Torrance Refinery Technology Workshop

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AGENDA

- Alkylation Background and Use in Torrance
- Modified Hydrofluoric Acid (MHF) Application at the Torrance Refinery
- Barrier Usage and Contribution to MHF Effectiveness
- Acid Reduction Factor (ARF) & Societal Risk Index (SRI)
- Next Steps
- Q/A

Confidential Business Information (CBI)

- The current Alkylation Technology was researched by Mobil Research and Development then became the Property of ExxonMobil when the companies merged.
- This technology was then sold to the PBF Energy and Torrance Refining Company by ExxonMobil.
- ExxonMobil maintain this technology as proprietary and therefore can not disclose without the permission of ExxonMobil and Honeywell/UOP
- COT is prevented from thoroughly disclosing the complete Alkylation technology chemistry used at the Torrance Refinery.

Why Do Refineries Have Alkylation Units?

- Refineries use many different types of processes to convert nature's complex petroleum mixtures to gasolines that burn cleanly and minimize air pollution.
- Alkylation is one of these processes that are able to help make clean fuels that minimize our "environmental footprint" and are required by CA regulations.

Alkylation History

- 1940's – Alkylation technology for high octane fuels for military aircraft
- Post WWII – Alkylate used as important component in lead-free fuels
- 1986 Goldfish Test – New concern over release and dispersion characteristics of anhydrous hydrogen fluoride (HF)
  - Torrance Fire Department requires Risk Management and Prevention Plan (RMPP) for HF use from Mobil made possible by new California legislation
- 1989 – City of Torrance files lawsuit against Mobil declaring the refinery a public nuisance

Alkylation History Cont.

- 1990 - Consent Decree Requirement – Must be as-safe/safer than the sulfuric acid alkylation (considered other viable alternative)
- 1991-1998 – Vetting by Court / Court Appointed Safety Advisor
- 1992-1993 - Mobil constructs a Pilot Plant at their Paulsboro
    - Refinery to validate Modified HF (MHF) development.
    - Based on chemistry, laboratory testing, and field testing: Using an additive, when mixed with HF, reduces its vapor-forming tendencies, with most of the HF "raining out" or landing on the ground within a short distance of a release.
- 1995 – 65% Airborne Reduction Factor (ARF) was target approved by the Court based on Court Appointed Safety Advisor vetting, laboratory tests, field tests, and testing of the Pilot Plant in Paulsboro, NJ.

Alkylation History Cont.

- 1991-1998 – Vetting by Court / Court Appointed Safety Advisor (Continued)
- 1995-1997 – Site Construction/Implementation at the Torrance Refinery
- 1997 – When scaled up to full production, unit operability/stability problems were encountered.
- 1998 –Required a reduction in additive concentration for unit stability from 65% to 50 % unbarriered ARF
  - Upgrades Applying Barrier Technology on Highest-Hazard Areas: Flanges, Recirculation Pumps, and Settlers in the Alkylation Unit

Protecting the Public

- Converting the Alkylation Unit to MHF doesn't make the process any faster, better, or more economic.

- The only reason for the conversion was to make things safer for the Torrance Community.

- ***MHF improves safety by changing- the way in which the mixture of liquids in the alkylation unit behave if accidently released.***

Common Alkylation Processes

- Contemporary Applications
  - Hydrofluoric Acid (HF)
  - Sulfuric Acid
- State-of-the-Art (1997) in HF Alkylation Technology Safety
  - Modified HF – Uses a Trade Secret “Additive” that works with HF catalyst
- Emerging Technologies Being Tested Elsewhere
  - Liquid Ionic Catalyst
  - Solid Catalyst
- TFD, Torrance Refining Company, and other agencies are monitoring these emerging technologies.

MHF Alkylation Unit Chemistry

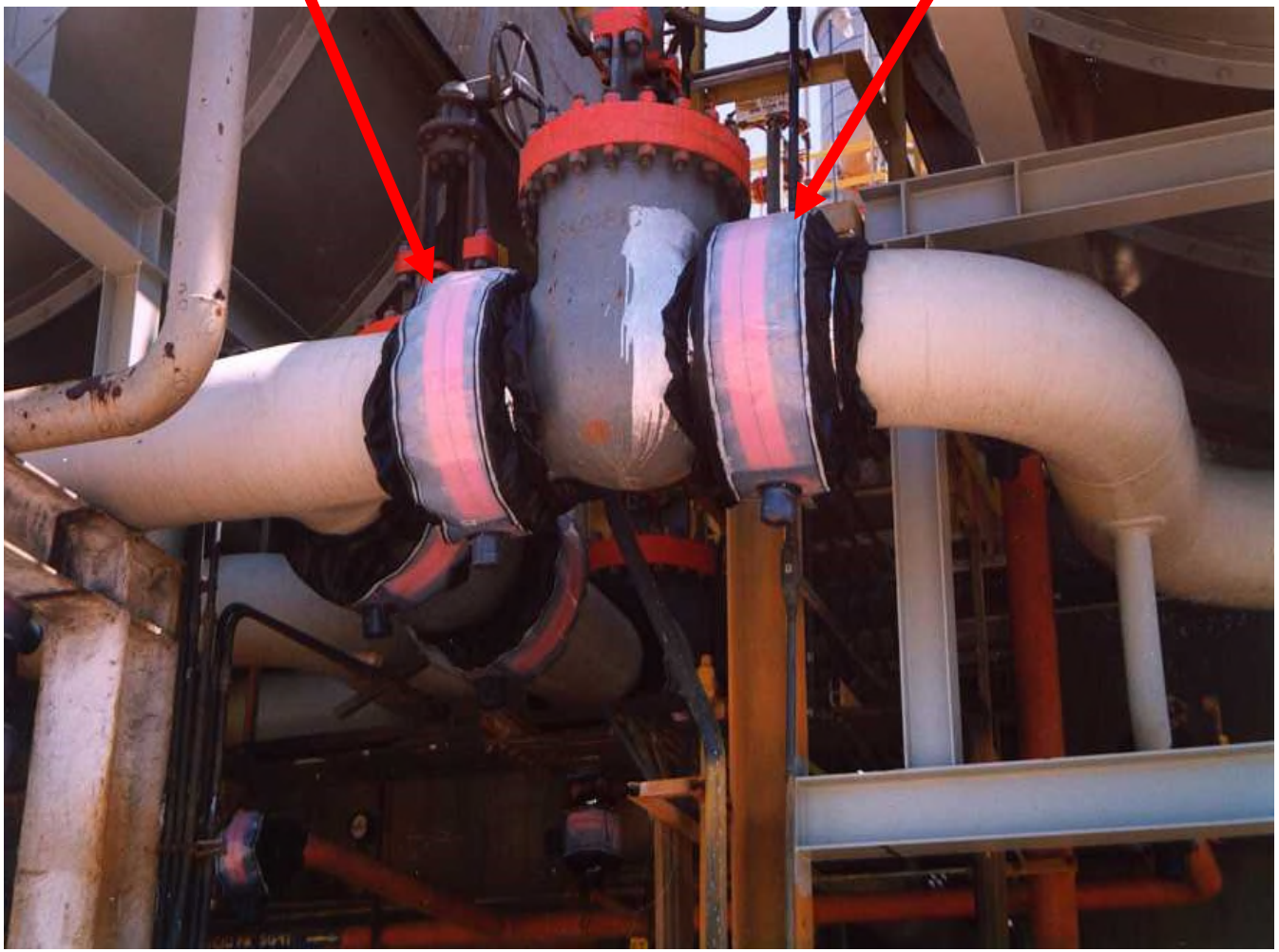
- Chemicals in Alkylation Unit
  - Normal HF (HF) is a colorless liquid that boils at 67.1F at sea level, but it is kept in its liquid state within the piping of the Alkylation Unit because it is under pressure
  - Hydrocarbon Mixture (HC)– Mostly isobutane, butylene, and propylene being catalyzed to create high-octane blending stock
  - "Additive" – Significantly decreases the potential hazard associated with an accidental release of Modified Hydrofluoric Acid (MHF)
  - ASO – Acid Soluble Oil
  - Water

MHF Alkylation Unit Chemistry - cont.

- 1994 Accepted Chemistry Yielding 65% ARF (all releases)
- 1998 Accepted Chemistry
    - Baseline Process Conditions Yielding 50% ARF (unbarriered releases)
    - 89% ARF is achieved for barriered releases
        - The application of flange shroud, settler pan, and recirculation pump enclosure barriers result in a level of safety the same or better than that approved in 1994.

Barrier Systems

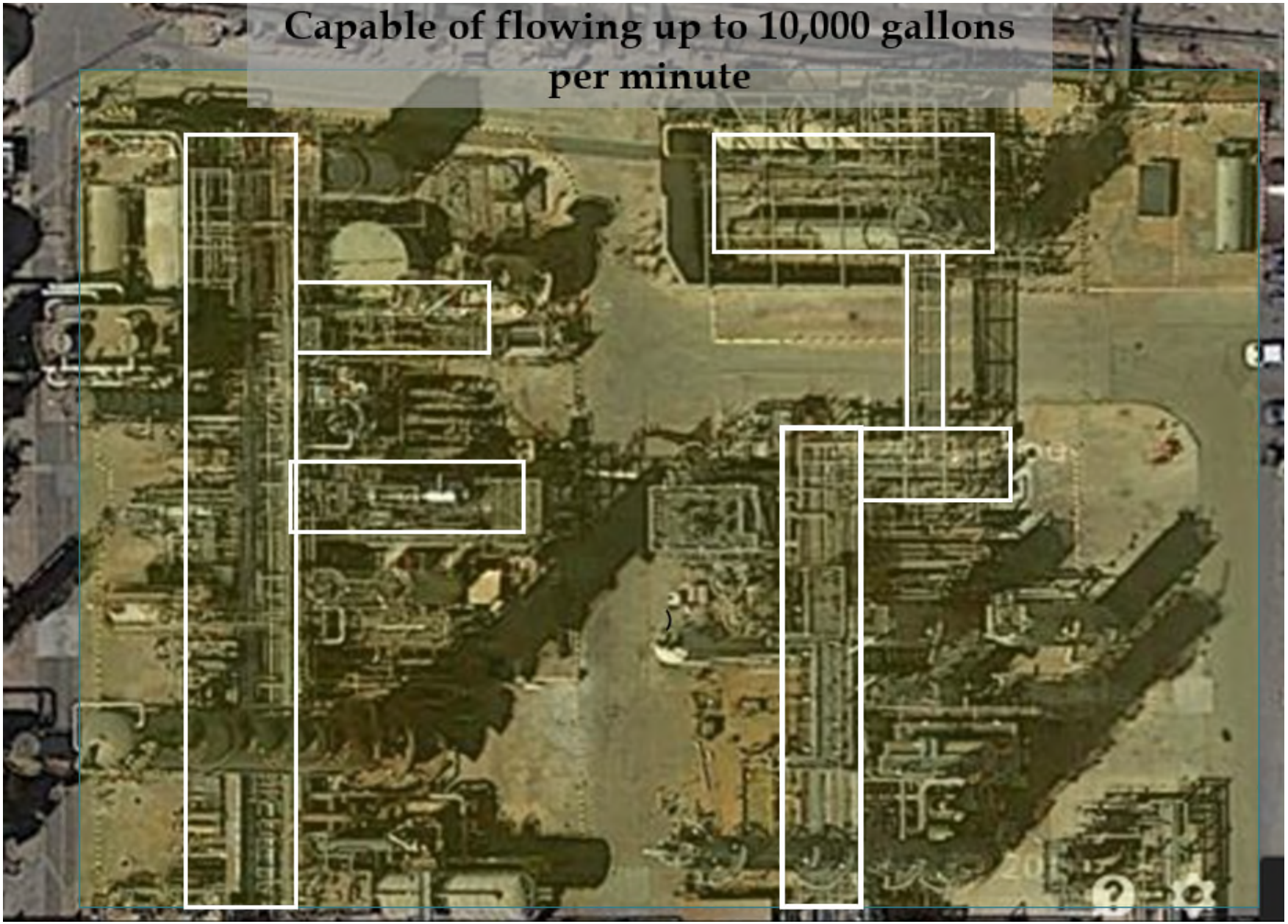
Flange Shrouds



Barrier Systems

Settler Pan

Water Deluge System



Airborne Reduction Factor (ARF)

- **Airborne Reduction Factor (ARF)** is a measure of the reduction in the amount of HF that will go airborne (as a fraction of the total HF released) in an incident.
- The larger the ARF, the less MHF is becomes airborne, and the lower the risk.
- ARF is primarily driven by:
  - HF Concentration
  - Additive Concentration
  - Water Concentration
  - Temperature
- ARF affects the severity (consequences) of a potential accidental release from the Alkylation Unit.
- Continuous monitoring of these properties through ARF reports sent to TFD daily

A Little Goes a Long Way

- Many things in the life are non-linear. At the grocery store, a gallon of milk doesn't cost 4 times the price of a quart. Non-linearity can also apply to chemistry and physics.
- For the Torrance Refinery Alkylation Unit, the additive's protective features are non-linear.
- Incremental safety benefits are greatest at lower concentrations. I.e., doubling the additive concentration does not double the safety improvement.
- So, with respect to additive concentration, "a little goes a long way." The first small percentages of additive have the most impact on ARF. This non-linearity is why the adjustment for operability in 1998 only reduced the ARF from 65% to 50%.

How Does ARF Protect Me

- MHF (1994) Original Additive Concentration

MHF + Pressure + Temp = 65% ARF

- MHF (1998) Revised Additive Concentration (unbarriered)

MHF + Pressure + Temp = 50% ARF

- MHF (1998) Revised Additive Concentration with Barriers

MHF + Pressure + Temp = 89% ARF

Societal Risk Index (SRI)

- ARF is a “release behavior” property of MHF that is a mass of chemical properties and process conditions.

- Societal Risk Index (SRI) is a measure of risk to the public – The lower the SRI, the lower the risk.
  - Measure risk as a function of severity and likelihood of impact to the Community
  - The MHF system is performing as designed and as approved by the Consent Decree

- Whereas, ARF influences the severity of a release event, SRI pulls together all potential release scenarios that could be envisioned by the designers, operators, and the Safety Advisor to balance consequences and likelihood to determine risk.

Societal Risk Index (SRI)

- SRI is Influenced by numerous design and operational characteristics that include:
  - Process Chemistry
  - Process Temperature and Pressure
  - Number of Acid delivery Trucks
  - Momentum Reduction Barriers – Flange Shrouds, Settler Pans, Recirculation Pump Enclosures
  - Firewater Monitors/Deluge Systems
  - Acid Evacuation System (AES)
  - HF Detectors

**TFD is notified if any of these elements are not fully functional, and immediate steps are taken to ensure the safety of public.*

Next Steps

- Continue to monitor the refinery safety systems as designed
- Continue to receive all compliance reports
- Create a Refinery Community Safety Agreement
- Summer 2017 - Strengthen the California Accidental Release Prevention Program (CalARP) and Process Safety Management (PSM) regulations

Next Steps - Continued

- The CalARP Program 4 requirements state that the refinery must evaluate Inherently Safe Technology (IST) and justify why application would be inappropriate. The City has the authority to contest, with reason, any justifications provided by the refinery as part of their Hazard Consequence Analysis (HCA).

- Ability for City to direct the Torrance Refinery to evaluate the need for the application of an inherently safer technology (e.g., liquid ionic technologies being considered for other US refineries)