AGENDA NO. 25

Status Update on PR 1410 – Hydrogen Fluoride Storage and Use at Petroleum Refineries

Governing Board Meeting

February 1, 2019
Diamond Bar, California

HF Background

- Hydrogen fluoride (HF) is a strong, potentially lethal acid
- HF is used to produce alkylate which is a blending component of high-octane gasoline
- Used at two California refineries: Torrance Refining and Valero
- Both refineries use modified HF (MHF), designed to reduce its exposure

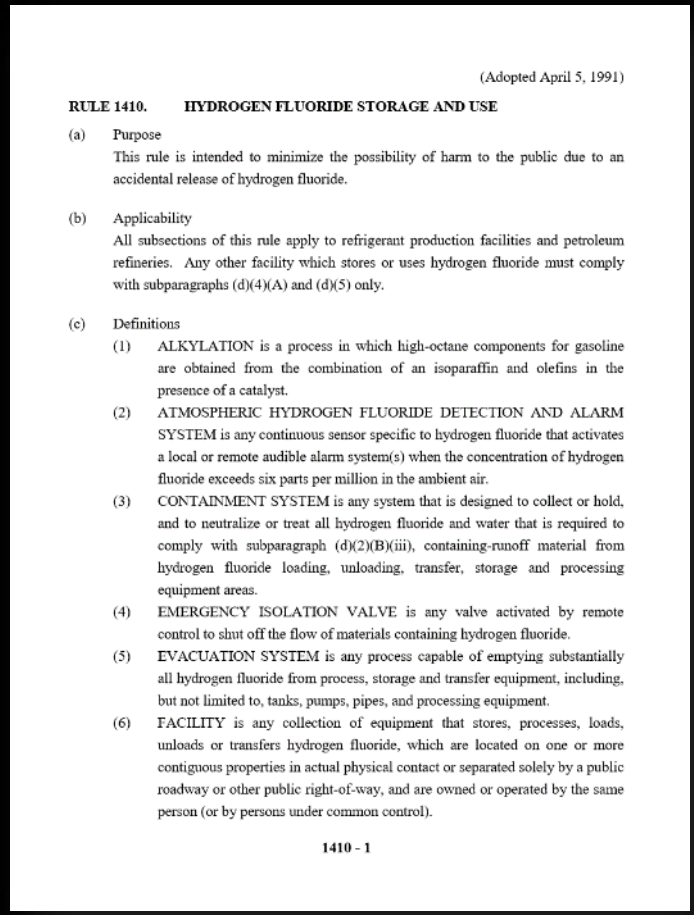
Torrance Refining

Valero

Approximate Volumes (gallons)		
	Valero (Wilmington)	Torrance Refining
Storage on-site	55,000	25,000
Use in acid settlers	7,000 with baffle	12,000 in two tanks

Regulatory Background

- April 1991 Board adopted Rule 1410 – Hydrogen Fluoride Storage and Use
  - Established a 7-year phase-out of HF unless a performance standard could be achieved
  - Required interim control measures
- Lawsuit challenged Rule 1410
  - SCAQMD's authority to phase out HF was upheld[1]
    - "[T]he Legislature clearly intended to vest AQMD with the authority to adopt preemptive measures designed to prevent air pollution episodes . . .."
  - Rule invalidated due to procedural error in circulating CEQA document



(Adopted April 5, 1991)

RULE 1410. HYDROGEN FLUORIDE STORAGE AND USE

(a) Purpose

This rule is intended to minimize the possibility of harm to the public due to an accidental release of hydrogen fluoride.

(b) Applicability

All subsections of this rule apply to refrigerant production facilities and petroleum refineries. Any other facility which stores or uses hydrogen fluoride must comply with subparagraphs (d)(4)(A) and (d)(5) only.

(c) Definitions

(1) ALKYLATION is a process in which high-octane components for gasoline are obtained from the combination of an isoparaffin and olefins in the presence of a catalyst.

(2) ATMOSPHERIC HYDROGEN FLUORIDE DETECTION AND ALARM SYSTEM is any continuous sensor specific to hydrogen fluoride that activates a local or remote audible alarm system(s) when the concentration of hydrogen fluoride exceeds six parts per million in the ambient air.

(3) CONTAINMENT SYSTEM is any system that is designed to collect or hold, and to neutralize or treat all hydrogen fluoride and water that is required to comply with subparagraph (d)(2)(B)(iii), containing-runoff material from hydrogen fluoride loading, unloading, transfer, storage and processing equipment areas.

(4) EMERGENCY ISOLATION VALVE is any valve activated by remote control to shut off the flow of materials containing hydrogen fluoride.

(5) EVACUATION SYSTEM is any process capable of emptying substantially all hydrogen fluoride from process, storage and transfer equipment, including, but not limited to, tanks, pumps, pipes, and processing equipment.

(6) FACILITY is any collection of equipment that stores, processes, loads, unloads or transfers hydrogen fluoride, which are located on one or more contiguous properties in actual physical contact or separated solely by a public roadway or other public right-of-way, and are owned or operated by the same person (or by persons under common control).

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[1] *Ultramar, Inc. v. South Coast Air Quality Management District*, 17 Cal. App. 4th 706-12 (1993).

Decision Not to Pursue Re-Adoption of Rule 1410

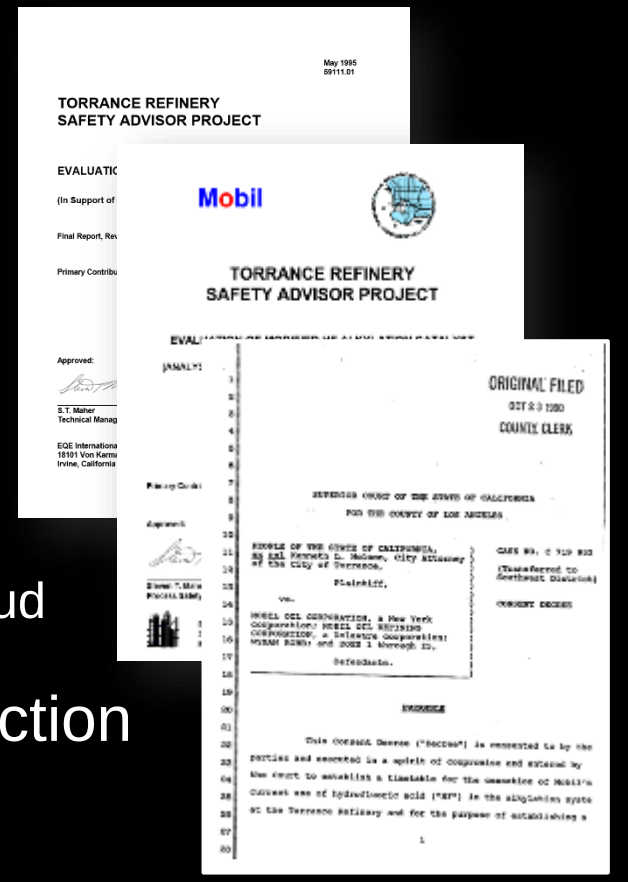
1991 Mobil Refinery[2] entered into a court consent decree

- Phase-out of HF by 1997 or
- Allow use of MHF if demonstrates no formation of dense vapor cloud

1999 Consent decree was changed to allow a significant reduction of the modifier

2003 SCAQMD signed MOU with Ultramar[3] to phase-out HF and allow use of MHF

2017 Torrance Refining provided SCAQMD with confidential information about MHF



[2] Currently Torrance Refining Company
[3] Ultramar is currently Valero

Events Leading to the Investigative Hearing in April 2017

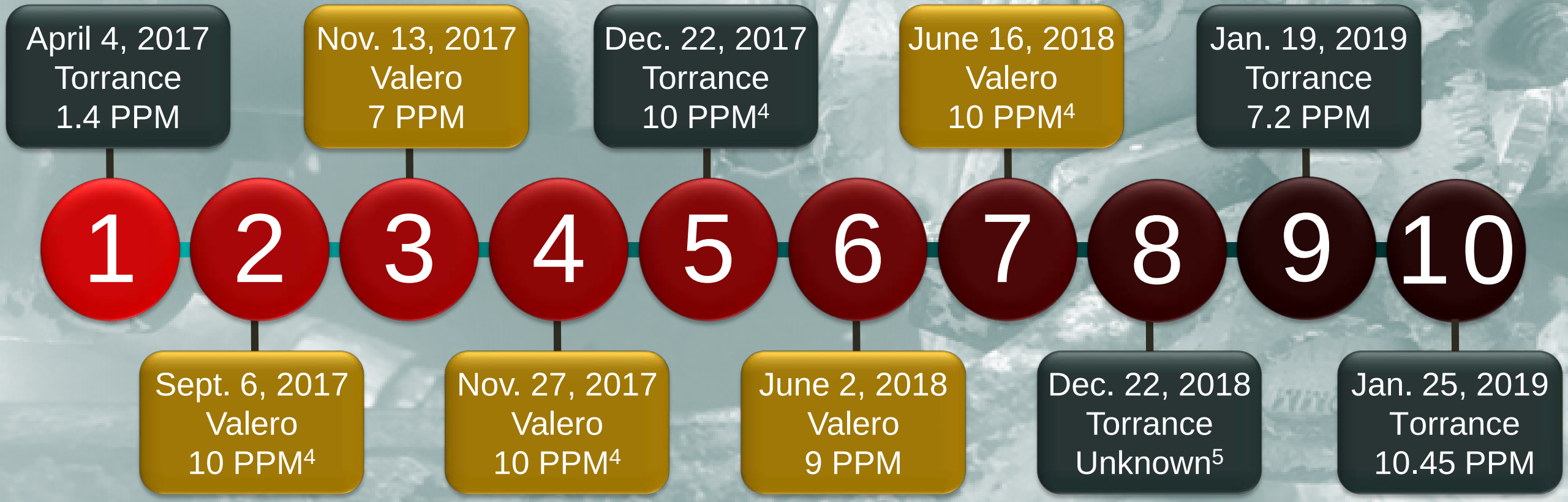
2015

"Near Miss" 40 ton debris lands within 5 feet from MHF tanks at Torrance Refining

2016-2017

Series of large flaring events and fire event that raised concerns about safety at Torrance Refining

10 MHF Leaks Since 2017



[4] HF point sensors can only measure up to 10 ppm. Concentrations could have been higher.

[5] 5 gallons of HF released at loading rack. No HF point sensors at loading rack. Closest HF point sensor is ~ 25 feet.

Public Process Following Investigative Hearing

1,300+ Comment Letters and Emails

- 500+ commenters opposing a phase-out
- 800+ commenters supporting a phase-out
- 7 letters from elected officials

4 Refinery Committee Meetings

- ~ 600 attendees per meeting
- ~ 80 commenters per meeting
- 8 expert presentations

Multiple Site Visits

- Observed current mitigation and safety measures at both refineries

9 Rule Working Group Meetings

- ~ 100 participants
- 3 meetings in the community
- 9 expert presentations

19 Individual Stakeholder Meetings

- 12 meetings with refineries
- 5 meetings with community groups
- 2 meetings with EPA/Cal OSHA

Why is HF usage at refineries a concern?

Refineries use large volumes of MHF…

2 inch hole could release 1,000 gallons in 2 minutes[6]

[6] Based on Goldfish Study, Test 1 – Unmitigated release of HF

Ground hugging cloud upon release…

Maximum concentration below 8 feet[7] within breathing height

[7] Based on Goldfish Study, Test 1 – Unmitigated release of HF

Rapid expansion of a vapor cloud upon release…

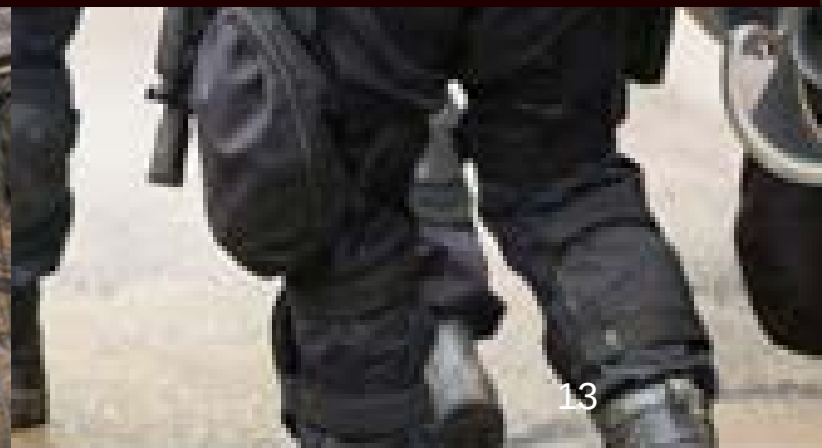
Tests have shown lethal concentrations can travel 2 miles[8]

[8] Based on Goldfish Study, Test 1, unmitigated, 1.65 inch release. Lethal concentration of 170 ppm for 10 minutes, USEPA Acute Exposure Guideline Level.

Large-scale unexpected incidents such as…

System Failures | **Natural Disasters** | **Intentional Acts**

Can lead to cascading failures



High population densities…

Greater potential for widespread human harm

Torrance Refining Company

245,000 People within 3 Miles
Nearest Residence ~0.3 miles

Valero Wilmington Refinery

153,000 People within 3 Miles
Nearest Residence ~0.8 miles

Uniquely hazardous health effects that result in deep tissue and bone damage…

Requires immediate and specialized treatment

New England Journal of Medicine

In 1986 Amoco and Allied Signal Corporation sponsored the “Goldfish” tests to assess HF release

Single release point was 1.65 inches (size of a golf ball)

1,000 gallons was released in 2 minutes

Ground hugging cloud travelled at wind speed of 18 feet per second

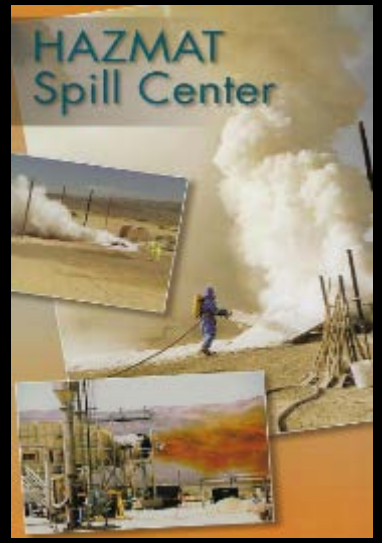
Cloud rapidly expanded upon release

HF concentration was twice the lethal level at 2 miles from release point

100% remained airborne

Field Tests

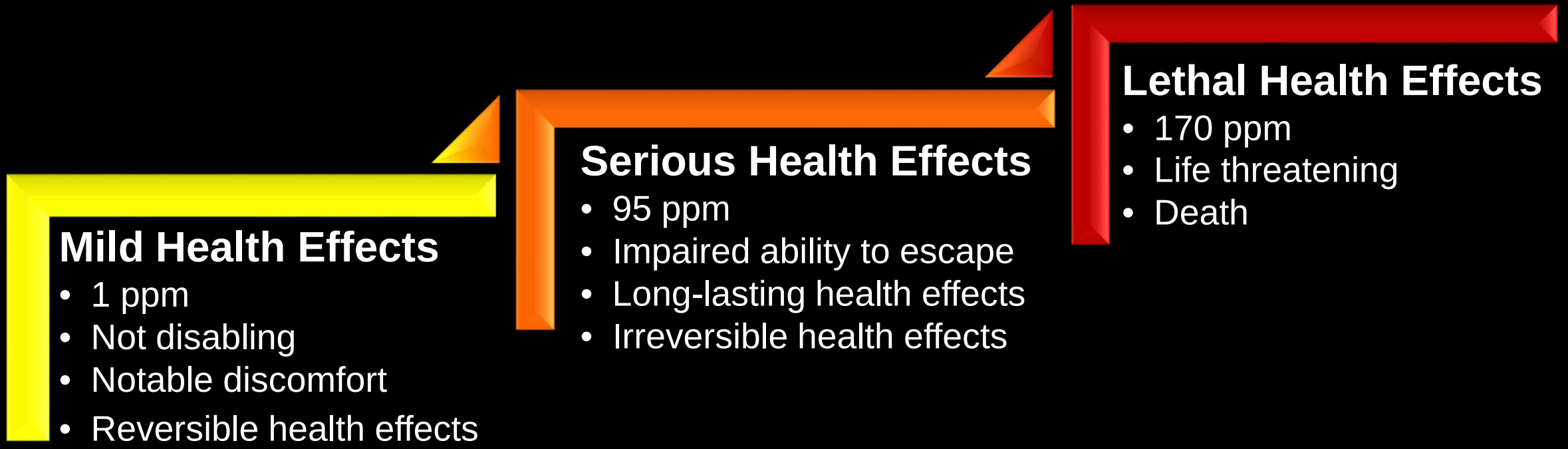
- Nevada Test Site
  - Goldfish test - large scale outdoor testing
  - Hawk Test - smaller wind tunnel tests on water spray mitigation
- Quest Consultants Inc. conducted two field tests for MHF[9] (1992-1993) in Oklahoma
  - Mobil and Phillips
  - Texaco and UOP



Nevada Test Site		
Name	**Year**	**Material**
Avocet	1978	LNG
Burro	1980	LNG
Coyote	1981	LNG
Desert Tortoise	1983	Ammonia
Eagle	1983	N_2O_4
Goldfish	1986	HF
Hawk	1988	HF

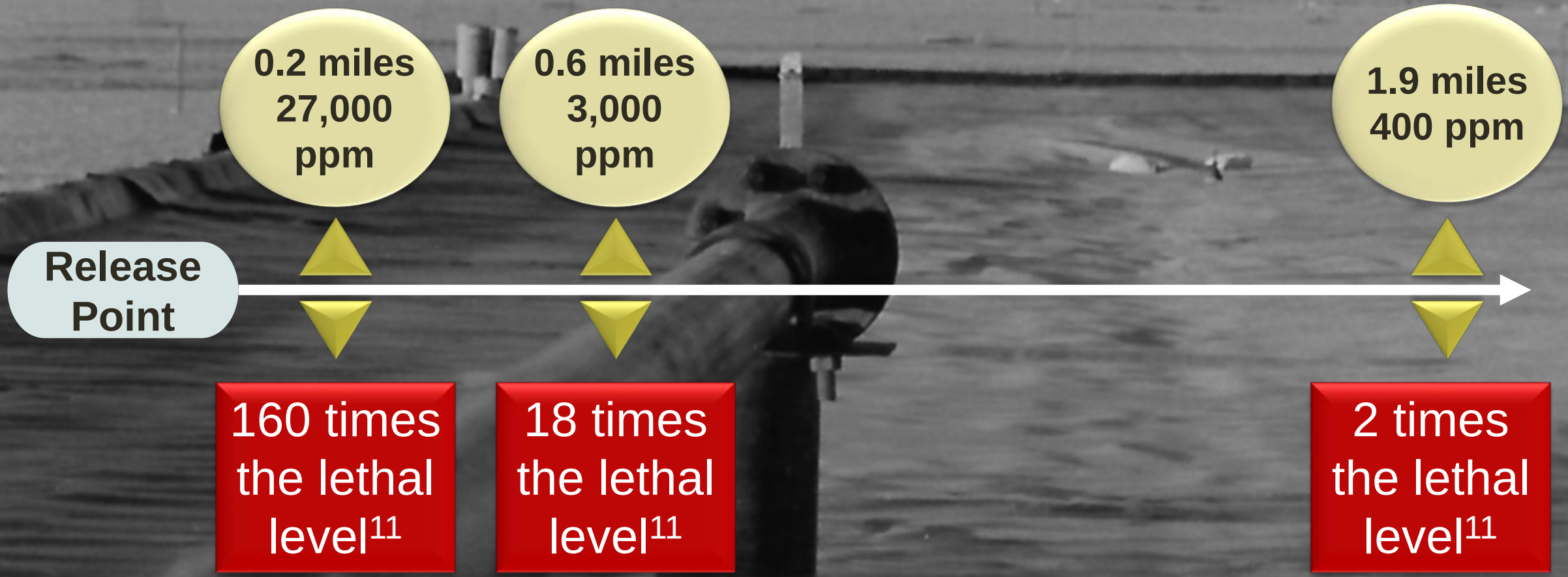
[9] Both field tests were not at the current operating conditions (temperature, pressure, and additive concentration) used at refineries.

Acute Exposure Levels for HF for 10 Minutes[10]



[10] USEPA Acute Exposure Guideline Levels

HF Levels Measured in Goldfish Study



[11] USEPA Acute Exposure Guideline Levels for 10 minutes exposure to HF

How much safer is MHF than HF?

Background on MHF

- Jointly developed by Mobil/Phillips in early 90's
- Modifier added to HF to reduce vapor-forming tendency
- Intent was for most of HF to rainout or fall to the ground
  - Initial additive concentration was ~30 percent, but led to "operational instability"[12]
  - Additive concentration decreased to ~7 percent
- Torrance Refining claims that 50% of MHF will rainout

[12] 1999 Torrance Refinery Safety Advisor Project Final Report

SCAQMD's Analysis of MHF

- Based on a review of technical documents and discussions with Torrance Refinery
  - Some, but uncertain, benefits of MHF
  - At most 35 percent benefit, but likely less
- No testing conducted at current operating conditions (additive concentration, pressure, and temperature)
- Most of the data is not publicly available
- Use of MHF is only one of many mitigation measures, but alone does not provide adequate safety for workers and community

HF and MHF Have Similar Concerns

- Ability of MHF to prevent formation of a vapor/aerosol cloud is highly uncertain
- Release of MHF will result in exposure to HF with same health effects
  - Any rainout will be HF liquid droplets
  - HF vapor cloud will still form
  - HF and MHF have same hazards and medical treatment

Honeywell

Material Safety Data Sheet

HYDROFLUORIC ACID, ANHYDROUS

1. CHEMICAL PRODUCT AND COMPANY IDENTIFICATION

PRODUCT NAME: Hydrofluoric Acid, Anhydrous

OTHER/GENERIC NAMES: HF, Anhydrous HF, AHF, Hydrogen Fluoride, HF Acid

PRODUCT USE: Chemical Derivatives, Alkylation Catalyst

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

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.

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 Additized HF

PRODUCT USE: Alkylation Catalyst

MANUFACTURER: Honeywell International
Industrial Products
101 Columbia Road
Box 1053

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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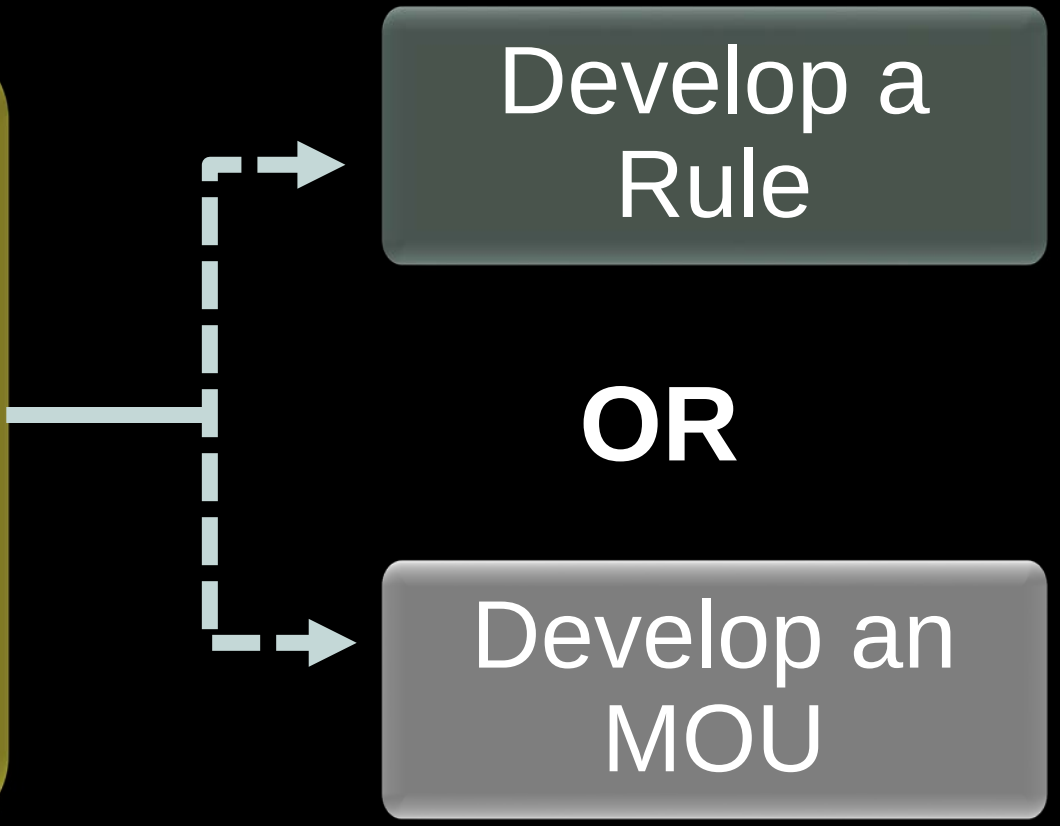
The Discussion

Direction from Refinery Committee

- Enhanced mitigation measures; and
- Phase-out MHF and explore option for a performance standard



Areas of General Agreement

HF and MHF are dangerous acids

Enhanced mitigation measures are needed

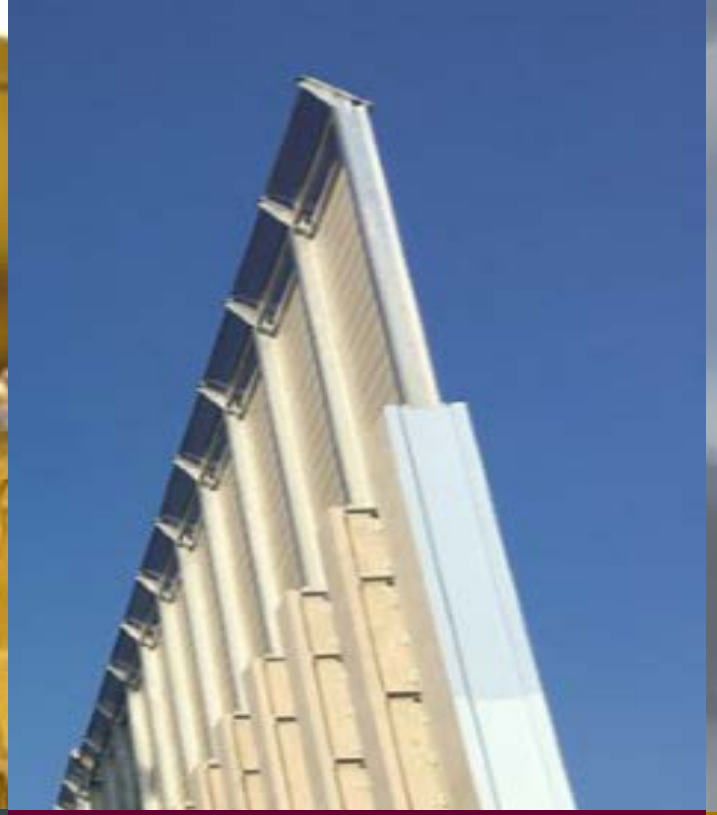
HF and MHF have the same health effects

Other than sulfuric acid, additional time needed for other alternative technologies

Overview of Enhanced Mitigation

Response Time

Added Redundancy



Enhanced Barriers

Enhanced Water

Alternative HF Technologies

Sulfuric Acid (Conventional)

- At 39 US refineries
- Safer than HF, but 50 more truck trips per day

Sulfuric Acid (Advanced)

- CD*Alky* uses 30-50% less acid – commercially proven
- ConvEx designed for HF conversion – not commercially proven

Solid Acid Catalyst

- Petrochemical plant in China
- 2,700 bpd startup in 2015

Ionic Liquid Catalyst

- Chevron, Salt Lake City
- Small pilot plant in 2005
- 5,000 bpd HF Alkylation conversion startup in 2020

Costs and Potential Market Impacts

- Torrance Refining's cost estimate of grassroots sulfuric acid unit[13]
  - $600 million for alkylation unit
  - $300 million for acid regeneration
- Valero has commented their facility has space constraints
- Advanced sulfuric acid units are expected to be substantially less
- Alternative technologies
  - Cost unknown
  - Torrance Refining views commercially viable as constructed at scale to California standards for two four-year turnaround cycles (Minimum of 12 years)
- Potential impacts to gasoline supply and cost
  - Any impacts would be temporary
  - Planned phase-out is different than an unplanned shutdown – less disruptive

[13] Burns and McDonnell - Alkylation Study & Estimate, 2017

Discussion on MHF Phase-Out

No Phase-out		Yes Phase-out
Alternative technologies not commercially proven		Longer implementation schedule with a technology assessment
Phase-out could result in a gasoline shortage		Lead time to plan - other options for alkylate supply
Refineries state they have and will continue to use MHF safely		Uncertain a consequential release can be mitigated
Refinery estimate: $900 million (Alkylation Unit and Acid Plant)		Lives at risk – cost of large release must be considered

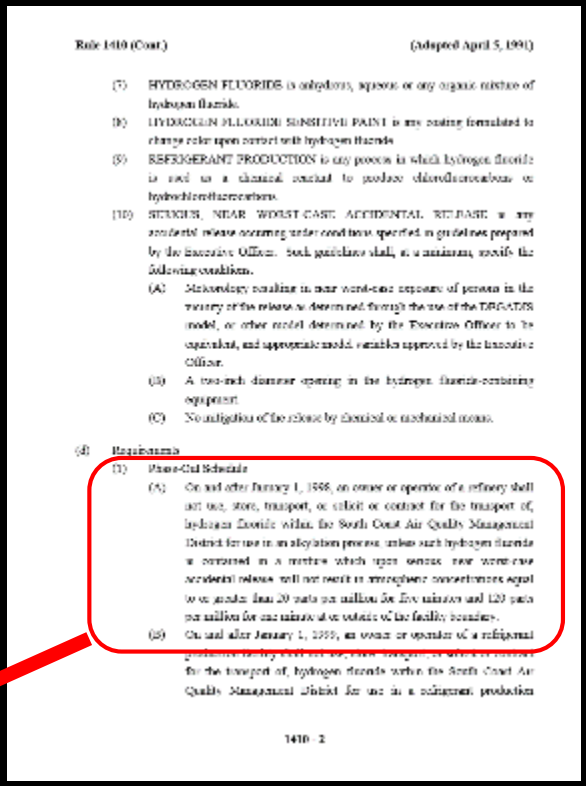
Uncertain that Enhanced Mitigation Can Protect the Community

- Can consequential release be mitigated?
- Can mitigation capture initial cloud?
- Can water be deployed rapidly?
- Can the mitigation system target exact location?
- Can the refineries supply enough water?
- Can sufficient redundancy guard against system failure?

What is a Performance Standard?

Performance Standard

- Benchmark that refineries would need to meet for continued use of MHF
- Needed to ensure enhanced mitigation can protect community
- Possible examples:
  - Concentration limit at fenceline or nearest receptor
  - Demonstrate MHF will not form dense vapor cloud
- 1991 Rule 1410 included a performance standard:
  - 20 ppm for 5 minutes; and
  - 120 ppm for 1 minute at the fenceline


Rule 1410 (Cont.) (Adopted April 5, 1991)

(f) HYDROGEN FLUORIDE is anhydrous, aqueous or any organic mixture of hydrogen fluoride.

(h) HYDROGEN FLUORIDE SENSITIVE PAINT is any coating formulated to change color upon contact with hydrogen fluoride.

(i) REFRIGERANT PRODUCTION is any process in which hydrogen fluoride is used as a chemical reactant to produce chlorofluorocarbons or hydrochlorofluorocarbons.

(m) SIGNIFICANT NEAR WORST-CASE ACCIDENTAL RELEASE is any accidental release occurring under conditions specified in guidelines prepared by the Executive Officer. Such guidelines shall, at a minimum, specify the following conditions:

(A) Meteorology resulting in near worst-case exposure of persons in the vicinity of the release as determined through the use of the DEGADIS model, or other model determined by the Executive Officer to be equivalent, and appropriate model variables approved by the Executive Officer.

(B) A two-inch diameter opening in the hydrogen fluoride-containing equipment.

(C) No mitigation of the release by chemical or mechanical means.

(d) Requirements

(1) Phase-Out Schedule

(A) On and after January 1, 1998, an owner or operator of a refinery shall not use, store, transport, or solicit or contract for the transport of, hydrogen fluoride within the South Coast Air Quality Management District for use in an alkylation process, unless such hydrogen fluoride is contained in a mixture which upon serious near worst-case accidental release will not result in atmospheric concentrations equal to or greater than 20 parts per million for five minutes and 120 parts per million for one minute at or outside of the facility boundary.

(B) On and after January 1, 1999, an owner or operator of a refinery [illegible] for the transport of, hydrogen fluoride within the South Coast Air Quality Management District for use in a refinery production

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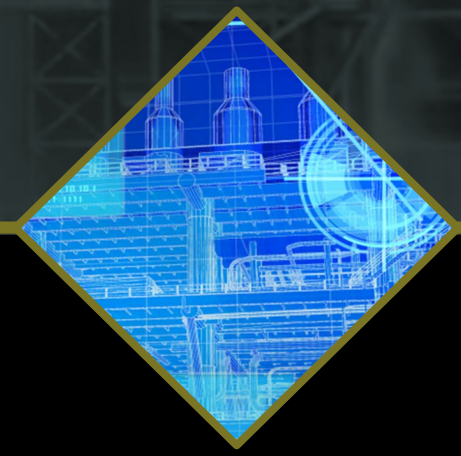
Three Key Elements of Performance Standard

Release Scenario

- Key parameters
  - Rate of release
  - Locations
  - Unit parameters

Standard

- Performance standard that must be met if MHF is released



Demonstration

- Demonstrate standard is met through
  - Modeling
  - Testing

Staff is Seeking Direction

- Continue with approach based on direction from Refinery Committee
  - Develop rule or MOU that requires refineries to:
    - Phase-out MHF within 5 to 7 years; or
    - Demonstrate, based on enhanced mitigation measures, that they meet a performance standard (to be developed) that ensures a consequential release will not impact the community