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

SCAQMD REFINERY COMMITTEE

January 20, 2018
Torrance, California

PUBLIC PROCESS

- Six working group meetings conducted since April 2017
- Presentations provided:
  - Refineries' Current Mitigations
  - CEC's Potential Transportation Fuel Supply and Price Impacts of HF Ban
  - API RP 751 Safe Operation of Hydrofluoric Acid (HF) Alkylation Units
  - Alternative Alkylation Technologies (DuPont/CB&I/Chevron)
  - Cal-OSHA Process Safety Management Regulation
  - TRAA's Modified HF (MHF)/HF Alkylation Dangers
  - SCAQMD's Proposed Rule Concepts
- Five technical discussion meetings with Torrance Refining Company (TORC)
- Two refinery site visits & Torrance refinery community/neighborhood tour
- Interagency meeting with US EPA and Cal-OSHA

GENESIS OF PR1410 RULEMAKING

- "Near-miss" accident at Torrance refinery on February 18, 2015
- Community concerns on the alkylation unit safety, potential HF release and corresponding risk
- Hazards and human health risk due to exposure to HF are greater than those of sulfuric acid
- Additional information made available
  - More studies and documentation on MHF
  - Viable alternative technologies have matured and are being implemented
- SCAQMD staff conducted independent assessment

	HF	Sulfuric Acid
Appearance	Colorless, fuming liquid/gas	Colorless, oily liquid
Vapor Density	0.7 (relative to air)	3.4 (relative to air)
Boiling Point	**67 °F**	**554 °F**
Hazards	Severe skin and deep tissue burns, changing the bone structure	Severe irritation and skin burn, carcinogenic
Rate of Onset	Immediate & delayed	Immediate
Isolating Distance*	At least 330 ft.	At least 150 ft.

** Isolate leak area in all directions as an immediate precautionary measure (source: https://cameochemicals.noaa.gov)*

"NEAR-MISS" ACCIDENT

Each settler tank contains 47,000 lb of MHF

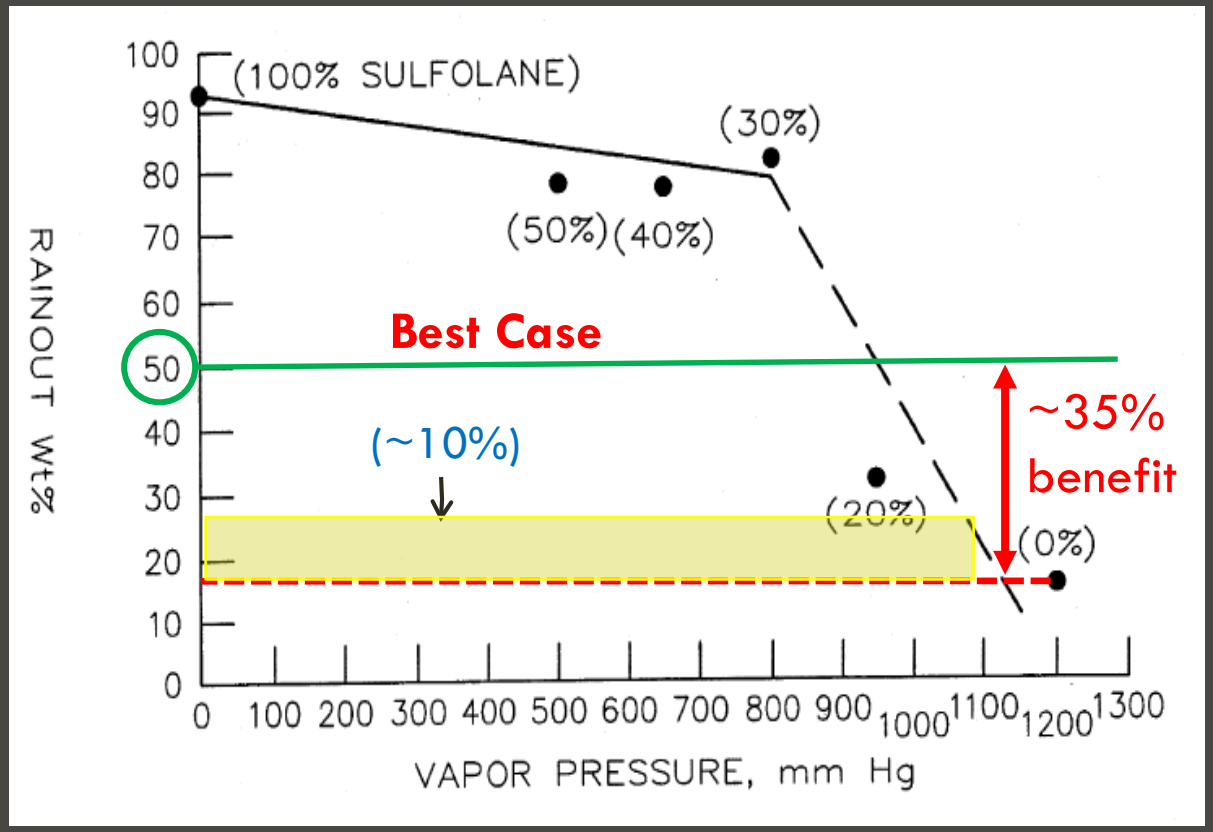
(Courtesy of the US Chemical Safety Board)

ASSESSMENT OF MHF TECHNOLOGY

- Staff has assessed the scientific information provided by TORC on MHF
- Assessing the safety of MHF technology is very complex and uncertainty still exists
- Summary results of MHF assessment:
  - Some, but uncertain, HF mitigation benefits offered by MHF (< 35%)
  - Ability to prevent formation of vapor/aerosol cloud is uncertain
    - ✓ Conditions of testing are different from current operating conditions
    - ✓ Large hole sizes were not considered
  - Ignoring all the uncertainties, best case scenario with all existing mitigation measures added at TORC, HF reduction is 89% leaving 11% released
- In case of breach in one settler tank at TORC, potential release of 5,200 lb HF assuming all passive mitigation functioning properly

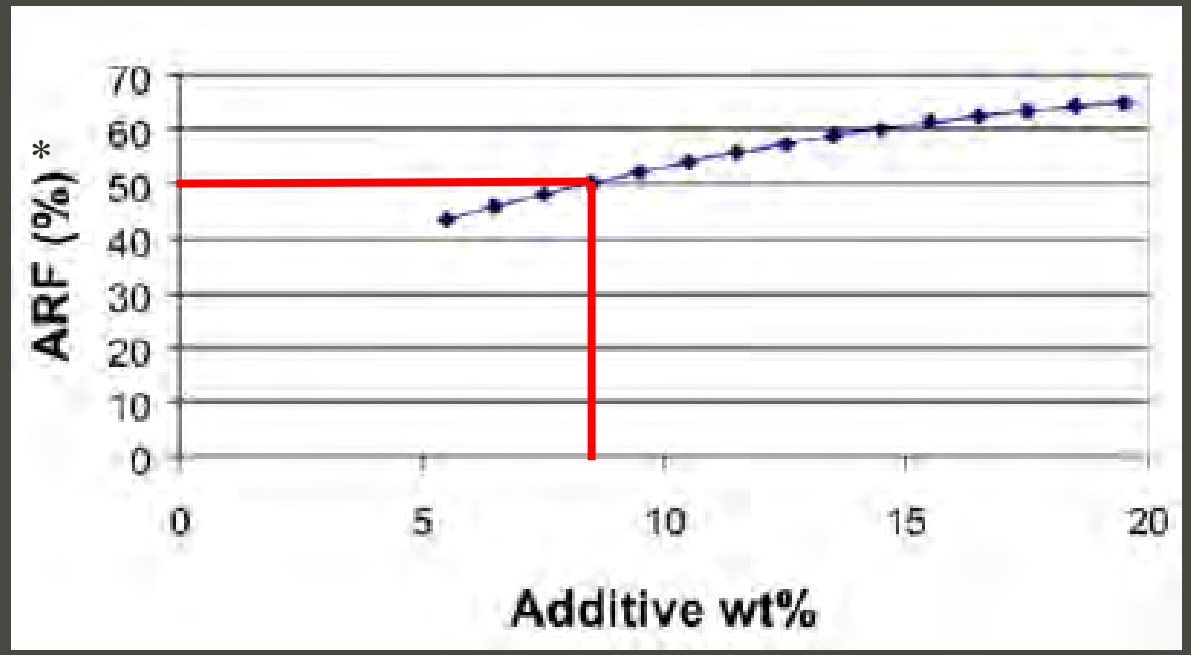
HF REDUCTION BENEFITS OFFERED BY MHF

Lab Tests and Modeling



(Phillips Petroleum Company 1995, US Patent 5,534,657)

Modeling Only (TORC)



(SCAQMD Meeting MHF Technology Discussion with TORC, May 4, 2017)

* Airborne Reduction Factor

INITIAL RULE CONCEPTS

- HF mitigation tiered at three different levels and with different timeline
  - Tier I Mitigation – Require existing mitigation with some enhancements
  - Tier II Mitigation – Above and beyond Tier I Mitigation (API recommendations)
  - Tier III Mitigation – Greatly enhanced protection (failsafe systems)
- Option to change to alternative technologies in lieu of Tier II and/or Tier III Mitigation

TIER I MITIGATION

- HF point sensors
- Alarm set points
- Open path monitors – 4 sided

  (TORC and/or Valero would need to install)
- Video cameras + monitor screens in remote control room
- HF sensitive paint
- Water mitigation

  (TORC would need to install water curtain)
- Acid evacuation system
- Emergency isolation block valves
- Backup power
- Baffles

  (TORC would need to install)
- Acid settler pans
- Flange shrouds

  (Valero would need to install)
- Pump barriers
- Safety audits

✓ Cost Range: $2.5 – $6 MM (for mitigation not yet installed)

TIER II MITIGATION

- Automated systems (water mitigation, emergency block valves) at alarm set points of HF sensors & open path monitors
- State-of-the-art high definition cameras (increase number of cameras & monitors)
- More HF sensors to compensate for non-operating sensors
- More comprehensive barriers (e.g., enclosure around acid settler tanks)

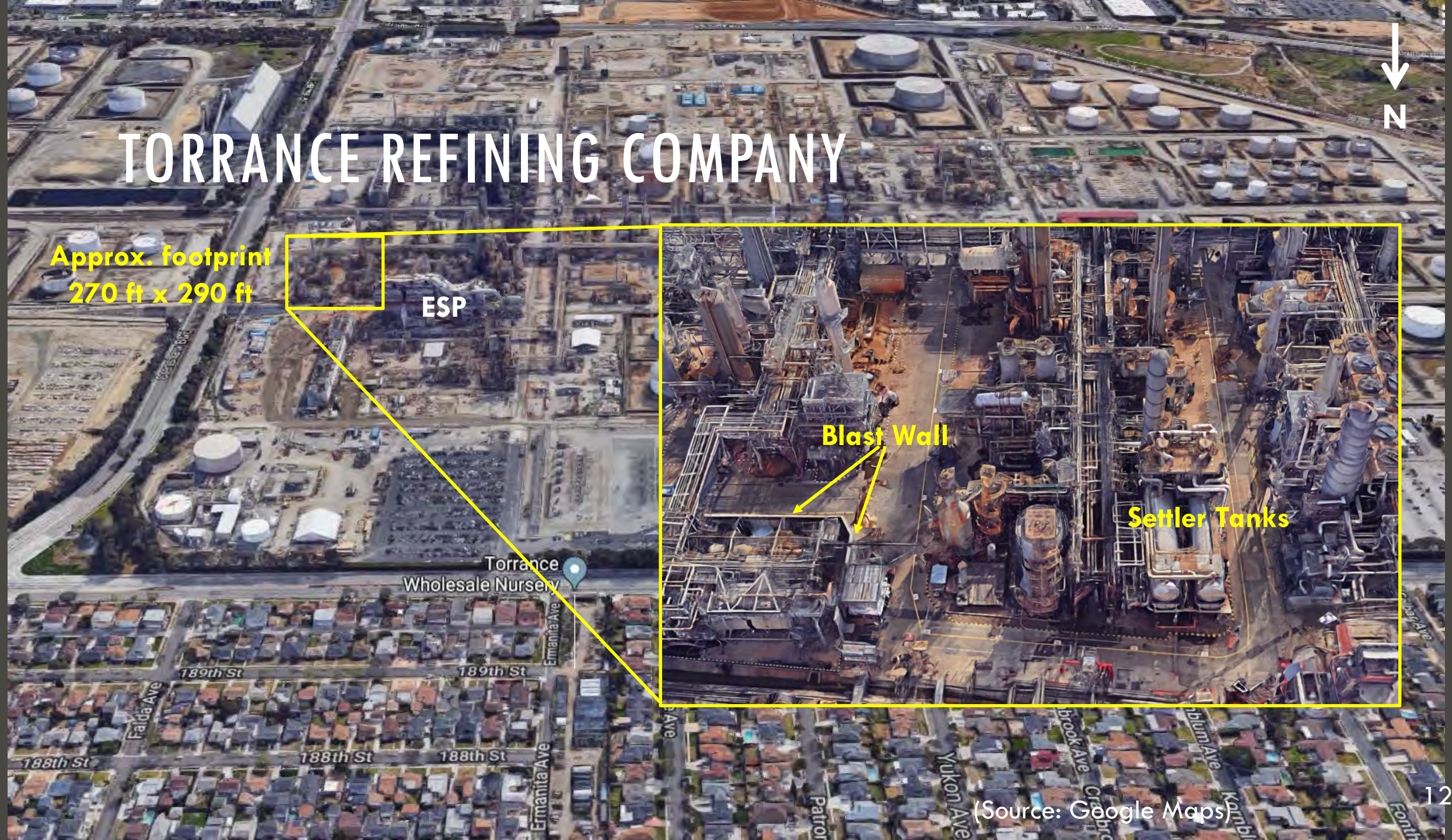
✓ Cost Range: $50 – $100 MM

TIER III MITIGATION (POTENTIAL APPROACHES)

- Complete, full enclosure of alkylation unit with roll-up doors, comprehensive water spray (worker safety), sensors & drainage capabilities
  - Possibly build whole new containment system parallel to existing unit to reduce downtime
  - Need to address potential "unintended secondary consequences" (e.g., flammable gases)
- Negatively pressured enclosure venting to scrubber with drainage
- Fully automated systems including acid evacuation at alarm set points
- Underground storage (acid dump tank, fresh storage, etc.)

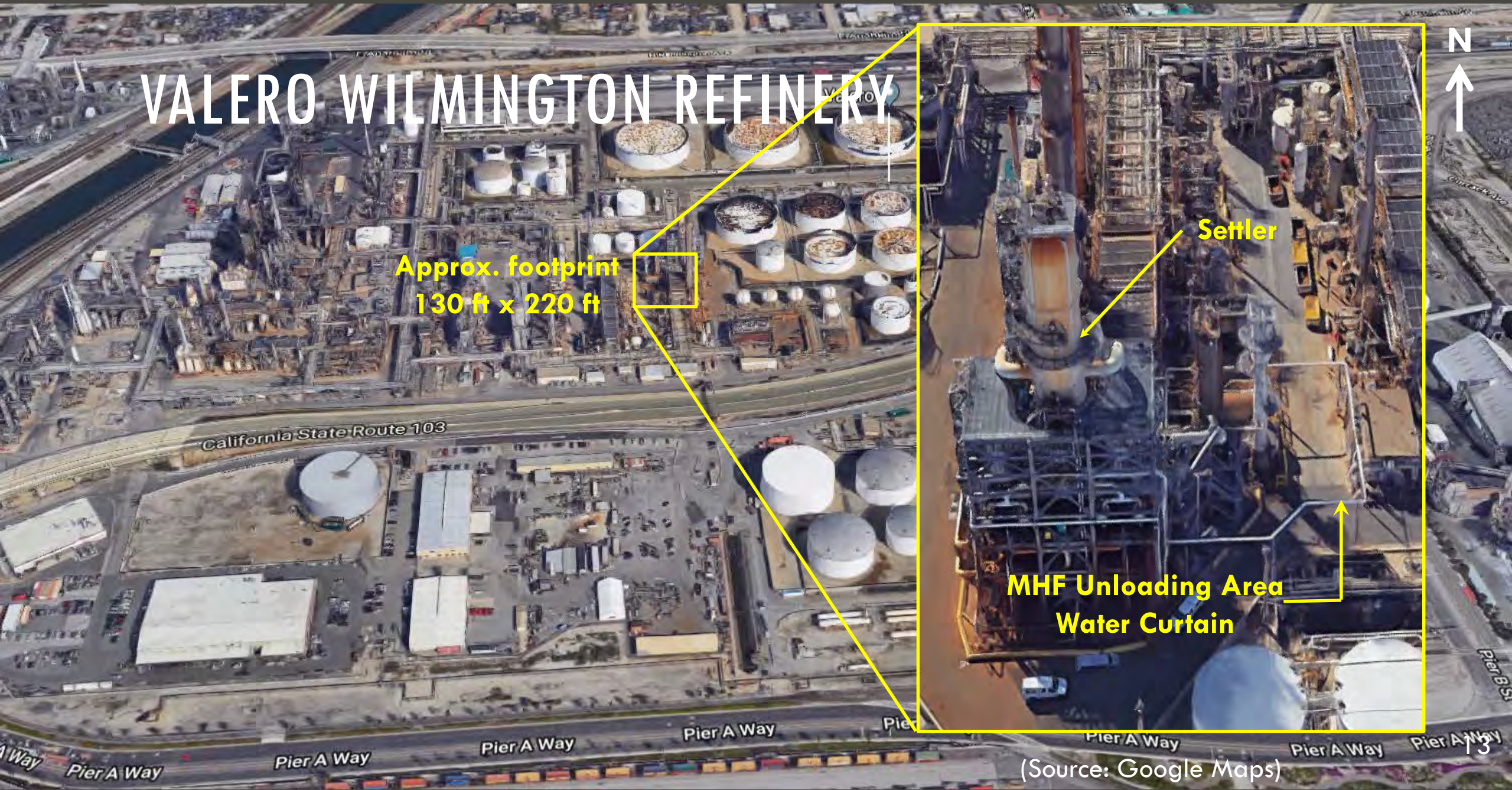
✓ Cost Range: $50 – $150 MM (based on chlorine gas containment and handling facility)

TORRANCE REFINING COMPANY



(Source: Google Maps)

VALERO WILMINGTON REFINERY



(Source: Google Maps)

COMPARISON OF ALTERNATIVES TO HF

Catalyst Type	Sulfuric Acid		Solid Acid	Ionic Liquid
Technology Name (Manufacturer)	CDAlky® (CB&I)	ConvEx℠ (DuPont/STRATCO)	AlkyClean® (CB&I)	ISOALKY™ (Chevron & UOP)
Cost	Less than conventional sulfuric acid unit (30–50% less acid consumption)	~40–60% less than a grassroots sulfuric acid unit	Information not available	Information not available
Associated Hazards	Sulfuric acid	Sulfuric acid	No known hazards	No known hazards
Commercial Applications/Status	One US Gulf Coast refinery start-up in 2020 at comparable capacity (23,000 b/d) and 13 refineries worldwide	None, new technology	Petrochemical plant in China at lower capacity (2,700 b/d)	Chevron Salt Lake City HF alkylation retrofit, with planned start-up in 2020 at lower capacity (5,000 b/d)

EXISTING COST ANALYSIS OF TECHNOLOGY CONVERSION

Conversion to sulfuric acid

Cost Range	Conditions	Reference
$100 – $200 MM	US Gulf Coast cost; Alkylation unit only	Norton Engineering (2016)
$210 – $330 MM	US Gulf Coast & Midwest costs; Alkylation unit (~23,000 b/d) and acid regeneration	DuPont (2018)
$600 – $900 MM	TORC cost; Alkylation unit and acid regeneration	Burns & McDonnell (2017)

POTENTIAL TIMING FOR IMPLEMENTATION

- 2018 – Rule adoption
- 6-12 months after adoption – Require Tier I Mitigation measures
- 2-3 years after adoption – Require Tier II Mitigation or alternative technology
- 2021 – Alternative technology assessment completed
- 8 years after adoption – Require Tier III Mitigation or alternative technology