechanical systems to limit potential leak rates to the atmosphere from failure of the seal. Provision should be made for monitoring large pump and driver vibration and bearing-housing temperatures so that failures that could result in emissions may be prevented. Alternative lubrication systems, such as oil mist, may also be beneficial in reducing bearing failures that may lead to seal failures.

Sealless pumps may require special maintenance procedures. In case of diaphragm rupture the lubricating oil can be contaminated with HF.

All pumps in HF service should be constructed of materials resistant to HF attack, such as carbon steel, Monel, and Hastelloy C-276. Specific parts that should be considered for HF-resistant alloy materials are the shaft, impeller, wear rings, throat bushing, and seal parts.

3.2.5 FLANGED JOINTS

Spiral-wound virgin polytetrafluorethylene-filled (PTFE-filled) Monel or flexible graphite-filled Monel gaskets should normally be used in HF service. Gasket dimensions should be per API Standard 601. Gaskets should be spiral wound with a PTFE, Monel, or carbon-steel inner ring to minimize acid intrusion between the flange faces.

If ring-type joint (RTJ) carbon-steel flanges are used, the rings should be ASME/ANSI soft iron rings of 90 maximum BHN. RTJ ring gaskets of fully annealed Monel are acceptable.

Spiral wound gaskets and studs should be replaced whenever a flange joint is broken. The flange gasket surfaces should be carefully inspected for corrosion or scale buildup and, if repaired, machined to the proper surface roughness.

Care should be taken not to overtighten bolts to minimize risk of bolt failure. Heat treated bolts (B7M or K-Monel) may be work-hardened and rendered subject to HF cracking if over-torqued. Type B7 bolts are capable of bending or warping flanges and causing leaks if over-tightened. Where B7M bolts are used for their resistance to

VVV 000008190

HF-induced cracking, a representative sample should be tested to insure compliance with hardness specifications.

As an aid to leak detection, all flanges, including valve bonnet flanges, in HF acid service should be coated with a paint that changes color when exposed to HF. This distinctively colored paint is also useful in identifying storehouse materials that have been certified suitable for HF service.

Gasket surfaces should be carefully cleaned and dried before being assembled as rust and dirt are rapidly attacked by HF acid and can result in a leak.

Avoid the use of flange covers, which can trap acid or acidic water where it can not be readily observed and removed.

3.2.6 HEAT EXCHANGERS

Only seamless tubes should be used in heat exchangers in HF service. Plugged tubes should be cut or drilled behind the tubesheet to prevent potential problems caused by hydrogen permeation. U-tube exchanger bends should be stress-relieved after fabrication.

3.2.7 GAUGE GLASSES

An air-cooled chlorofluoroethylene polymer (for example, Kel-F) shield should be used to protect the glass on gauge glasses exposed to HF. An air-cooled shield has a higher allowable temperature limit than other types. Gaskets should be PTFE or flexible graphite. In general the use of gauge glasses should be minimized.

3.3 Equipment Maintenance

3.3.1 GENERAL

A preventive and predictive maintenance program should be in effect for HF alkylation units. This program should be used to establish proper inspection and maintenance intervals for equipment in HF service. Particular attention should be given to sealing devices on HF-service pumps and to flanged joints. Liscensor information should be the basis for determining what constitutes HF service.

3.3.2 TEMPORARY REPAIRS

Temporary repairs in acid service, including leak repair clamps, should be used only after approval by the appropriate level of management. When temporary piping or clamps are used, they should be documented and monitored by operators and/or inspectors on a scheduled basis and removed at the first opportunity. Operations and maintenance personnel who may be called upon to do HF leak

vvv 000008191

clamping should be trained in the use of leak clamping and pumping equipment, including criteria for changeout of bolts exposed to HF and in use of personal protective clothing and breathing apparatus. Bolts exposed to HF should be replaced.

3.3.3 SAFETY RELIEF VALVES

A written procedure should be developed for safety relief valve (SRV) maintenance. All SRVs should be tested and results documented at least every five years. Procedures should require management approval for any SRV to be taken out of service while the unit is operating. Special procedures are needed to accomplish this safely. Consider prepping SRVs before cleaning or disassembly to determine actual popping pressure. Failures to function as specified should be examined, cause determined, SRVs repaired and the testing frequency modified if necessary.

If rupture discs are used below SRVs, a high-pressure alarm or other means to detect disc leakage should be included in each such installation. Rupture discs should be replaced whenever the SRV is removed.

Radiography or other verification methods should be used each time the isolation block valves before and after a SRV are reopened to insure that the isolation valves are actually open.

3.3.4 ISOLATION AND NEUTRALIZATION

Written procedures should be developed for preparing equipment for maintenance. These procedures should include equipment neutralization, purging, and isolation prior to turning over to maintenance personnel.

3.3.5 MATERIAL REMOVED FROM UNIT

Valves and other equipment to be taken out of the alkylation unit battery limits should be opened, packing removed, bonnet bolting loosened, and other areas where HF may be pocketed disassembled. The equipment should be neutralized and tagged with a caution tag, indicating that the equipment has been in HF service and has been neutralized. Protective clothing requirements should be specified for further disassembly of such neutralized equipment on the unit or in the shop.

Fork lifts, metal scaffolding, and other equipment used in areas of HF service should be hosed down or neutralized after use. The use of wooden scaffolding should be avoided because wood absorbs HF and can not be neutralized fully.

VVV 000008192

Scrap materials potentially contaminated with HF should be stored in a segregated HF scrap weathering area. A written log of scrap materials entering and leaving the HF scrap area should be kept. Persons receiving HF scrap materials should be advised in writing of the hazards of HF.

3.3.6 LIFTS

Using a crane to lift heavy materials over piping and equipment containing HF should be avoided. If necessary, such a lift should be considered critical and appropriate management approval obtained. A written rigging plan should be prepared and reviewed covering details such as possible alternatives, crane placement, sewer line location, possible alternatives, crane mechanical condition and capability. Synthetic slings should not be used.

3.3.7 EQUIPMENT IN SERVICE

HF-containing vessels and piping should not be welded, hot tapped, or peened while in service. These operations have the potential for introducing localized corrosion sites or areas of uncontrolled hardness which may result in leaks.

3.4 Inspection of Unit Equipment

A written procedure for inspection of each operating unit is highly recommended, along the lines suggested below.

3.4.1 INSPECTION FREQUENCY

All unit equipment should be inspected for in-service defects, deformities, and damage from process exposure. The frequency of inspection should be determined from unit records; or where such records are absent (new units) or inadequate, per Table 1.

3.4.1.1 Modified Inspection Frequency

The inspection frequencies in Table 1 may be modified by evaluating inspection records and adjusting frequencies based on these documented data. Another basis for extending the inspection frequency is the use of HF corrosion-resistant materials. Conditions that warrant more frequent inspections are carbon steel exposed to high temperature ($>160^{\circ}\text{F}$) with HF, high water content (>2 percent) with HF, vapor spaces with HF, dead legs or startup lines exposed to HF, or Monel exposed to HF contaminated with oxygen. These conditions are presented for guidance only; documented plant history should govern inspection frequencies. In no case, however, should

Table 1—Inspection Frequencies for Equipment in HF Alkylation Service

Equipment	Service	Inspection	Recommended Maximum Interval (Years)
Pressure vessels	HF<160°F	Internal	10
Pressure vessels, steel	HF>160°F	Internal	5
Flanges	All HF	Gasket surface	10
Piping, all sizes ^a	HF<160°F	External	5
Piping, steel, all sizes ^a	HF>160°F	External	2
Piping, less than 2 inches ^a	All HF	Joints	5
Bleeder, vent connections, and instrument taps	All HF	Radiography	2
Rotating equipment	All HF	Internal	5
Valves	All HF	Internal	10
Exchanger tube bundles	All HF		10
Vessel and supports	All<200°F	External under insulation	5
Fired heaters and stacks	All	Internal	10
(If burning ASO)	All	Internal	4

^aSpecial steps should be taken to ensure that dead legs and startup lines are not overlooked.

VVV 000008194

frequencies be longer than one half the remaining equipment life as computed per API Standard 510, Section 4.

3.4.1.2 Pressure Vessels

All pressure vessels should be inspected per applicable API, ASME, and ANSI codes; for example, Section VIII of the ASME Code, API Standard 510, API Recommended Practices 571-576, and API Standard 2510. New construction inspection should be per Section VIII of the ASME Code. The inspection practices outlined in this document are a supplement to, rather than a replacement of, routine refinery inspection practices.

Carbon steel pressure vessel welds and HAZ exposed to HF may be subject to cracking. These welds should be initially inspected by wet fluorescent magnetic particle (WFMP) methods and reinspected by this method every 10 years thereafter. At each vessel entry, the vessel walls should be visually inspected for hydrogen blistering, and a portion of the surface should be ultrasonic thickness (UT) tested.

Any repairs to vessels should be WFMP tested and then spot tested every scheduled turnaround thereafter or until WFMP inspections have sufficiently established the safety and reliability of the vessel such that a normal inspection frequency may be resumed.

Weld and HAZ hardness is of particular concern in vessels exposed to HF at all concentrations because of the tendency of hard welds to crack. New vessel welds and repair welds should be PWHT or spot hardness tested to insure that they are below specification limits.

External thickness testing of vessel walls should be done in conjunction with scheduled turnarounds or every five years, whichever is less.

3.4.1.3 Welding Steel Exposed to HF

Steels exposed to HF may be saturated with hydrogen. Proper attention to degassing and preheating before welding will improve weld quality.

If PWHT is performed on welds that have been exposed to HF, such welds should be inspected after stress relief to check for cracks aggravated by PWHT. Consider radiographic, WFMP or UT inspection methods.

VVV 000008195

3.4.1.4 Heat Exchangers

Heat-exchanger shells should be considered pressure vessels for inspection purposes.

3.4.1.5 Piping Two Inches and Larger

Piping two inches and larger in HF service should be thickness gauged as indicated in Table 1, or at one-half of the calculated remaining life, whichever is less. Piping welds and HAZ for new construction and repairs should be fully radiographed, and hardness tested to determine the need for PWHT.

3.4.1.6 Piping Less Than Two Inches

Piping less than two inches, dead legs, and startup lines in HF service should be identified and inspected on a schedule as indicated in Table 1. Every effort should be made to eliminate dead legs.

Small piping inspection should follow the guidelines below:

- a. Screwed joints should be disassembled, cleaned, and inspected visually. Radiography is an acceptable alternative. Male and female threads should be checked with a ring or plug gauge. PTFE tape, or an alternative equivalent, should be used with screwed joints that are not seal welded.
- b. Welded joints exposed to HF should be radiographed after construction or repair to reveal cracking, lack of penetration, undercut, or slag. Refer to ASME B31.3 for criteria. Piping welds that may be exposed to HF should be hardness checked.
- c. Bleeder and vent connections exposed to stagnant process fluids should be radiographed per Table 1. These connections should be eliminated where possible.
- d. Seal welds, if present, should be inspected to insure all threads are covered by weld metal.

3.4.1.7 Valves

Valves in HF service should be inspected for erosion-corrosion damage per Table 1. Valve stuffing box bores should be inspected for enlargement from uniform corrosion. Packing should not be reused.

Maintenance procedures should include qualification and testing for shops used to repair HF service valves.

3.4.1.8 Flanges

Flanges in HF service should be inspected for corrosion of the gasket surface per Table 1. Tightly adherent scale may mask

VVV 000008196

corrosion and should be removed. Spiral wound gaskets and bolts should be replaced whenever the flanged joint is broken.

3.4.1.9 Pumps and Rotating Equipment

Pumps and rotating equipment in HF service should be inspected for erosion-corrosion damage to case and rotating parts per Table 1.

3.4.1.10 Fired Heaters

Fired heaters and stacks should be internally inspected per Table 1. Furnace tube inspection should include bulging, bowing, and internal and external corrosion measurement.

3.4.1.11 Fireproofing

Fireproofing of vessel supports, critical valves, instruments, and electrical runs should be inspected as outlined in API Publication 2218. Consider spot checking for corrosion under insulation and fireproofing.

3.4.1.12 Additional Inspections

Additional inspections should be carried out whenever operational changes or process upsets occur that could cause increases in corrosion damage of equipment. Examples of such changes or upsets include excessive water content in acid, acid carryovers, and temperature excursions.

3.4.2 INSPECTOR QUALIFICATION

Inspection of equipment covered by this document should be performed either by qualified inspection personnel or under the direct supervision of such personnel. Qualification should include API Standard 510 and/or National Board Certification. Equivalent foreign credentials may also be accepted. Nondestructive testing certification through the American Society for Non-Destructive Testing is also beneficial. All inspection personnel should receive training in the personnel hazards associated with handling or entering equipment exposed to HF. They should receive a copy of the refinery/unit procedures covering personal protective clothing, confined-space entry, and HF safety.

3.4.3 OPERATOR SURVEILLANCE

Another key element of release prevention is surveillance by the unit operators for evidence of minute HF leakage. Operators should be alert for such signs as HF sensitive paint that has changed color,

VVV 000008197

buildup of corrosion products between flanges, and the distinctive odor of HF. Repairs should be made without delay. Consider including in unit operating procedures a checklist of remote or limited access valves and instrument connections that should be regularly checked for leakage. Dilute ammonia water sprays and wet litmus paper are common means of detecting HF wisps.

3.4.4 STOREHOUSE MATERIALS

A quality assurance program should be used to identify, segregate, and insure the quality and proper warehouse storage of materials specific to the HF alkylation unit. A segregated storage area for these materials should be considered.

3.5 Record Keeping

3.5.1 INSPECTION RECORDS

For an effective inspection program, complete records of inspection results shall be kept. API Standard 510 and Recommended Practice 574 contain examples of inspection record forms.

3.5.2 EQUIPMENT WORK LIST

A list of valves, instruments, controls, and safety devices requiring service, and of temporary repairs and clamps installed in the unit should be maintained in the unit. This list should be reviewed at a frequency that will ensure that the conditions are remedied at the appropriate opportunity.

3.5.3 UNIT DOCUMENTATION

A copy of the unit piping and instrument diagrams and appropriate electrical diagrams should be kept in the unit control center to assist operators, maintenance and inspection personnel in locating blinds, isolation valves, pressure-relief devices, tag-outs and other safety and control equipment. These documents should be kept up-to-date as a part of the Management of Change procedure.

VVV 000008198

SECTION 4—TRANSPORTATION AND INVENTORY CONTROL

4.1 Refiner-Shipper Cooperation

During shipping and to some extent during unloading of fresh HF acid, the shipper's equipment is not protected by the refiner's safety and leak mitigation systems. The refiner and the acid supplier and shipper should actively cooperate to insure that these operations are performed safely. Some suggested elements of that cooperation, dealing primarily with truck transport, are included below.

4.1.1 SHIPPING CONTAINERS

HF acid suppliers and shippers should use equipment designed, inspected, and maintained according to Chemical Manufacturers Association procedures, as developed and amended. Shipping containers should be dedicated to HF service.

4.1.2 ROUTES

HF shippers should plan a route to the refinery that will minimize transportation risk. They should adhere to this route. Containers should be closely tracked en route. Routes within the refinery should be jointly planned and should include a safe holding area in the refinery for early deliveries.

4.1.3 HOSES AND VALVES

Trucks for HF acid transportation should be equipped with hoses suitable for acid unloading and for pressurizing the transport container. These should have a minimum working pressure of at least 150 pounds per square inch gauge and should be inspected and leak tested prior to each use. The test results should be recorded. Containers should have air-to-open remote-operated valves on all outlet connections and an air-to-open remote-operated valve or a check valve on the nitrogen-pressuring connection. All external root valves should be enclosed in a protective housing and should be cappable.

4.1.4 PERSONNEL AND CLOTHING

The refiner-shipper agreement should include the number of people accompanying each shipment of acid. Shippers shall provide safety equipment and clothing for their drivers. Refer to section 2.5.1.2 covering PPE. The agreement should include the number of

VVV 000008199

backup personnel needed during the unloading and an outline of the duties of each participant in case of upset or emergency.

4.1.5 TRAINING

Driver training should include the hazards of HF, first aid, unloading procedures, and operation of the safety features of the shipping container. Training and testing programs should be ongoing. Certification of such training should be made available to the refiner upon request.

4.1.6 EMERGENCY PROCEDURES

The refiner should notify and review with the drivers appropriate unit/refinery safety and evacuation procedures.

4.2 HF Unloading

The safe unloading of acid into the unit is of utmost importance to the success of the refiner's hazards management program. The unloading station should be carefully designed to minimize risk of accidental release. Clearly written operating procedures should be in place to insure that all steps in the unloading process are done safely. Appendixes C and E of this practice list some of the procedural and design considerations for truck transport unloading which may help refiners develop their own programs.

4.3 Inventory Control

Fresh HF acid inventory in the plant should be minimized. A part of this effort should include close scheduling with the acid supplier to ensure that timely deliveries are received. A key part of acid inventory control is careful monitoring of acid levels in the unit inventory. Radioactive level devices have proven effective in monitoring levels in acid storage vessels.

VVV 000008200

SECTION 5-RELIEF, UTILITY, AND MITIGATION SYSTEMS

5.1 Relief and Neutralization Systems

5.1.1 GENERAL

The volatile nature of HF means that it can be efficiently recovered from the fractionation columns in the unit. It also means that the vents, products, and byproducts from the unit may contain acid or organic fluorides and thus present a possibility of a release of HF. Each operating unit should have facilities to control, neutralize, or otherwise mitigate any hazard from the process byproducts.

5.1.2 ACID-SOLUBLE OIL NEUTRALIZATION

Acid-soluble oil (ASO) or polymer from the acid regeneration system may contain a small amount of free HF acid and/or an HF/water azeotrope. This may make the ASO corrosive and should be recognized when handling this material. Consider neutralizing, washing, or otherwise treating the acid in ASO to minimize potential corrosion problems. The method of treatment should be covered in the operating procedures.

5.1.3 PRESSURE RELIEF AND FLARE SYSTEMS

Overpressure vents from the acid-containing parts of the alkylation unit will contain some HF. These streams should be routed through a scrubber to remove the acid before the hydrocarbons are released to the flare. The capacity of this scrubber should be reviewed whenever significant process changes are made in the unit. The flare system should be inspected for corrosion if it is inadvertently exposed to HF.

5.1.4 PRODUCT TREATMENT

Products from an HF alkylation unit may contain small amounts of organic fluoride or free HF. These streams should be treated to reduce downstream corrosion potential. Product specifications may require testing to insure adequate fluoride removal.

5.1.4.1 Alkylate

HF contamination of alkylate is unlikely, but the rundown tankage should be checked periodically for low pH in the water heel. This check is particularly important if the alkylate is untreated, or after

VVV 000008201

a unit upset. Consider adding a small amount of alkali to the water heel in the tank to reduce corrosion to the tank floor.

5.1.4.2 Propane and Butane

Propane and butane products are normally treated by passing first through alumina defluorinators to destroy organic fluorides, and then through alkali (caustic) to remove any remaining HF. Some potential hazards that should be considered when writing operating procedures for this part of the process include:

- a. Misoperation in the unit may allow significant quantities of HF into the alkali treater. The heat of reaction in the treater may be high enough to cause product vaporization which can increase pressure and cause equipment damage. Consider installing alarms to warn of such a situation.
- b. Solid alkali forms a thick brine upon reaction with HF that can spatter violently if drained carelessly into the sewer.
- c. Arsenic introduced with the fresh acid may deposit on the defluorinator alumina and can present a hazard when handling spent alumina.

5.1.5 PROCESS DRAINS AND NEUTRALIZATION

Process drains may contain HF and therefore should be monitored for need to neutralize before release to the waste water treatment plant. Units should have a neutralization basin or pit for acid area drains. Alkali neutralization may result in insoluble fluoride salts, which may cause plugging. If acidic drains are allowed to mix with sulfidic drains from other areas, a release of hydrogen sulfide can result. Operating procedures should address these possibilities, as well as disposal of fluoride salts.

5.2 Utility Systems

5.2.1 GENERAL

The utility systems in an HF alkylation unit are important because unexpected contamination of the process by the utilities can have a significant influence on unit corrosivity and safety. Conversely, contamination of the utility systems with HF may spread acid hazards beyond unit limits. Procedures should be in place that define how utility connections to processes are to be made and monitored.

VVV 000008202

5.2.2 COOLING WATER

Operating with cooling-water pressure higher than the process pressure should be avoided, if possible. Leaking cooling water through exchangers into the process can quickly increase unit acid corrosivity and present the potential for unit upsets. Acid sampling and inspection frequencies should reflect this possibility.

Operating with cooling-water pressure below process pressure is preferred but risks leaking acid into the cooling water system. Consider pH, fluoride ion or other monitors in the cooling-water system to warn of this occurrence.

5.2.3 STEAM SYSTEMS

Where high-pressure steam exchangers are used, potential water leakage into the process should be considered. As with cooling water, this possibility should be considered in setting acid sampling and equipment inspection frequencies.

5.2.4 CONDENSATE SYSTEMS

Onstream pH or other monitors are recommended in the condensate system to provide an early indication of an acid leak. Operating procedures should include manual testing with pH paper.

5.2.5 NITROGEN SYSTEMS

Nitrogen used in the HF alkylation unit should be periodically tested for oxygen, which accelerates unit corrosion. Special care should be taken to avoid leakage of HF into the nitrogen or purge gas system used to unload fresh acid.

5.2.6 BREATHING AIR

Breathing air should meet at least the requirements for Grade D breathing air as defined by the latest edition of CGA G-7.1. Breathing air may be supplied from cylinders or from a special, dedicated compressor. If a compressor is used, provision should be made for appropriate air quality monitors on the inlet air stream and for an emergency back-up supply in case of a power failure.

5.2.7 ELECTRICAL SYSTEMS

A secure power supply should be provided for critical instruments and unit control systems, where electrically powered.

VVV 000008203

Consider locating an alternate means of remotely stopping pump-drivers at least fifty feet from the affected pumps to provide an emergency means of remotely stopping critical pumps.

5.2.8 INSTRUMENT AIR SUPPLY SYSTEMS

Back-up air or other gas supply should be provided for critical air-powered instruments and unit control systems.

5.3 Mitigation Systems

5.3.1 GENERAL

Despite the best program of design, maintenance, and inspection, and the highest level of training, there still may exist a very remote possibility of a release of HF. Early detection and rapid mitigation of the release should, therefore, be included in the refiner's program for process hazards management of the HF alkylation unit.

5.3.2 MONITORING AND DETECTION SYSTEMS

The reliable and early detection of an HF release is an important component of an effective system for the protection of both refinery employees and the surrounding community. Detection is also key in the implementation of mitigation measures. Each HF alkylation unit should have a comprehensive leak-detection system. Such a system may include closed-circuit TV, point sensors, open-path sensors, and other imaging systems as deemed appropriate for the unit. Operating procedures should specify system testing frequencies and proper alarm responses. This system should provide coverage for all process areas containing HF, as well as storage and loading or unloading areas. Appendix F outlines some factors affecting detection system design and component selection.

5.3.3 RELEASE MITIGATION SYSTEMS

Accidental releases of HF can be mitigated by a number of techniques including, but not limited to, water application, diking, foam or chemical application, vapor barriers, acid refrigeration, remote isolation, rapid deinventory systems, etc. The selection of mitigation technique(s) to apply will depend on a variety of site-specific and release-specific factors. For example, a pressurized release of superheated liquid HF is likely to result in an aerosol vapor cloud, thus negating the use of dikes or vaporization reduction chemicals. A low-pressure subcooled HF liquid release is likely to form a liquid pool and, as such, containment in conjunction with

VVV 000008204

vapor suppression techniques may provide adequate short term mitigation.

5.3.4 WATER MITIGATION SYSTEMS

A tested and effective HF release mitigation tool is the application of large quantities of water to the leak. A refinery's hazards management program should consider such a water application system specifically designed for HF mitigation. Water can be applied by either a system of fixed-spray curtains, by water monitors, or by some combination, depending on local considerations. Appendix G discusses some parameters which should be considered in the design of a water-application system for mitigating the impact of an HF release.

Any system designed for applying large quantities of water to an acid release should also provide for the safe handling of the contaminated runoff water.

Any water mitigation system should be fully testable. Operating procedures should specify test procedures and frequencies.

5.3.5 EMERGENCY ISOLATION VALVES

The magnitude of any HF release from an HF alkylation unit can be reduced if valves exist to isolate quickly the major inventories of acid. A refinery's hazard management program should consider installation of remotely operated emergency block valves (EBVs). These EBVs should be located so that large inventories and credible potential leak sources can be safely isolated. The goal is to be able to remove sources of acid, or of pressure, from the release site. Safe pressure relief of equipment isolated by EBVs should be included in the design. Appendix H discusses some of the parameters that may be helpful in locating EBVs and in designing the installation. As with any emergency system, testability of the elements is an important part of the design.

5.3.6 ACID DEINVENTORY SYSTEMS

5.3.6.1 General

The duration, and thus the magnitude, of an HF release can be reduced if the acid in the leaking section of the unit can be moved quickly to a safe location. A refinery's hazards management program should consider facilities to permit rapidly moving acid and entrained hydrocarbon from leaking equipment into safe equipment.

The fundamental purpose of any system to remove the acid content of a vessel is to reduce the time during which that vessel

may be leaking acid. The number of design variables in a deinventory system is too great to present details in this recommended practice. However, a number of general factors, listed below, should be considered in the design of such a system. Licensors of HF alkylation technology may also provide design assistance.

5.3.6.2 Deinventory Time

The time allowed for the acid movement should be short. The time decision will also impact the water-mitigation system design.

5.3.6.3 Extent of Movement

The extent of acid movement should be settled early in the design process. It may be sufficient to move most of the acid involved in a release rather than trying to move all of the trapped acid.

5.3.6.4 Motive Force

Moving acid requires a motive force that will be available during a release incident. The options available include gravity, existing pumps manifolded into appropriate low spots, new pumps installed for this purpose, hydrocarbon pressure, vacuum, nitrogen pressure, and others.

5.3.6.5 Vessels Included

The selection of vessels that will be connected to the rapid deinventory system depends on the location of credible releases and the installation of EBVs to isolate release sources. The acid deinventory system and EBV installations should be coordinated to ensure that the overall mitigation system functions properly.

5.3.6.6 Receiving Vessels

A key consideration is where the acid and entrained hydrocarbons will go. The options, depending on the volume to be moved and the sizes of vessels, could include the acid storage drum, settler, iso stripper, depropanizer or a dedicated on- or off-site vessel.

5.3.6.7 Venting

The vessel(s) receiving the acid may need provision for venting and neutralizing vapors generated during the movement of acid.

5.3.6.8 Pressure Relief

Safety-relief-valve capacity and location should be reviewed during the design phase of a deinventory system. Changing the

vvv 000008206

service of a vessel during an emergency or installing additional valves into a piping system may change the pressure-relief needs of the equipment involved.

5.3.7 HAZARD ANALYSIS

Mitigation systems are changes in the facility and should be subject to some form of PHA, as outlined in 1.1.2. Some of the special considerations for mitigation systems are the effects of high pressure water sprays on instruments and other equipment, handling of high volume water run-off, the effects of inadvertent closure of EBV's, and the potential risks of moving acid to on-site locations not normally containing large acid inventories or to off-site locations.

VVV 000008207

SECTION 6—REFERENCES

6.1 Standards, Codes, and Specifications

The most recent editions of the following standards, codes, and specifications are cited in this recommended practice.

ACGIH¹

Threshold Limit Values and Biological Exposure Indices

AIHA²

Emergency Response Planning Guidelines

API

- Std 510 Pressure Vessel Inspection Code: Inspection, Rating, Repair, and Alteration
- RP 571 Conditions Causing Deterioration or Failure (in press)
- RP 572 Inspection of Pressure Vessels, Heat Exchangers, Condensers, and Coolers (in press)
- RP 573 Inspection of Fired Boilers and Heaters (in press)
- RP 574 Inspection of Piping, Tubing, Valves, and Fittings
- RP 575 Inspection of Atmospheric and Low-Pressure Storage Tanks (in press)
- RP 576 Inspection of Pressure-Relieving Devices (in press)
- Std 601 Metallic Gaskets for Raised-Face Pipe Flanges and Flanged Connections (Double-Gasketed and Spiral-Wound)
- RP 750 Management of Process Hazards
- Publ 2218 Fire Proofing Practices in Petroleum and Petrochemical Processing Plants
- Std 2510 Design and Construction of Liquefied Petroleum Gas (LPG) installations

ASME³

B31.3 Chemical Plant and Petroleum Refinery Piping
Boiler & Pressure Vessel Code, Section VIII, "Pressure Vessels"

CGA⁴

G-7.1 American National Standard Commodity Specification for Air

National Board⁵

National Board Inspection Code

VVV 000008208

NIOSH⁶

90-117 NIOSH Pocket Guide to Chemical Hazards
Occupational Health Guideline for Hazardous Chemicals: Hydrogen
Fluoride

OSHA⁷

Occupational Safety and Health Standards (29 Code of Federal
Regulations Parts 1910.38, "Employee Emergency
Plans and Fire Prevention Plans"; 1910.120,
"Hazardous Waste Operations and Emergency
Response"; 1910.132, "General Requirements";
1910.133, "Eye and Face Protection"; 1910.134,
"Respiratory Protection"; 1910.135, "Occupational
Head Protection"; 1910.136, "Occupational Foot
Protection"; 1910.1000, "Air Contaminants";
1910.1200, "Hazard Communication"; and
1910.1450, "Occupational Exposure to Hazardous
Chemicals in Laboratories")

6.2 Books, Articles, and Reports

1. "The Use of Hydrofluoric Acid in the Petroleum Refining Alkylation Process," Policy Statement, American Petroleum Institute, Washington D.C., March 1990, **pp.?**
2. "Process Safety Management of Highly Hazardous Chemicals," 55 Federal Register 29,150 (1990) (to be codified at 29 Code of Federal Regulations Part 1910.119).
3. Guidelines for Hazard Evaluation Procedures, Second Edition with Worked Examples, American Institute of Chemical Engineers, New York, (in press), **pp.?**
4. D.N. Blewitt, R.P. Koopman, T.C. Brown, and W.J. Hague, "Effectiveness of Water Sprays on Mitigating Hydrofluoric Acid Releases," Paper presented at the 1987 CCPS Vapor Cloud Conference, **City?**, November 1987.
5. K.W. Schatz and R.P. Koopman, "Effectiveness of Water Spray Mitigation Systems for Accidental Releases of Hydrogen Fluoride—Summary Report," Volumes I-VIII, Industry Cooperative HF Mitigation/Assessment Program, June 1989, **pp.?**
6. G. Heskestad et al., Dispersal of LNG Clouds with Water Spray Curtains. Annual Report—Phase 1, Factory Mutual Research Corporation for GRI, **City?**, August 1982, **pp.?**
7. P.A. Moore and W.D. Rees, "Forced Dispersion of Gases by Water and Steam," Paper presented at the International Chemical Engineering Symposium, **City?**, November 1981.

vvv 000008209

APPENDIX A—ELEMENTS OF A COMPREHENSIVE AUDIT

Comprehensive auditing means a periodic review of a representative sampling of the systems and procedures in place in an HF alkylation unit. Consider including the following elements when developing an audit process.

- a. Initial walk-through of the unit to look at:
 1. Layout of fire fighting access, escape routes, emergency vent discharge location, distance to other areas of concern, housekeeping, isolation of surface drains, access to potential leak sites, and so forth.
 2. Labeling of lines, key valves, instrument settings, alarms and trips, emergency shutoffs, unit access limits and warnings, and the like.
 3. Safety equipment including fire extinguishers, hydrants and hoses, respiratory gear, personal protective clothing, grounding, emergency communications systems, safety showers, eyewash stations, mitigation equipment, first-aid equipment, etc.
- b. Systems review
 1. Review process control for specification of normal control ranges, system software and backup, instrument and equipment redundancy, P&ID currency, and instrument reliability history.
 2. Review detection systems for mechanical condition, testing, repair, calibration frequency, and frequency of nuisance trips.
 3. Review mitigation systems for mechanical condition, repair history, fire protection, and testing.
- c. Review operating procedures covering all appropriate operating activities for technical correctness, clarity, ease with which they can be followed, and completeness. Check date of last review and inclusion of changes to the unit. Also review log books, checklists, work and entry permit procedures, training manuals and materials, and other records.
- d. Review maintenance procedures and preventive and predictive maintenance records covering mechanical equipment, piping, equipment trips, vessels, interlocks, SRV testing, detection devices, mitigation systems, equipment neutralization, and PPE use in the shop area.
- e. Review inspection procedures, methods, and schedules. Records should be up-to-date and reflect the current condition of the unit. Review reports of inspection findings and status of recommendations.

VVV 000008211

FOOTNOTES

¹American Conference of Governmental Industrial Hygienists, 6500 Glenway Avenue, Building D-7, Cincinnati, Ohio 45211-4438.

²American Industrial Hygiene Association, P.O. Box 901010, Cleveland, Ohio 44190.

³American Society of Mechanical Engineers, 345 East 47th Street, New York, New York 10017.

⁴Compressed Gas Association, 1235 Jeff Davis Highway, Arlington, Virginia 22202-3269.

⁵National Board of Boiler and Pressure Vessel Inspectors, 1055 Crupper Avenue, Columbus, Ohio 43229.

⁶National Institute for Occupational Safety and Health, U.S. Department of Health and Human Services, 4676 Columbia Parkway, Cincinnati, Ohio 45226.

⁷Occupational Safety and Health Administration, U.S. Department of Labor. The *Code of Federal Regulations* is available from the U.S. Government Printing Office, Washington, D.C. 20402.

VVV 000008210

- f. Conduct interviews with key operations, engineering, maintenance, and inspection personnel concerning maintenance, quality control, safety, training, operational procedures, control of changes, emergency procedures or simulations, and other matters not easily found in unit records. Interviews should be structured to elicit any concerns that people may have; to determine that they are familiar with applicable operating and maintenance procedures, safety and emergency plans, etc.; and to assess the effectiveness of training programs.
- g. Review the emergency response plan and documentation of the drills to determine effectiveness. Consider such matters as notification procedures, response, agency interaction, and community outreach. Consider visiting first-aid and medical response sites. Verify that first-aid kits contain up-to-date materials and that personnel are trained in their use.
- h. Include other items as appropriate to the site.

VVV 000008212

APPENDIX B—EXPOSURE LIMITS FOR HF ACID

The limits outlined in Table B-1 are those in effect at the time of publication of this recommended practice, be sure to check for latest editions. Definitions of the terms and application of the limits should be taken directly from the references and regulations.

VVV 000008213

Table B-1—Exposure Limits

Agency	Reference Number ^a	Level	Duration	Concentration In PPMV
OSHA	b	PEL	8 hour TWA	3 (as F)
OSHA proposed	[2]	STEL	15 minute TWA	6
ACGIH	c	TLV ceiling ^d	8 hours/day	3
NIOSH/OSHA	e	IDLH	≤30 minutes	30
AIHA	f	ERPG-19	≤60 minutes	5
	f	ERPG-29	≤60 minutes	20
	f	ERPG-39	≤60 minutes	50

Notes:

PPMV=parts per million volume; OSHA=Occupational Safety and Health Administration; PEL=permissible exposure limit; TWA=time weighted average; STEL=short-term exposure limit; ACGIH=American Conference of Governmental Industrial Hygienists; TLV=threshold limit value; NIOSH=National Institute for Occupational Safety and Health; IDLH=immediately dangerous to life and health; AIHA=American Industrial Hygiene Association.

^aSee Section 6 for reference information.

^bSee 29 Code of Federal Regulations Part 1910.1000.

^cSee ACGIH's Threshold Limit Values and Biological Exposure Indices.

^dA ceiling is a concentration that should not be exceeded during any part of the working exposure.

^eSee NIOSH Pocket Guide to Chemical Hazards and Occupational Health Guideline for Hazardous Chemicals: Hydrogen Fluoride.

^fSee AIHA's Emergency Response Planning Guidelines.

gERPG=Emergency Response Planning Guidelines. ERPG levels are as follows:

1. ERPG-1=the maximum airborne concentration below which it is believed that nearly all individuals could be exposed for up to one hour without experiencing other than mild, transient adverse health effects or without perceiving a clearly defined objectionable odor.
2. ERPG-2=the maximum airborne concentration below which it is believed that nearly all individuals could be exposed for up to one hour without experiencing or developing irreversible or other serious health effects or symptoms which could impair an individual's ability to take protective action.

VVV 000008214

3. ERPG-3=the maximum airborne concentration below which it is believed that nearly all individuals could be exposed for up to one hour without experiencing or developing life-threatening health effects.

VVV 000008215

APPENDIX C-ACID TRUCK UNLOADING PROCEDURES

Various hazard reviews of HF alkylation units have identified acid unloading as having a higher potential for HF release than most other procedures in the unit. Because of this, acid unloading should follow a carefully written procedure. Nitrogen-pressured unloading is the most commonly used procedure; however, other procedures, such as pumped unloading, are also used.

The following is one possible procedure for nitrogen-pressured HF unloading. The details may vary from unit to unit. This procedure is written to accommodate the type of unloading station described in Appendix E.

1. Class C protective clothing should be available to refinery personnel and the drivers. It should be worn by all personnel involved during critical phases of the acid unloading.
2. A minimum of two people should be available full-time for HF acid unloading. At least one qualified person from the refinery HF alkylation unit should participate.
3. Prior to delivery of acid, unit operators should verify that all acid tank try-cocks, process valves, and the nitrogen pressure controller are properly configured and operable. The acid storage-vessel level should be checked to insure that there is room for the volume of fresh HF acid to be received. The contents of the transport container should be verified as being anhydrous HF acid.
4. The safety shower and eye-wash station in the transport unloading area should be tested prior to unloading.
5. HF acid transport containers should be unloaded during daylight hours, except where lighting in the unloading area is at daylight levels and adequate staff are available for emergency response.
6. The unit operators should insure that there is adequate neutralization capacity in the neutralization section.
7. When the transport container is spotted at the unloading area, set the brakes, chock the wheels, hook up the bonding wire, post warning signs, and isolate the area.
8. For truck deliveries, remove the keys from the tractor to a safe location controlled by the unit operator.
9. If pressure in the acid storage vessel is high enough to impede unloading, the operator may vent to the neutralization section to achieve a pressure low enough to speed up unloading.
10. Insure that both the transport container remote-operated valves and the unit remote isolation valve are operable.

VVV 000008216

11. Safety relief valves on HF acid transport containers from different vendors may be set at different pressures. The Alkylation unit nitrogen pressure regulator and SRV should be set at a point below the transport-vessel SRV to avoid venting HF-laden gas. The nitrogen header should be blown down prior to hook-up to confirm that it is water-free.

12. Unit operators and the truck driver (where applicable) should verify that all systems are depressured on their respective ends before making a hook-up. Then the blind flanges on the acid unloading line and the nitrogen pressure inlet line should be carefully removed. Flange connections should be visually inspected. The acid unloading and the nitrogen lines should be connected to their respective openings using new, solid, one-eighth-inch thick PTFE or PTFE-coated steel gaskets and new B7M bolts. Before these lines are used, it is desirable to test both the nitrogen and acid unloading systems by pressuring with nitrogen, using a crossover between the nitrogen line and the acid unloading line. Check all connections with a liquid leak detector, such as a soapy water solution. Following the leak test, depressure the system to a safe location and secure it.

13. Unit operators should insure the proper line-up to the acid storage vessel. The valve at the end of the unloading line at the unit unloading manifold should remain closed at this time.

14. The dome on the transport container should be slowly swung open in case the valve stems are leaking HF into the dome.

15. Before opening the liquid discharge valve, pressure the transport container with nitrogen to a pressure higher than the acid storage vessel. This step will prevent a backflow of liquid or gas into the transport container from the acid storage vessel.

16. Slowly open the unit manifold acid valve and inspect the fittings for leaks. Check all connections with a leak detector, e.g., 10-percent ammonia solution. If there are no leaks, slowly open the transport-container-dome acid valve, permitting acid to flow into the acid storage vessel.

17. Using the pressure regulator, increase the nitrogen pressure to the transport container as needed to maintain flow.

18. Unit operators should check the nitrogen pressure of the transport container periodically during the unloading operation. They should also check the pressure and level of acid in the acid storage vessel to insure that acid is being received and that there is ample room for the amount being unloaded. When the transport container is empty, the storage-vessel pressure will equalize with the container's pressure. The transport-container gauge pressure will

VVV 000008217

fall quickly, and the hose may move around when the container is empty.

19. Upon completion of the acid transfer, block in the acid storage vessel by closing the unloading line at the vessel. Close the nitrogen inlet valve upstream of the pressure regulator, and check the level of acid in the acid storage vessel to be sure that the amount unloaded agrees with the amount specified by the bill of lading.

20. Vent the pressure in the transport container to the neutralization section using the unloading line and the appropriate vent line. The pressure should gradually reduce to 20 pounds per square inch gauge or less during the venting operation.

21. Close the transport-container's nitrogen valve and acid unloading valve. Then close the vent line to the acid relief header and the valves at the end of the nitrogen and the unloading lines at the unit manifold. Check that these lines are depressured by opening appropriate drains.

22. Then cautiously disconnect the hose fittings to the transport container and stow away. Replace blind flanges at the transport container and at the unloading manifold using new PTFE gaskets and new bolts. Seal the transport container's dome for return shipment. Wash down any spilled acid into the area acid drain.

23. Release the brakes and remove the warning signs and the chocks on the transport container when it is ready to depart.

24. For tank-truck shipments, return the keys to the driver after all piping has been disconnected and the hoses secured.

25. For rail-car shipments, reverse the placard on the tank car.

VVV 000008218

APPENDIX D-EXAMPLES OF TASKS FOR EACH CLOTHING CLASS

Below are some examples of work normally done in each of the four classifications of personal protective clothing defined in this recommended practice.

- a. Class A clothing—Examples of routine work include but are not limited to: reading meters and gauges in the field; routine visual inspections of the unit; unloading or dumping alumina; repair of equipment that has been opened, disassembled, and neutralized so that no acid can be trapped within; work on non-acid equipment in area if there is no other acid-area work going on nearby; reassembly of thoroughly cleaned acid equipment; welding on equipment that has been properly prepared for welding; and painting.
- b. Class B clothing—Examples of routine work include but are not limited to: greasing of valves; washing down; sample collection of non-acid-containing materials; pump work after blinding has been completed and cover plate removed; reboiler work (after column manways have been opened); opening manways on vessels; dismantling safety relief valves (when there is no potential for trapped acid); disassembly of acid equipment that has been opened and neutralized, including exchangers and condensers with HF-containing tubes that are known to be unplugged.
- c. Class C clothing—Examples of routine work include collecting samples containing a potentially harmful quantity of HF; changing pressure gauges in acid areas; blinding and other opening of lines where equipment has been depressured; work on any acid equipment which is not blinded at the first flange; initial opening of equipment after blinding (includes exchanger heads, manways, and flanges); work on small piping manifolds until certain that no HF can be trapped inside equipment (includes work on meters and meter manifolds and valves, disassembly of pumps, and disassembly of exchangers and reboilers that contain acid until tubes are unplugged).
- d. Class D clothing—Examples of work include pump-seal or valve-packing failure and working in close proximity to leaks that require lines or equipment to be isolated.

The following step-wise procedure is recommended for the removal of protective clothing:

- a. Neutralize boots and gloves.
- b. Remove face shield and hard hat.
- c. Remove rubbers/boots.

VVV 000008219

- d. Remove outer clothing.
- e. Remove gloves.

VVV 000008220

APPENDIX E—DESIGN FEATURES OF AN ACID TRUCK UNLOADING STATION

Unloading of HF acid into an alkylation unit is one of the more hazardous procedures in the routine operation of the unit. A carefully designed unloading station can greatly reduce the risk of an HF release during this operation. Nitrogen-pressured unloading is probably the most common method, although other procedures are also used.

The following are desired features for a nitrogen-pressured HF acid unloading station. Details may vary from unit to unit. This discussion is not intended to preclude the use of other unloading systems, such as pumped unloading.

- a. The unloading vehicle should have clear access to the unloading facility at the unit.
- b. The unloading facility or transportation vehicle should include means, such as wheel chocks, for positively fixing the vehicle.
- c. An emergency shower and eye-wash station should be readily accessible (between 10 and 50 feet) from the unloading station. Alarms activated by the shower and eye wash will alert operators in the control room to a possible upset.
- d. Utility water via a hose station should be available for washdown and flushing.
- e. Nitrogen should be provided at a pressure suitable for unloading the transportation container into the storage facility. The nitrogen header should have a SRV set at least 20 percent below the transport container SRV setting. There should be provision, such as check valves, to exclude backup of acid or any material through the nitrogen or other systems to other refinery areas. The nitrogen supply should have a restrictive device that will allow unloading in a reasonable time, but prevent high nitrogen flow through the transfer hose when the transport vessel is empty.
- f. Where access to the transport is from a top platform, there should be egress possible in at least two directions. Stairways are preferred over ladders.
- g. There should be water mitigation facilities that can be directed on the unloading facility in the event of a release.
- h. There should be a connection from the unloading line to the acid scrubber for venting after unloading or for emergency depressuring.
- i. Provision should be made to monitor the pressure in the acid storage vessel during the unloading.

VVV 000008221

j. Unloading piping should be arranged to minimize dead legs where acid may accumulate.

k. Valves should be provided to allow tightness testing with nitrogen of the connections from the unloading manifold to the transport vessel. A pressure indicator should be included, visible from the unloading station, to facilitate testing and monitoring during the unloading.

l. The connecting hoses or lines from the unit unloading manifold to the transport container should allow for vertical movement due to decreasing load on the container springs during unloading.

m. A remote-operated valve should be provided as the last valve before the acid hose connection on the unit unloading manifold.

n. There should be an atmospheric vent valve facing downward and located at the low point of the unit unloading manifold for final depressuring after completion of unloading and venting to the acid neutralizer.

VVV 000008222

APPENDIX F—MONITORING AND DETECTION SYSTEMS

F.1 General

A system to provide for the early detection of an accidental release is an essential part of any HF alkylation unit hazards management plan. The design of a detection system should reflect its particular purpose and site-specific factors.

Some of the operating characteristics desired in a system for monitoring air quality may be quite different from those wanted for the detection of an accidental release. For example, there will be less need for rapid response and early-warning capabilities for the air-monitoring system. Also, while the reasonably precise measurement of concentration is an important factor in a monitoring system, it is much less critical in the early detection of an accidental release.

In all cases, the design of a detection system and the choice of specific components should reflect the details of the process and the refinery setting. Possible interference from other chemical compounds and site meteorological conditions should be taken into consideration. Factors such as the range of possible ambient temperatures and relative humidity levels can significantly affect the performance of system components and, therefore, should be included in component selection and design.

F.2 System and Component Performance Characteristics

The desired performance characteristics should be considered in the selection of the components and in the design of the detection system. Key design issues for a system include the following:

- a. Detector type.
- b. Detection range.
- c. Selectivity.
- d. Response time.
- e. Stability.
- f. Reliability, in terms of:
 1. Maintainability.
 2. Compatibility with refinery environment.
 3. Experience in similar applications.

(Similar issues should be addressed for both an air-quality monitoring and an accidental release detection system. Because the focus of this recommended practice is risk reduction, the remainder

VVV 000008223

of this section will address a system for early identification and warning of an acute accidental release.

F.3 Detector Type

The traditional HF detection system has been based on the electrochemical point sensor; but as of this writing, a number of other promising detector types are under development. Detection systems are generally based on one or more of the following general detector types:

- a. Point sensors – These devices will respond to HF only at their specific location. The response signal is usually proportional to the HF concentration.
- b. Open path – These detectors will respond to the presence of HF anywhere along a line-of-sight path between a transmitting device and a receiver. Such devices do not provide point concentrations but rather respond to the cumulative quantity of HF in the open path. Open-path detectors are useful for perimeter monitoring.
- c. Imaging – These detectors are based on the visual or infrared image generated by a cold, dense HF release. These systems are useful for identifying or confirming a large release, establishing the exact location and remotely directing the initial mitigation activities.

F.4 Detection Range

When HF detectors are used for early leak detection, as opposed to personal hygiene monitoring, a set point of about 10 ppm is desirable to activate an HF alarm. Primary detection devices typically operate over a range of about 0-20 ppm. Although the local HF concentration of an accidental HF release may be substantially higher than 20 ppm, the objective is early detection of a release, not determination of exact concentrations.

F.5 Selectivity

If other compounds may be present in the area being monitored, a detection system should be HF-specific to the extent possible so that the presence of other gases does not affect the detector's response. Frequent spurious activation of the detector's alarm system is likely to result in the operators losing confidence in the detection system.

VVV 000008224

F.6 Response Time

It is important to note that device response time may be affected significantly by ambient conditions. For example, humidity will affect the response time of some detector types by many seconds, particularly at the lower end of the detection range. A detector should be capable of responding effectively under all conditions likely to be experienced at a given site.

A second consideration of response time involves the system response time, which is the length of time from a significant HF release until the mitigation procedure is activated. This time will be a function of system deployment, device response time, and activation strategy. System response time should be as low as possible to minimize the downwind impact of an HF release.

F.7 Stability

Detectors should have good stability. If there is a significant zero or span drift over time, the detector will require frequent calibration to minimize inaccurate readings and spurious alarms.

F.8 Reliability

It is very important to consider the reliability of a detector in terms of maintainability, compatibility with the refinery environment, and proven performance. If a detector is not properly calibrated and maintained, it may fail to respond in the event of a release. Detector elements may deteriorate or be consumed over time, or may become poisoned by other gases, so that the response to a release is impaired. A schedule of periodic maintenance and recalibration should be established. Since the detector will most likely be installed outdoors, it should be able to withstand local weather and environmental conditions and meet appropriate electrical classifications for the location. The components that may come in contact with HF should be constructed of suitable materials. Also, any device chosen should be suitable for the hazardous-area classification where installed.

For any system to function properly over time, the instrument mechanics who will maintain it should be well trained in the purpose and design details of all the components.

The reliability of the entire system, as well as the detector itself, should be high. For example, an uninterruptible power supply should be provided wherever possible.

VVV 000008225

F.9 Deployment

The components of a detection system should be deployed in such a way as to meet the performance characteristics described above. In general, this will require consideration of refinery/unit geometry, prevailing weather conditions, potential leak sources and release rates, maintenance requirements and access needs, mitigation system characteristics, and other features relevant to the site. In some cases, a single detector type will not provide all the desired characteristics. An integrated system of multiple device types may be useful in such cases. One device may provide a capability lacking in another and vice versa. The relative features and capabilities of the different detector types should be reflected in the system layout when multiple types are used.

F.10 Visual Detection

Although not usually considered detection devices, television cameras can be useful tools for alerting operators to vapor clouds and other emergency situations. When used in conjunction with the detection systems described above, TV cameras can significantly improve the operator's ability to assess a potential emergency and to determine its exact location and scope. Cameras are also valuable for directing and observing the effects of mitigation measures. When TV cameras are employed, they should have remote pan and zoom capability and be located to cover strategic portions of the unit. Monitor screens should be located in the unit control room where operators can readily see them.

VVV 000008226

APPENDIX G—WATER MITIGATION SYSTEMS

G.1 General

Water-spray mitigation is one of several mitigation techniques available to reduce the consequences of a release of an HF cloud. For this purpose, water can be applied either by fixed-spray curtain systems or water monitors or both, depending on site-specific needs. Both methods have been tested and evaluated in a series of large-scale studies. "Effectiveness of Water Sprays on Mitigating Hydrofluoric Acid Releases" provides an overview of tests conducted in 1986 at the USDOE facility at Frenchman Flats, Nevada, and "Effectiveness of Water Spray Mitigation Systems for Accidental Releases of Hydrogen Fluoride—Summary Report" provides a detailed accounting of a series of over 80 parametric tests conducted in 1988 at the same USDOE facility.[4,5] Volume VIII of "Effectiveness of Water Spray Mitigation Systems for Accidental Releases of Hydrogen Fluoride—Summary Report" contains data on over 200 wind tunnel tests on monitors. This series of tests evaluated a variety of issues including system geometry effects, water-spray curtain and water-monitor performance, effects of water-droplet size and effect of water-to-acid volumetric ratios on acid removal efficiency.

G.2 Effectiveness of Water Mitigation Mechanisms

Studies evaluating water application systems have identified the two primary mitigation phenomena as:

- a. Direct removal of HF from the release plume by chemical absorption, resulting in a reduction in the amount of acid moving downwind.
- b. Entrainment of air induced by the movement of the water droplets, resulting in dilution of the plume and lowering the downwind HF concentration.

For HF, direct removal appears to be the primary mechanism due to HF's hygroscopic nature.

Studies of released gases cited in Dispersal of LNG Clouds with Water Spray Curtains, Annual Report—Phase 1 and "Forced Dispersion of Gases by Water and Steam" have clearly indicated the benefits of air entrainment in reducing concentrations in a plume.[6,7] However, these dilution effects are only important near the point of release.

The mitigation tests cited in "Effectiveness of Water Spray Mitigation Systems for Accidental Releases of Hydrogen Fluoride—

vvv 000008227

Summary Report" indicate that removal efficiencies of 90 percent or greater can be achieved using either fixed water sprays or water monitors. The percent of removal achieved for a given system design will be primarily a function of the water-to-acid ratio supplied to the plume.

G.3 Design Considerations

A series of factors should be analyzed in designing an effective water mitigation system. The design will be highly dependent on the individual site details. The degree of mitigation desired will depend on refinery setting, local topography, and proximity to the public. The general analysis should include the following:

- a. Compilation of process and mechanical design information.
- b. Conduct of a Process Hazards Analysis.
- c. Development of credible release scenarios.
- d. Development of local weather design data.
- e. Compilation of site topography and population locations.
- f. Conduct of a consequence analysis.
- g. Determination of desired mitigation effectiveness.
- h. Design of water supply, application, and disposal systems.
- i. Considerations for initiation and control accessibility.
- j. Special considerations.

G.4 Development of Credible Release Scenarios

Based on the findings of the Process Hazards Analysis, a list of credible release scenarios may be developed. For each release scenario, information should be developed to define the potential release, including release rate, release duration, HF release concentration, release height, jet velocity if appropriate, initial temperature, and an estimate of the likelihood that the released acid will form an aerosol or a liquid pool. Release duration may also be a function of isolation and deinventory systems installed.

G.5 Conduct of Consequence Analysis

A consequence analysis using appropriate atmospheric plume dispersion models should be conducted to determine potential off-site impacts associated with each release scenario of interest. Analysis should include potential downwind dosage as well as concentration.

VVV 000008228

G.6 Determination of Water Effectiveness

Based on the results of the consequence analysis, an estimate of the desired water-removal efficiency can be made. Using the information provided in "Effectiveness of Water Spray Mitigation Systems for Accidental Releases of Hydrogen Fluoride-Summary Report," an estimate of the water application rates needed for each release scenario can be made.

G.7 Layout of Water Application Systems

Each release site of interest can be marked on the unit plan drawings. Once completed, the plan drawing will provide an indication of the areas with the greatest density of release points. Use this release density information in combination with wind-direction data to help select locations for fixed water sprays or water monitors. With water monitors, multiple monitors should be used to supply water to each potential major release location. Fixed water spray headers should be designed to effectively use the water to block passage of the release and to inject maximum air into the vapor cloud.

G.8 Special Considerations

Other factors to be considered in completing the design include:

1. Compatibility of desired water rates with facility fire fighting system capacity.
2. Use of TV monitors to help direct and control water application systems.
3. Impoundment and neutralization facilities for acidic run-off water generated during HF release mitigation.
4. Area drainage requirements.
5. Special designs for areas requiring freeze protection.
6. Provision for periodic testing of the full system.
7. Any local regulations that might apply to this sort of installation.

VVV 000008229

APPENDIX H-EMERGENCY ISOLATION OF AN HF RELEASE

H.1 General

The magnitude of an HF release can be reduced in volume as well as time by providing block valves for isolation of the various acid-containing parts of the unit. LPG releases may also be reduced by isolating major inventory sources. An HF alkylation unit's process hazards management plan should consider installing emergency block valves (EBVs) or remote operators on existing valves at appropriate locations per the following guidelines.

H.2 Determining EBV Locations

Consider the following steps in establishing the need for new or retrofitted remote-operated EBVs in the alkylation unit:

- a. Identify vessels or other containers where HF acid is stored in quantities large enough to cause a significant downwind hazard if released.
- b. Identify other equipment where some likelihood of a release exists. Acid service pumps are a good example.
- c. Identify all lines connected to the above equipment or vessels which should be isolated and blocked to remove (1) sources of acid feeding the release and (2) sources of pressure that if blocked would reduce the release rate.
- d. Identify existing valves which might be retrofitted with remote operators to provide EBVs.
- e. Identify the remaining locations where new EBVs are desirable.

H.3 Designing EBV Installations

Consider the following mechanical factors when designing EBV installations:

- a. Quarter-turn valves may close more quickly and be less liable to foul with fluoride scale than gate valves. However, quarter-turn valves with PTFE sleeves may leak through if exposed to an extended fire, while gate valves with metal-to-metal seats should not leak from fire exposure.
- b. Valve operators may need backup motive power (electricity, air, nitrogen or other) so that they will be available during an upset when primary power is lost.
- c. EBVs should be fully testable, from the remote initiation switch to the valve movement. Consider how much movement is necessary to verify operability. Valves where the seating surfaces can trap

VVV 000008230

scale probably need full stroking, while other valve designs may be verified with partial stroking.

- d. Consider adding position switches to valves to notify the operator when the desired movement has taken place.
- e. Consider locating EBV controls and position lights, as well as other mitigation controls, on a single panel with a schematic flow diagram of the unit so the operator can quickly assess the status of emergency control equipment during an incident.
- f. Consider combining EBVs into logical systems with a single initiation switch where appropriate; for example, pump suction and discharge valves and the pump driver power.
- g. Both the EBV and its motive power source should be protected from damage from fire or impact during an incident.
- h. Note that adding valves in a unit may isolate a piece of equipment from its safety relief valve. SRV and neutralization systems should be reviewed after EBV locations have been established.
- i. Consider fitting quarter turn valves with position indicating flags which allow the position of the valve to be more readily determined from a distance or by video.

VVV 000008231

APPENDIX I-BIBLIOGRAPHY

- Blewitt, D.N., Petersen, R.L., and Heskestad, G., "Evaluation of Water Spray Mitigation for an Industrial Facility," Paper presented at 1991 International Conference and Workshop on Modeling and Mitigation--The Consequences of Accidental Releases of Hazardous Materials, Center for Chemical Process Safety, **City?**, 1991.
- Degnan, T.F., Materials of Construction for Hydrofluoric Acid and Hydrogen Fluoride, Process Industries Corrosion, National Association of Corrosion Engineers, Houston, Texas, 1986.
- Diener, R., and Van Zele, R.L., Industry Cooperative Hydrogen Fluoride Mitigation & Ambient Impact Assessment Program--Summary Report, The Industry Cooperative HF Mitigation/Assessment Program Steering Committee (NTIS No. DE90011208), 1989.
- Fthenakis, V.M., A Theoretical Study of Absorption of Toxic Gases by Spraying, American Institute of Chemical Engineers, **City?**, 1989.
- Fthenakis, V.M., Schatz, K.W., and Zakkay, V., "Modeling of Water Spraying of Field Releases of Hydrogen Fluoride," Paper presented at 1991 International Conference and Workshop on Modeling and Mitigation--The Consequences of Accidental Releases of Hazardous Materials, Center for Chemical Process Safety, **City?**, 1991.
- Hanna, S.R., and Drivus, P.J., Guidelines for Use of Vapor Cloud Dispersion Models, American Institute of Chemical Engineers, **City?**, 1987.
- Hanna, S.R., and Strimatis, D.G., Workbook of Test Cases for Vapor Cloud Dispersion Models, American Institute of Chemical Engineers, **City?**, 1989.
- Materials for Receiving, Handling, and Storing Hydrofluoric Acid, Committee Report 5A171, National Association of Corrosion Engineers, Houston, Texas, 1983.
- McFarlane, K., "Development of Plume and Jet Models," Paper presented at 1991 International Conference and Workshop on Modeling and Mitigation--The Consequences of Accidental Releases of Hazardous Materials, Center for Chemical Process Safety, **City?**, 1991.
- Meroney, R.N., "Numerical Simulation of Mitigation of HF Cloud Concentrations by Means of Vapor Barriers and Water Spray

VVV 000008232

Curtains," Paper presented at 1991 International Conference and Workshop on Modeling and Mitigation--The Consequences of Accidental Releases of Hazardous Materials, Center for Chemical Process Safety, **City?**, 1991.

Moser, J.H., Blewitt, D.N., Steinberg, K.W., and Petersen, R.L., "HF HEGADIS Simulation of Dense Gas Dispersion From a Wind Tunnel--Modeled Oil Refinery," Paper presented at 1991 International Conference and Workshop on Modeling and Mitigation--The Consequences of Accidental Releases of Hazardous Materials, Center for Chemical Process Safety, **City?**, 1991.

Puttock, J.S., McFarlane, K., Prothero, A., Roberts, P.T., Rees, F.J., Witlox, H.W.M., and Blewitt, D.N., "HGSYSTEM Modeling Package," Paper presented at 1991 International Conference and Workshop on Modeling and Mitigation--The Consequences of Accidental Releases of Hazardous Materials, Center for Chemical Process Safety, **City?**, 1991.

Roberts, P.T., Puttock, J.S., and Blewitt, D.N., Gravity Spreading and Surface Roughness Effects in the Dispersion of Dense-Gas Plumes, American Institute of Chemical Engineers, **City?**, 1990.

Schuyler, R. L., Hydrogen Blistering of Steel in Anhydrous Hydrofluoric Acid, Materials Performance, NACE, Houston, Texas, April 1979.

Spice, T.O., and Havens, J., Modeling Aerosol Dispersion for Accidental Consequences Analyses, American Institute of Chemical Engineers, **City?**, 1990.

Witlox, H.W.M., "Recent Development of Heavy-Gas Dispersion Modeling," Paper presented at 1991 International Conference and Workshop on Modeling and Mitigation--The Consequences of Accidental Releases of Hazardous Materials, Center for Chemical Process Safety, **City?**, 1991.

Witlox, H.W.M., McFarlane, K., Rees, F.J., and Puttock, J.S., Development and Validation of Atmospheric Dispersion Models for Ideal Gases and Hydrogen Fluoride. Parts I, II, and III, Shell Research Ltd., **City?**, 1990.

VVV 000008233