

Status Update on PR1410 – Hydrogen Fluoride Storage and Use at Petroleum Refineries



SCAQMD REFINERY COMMITTEE

September 22, 2018
Wilmington, California

SUMMARY OF APRIL 28TH 2018 REFINERY COMMITTEE MEETING

- SCAQMD staff presented two possible rule concepts
 - ❑ Tier I+ mitigation and phase-out MHF in 5 years
 - ❑ Tier I/II+ mitigation and phase-out MHF in 6–8 years
- Refinery Committee directed to staff:
 - ❑ Pursue release of MHF testing and technology documentation from Honeywell
 - ❑ Provide information on HF usage in other industries
 - ❑ Develop Tier I/II+ mitigation rule requirements
 - ❑ Provide information on seismic/terrorism risk at refineries
 - ❑ Report back on Regulatory vs. MOU approach

SCAQMD MEETINGS SINCE THE LAST REFINERY COMMITTEE

Working Group Meetings

June 20, 2018
(Tier I Mitigation)

September 6, 2018
(Tier II+ Mitigation)

Refinery Meetings with Staff

Torrance Refining Company
August 28, 2018
September 13, 2018

Community Meetings with Staff

Torrance Refinery Action Alliance
August 31, 2018

RELEASE OF MHF TESTING AND TECHNOLOGY DOCUMENTATION FROM HONEYWELL

RESPONSE:

- May 2018: Requested information from Honeywell
- June 2018: Honeywell said permission needed from ExxonMobil (technology developer)
- August 2018: ExxonMobil “does not consent to the public disclosure in any form (redacted or not)” and claims documents contain trade secret and confidential business information
- Staff is still exploring options to make information public

OTHER USES OF HF IN THE BASIN

RESPONSE:

- Identified ~50 facilities that use HF in the Basin
 - Aerospace, metal finishing and fabrication, semiconductor, glass etching*
 - Concentrations less than 50%**
 - Usage less than 5 gallons monthly
 - Used at temperatures below boiling point
- Comparison to refinery usage
 - Concentrated HF (>80%) with additive
 - Used at temperatures above boiling point and under pressure
 - >20,000 gallons of MHF on-site

* SCAQMD permit database 2011–2017 and Annual Emissions Reporting data

** U.S. EPA Risk Management Program requires HF concentrations 50% or more to provide off-site consequence analysis

SCAQMD STAFF'S APPROACH FOR MITIGATION MEASURES

- Must mitigate a large consequential release
- Build upon existing mitigation
- Sufficient redundancy to address a catastrophic event with cascading effects such as fire, damage to mitigation system, loss of power, communication, transportation access, etc.
- Proposed implementation of all mitigation by 2021

OVERVIEW OF KEY SCAQMD RECOMMENDED MITIGATION ENHANCEMENTS

- Improved monitoring for early detection
- Enhanced video
- Automatic water activation
- Improve response time for Rapid Acid Dump
- Physical barrier around key MHF usage areas to minimize dispersion and improve water effectiveness

Reduce Response Time

Enhanced Water Mitigation

Enhanced Physical Barriers

Added Redundancy

- Upgrade water mitigation to a water to HF ratio of 60:1
- Multi-layer water
- Varying heights
- All high risk areas
- Back-up power
- Back-up water supply
- Redundant pumps
- Redundant surveillance

CHALLENGE OF WATER MITIGATION

- Properly designed water mitigation can reduce HF up to 95%* if:
 - ❑ 60 gallons of water is applied to every 1 gallon of HF released (60:1 water to HF ratio)
 - ❑ This means that 30,000 gallons per minute of water is needed for a 500 gallon per minute release of HF
- Challenges
 - ❑ Designing a mitigation system that can apply enough water at the right locations for a large release
 - ❑ Ensuring the amount of water needed can be sustained throughout the release
 - ❑ Ensuring there is sufficient redundancy for water and power if there is a system failure or delayed response to applying water



* *Water Spray Mitigation of Hydrofluoric Acid Releases, Schatz and Koopman, 1990 and Effectiveness of Mitigation Systems in Reducing Hazards of Hydrogen Fluoride Leaks, Quest Consultants Inc., 1995*

CONSIDERATIONS FOR USE OF MHF

- Ability of MHF to prevent formation of a vapor/aerosol cloud is uncertain*
 - ❑ Some, but uncertain, HF mitigation benefits offered by MHF (<35%)
 - ❑ Conditions of testing are different from current operating conditions
 - ❑ Large hole sizes were not considered
- A release of MHF will still result in exposure to HF**
 - ❑ Liquid droplet “rainout” and vapor cloud will be HF
 - ❑ Material Safety Datasheets for HF and MHF lists the same hazards and medical treatment

* Staff presentation at January 20, 2018 Refinery Committee

** Staff presentation at April 28, 2018 Refinery Committee

Honeywell

Material Safety Data Sheet

MODIFIED HYDROFLUORIC ACID

1. CHEMICAL PRODUCT AND COMPANY IDENTIFICATION

PRODUCT NAME: Modified Hydrofluoric Acid

OTHER/GENERIC NAMES: MHF, Modified HF, Modified Hydrogen Fluoride, Modified HF Acid, Acidized HF

PRODUCT USE: Alkylation Catalyst

MANUFACTURER: Honeywell International
Industrial Products
101 Columbia Road
Box 1053
Morristown, New Jersey 07962-1053

FOR MORE INFORMATION CALL:
(Monday-Friday, 8:00am-4:30pm EST)
HF Technical Service Department
800-422-5902
Or visit the Honeywell HF website:
<http://www.HFacid.com>

IN CASE OF EMERGENCY CALL:
For Medical Emergencies
(24 Hours/Day, 7 Days/Week)
800-498-5701
For Transportation Emergencies:
800-224-9300 (CHEMTREC for US)
613-996-6666 (CANUTEC for Canada)

2. COMPOSITION/INFORMATION ON INGREDIENTS

INGREDIENT NAME	CAS NUMBER	WEIGHT %
Hydrofluoric Acid	7664-39-3	85
Sulfolane	126-33-0	15

Trace impurities and additional material names not listed above may also appear in the Regulatory Information Section 15 towards the end of the MSDS. These materials may be listed for local "Right-To-Know" compliance and for other reasons.

3. HAZARDS IDENTIFICATION

EMERGENCY OVERVIEW: Clear, colorless, corrosive fuming liquid with an extremely acrid odor. Forms dense white vapor clouds if released. Both liquid and vapor can cause severe burns to all parts of the body. Specialized medical treatment is required for all exposures.

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CONSIDERATIONS FOR USE OF MHF *(CONTINUED)*

- Torrance Refining Company and Valero are located in densely populated areas*
- Accidents happen*
- Uncertain if a large consequential release can be mitigated
- Conflicting “shelter in place” procedures for chemical release versus post-earthquake safety to evacuate the building

Torrance Refining Company



Alkylate: 25,500 BPD
245,000 People within 3 Miles
Nearest Residence 1,500 Feet

Valero Wilmington Refinery



Alkylate: 20,000 BPD
153,000 People within 3 Miles
Nearest Residence ~4,100 Feet

* Staff presentation at April 28, 2018 Refinery Committee

MEDICAL TREATMENT OF HF

- Potential exposure can be to dermal (skin), eyes, or inhalation
- Local hospitals can treat HF exposure
- Patients with significant HF exposure will need to be transported to a burn unit
- One hospital with a burn unit within a 10 mile radius
 - ❑ Torrance Memorial Medical Center (8 beds)
- Three hospitals with burn units within a 10 to 30 mile radius
 - ❑ LAC+USC Medical Center (21 beds)
 - ❑ University of California, Irvine Medical Center (16 beds)
 - ❑ Grossman Burn Center/Santa Ana (5 beds)

SUPPLY OF CALCIUM GLUCONATE (ANTIDOTE TO TREAT HF BURNS)

- Calcium gluconate is currently on the national shortage list of medications*
- All local hospitals have calcium gluconate – but amount is unknown
- For significant inhalation exposure – nebulizer every 4 hours for 48 hours**
- LA County Emergency Medical Services can treat approximately 500 single treatments
 - Treat ~40 people if significant inhalation exposure



* U.S. Food and Drug Administration, FDA Drug Shortages

** Recommended medical treatment of hydrofluoric acid, Honeywell, Version 7.0, 2018

CONSIDERATIONS FOR PHASING OUT HF

(DISCUSSED AT APRIL 2018 REFINERY COMMITTEE MEETING)

- Estimated cost impact is between \$300 and \$600 million*
- Potential market impacts
 - ❑ Any impacts would be temporary
 - ❑ Planned phase-out is different than an unplanned shutdown – less disruptive
- Possible schedule
 - ❑ Sulfuric acid alkylation: 4 to 6 years
 - ❑ Emerging technology (Solid Acid Catalyst and Ionic Liquid Catalyst): 10 to 12 years

* Conversion of a HF Alkylation unit to a Sulfuric Acid Alkylation unit must include a thorough review of the entire unit in order to determine if any equipment can be re-used. It is expected that the Fractionation section of the HF Alkylation Unit may be able to be re-used, but further evaluation, especially of metallurgy requirements between the two technologies would need to be conducted (Norton Engineering, Alkylation Technology Study, 2016). \$300 million is based on cost of post-processing equipment included in the Burns & McDonnell Alkylation Study & Estimate, 2017.

POSSIBLE OPTIONS

Implement Enhanced Mitigation Measures (No Performance Standard)

- Implement enhanced mitigation measures

Implement Enhanced Mitigation Measures with Performance Standard

- Implement enhanced mitigation measures
- Conduct testing of MHF and efficacy of mitigation to minimize risk of large consequential release

Implement Enhanced Mitigation AND Phase-out MHF if Performance Standard Cannot be Met

- Implement enhanced mitigation measures
- Phase-out MHF unless testing of MHF and efficacy of mitigation minimizes risk of large consequential release

Implement Enhanced Mitigation Measures and Phase-out MHF (No Performance Standard)

- Implement enhanced mitigation measures
- Phase-out MHF

BIOS AND GENERAL OVERVIEW OF GUEST PRESENTERS

KENNETH W. HUDNUT, PH.D.



- Ph.D. in Geology from Columbia University and A.B. in Earth Sciences from Dartmouth
- Former Science Advisor for Risk Reduction for the Earthquake Science Center for the United States Geological Survey (USGS)
- Currently USGS Geophysicist that has studied earthquakes for over 30 years
- Served multiple terms on the board of the Southern California Earthquake Center

DR. HUDNUT'S PRESENTATION WILL DISCUSS

- Faults near the two refineries
- What is considered a major earthquake and possible effects
- Possibility of a major earthquake near Torrance Refining Company and Valero refineries
- Possible secondary effects associated with a major earthquake

RONALD P. KOOPMAN, PH.D., P.E.



- Ph.D. in Applied Physics from the University of California at Davis, M.S. Nuclear Engineering and B.S. in Mechanical Engineering from the University of Michigan
- Retired Manager and Senior Scientist at Lawrence Livermore National Laboratory (36 years) conducting experiments involving large-scale releases of hazardous gases at the Department of Energy Spill Test Facility in Nevada
 - ▣ Managed and conducted large-scale field experiments with HF releases – referred to as the “Goldfish Test”
- Published papers on release experiments of hazardous gases and HF water mitigation
- Currently the Principal of Hazard Analysis Consulting

DR. KOOPMAN'S PRESENTATION WILL DISCUSS

- The 1986 Goldfish Test
 - Dispersion of HF as a dense vapor cloud
 - Use of water spray mitigation
- Water spray mitigation of HF releases – referred to as the Hawk Study (Small-scale testing of water mitigation)

JOHN B. CORNWELL



- M.S. in Mechanical Engineering and B.S. in Chemical Engineering from the University of Texas at Austin
- Currently an Engineer at Quest Consultants Inc. directing the development and use of consequence and risk analysis software for modeling the impacts associated with toxic and flammable fluid releases
- Quest oversaw large scale outdoor testing to determine the effects of additives on suppressing aerosol formation during release of superheated hydrogen fluoride
- Published technical and analytical papers on HF and the effectiveness of mitigation
- Over 30 years of experience in the fields of consequence and risk analysis

MR. CORNWELL'S PRESENTATION WILL DISCUSS

- Experience with conducting HF and MHF testing
- Type of testing needed to understand the effects of a large scale release of MHF with and without mitigation from an acid settler
 - ❑ Key parameters and considerations for testing
 - ❑ Timeframe (engineering, implementation, and final report)
 - ❑ Estimated cost

MICHAEL MASTRANGELO



- Program Director, Institutional Preparedness at the University of Texas Medical Branch (UTMB)
- Responsible for all aspects of preparedness at UTMB which is the only Level 1 trauma and burn center in the region
- Developed the Annual Hydrofluoric Acid Symposium and Exercise for University of Texas Medical Branch (Since 2014)
- Serves on many regional, state, and national emergency preparedness committees and received numerous awards for his innovative work

MR. MASTRANGELO'S PRESENTATION WILL DISCUSS

- Background about UTMB Galveston Annual HF Symposium
 - ❑ Why HF Symposium was initiated
 - ❑ Key objectives and findings of the HF Symposium
- Key concerns about a large release of HF
 - ❑ Potential health impacts
 - ❑ Emergency response and treatment
 - ❑ Challenges