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

Approximate Volumes (gallons)

<table>
<thead>
<tr>
<th></th>
<th>Valero (Wilmington)</th>
<th>Torrance Refining</th>
</tr>
</thead>
<tbody>
<tr>
<td>Storage on-site</td>
<td>55,000</td>
<td>25,000</td>
</tr>
<tr>
<td>Use in acid settlers</td>
<td>7,000 with baffle</td>
<td>12,000 in two tanks</td>
</tr>
</tbody>
</table>
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

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

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\(^2\) 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

Source: LA Times
10 MHF Leaks Since 2017

1. April 4, 2017
   Torrance
   1.4 PPM

2. Nov. 13, 2017
   Valero
   7 PPM

3. Dec. 22, 2017
   Valero
   10 PPM

4. June 2, 2018
   Valero
   9 PPM

5. June 16, 2018
   Valero
   10 PPM

6. Dec. 22, 2018
   Torrance
   Unknown

7. Jan. 19, 2019
   Torrance
   7.2 PPM

8. Jan. 25, 2019
   Torrance
   10.45 PPM

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

9 Rule Working Group Meetings
- ~ 100 participants
- 3 meetings in the community
- 9 expert presentations

Multiple Site Visits
- Observed current mitigation and safety measures at both refineries

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\textsuperscript{7} within breathing height

\textsuperscript{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$^8$

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$^8$ 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
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

<table>
<thead>
<tr>
<th>Name</th>
<th>Year</th>
<th>Material</th>
</tr>
</thead>
<tbody>
<tr>
<td>Avocet</td>
<td>1978</td>
<td>LNG</td>
</tr>
<tr>
<td>Burro</td>
<td>1980</td>
<td>LNG</td>
</tr>
<tr>
<td>Coyote</td>
<td>1981</td>
<td>LNG</td>
</tr>
<tr>
<td>Desert Tortoise</td>
<td>1983</td>
<td>Ammonia</td>
</tr>
<tr>
<td>Eagle</td>
<td>1983</td>
<td>N(_2)O(_4)</td>
</tr>
<tr>
<td>Goldfish</td>
<td>1986</td>
<td>HF</td>
</tr>
<tr>
<td>Hawk</td>
<td>1988</td>
<td>HF</td>
</tr>
</tbody>
</table>

\(^9\) 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\textsuperscript{10}

**Mild Health Effects**
- 1 ppm
- Not disabling
- Notable discomfort
- Reversible health effects

**Serious Health Effects**
- 95 ppm
- Impaired ability to escape
- Long-lasting health effects
- Irreversible health effects

**Lethal Health Effects**
- 170 ppm
- Life threatening
- Death

\textsuperscript{10} USEPA Acute Exposure Guideline Levels
HF Levels Measured in Goldfish Study

Release Point

- 0.2 miles, 27,000 ppm: 160 times the lethal level\textsuperscript{11}
- 0.6 miles, 3,000 ppm: 18 times the lethal level\textsuperscript{11}
- 1.9 miles, 400 ppm: 2 times the lethal level\textsuperscript{11}

\textsuperscript{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”\(^\text{12}\)
  ○ Additive concentration decreased to ~7 percent
• Torrance Refining claims that 50% of MHF will rainout

\(^\text{12}\) 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
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.
The Discussion
Direction from Refinery Committee

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

Develop a Rule

OR

Develop an MOU
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
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)
- CDAlky 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\(^\text{13}\):
  - $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**
- Alternative technologies not commercially proven
- Phase-out could result in a gasoline shortage
- Refineries state they have and will continue to use MHF safely
- Refinery estimate: $900 million (Alkylation Unit and Acid Plant)

**Yes Phase-out**
- Longer implementation schedule with a technology assessment
- Lead time to plan - other options for alkylate supply
- Uncertain a consequential release can be mitigated
- 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

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**Rule 1410 (1991)**

- **Concentration limit at fenceline or the nearest receptor:**
  - 20 ppm for 5 minutes; and
  - 120 ppm for 1 minute at the fenceline.

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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:
    o Phase-out MHF within 5 to 7 years; or
    o 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