U.S. Chemical Safety and
Hazard Investigation Board

Fire and Explosions at Philadelphia Energy Solutions Refinery Hydrofluoric Acid Alkylation Unit

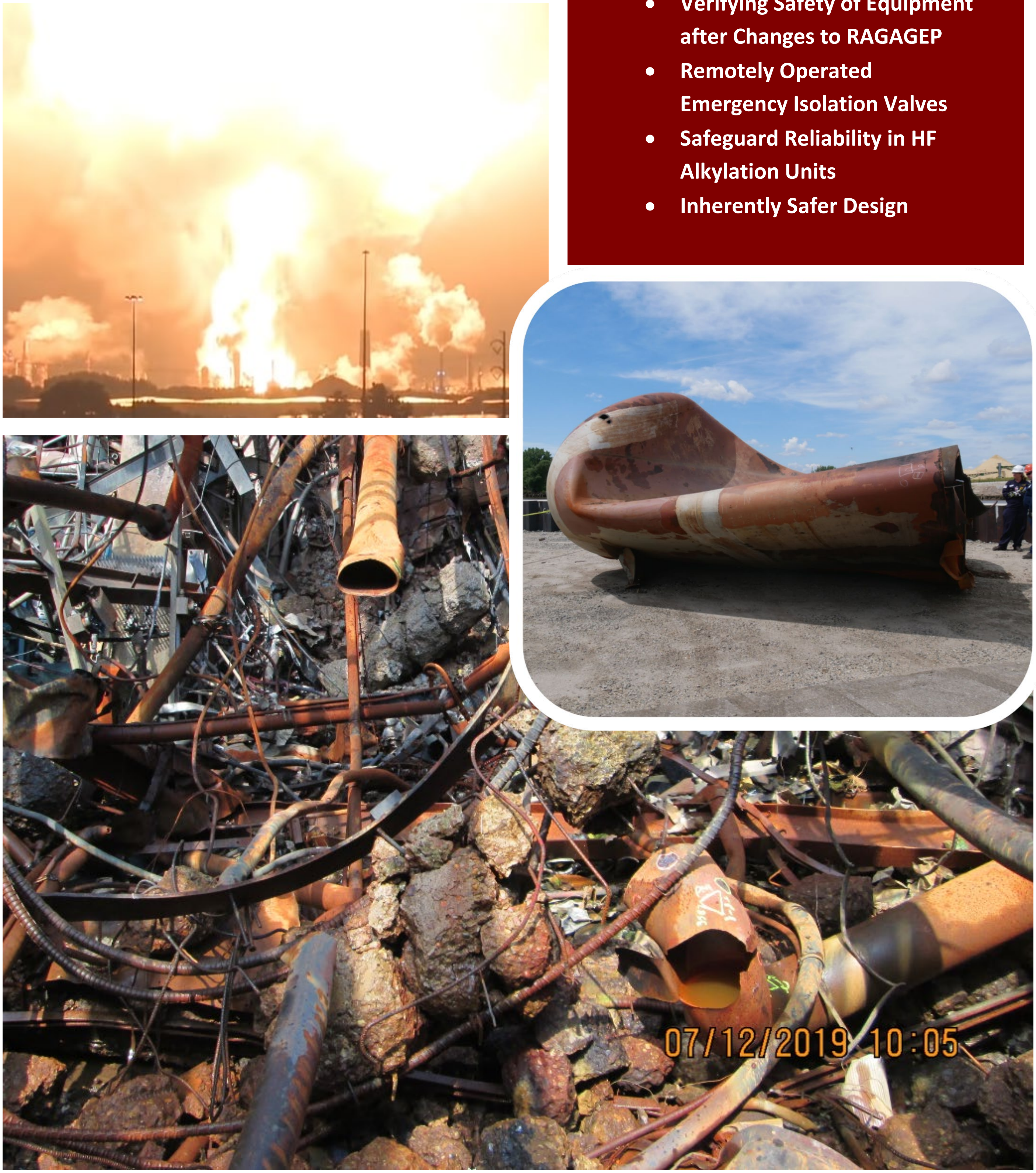
Philadelphia, Pennsylvania | *Incident Date: June 21, 2019* | **No. 2019-04-I-PA**

Investigation Report

Published: October 11, 2022

SAFETY ISSUES:

- Mechanical Integrity
- Verifying Safety of Equipment after Changes to RAGAGEP
- Remotely Operated Emergency Isolation Valves
- Safeguard Reliability in HF Alkylation Units
- Inherently Safer Design



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Abbreviations

API	American Petroleum Institute
BLEVE	boiling liquid expanding vapor explosion
bph	barrels per hour
CCPS	Center for Chemical Process Safety
CML	condition monitoring location
CSB	U.S. Chemical Safety and Hazard Investigation Board
EPA	U.S. Environmental Protection Agency
HF	hydrofluoric acid or hydrogen fluoride
IDLH	Immediately Dangerous to Life or Health
OSHA	Occupational Safety and Health Administration
PES	Philadelphia Energy Solutions
ppm	parts per million
PSM	Process Safety Management
RAD	rapid acid deinventory
RE	residual elements
RMP	Risk Management Plan
RP	Recommended Practice
TSCA	Toxic Substances Control Act

Glossary

The terms listed below are ***emphasized*** in the report at first usage.

Alloying (Alloy) Elements — Elements intentionally added to a metal such as steel to achieve particular properties or meet material specifications.

Boiling liquid expanding vapor explosion (BLEVE) — The "sudden loss of containment of a pressure-liquefied gas existing above its normal atmospheric boiling point at the moment of its failure, which results in rapidly expanding vapor and flashing liquid. The release of energy from these processes (expanding vapor and flashing liquid) creates a pressure wave" [1, p. 311].

Circuits — Piping sections that are exposed to similar process conditions, are made of the same material of construction, and are subject to the same expected damage mechanisms.

Component (Piping) — A portion of piping between welds or flanges. Piping components include straight run piping and pipe fittings.

Condition monitoring location (CML) — A designated area of equipment where periodic thickness examinations are conducted. Each CML represents as many as four inspection locations located circumferentially around piping. CMLs are also referred to as thickness monitoring locations (TMLs). CMLs were historically referred to as corrosion (rather than condition) monitoring locations, and that terminology is sometimes still used within the industry.

RAGAGEP — Recognized and Generally Accepted Good Engineering Practices. RAGAGEP can include widely adopted codes, consensus documents such as American Petroleum Institute (API) standards, non-consensus documents such as manufacturer recommendations, and internal company standards [2].

Residual Elements (RE) — Contaminating elements such as nickel, copper, and chromium that are a result of steel manufacturing processes using scrap metal. Concentrations of these residual elements in carbon steel above an established baseline can increase corrosion rates of carbon steel exposed to hydrofluoric acid.

Executive Summary

On the morning of June 21, 2019, a pipe elbow in the Philadelphia Energy Solutions (PES) hydrofluoric acid (HF) alkylation unit ruptured. A large vapor cloud—composed of about 95% propane, 2.5% HF, and other hydrocarbons—engulfed part of the unit. The vapor cloud ignited two minutes after the start of the release, causing a large fire. The control room operator then activated the Rapid Acid Deinventory (RAD) system, a safety system that causes HF to be routed to a separate drum in the event of a loss-of-containment incident or other emergency. The activation of the RAD system successfully drained about 339,000 pounds (43,260 U.S. gallons) of hydrofluoric acid from the unit to the RAD drum.

The control room operator then tried to remotely turn on the water pumps that fed the elevated HF mitigation water cannons, which are designed to reduce airborne HF through vapor suppression, but the water pumps did not turn on. The control system communication to the water pumps had failed at the time of vapor cloud ignition, and a backup power system in the unit had also failed, preventing the ability to remotely operate the water spray HF mitigation system.

Three explosions then occurred in the unit. Evidence indicates these explosions were secondary events caused by the fire. The third explosion was the largest and occurred when a vessel, called V-1, containing primarily butylene, isobutane, and butane, violently ruptured. A fragment of the V-1 vessel weighing approximately 38,000 pounds flew across the Schuylkill River, and two other fragments, one weighing about 23,000 pounds and the other 15,500 pounds, landed in the PES refinery.

About 40 minutes into the release, a refinery worker was able to manually turn on the water pump that supplied the HF mitigation water cannons, which then allowed the elevated water spray HF mitigation system cannons to start spraying water into the unit to help suppress the released HF. The fire was extinguished the following day, on Saturday June 22, at about 8:30 a.m.

Low-concentration HF was present in some of the process piping and equipment that failed during the incident, causing HF to release to the atmosphere. PES estimated that 5,239 pounds of HF released from piping and equipment during the incident. It estimated that 1,968 pounds of the released HF was contained by water spray within the unit and was processed in the refinery wastewater treatment plant, and that 3,271 pounds of HF released to the atmosphere and was not contained by water spray. PES also estimated that about 676,000 pounds of hydrocarbons released during the event, of which an estimated 608,000 pounds were combusted.

The HF alkylation unit was severely damaged by the fire and explosions. Marsh JLT Specialty reported that the incident resulted in an estimated property damage loss of $750 million, and the 2020 Marsh JLT Specialty report ranked the PES incident as the third-largest refinery loss to occur worldwide since 1974 [3]. Five workers and a firefighter experienced minor injuries during the incident and response. The CSB is unaware of any off-site impacts from the HF release. On June 26, 2019, PES announced that the refining complex would be shutting down [4].

Federal, state, and local agencies that responded to or investigated the incident include the U.S. Chemical Safety and Hazard Investigation Board, the Occupational Safety and Health Administration (OSHA), the U.S. Environmental Protection Agency (EPA), the Bureau of Alcohol, Tobacco, Firearms and Explosives (ATF), the

Pennsylvania Department of Environmental Protection, The City of Philadelphia Department of Public Health Air Management Services, the Philadelphia Fire Department, and the Philadelphia Police Department.

Safety Issues

The CSB's investigation identified the safety issues below.

- **Mechanical Integrity.** A steel pipe elbow containing high concentrations of nickel and copper had become severely thin from HF corrosion and ruptured to initiate the incident. Carbon steel with high nickel and copper content is known within the industry to corrode faster from contact with HF than carbon steel with lower nickel and copper content. While the PES pipe elbow had become severely thin from corrosion, adjacent piping components lower in nickel and copper content had not corroded as quickly and were not thin. At the time of the incident, published industry standards and recommended practices did not require refineries to conduct 100% component inspection of carbon steel piping in HF service to identify any piping components corroding and thinning faster than others, which as shown by this incident, can lead to hazardous loss of containment events. After the incident, API RP 751 *Safe Operation of Hydrofluoric Acid Alkylation Units* was revised to include a new requirement for refiners to develop a special emphasis inspection program to inspect all individual carbon steel piping components and welds in identified HF alkylation corrosion zones to identify areas of accelerated corrosion. This new requirement should help prevent future failures of steel piping with high nickel and copper content in HF alkylation units. (Section 2.1)

- **Verifying Safety of Equipment after Changes to RAGAGEP.** The seminal research presented in the 2003 NACE paper 03651 *Specification for Carbon Steel Materials for Hydrofluoric Acid Alkylation Units* directly led to changes in industry guidance quantifying the levels of nickel and copper in steel that could be considered safe for use in HF alkylation units. However, prior to the incident, API RP 751, Sunoco, and PES did not effectively respond to these advancements in industry knowledge by ensuring the safety of existing facilities through requiring all carbon steel piping circuit components to be inspected. Both the OSHA PSM and EPA RMP regulations require companies to determine that their equipment is designed, maintained, inspected, tested, and operating in a safe manner when new safety information is discovered and published in Recognized and Generally Accepted Good Engineering Practice (RAGAGEP) documents. To prevent catastrophic incidents, companies and industry trade groups must take swift action to ensure process safety when new knowledge on hazards is published. These actions must include ensuring that facilities built before the new knowledge was published are still safe to operate. (Section 2.2)

- **Remotely Operated Emergency Isolation Valves.** Based on the thinning of the V-1 vessel steel, the CSB concluded that a jet flame from the ruptured elbow impinged upon the bottom of the V-1 vessel, causing the steel to stretch and thin until the vessel ruptured. The large hydrocarbon sources downstream of the failed elbow could not be remotely or automatically isolated, and therefore PES was unable to stop the jet flame in a timely manner to prevent the V-1 vessel rupture. (Section 2.3)

- **Safeguard Reliability in HF Alkylation Units.** The PES water spray HF mitigation system was damaged during the incident and could not be remotely activated. The damage to the PES water spray HF mitigation system demonstrates that "active" safeguards—or safeguards that require a person or technology to trigger their activation—have the potential to fail in major incidents involving fires and explosions. (Section 2.4)

- **Inherently Safer Design.** Technologies are being developed that could be a safer alternative to HF and sulfuric acid alkylation, including composite ionic liquid catalyst alkylation technology, solid acid catalyst alkylation technology, and the new ionic liquid acid catalyst alkylation technology developed by Chevron, which is now operating at commercial scale at Chevron's Salt Lake City refinery. While EPA has previously issued requirements for companies to evaluate inherently safer technologies, there is currently no Federal regulatory requirement for petroleum refineries to evaluate inherently safer design strategies to reduce the risk of serious accidental releases. (Section 2.5)

Cause

The CSB determined the cause of the incident was the rupture of a steel piping component with high nickel and copper content that had corroded from HF and thinned faster than adjacent piping components with lower nickel and copper content. The ruptured pipe released propane and toxic hydrofluoric acid to the atmosphere.

Contributing to the incident was the lack of requirements by the American Petroleum Institute, Sunoco, and PES, to inspect all existing carbon steel piping circuit components to ensure they could safely operate in HF service after the industry began quantifying the levels of nickel and copper in steel that could be considered safe for use in HF alkylation units in 2003.

Contributing to the severity of the incident was the absence of remotely operated emergency isolation valves to isolate large sources of hydrocarbons, and incident-induced damage to the water mitigation system that limited PES's ability to suppress released HF during the incident.

Recommendations

To U.S. Environmental Protection Agency

Develop a program that prioritizes and emphasizes inspections of refinery HF alkylation units, for example under EPA's National Compliance Initiative called Reducing Risks of Accidental Releases at Industrial and Chemical Facilities. As part of this program, verify that HF alkylation units are complying with API RP 751 *Safe Operation of Hydrofluoric Acid Alkylation Units*, including but not limited to the implementation of a special emphasis inspection program to inspect all individual carbon steel piping components and welds to identify areas of accelerated corrosion; the protection of safety-critical safeguards and associated control system components, including but not limited to wiring and cabling for control systems and primary and backup power supplies, from fire and explosion hazards including radiant heat and flying projectiles; and the installation of remotely-operated emergency isolation valves on the inlet(s) and outlet(s) of all hydrofluoric acid containing vessels, and hydrocarbon containing vessels meeting defined threshold quantities.

Revise 40 C.F.R. Part 68 (EPA Risk Management Plan) to require new and existing petroleum refineries with HF alkylation units to conduct a safer technology and alternatives analysis (STAA) and to evaluate the practicability of any inherently safer technology (IST) identified. Require that these evaluations are performed every 5 years as a part of an initial PHA as well as PHA revalidations.

Per the requirements in EPA Rule *Procedures for Prioritization of Chemicals for Risk Evaluation Under the Toxic Substances Control Act*, initiate prioritization to evaluate whether hydrofluoric acid is a High-Priority Substance for risk evaluation. If it is determined to be a High-Priority Substance, conduct a risk evaluation of hydrofluoric acid to determine whether it presents an unreasonable risk of injury to health or the environment. If it is determined to present an unreasonable risk of injury to health or the environment, apply requirements to hydrofluoric acid to the extent necessary to eliminate or significantly mitigate the risk, for example by using a methodology such as the hierarchy of controls.

To American Petroleum Institute

Update API RP 751 *Safe Operation of Hydrofluoric Acid Alkylation Units* to require the following:

a. Protection of critical safeguards and associated control system components, including but not limited to wiring and cabling for control systems and primary and backup power supplies, from fire and explosion hazards, including radiant heat and flying projectiles; and

b. Installation of remotely-operated emergency isolation valves on the inlet(s) and outlet(s) of all hydrofluoric acid containing vessels, and hydrocarbon containing vessels meeting defined threshold quantities.

To ASTM International

Revise ASTM A234 to incorporate supplementary requirements for piping used in HF service, as defined in HF supplementary requirements S9.1 through S9.7 in ASTM A106 version 19a.

1 Factual Information

This section details the facts gathered by the CSB investigation team.

1.1 Philadelphia Energy Solutions Refinery History

The Philadelphia Energy Solutions (PES) Refining Complex—comprised of two separate refineries, Point Breeze and Girard Point (**Figure 1**)—has a history spanning over 150 years under various companies' ownership. In 1866, Atlantic Petroleum Company built four warehouses at the Point Breeze location with the capacity to store up to 50,000 barrels of refined oil product, which at that time was primarily kerosene used in lamps. In 1870, Atlantic Petroleum Company changed its name to Atlantic Refining Company and established its first refining units at the site. By 1915 it was producing gasoline for cars and by 1918 aviation fuel for use in World War I.

In 1920, Gulf Oil began operations at the Girard Point location. By 1927 the facility was refining 31,000 barrels of gasoline and other products per day.

In 1966, Atlantic Refining Company merged with Richfield Oil Company, becoming ARCO. In the mid-1980s, Gulf Oil was bought by Chevron [5], and the Girard Point refinery was renamed the Chevron USA Philadelphia refinery. In 1985, Dutch oil trader John Deuss purchased the Point Breeze refinery from ARCO.

In 1988, Sunoco purchased the Point Breeze refinery from Deuss. In 1994, Sunoco also purchased the Girard Point refinery from Chevron. In 1995, Sunoco consolidated the two facilities into one refining complex. The facility operated under Sunoco for 17 years, until it was purchased in 2012 by PES. In 2019, the refining complex could process 335,000 barrels of crude oil per day and was the largest oil refining complex on the U.S. East Coast [6]. At the time of the incident, there were approximately 1,026 people employed at PES.[a]

In January 2018, PES filed for bankruptcy [7]. The company reorganized and emerged from bankruptcy on August 7, 2018. On June 21, 2019, the pipe failure, fire, and explosions that are the subject of this report occurred in the PES Girard Point refinery. On June 26, 2019, PES announced it would shut down the refining complex [4]. On July 22, 2019, PES again filed for bankruptcy [8]. In February 2020, a U.S. bankruptcy court judge approved the sale of the PES refinery to Hilco Redevelopment Partners [9]. As of the date of this report, Hilco Redevelopment Partners is demolishing the refinery and plans to repurpose the site [10].

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[a] There were 612 hourly workers and 414 salary employees at PES.

Figure 1. Overhead view of the PES refinery in Philadelphia, Pennsylvania. (Credit: Google Earth with annotations by CSB)

1.2 Background on Alkylation and Hydrofluoric Acid

Alkylate is a high-octane blending component for gasoline. Gasoline with a high-octane rating experiences less autoignition in engines, called "engine knock [11]." The octane rating of gasoline is a key part of the fuel grade selected at the gasoline pump (**Figure 2**).

As shown in **Figure 3**, producing alkylate for gasoline typically requires reacting an olefin—a hydrocarbon with a double bond (e.g., propylene, butylene)—with isobutane using an acid catalyst, either sulfuric or hydrofluoric acid. The alkylate product is a branched hydrocarbon with single bonds [12].[a]

Figure 2. Octane ratings at a gasoline pump.

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[a] HF alkylation was first commercialized in the early 1940s [17, p. 15].

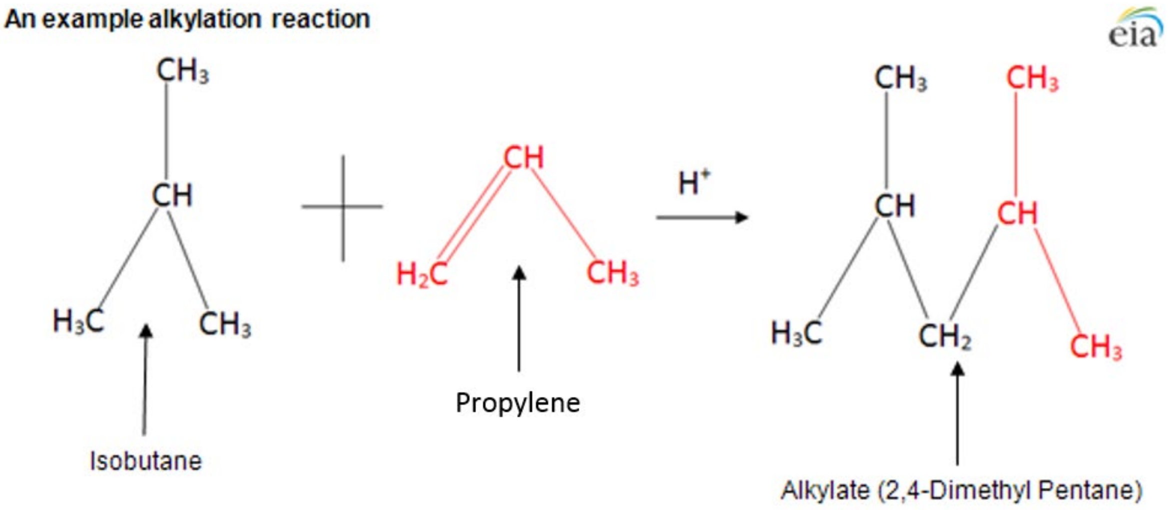

Figure 3. Example alkylation reaction. (Credit: U.S. Energy Information Administration [12])

Both acids typically used in refinery alkylation units—hydrofluoric acid and sulfuric acid—have associated risks. Hydrofluoric acid is particularly hazardous in the event of a major release because it is highly toxic and is a vapor at atmospheric conditions.[a] Hydrofluoric acid is immediately dangerous to life or health (IDLH) at 30 parts per million (ppm) [13]. Upon physical contact with skin, HF penetrates the skin and causes destruction to deep tissue layers and bone. Fatalities have been reported from an HF skin exposure to as little as 2.5% of body surface area [14, p. 5]. If inhaled, HF can cause severe lung injury and pulmonary edema—fluid in the lungs—which can result in death [14, p. 2]. Sulfuric acid is highly corrosive and can cause skin burns and other injuries upon contact [15]. However, it is a liquid at atmospheric conditions[b] and does not form a significant vapor cloud upon release.

1.3 PES Refinery HF Alkylation Unit Process Description

The PES HF alkylation unit process is described below and is accompanied by a simplified process flow diagram (**Figure 4**). The equipment shown in red in the figure is the HF alkylation reaction section and the rapid acid deinventory drum, to which the HF can be routed in the event of a loss-of-containment incident or other emergency.

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[a] Hydrofluoric acid has a boiling point of 67 °F at atmospheric pressure, and a vapor pressure of 783 mmHg [13].

[b] Sulfuric acid has a boiling point of 554 °F at atmospheric pressure, and a vapor pressure of 0.001 mmHg [91].

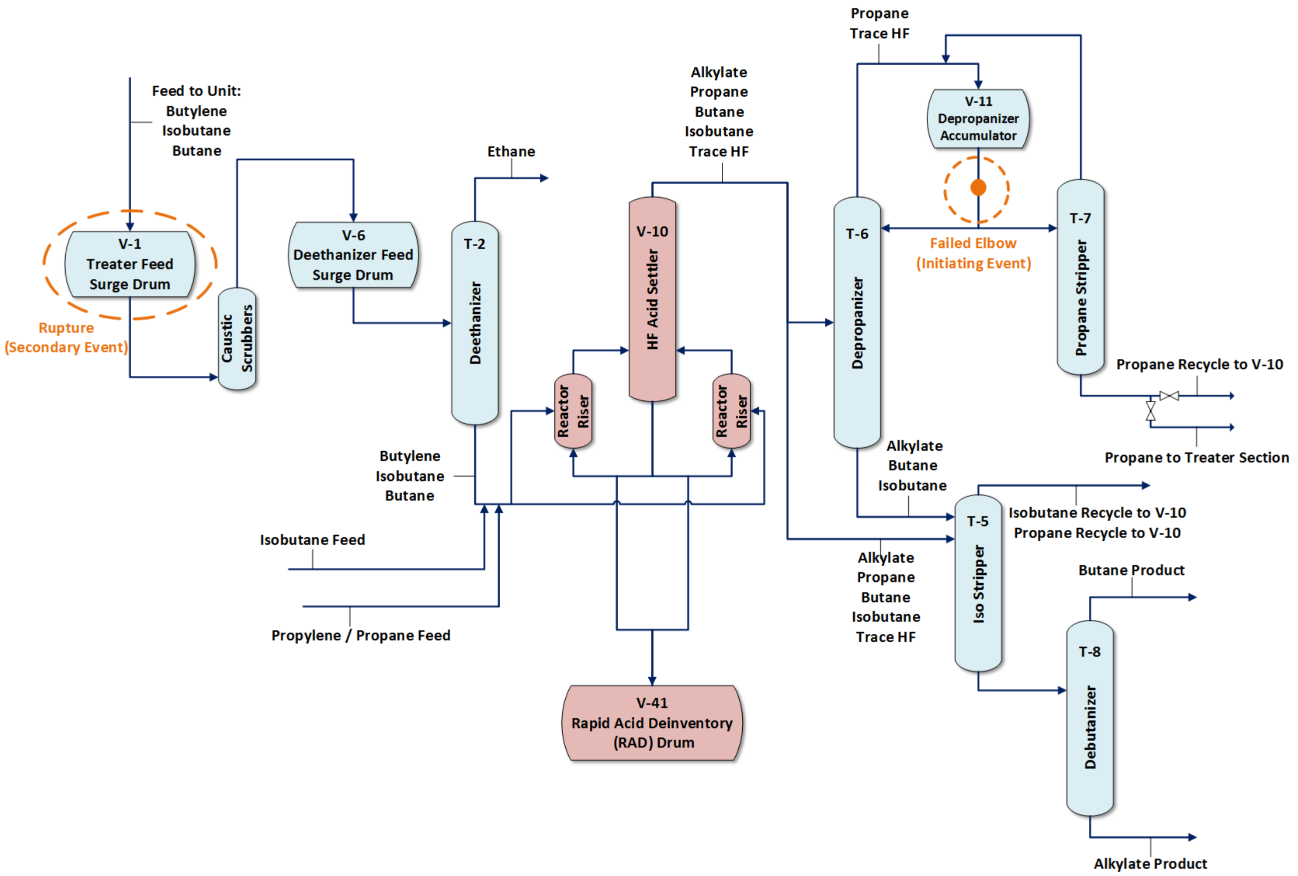

Figure 4. Simplified process flow diagram of the PES HF alkylation unit. (Credit: CSB)

The feed entering the PES HF alkylation unit was comprised primarily of butylene, isobutane, and butane, with smaller amounts of other light hydrocarbons. The feed first entered V-1, the treater feed surge drum, and was then fed to process treatment vessels. Downstream of the deethanizer column, T-2, additional isobutane and propylene were fed to the hydrocarbon stream, which was then fed to the V-10 HF acid settler reactor risers.

In the reactor risers, the hydrocarbon feed was mixed with HF, which catalyzed the reaction between the olefins (propylene and butylene) and isobutane to produce alkylate. The alkylate product, the remaining hydrocarbons, and the HF then entered the V-10 HF acid settler, where the HF separated from the hydrocarbon mixture due to the differences in density between the HF (heavier) and hydrocarbons (lighter). The HF returned to the reactor risers, continuously circulating through the acid circulation loop.

The alkylate / hydrocarbon mixture and trace HF then was fed to multiple distillation columns and strippers, as shown in **Figure 4**. The bottoms product of the debutanizer (T-8) was the end alkylate product, to be used as a blending component for gasoline.

The unit was also equipped with a rapid acid deinventory (RAD) system to quickly deinventory HF from the V-10 HF acid settler and associated equipment.[a] The RAD system was installed in 2002 and was designed to

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[a] API RP 751 *Safe Operation of Hydrofluoric Acid Alkylation Units* recommends that facilities consider installing rapid acid deinventory systems as a potential mitigation measure, to be part of the facility's overall hydrofluoric acid release mitigation system [17, p. 37].

deinventory the system in seven to eight minutes to a large vessel called the RAD drum. The RAD drum was sized to store all of the unit's bulk HF and almost all of the hydrocarbons from the V-10 HF acid settler. The RAD system was designed to be manually activated by an operator, and could be activated from three separate locations: (1) the central control room, (2) the alkylation unit's blast-resistant local control room, and (3) a remote instrument enclosure building outside the unit boundary. The unit was also equipped with a water mitigation system that used elevated water cannons that were designed to spray water into the unit to contain released HF through vapor suppression.[a,b] The water mitigation system was designed to be manually, remotely activated from the central control room.

As will be described in this report, this incident occurred when a pipe elbow ruptured in the HF alkylation unit. The elbow was part of the piping between V-11, the depropanizer accumulator, and T-6, the depropanizer distillation column and T-7, the propane stripper (**Figure 5**). The elbow was on the discharge piping from a pump (one of two pumps in this system labeled P14-A and -B) that was not operating at the time of the incident. At the time of the event, this piping was at a pressure of about 380 psig and a temperature of about 100°F. The approximate design composition of process fluid in the piping is shown in **Table 1.**

Although there were emergency isolation valves on the suction (inlet) of each of the P-14 pumps, there were no emergency isolation valves downstream of the pumps, between the pumps and columns T-6 and T-7. Those large hydrocarbon sources downstream of the failed elbow could not be remotely or automatically isolated.

Table 1. Design composition of the process fluid in the piping containing the failed elbow.

Material	**Weight Percent**
Propane	94.7
Hydrofluoric Acid	2.5
Additional Hydrocarbons	2.8

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[a] API RP 751 *Safe Operation of Hydrofluoric Acid Alkylation Units* requires HF alkylation units to be equipped with remotely activated and remotely controlled water spray mitigation systems [17, p. 35].

[b] "[A]pplying high volumes of water to any release of HF will significantly reduce the airborne fraction of the HF released and provide an effective tool for mitigating the effects of an HF release. […] At a minimum, the required water mitigation system… should be specifically designed for HF mitigation" [17, p. 37].

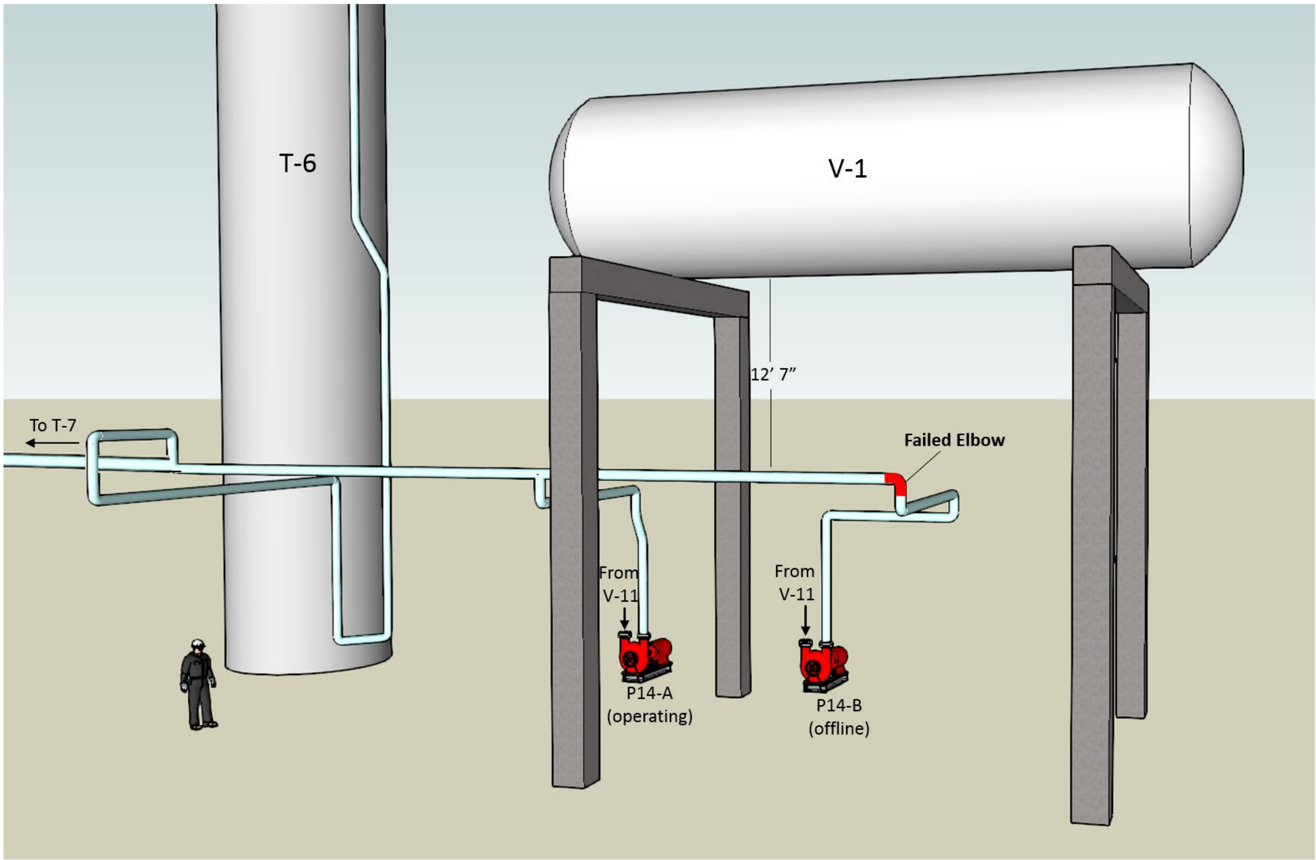

Figure 5. Model of the piping **circuit** containing the failed elbow. (Credit: CSB)

1.4 Incident Description

1.4.1 Initial Release

On Friday, June 21, 2019, the HF alkylation unit was reportedly operating normally. At 3:34 a.m., the control room operator, located in the refinery central control room, which was not in the HF alkylation unit, performed a routine process configuration change to route the T-7 propane stripper bottoms product out of the unit to treatment for storage. This process change would send excess propane circulating in the unit to product storage.

As part of this same operation, at 3:55 a.m. the control room operator increased the feed to the T-7 propane stripper from 73 barrels per hour (bph) to 78 bph. Five minutes later, at 4:00 a.m., the control room operator further increased the feed to the T-7 propane stripper, from 78 bph to 80 bph (**Figure 6**). There were no abnormal process deviations or upsets recorded during this operation.

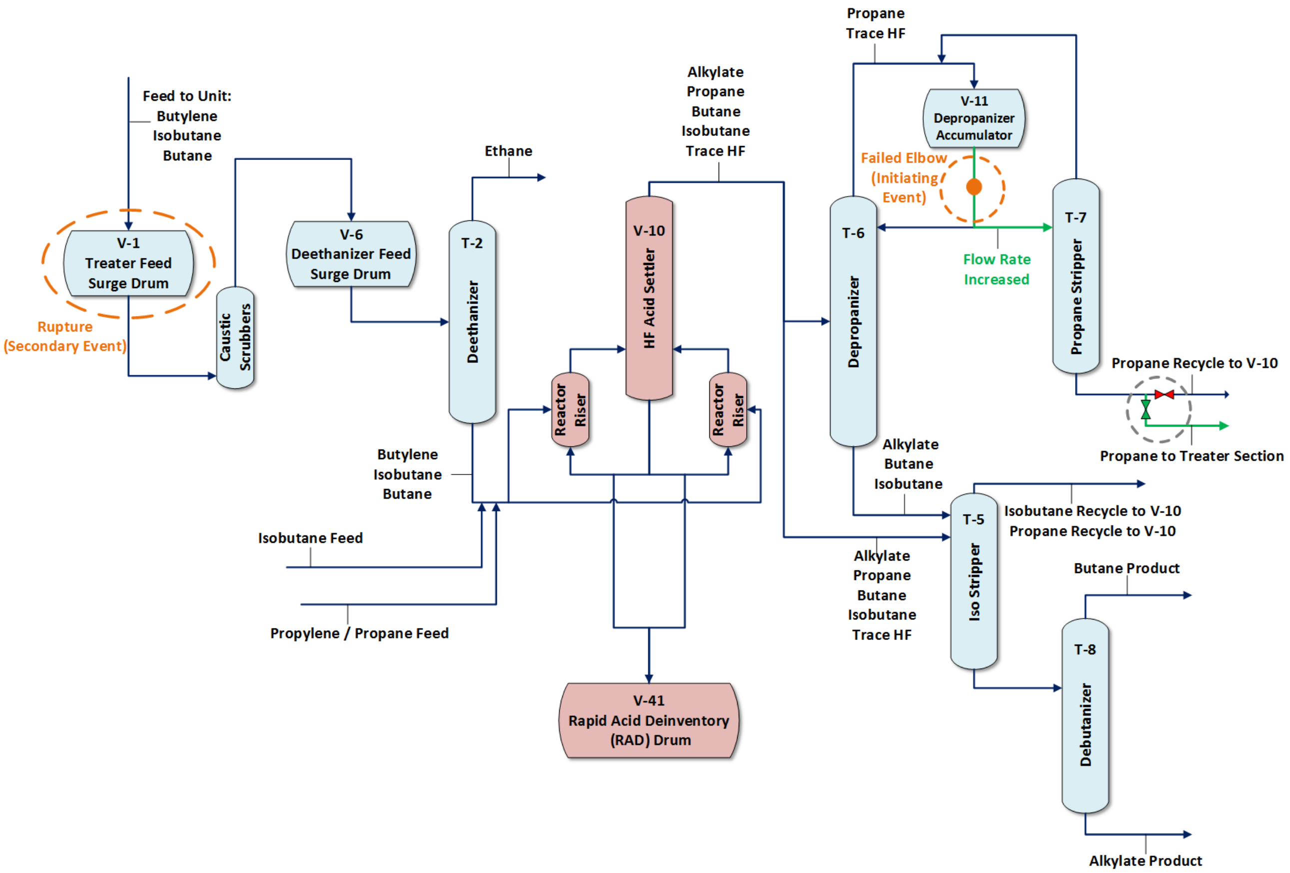

Figure 6. Process changes made immediately before the incident. (Credit: CSB)

About three seconds after the operator increased the T-7 feed to 80 bph, at 4:00:16 a.m. an elbow on the discharge piping of pump P14-B ruptured (**Figure 7**). An incident timeline can be found in **Appendix A**, which includes the process data and operational events preceding and during the incident.

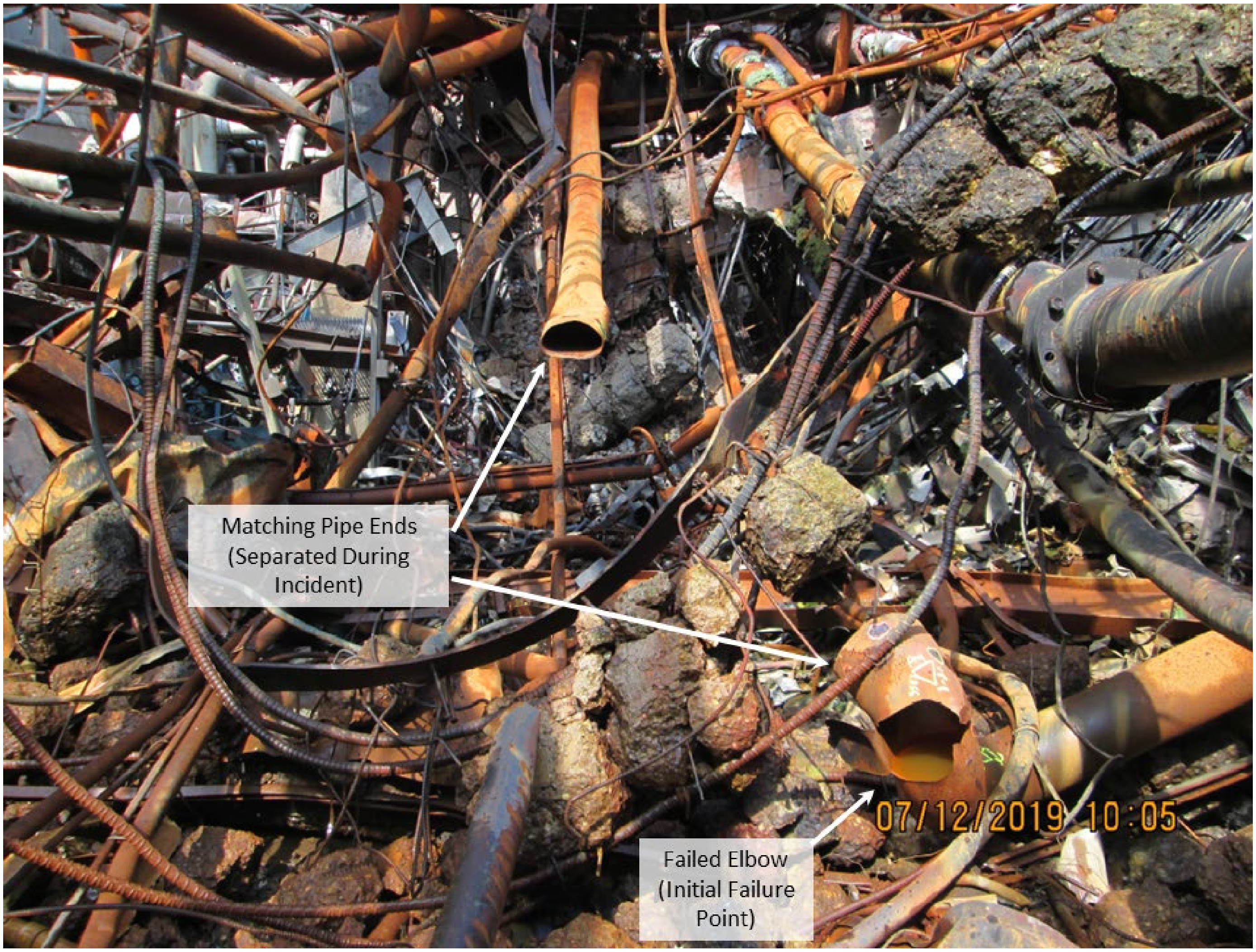

Figure 7. Photo of the ruptured pipe elbow found post-incident. (Credit: PES)

In total, there were three field operators in the alkylation unit at the time of the incident (field operator 1, field operator 2, and field operator 3). Field operators 1 and 2 were inside the HF alkylation unit's blast resistant local control room ("local control room"), and field operator 3 was just outside the local control room. Field operator 3 heard a "bang" and all heard a roaring noise, described by field operator 2 as if something high pressure "let go." Upon hearing the noise, field operator 3 went through the local control room and the old control room and opened the door to the unit (**Figure 8**). Field operator 3 saw a large vapor cloud at least 10 feet high, which had engulfed part of the unit (**Figure 9**). Based on the approximate design composition of process fluid in the piping, this vapor cloud was composed of about 95% propane and 2.5% HF, the balance being other hydrocarbons (see process fluid composition in Section 1.3). Field operator 3 then immediately ran back to the local control room and called the emergency response line to report the release. In **Figure 8** below, the orange circles show the locations of the field operators. The red line depicts the path taken by field operator 3 to see the release. The yellow star is the location of the ruptured pipe elbow, where the release originated.

Figure 8. Locations of field operators at the time of the release. (Credit: Google Earth with annotations by CSB)

Figure 9. Security camera footage of leaking process fluid forming a large ground-hugging vapor cloud that surrounded some sections of the unit. (Credit: PES)

1.4.2 Worker Response

The first indication that the control room operator received of an abnormal process event was alarms on the control screen. The alarms that activated in the control system in the first few seconds were:

- Vibration spike on the offline spare depropanizer reflux pump, P14-B
- Low flow alarm on the propane stripper feed line
- Vibration spike on the running depropanizer reflux pump, P14-A

Soon after the control room operator acknowledged the flow and vibration alarms, the control room operator saw a continuous and rapid succession of alarms from various equipment and sensors in the unit, including hydrofluoric acid-in-air detectors. The control room operator called field operator 3 and stated, “I think I lost flow on P-14.” Field operator 3 responded that it was a bigger event than that, but the control room operator did not understand the response because field operator 3’s voice was garbled over the radio. At 4:01 a.m., field operator 3 called the communications center to report that the unit had had “a major release.” The emergency response team mobilized to go to the unit.

At this point, the three field operators were in the local control room at the unit. Field operator 2 opened the north door (facing away from the unit) and saw that the hydrocarbon vapor cloud had surrounded the local control room. Field operator 2 then shut the door, remaining inside. Field operator 1 then opened the same north door. Shortly after the field operator stepped out the door, at 4:02:06 a.m., the vapor cloud ignited. Field operator 1 was blown back into the local control room and fell to the floor. Flames entered into the doorway of the local control room and then went out.

The control room operator was looking at camera footage of the unit and saw a flash. The cameras viewing the unit then went black immediately, making it difficult to determine what was going on in the unit. At this point, the control room operator knew there was a process problem in the unit but did not know the extent of the incident.

In the unit, field operator 3 opened the north door of the local control room. The field operator could see flames but saw a path to escape. All three field operators ran from the local control room out the north door and escaped from the unit.

Field operator 2 then told the control room operator over the radio to activate the RAD and shut everything down in the unit. At 4:02:37 a.m., the control room operator activated the RAD system, which drained about 339,000 pounds (43,260 U.S. gallons) of hydrofluoric acid from the unit to the RAD drum. This activation of the RAD system occurred two minutes and 21 seconds after the release started, and 31 seconds after ignition. This two minute and 21 second response time was within the PES target operator response time of two minutes and 30 seconds. The control room operator then activated the second safety interlock at 4:03:21 a.m., which shut down acid service pumps and closed remote-operated valves to “safe” the acid section of the unit.

At 4:06 a.m., Incident Command was established by the emergency responders. The responders positioned a fire engine and began opening fixed fire monitors on the south side of the unit. The monitors and fire engine sprayed water into the unit both to cool hydrocarbon-containing equipment and to control the fire.[a]

At 4:12 a.m., the control room operator tried to remotely turn on the water pumps that fed the elevated HF mitigation water cannons, which were designed to reduce airborne HF through vapor suppression,[b,c] but the water pumps did not turn on. The control system communication to the water pumps had failed at 4:02:06 a.m. (time of ignition) and a backup power system in the unit—the uninterruptible power supply (UPS)—also failed nine seconds later at 4:02:15.[d] Field operator 1 tried to walk to the water pumps to manually turn them on, but the operator could not get to the pumps because the fire made that area too hot to enter (**Figure 10**).

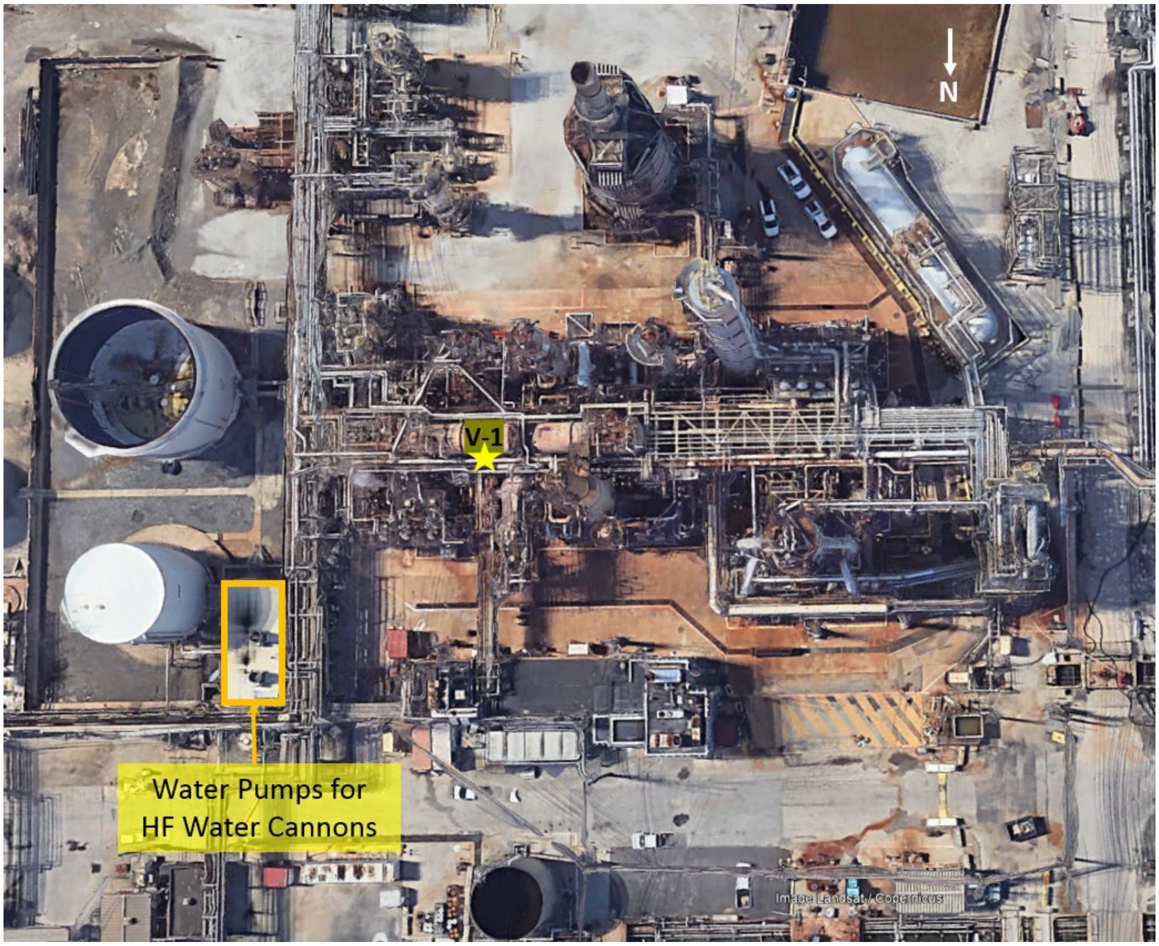

Figure 10. Location of (1) the water pumps that fed the hydrofluoric acid mitigation water cannons (yellow rectangle), and (2) the location of the ruptured elbow from which the process release originated (yellow star). (Credit: Google Earth with annotations by CSB)

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[a] The emergency response team used an underground firewater system to support firefighting efforts.

[b] API RP 751 *Safe Operation of Hydrofluoric Acid Alkylation Units* requires HF alkylation units to be equipped with remotely activated and remotely controlled water mitigation systems [17, p. 35].

[c] "[A]pplying high volumes of water to any release of HF will significantly reduce the airborne fraction of the HF released and provide an effective tool for mitigating the effects of an HF release" [17, p. 37].

[d] The PES alarm data states "UPS Failure" at 4:02:15 a.m.

At 4:15 a.m. an explosion occurred in the unit (**Figure 11**). Based on the fact that the unit was operating normally before the elbow rupture and that there was fire in the unit at the time of this explosion, it appears to have been a secondary event caused by the fire. Another explosion occurred at 4:19 a.m., which also appears to have been an additional secondary event caused by the fire.

Figure 11. Surveillance video stills of explosions in the unit. (Credit: PES)

At 4:22 a.m., a third, and the largest, explosion occurred when the V-1 treater feed surge drum, containing primarily butylene, isobutane, and butane, violently ruptured (**Figure 12** and **Figure 13**). A fragment of the vessel weighing approximately 38,000 pounds flew across the Schuylkill River, and two other fragments, one weighing about 23,000 pounds and the other 15,500 pounds, landed in the PES refinery (**Figure 14**). This was also a secondary event caused by the fire. In **Figure 14**, the fragment 1 photo was taken after the fragment was recovered from the bank of the river and relocated to the PES refinery. The deformation of fragment 1 appears to be consistent with the deformation expected from its impact with the riverbank.

Figure 12. Video still of the V-1 explosion. (Credit: NBC10 Philadelphia [16] with annotations by CSB)

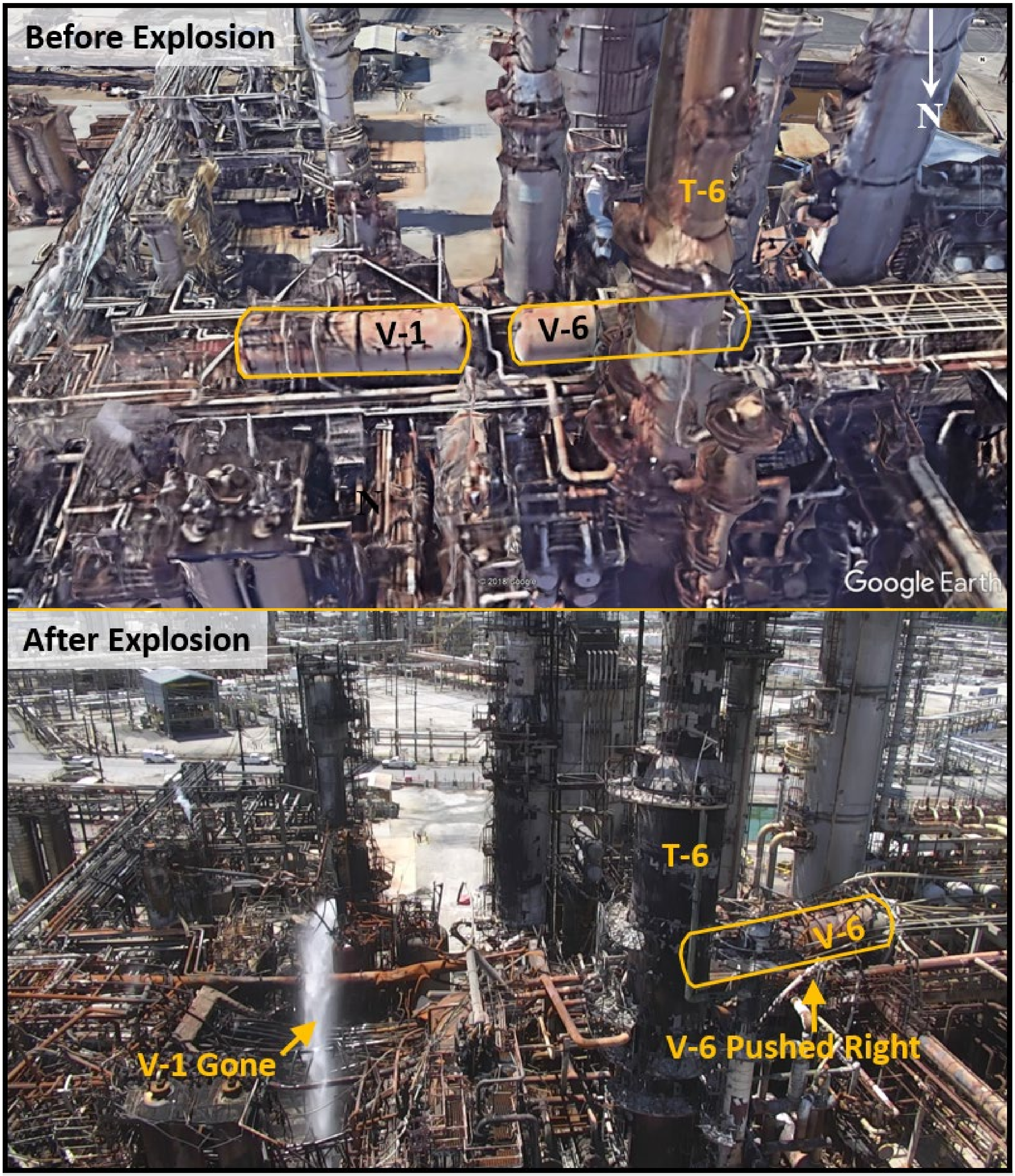

Figure 13. Comparison of the incident scene pre-incident and post-incident. (Top photo credit: Google Earth. Bottom photo credit: PES. annotations by CSB)

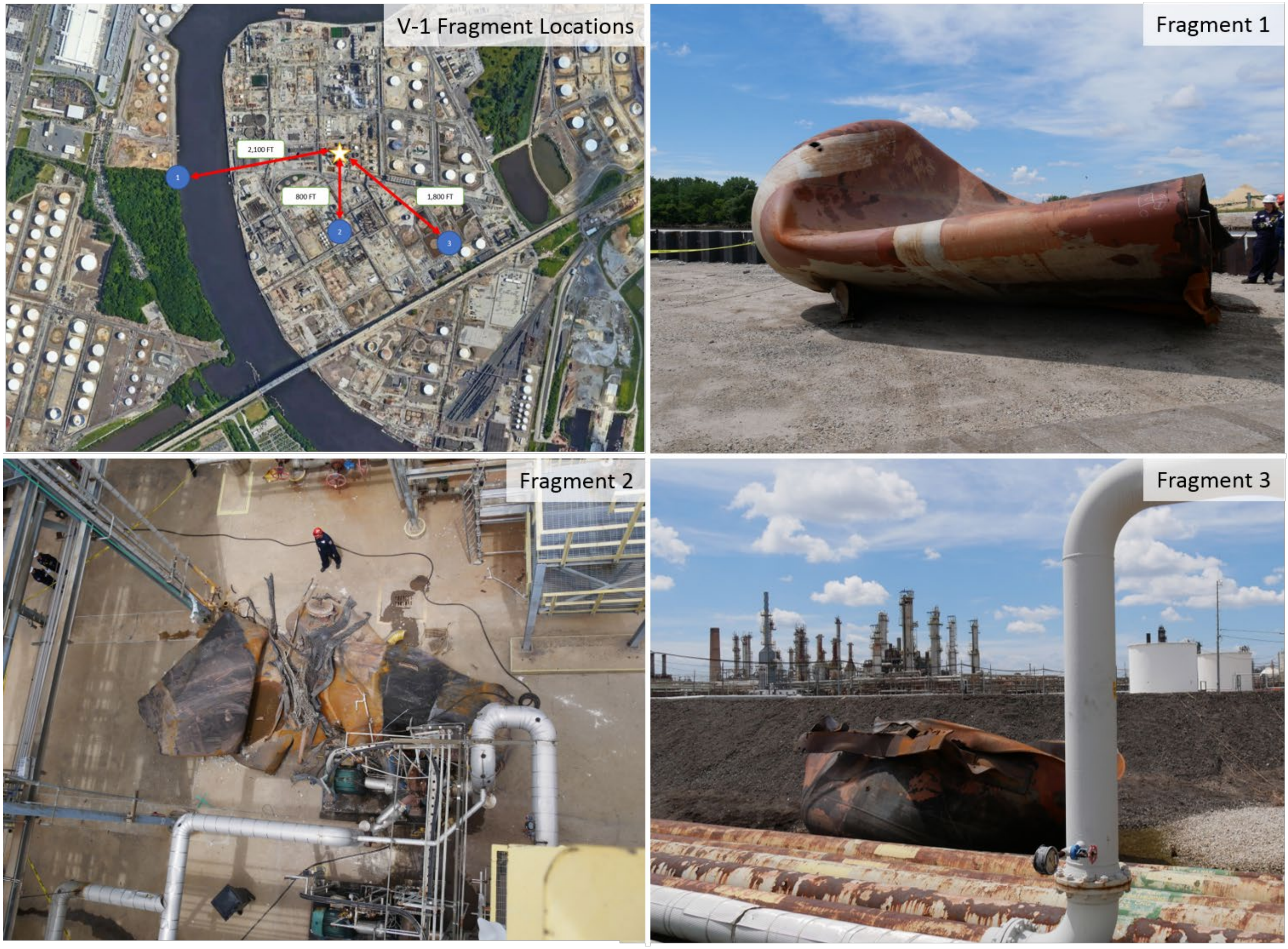

Figure 14. Locations and photos of the post-incident V-1 vessel fragments. (Top left photo credit: Google Earth with annotations by CSB. Credit for other photos: CSB)

At about 4:39 a.m., the alkylation unit shift supervisor entered the alkylation unit in firefighting protective gear called “bunker gear” and manually turned on the water pump (**Figure 10**) that supplied the HF mitigation water cannons, which then allowed the elevated hydrofluoric acid water mitigation cannons to start spraying water into the unit to help suppress the released HF.

Additional firefighters from the PES emergency response team arrived at the unit to continue efforts to put the fire out. Firefighters from the Philadelphia Fire Department and the local Industrial Firefighting Group also came to the scene and assisted in putting out the fire. Refinery operators put on bunker gear and manually closed isolation valves at the battery limits of the unit to stop the flow of hydrocarbons and steam into the unit. The fire was extinguished the following day, on Saturday, June 22, at about 8:30 a.m.

After the incident, PES hired a company that specializes in chemically cleaning alkylation units to develop a process to neutralize the HF contained in the RAD drum. The company reacted the hydrofluoric acid with a base (a material with a high pH), to produce water and a salt. The neutralization process began on Wednesday, August 7, 2019, and was completed on Tuesday, August 27, 2019.

1.4.3 Incident Consequences

Low-concentration HF was present in some of the process piping and equipment that failed during the incident, causing HF to release to the atmosphere. PES estimated that 5,239 pounds of HF released from piping and equipment during the incident. It estimated that 1,968 pounds of the released HF was contained by water spray within the unit and was processed in the refinery wastewater treatment plant, and that 3,271 pounds of HF released to the atmosphere and was not contained by water spray.[a] PES also estimated that about 676,000 pounds of hydrocarbons released during the event, of which an estimated 608,000 pounds were combusted.

In addition, flying projectiles, such as those produced by the V-1 rupture, have the potential to impact and puncture equipment containing potentially hazardous substances.[b] During the incident, projectiles flew up to 2,100 feet from their original location. Fragment 2, shown in **Figure 14**, landed between large equipment containing cumene and other chemicals. Cumene is toxic and flammable,[c] and a major cumene release at the PES refinery could have caused subsequent fire and explosions. In addition, the HF acid settler and the RAD drum were about 140 feet and 200 feet from V-1, respectively, and therefore had the potential to be impacted by flying projectiles.

The HF alkylation unit was severely damaged by the fire and explosions. Marsh JLT Specialty reported that the incident resulted in an estimated property damage loss of $750 million, and the 2020 Marsh JLT Specialty report ranked the PES incident as the third-largest refinery loss to occur worldwide since 1974 [3].

Five workers experienced minor injuries during the incident and response. A Philadelphia firefighter who responded to the PES refinery fire contacted the CSB and reported having experienced breathing problems two days after the fire; the individual has since been treated. The CSB is unaware of any off-site impacts from the HF release.

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[a] In October 2019, the Interagency Modeling and Atmospheric Assessment Center (IMAAC), an entity led by the Federal Emergency Management Agency (FEMA), modeled the June 21, 2019 release of HF from the PES facility. IMAAC concluded that “significant HF [concentrations] was unlikely to have crossed the facility perimeter [as a result of the incident].” The modeling results indicate that the “modeled HF concentrations outside the facility perimeter [as a result of the incident] were low, on the order of a few parts per billion (ppb) or below ….. These levels are considerably below generally accepted health hazards for HF.” IMAAC stated that “significant HF was unlikely to have crossed the facility perimeter … due to the fact that the wind speeds were relatively light and the terrain is not particularly steep, so the gas simply can’t move far enough in 2 minutes [before the ignition] to get off the property.” The CSB emphasizes that a specific set of circumstances contributed to the modeled low HF concentration offsite during the event, but that these specific circumstances will not always be present during releases of HF. It is plausible that during the PES event, a different combination of weather and terrain conditions could have led to a hazardous offsite concentration of HF. In addition, a 1995 study by Quest Consultants found that “the distances to ERPG-3 [an emergency response worst-case planning level] for HF range from 5.2 miles (8.3 km) to 2.2 miles (3.5 km) under worst-case conditions when various mitigation options and compositions are available [in the releases studied] [43].” These results indicate that significantly large off-site regions could be affected by HF releases from HF alkylation units.

[b] For example, explosion debris punctured a steel asphalt tank at the Husky Superior Refinery in 2018, creating a large fire. The Husky Superior Refinery uses hydrofluoric acid in its alkylation unit. The hydrofluoric acid storage tank at the Husky Superior Refinery is located about 150 feet from the equipment that ruptured in the explosion. Neither the hydrofluoric acid tank nor the water curtain equipment surrounding the hydrofluoric acid tank, used to provide water suppression in the event of an acid leak, were impacted by explosion debris, but they were located closer to the ruptured equipment than the asphalt tank that was punctured by the explosion debris [50]. The CSB considers the Husky incident a “near miss” event—it is possible that the hydrofluoric acid equipment could have been punctured by explosion debris. In 2015, a flying projectile came in close proximity to HF settlers at the ExxonMobil Torrance refinery, which was another near-miss HF release event.

[c] Cumene is a colorless liquid with a sharp odor that irritates the eyes, skin, and mucous membranes and in some instances can lead to narcosis or coma. Cumene is immediately dangerous to life or health at 900 ppm. Cumene is also flammable [92].

1.5 Failed Pipe Elbow

The failed pipe elbow was found in the PES HF alkylation unit after the incident. The CSB performed metallurgical testing of the elbow. The testing found that the failed steel elbow had a high nickel and copper content.

The original thickness of the elbow and adjacent piping was 0.322 inch when it was installed in 1973. Thickness measurements of the ruptured elbow show that the piping had a minimum wall thickness of 0.011 inch,[a] which is less than 7% of the PES default retirement thickness of 0.180 inch —the thickness at which PES removes and replaces piping. The ruptured elbow operated in a portion of the alkylation unit containing “trace acid” as defined by API Recommended Practice (RP) 751 *Safe Operation of Hydrofluoric Acid Alkylation Units* [17, p. 47], at temperatures of around 100°F and HF acid concentrations of around 2.5 weight percent.

Figure 15. The ruptured elbow as found in the PES alkylation unit after the incident (left, outlined in red) and the same rupture during metallurgical testing (right).

The elbow that ruptured (shown in **Figure 15**) and the other piping ***components*** within its circuit were installed around 1973. The original specification[b] for this piping required fittings such as elbows to be constructed of “ASTM A234, Grade WPB, weight to match pipe.” ASTM A234 *Standard Specification for Factory-Made Wrought Carbon Steel and Ferritic Alloy Steel Welding Fittings* is an industry standard for pipe fittings, such as elbows. The CSB metallurgical examination of the ruptured elbow confirmed that the pipe elbow was stamped as grade “WPB.” The metallurgical examination also identified a faint stamp behind the more prominent “WPB” stamp, which appears to say “YOLOY” (**Figure 16**). YOLOY is a trade name for a particular low-***alloy*** steel put on the market in 1934 by Youngstown Sheet and Tube Company [18, p. 11]. YOLOY is a different specification

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[a] 0.011 inch is about half the thickness of a credit card.

[b] The specification, called Foster Wheeler Specification F (developed in 1972), was for piping containing cold HF acid and hydrocarbon mixtures.

of steel from ASTM A234 WPB, and its composition matches the specification ASTM A234 WPR, which was established in 1980, after the elbow's installation [19, p. 7].[a]

Figure 16. Photo of specification stamps on the failed elbow. "YOLOY," highlighted with red, is faintly visible behind the "WPB" stamp.

1.6 PES Inspection Program

Piping systems are comprised of many different components, including straight piping, fittings, valves, and flanges. Refineries then classify sections of piping into circuits, which are piping sections that are exposed to similar process conditions, are made of the same material of construction, and are subject to the same expected damage mechanisms. Within each piping circuit, refineries specify ***condition monitoring locations*** (CMLs), which are inspection points to monitor for damage mechanisms such as corrosion, for example by measuring the thickness of the pipe wall. In piping circuits subject to uniform corrosion, the industry piping code API 570 *Piping Inspection Code: In-service Inspection, Rating, Repair and Alteration of Piping Systems* allows for fewer CMLs, and for circuits susceptible to localized corrosion, more CMLs are needed [20].

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[a] ASTM A234 WPR (1980) specifies the following material composition (in percentages): 0.20 (max) Carbon, 0.40-1.05 Manganese, 0.045 (max) Phosphorus, 0.050 (max) Sulfur, 1.60-2.24 Nickel, and 0.75 – 1.25 Copper.

When CMLs were first specified for the PES refinery HF alkylation unit in 1973 (at that time, the refinery was owned by Gulf Oil), the inspection group based the inspection program on the piping being susceptible to a uniform corrosion mechanism and selected representative CMLs to monitor corrosion of the piping. Since 1973, the various refinery owners added additional CMLs. In 2002, the piping circuit containing the failed elbow contained 41 CMLs, and by 2019 the circuit contained 141 CMLs. **Figure 17** shows the portion of the piping circuit that contained the failed elbow, indicating CML locations and the most recent thickness measurements. There was not a CML on the elbow that failed.

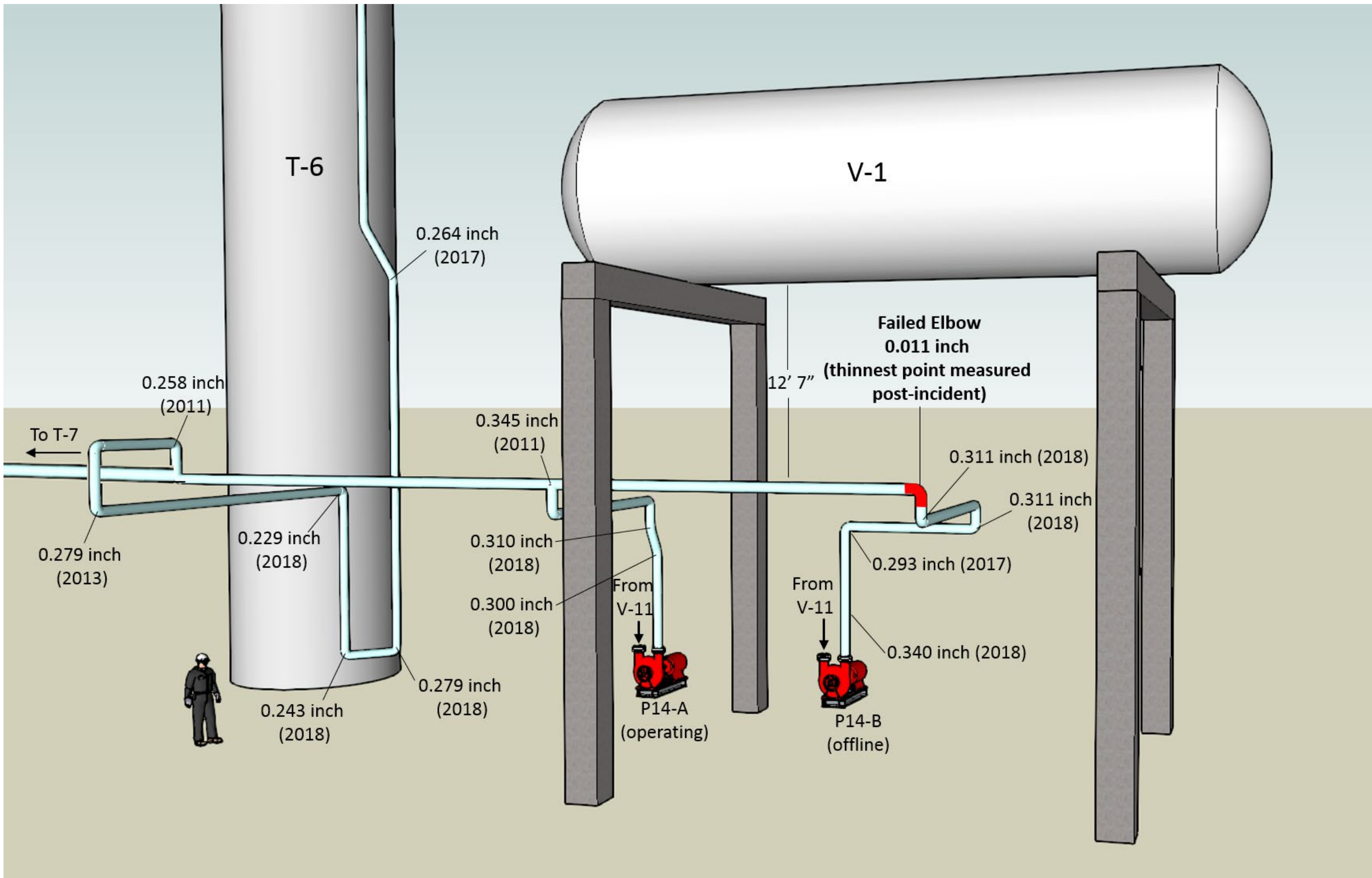

Figure 17. Model of the piping circuit containing the ruptured elbow, showing the most recent thickness measurements at designated Condition Monitoring Locations (CMLs). (Credit: CSB)

1.7 Damage to Water Spray HF Mitigation System

The PES HF alkylation unit was equipped with a water spray mitigation system. This system was a critical safeguard in the event of an HF release, as it was designed to reduce airborne HF through vapor suppression[a, b] to prevent it from traveling offsite. During the incident, this critical safeguard was damaged. Plant data show that the control system communication to the water pumps had failed at 4:02:06 a.m. (time of ignition) and a backup power system in the unit—the uninterruptible power supply (UPS)—also failed nine seconds later, at

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[a] API RP 751 *Safe Operation of Hydrofluoric Acid Alkylation Units* requires HF alkylation units to be equipped with remotely activated and remotely controlled water mitigation systems [17, p. 35].

[b] "[A]pplying high volumes of water to any release of HF will significantly reduce the airborne fraction of the HF released and provide an effective tool for mitigating the effects of an HF release" [17, p. 37].

4:02:15. When the control room operator tried to turn on the water pumps that fed the elevated HF mitigation water cannons at 4:12 a.m., the water pumps did not turn on. The system had to be manually turned on in the field by a shift supervisor wearing firefighting protective gear, which occurred at about 4:39 a.m.

1.8 V-1 Explosion and Observed Damage to V-1 Fragments

During the incident, at 4:22 a.m., the V-1 treater feed surge drum, containing primarily butylene, isobutane, and butane, violently ruptured. A fragment of the vessel weighing approximately 38,000 pounds flew across the Schuylkill River, and two other fragments, one weighing about 23,000 pounds and the other 15,500 pounds, landed in the PES refinery. After the incident, CSB investigators analyzed the V-1 fragments. The investigators observed thinning of the bottom portion of the V-1 fragments, as shown in **Figure 18**. Fragment 2 had been cut into two pieces before being relocated to the location shown in **Figure 18**. The observed thinning of the V-1 vessel is consistent with what would be expected from a jet flame impinging on the vessel from the ruptured elbow, as shown in **Figure 19**. A jet flame (or jet fire) is a "pressurized stream of combustible gas or atomized liquid … that is burning. […] A jet fire is usually [] localized, but very destructive to anything close to it [21, pp. 87-88]." The pipe that ruptured was at a pressure of about 380 psig, which supplied the pressurized gas fueling the jet flame that impinged on the V-1 vessel (**Figure 19**).

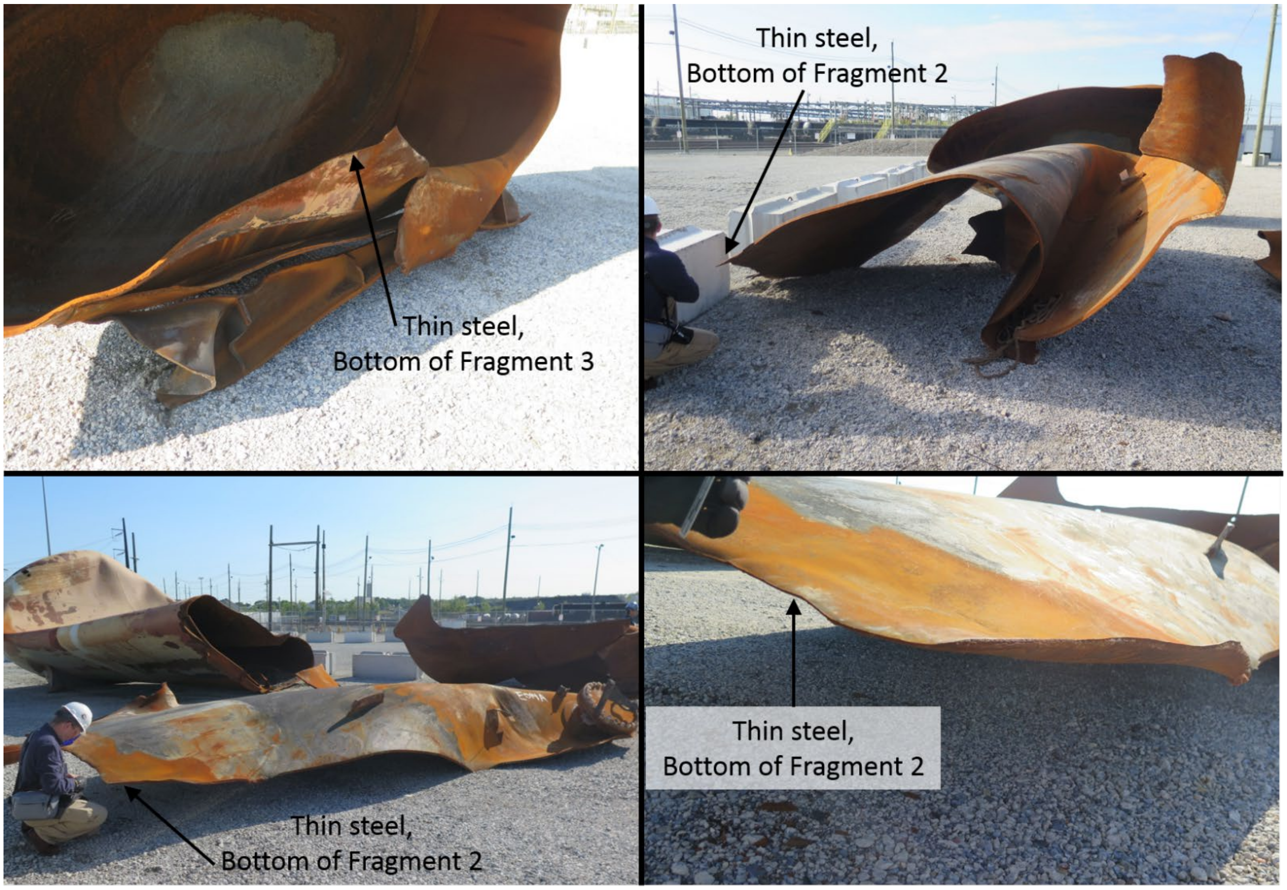

Figure 18. Photos of recovered fragments of V-1. (Credit: CSB)

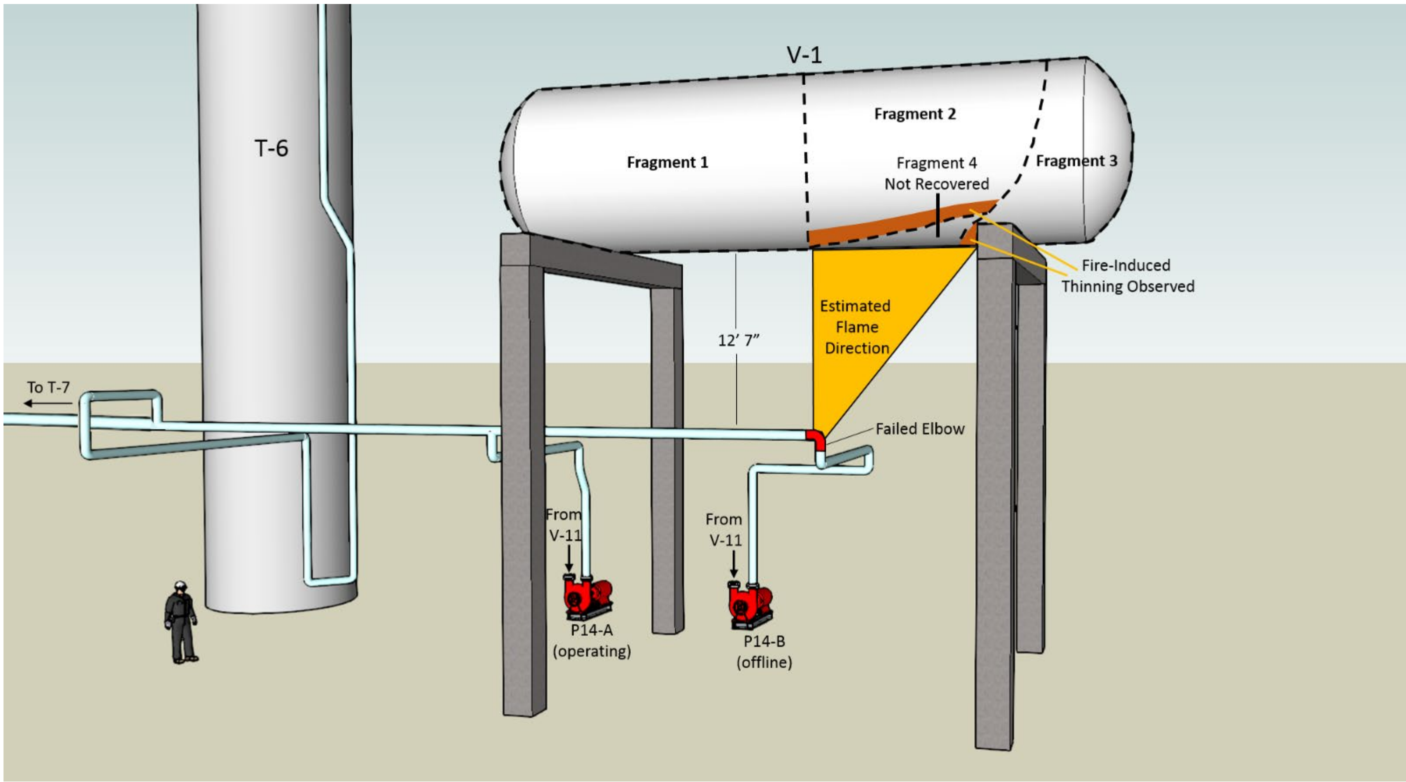

Figure 19. Locations of observed V-1 thinning, and depiction of the estimated flame size originating from the failed elbow, which impinged on the bottom of V-1. (Credit: CSB)

At the start of the incident, V-1 was about 53% liquid-full of primarily butylene, isobutane, and butane, and the internal pressure was 37 psig.[a] The V-1 pressure indicator's last reading was at 4:02:00 a.m., and then failed at about the time of ignition. The level indicator's last reading was at 4:02:45 a.m. before failing during the fire, last indicating that V-1 was about 25% liquid-full, but this reading may not be reliable due to the fire's effect on the instrumentation.[b] The V-1 pressure and level data are shown in **Figure 20**. V-1 was not equipped with thermal insulation for protection from fire.

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[a] The pressure relief valve for the V-1 surge drum was set to open at an internal V-1 pressure of 155 psig, designed for an external fire overpressure scenario.

[b] The last liquid level reading measured in V-1 was 25.5 %, at 4:02:45 a.m. This value is not a reliable indication of the liquid level, however, because the data shows the liquid level dropped from about 52% full to 25.5% full in about 15 seconds, which is unlikely. The ongoing fire likely affected this measurement to read an incorrect value.

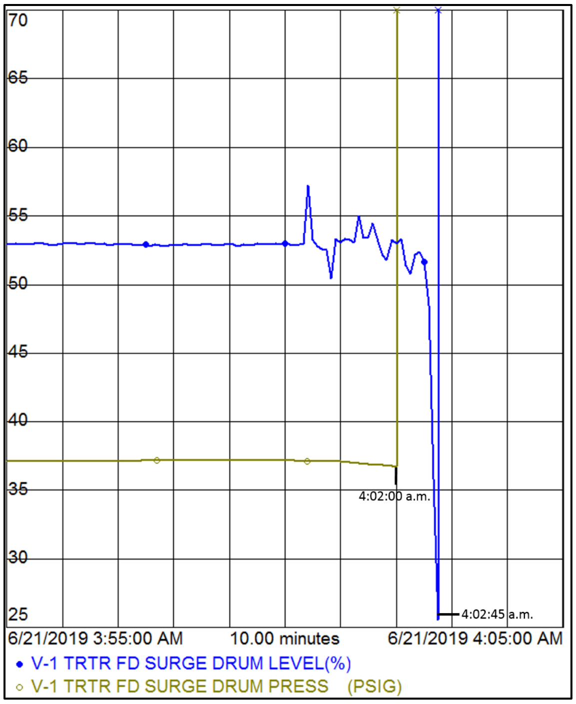

Figure 20. V-1 internal pressure and level before and during the incident. (Credit: CSB)

1.9 Weather at Time of Incident

At 3:54 a.m. on June 21, 2019 in Philadelphia, Pennsylvania, it was 72°F, there was an 8 mile per hour southwesterly wind, and it was mostly cloudy [22].

1.10 Similar Facilities in the United States

Of the 155 U.S. petroleum refineries currently in operation as of the date of this report, 46 operate HF alkylation units.

1.11 Description of Surrounding Area

Figure 21 shows the PES refinery and depicts the primarily urban area within one, three, and five miles[a] of the refinery boundary. Summarized demographic data for the area within one mile of the PES refinery boundary is shown below in **Figure 21**. More detailed demographic information can be found in **Appendix D**.

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[a] A 1995 study by Quest Consultants found that "the distances to ERPG-3 for HF range from 5.2 miles (8.3 km) to 2.2 miles (3.5 km) under worst-case conditions when various mitigation options and compositions are available [in the releases studied] [43]." ERPG-3 refers to the maximum airborne concentration below which nearly all individuals could be exposed for up to one hour without experiencing or developing life-threatening health effects. ERPG-3 is a worst-case planning level. Exposure to concentrations above the ERPG-3 level will be lethal to some members of the community [101].

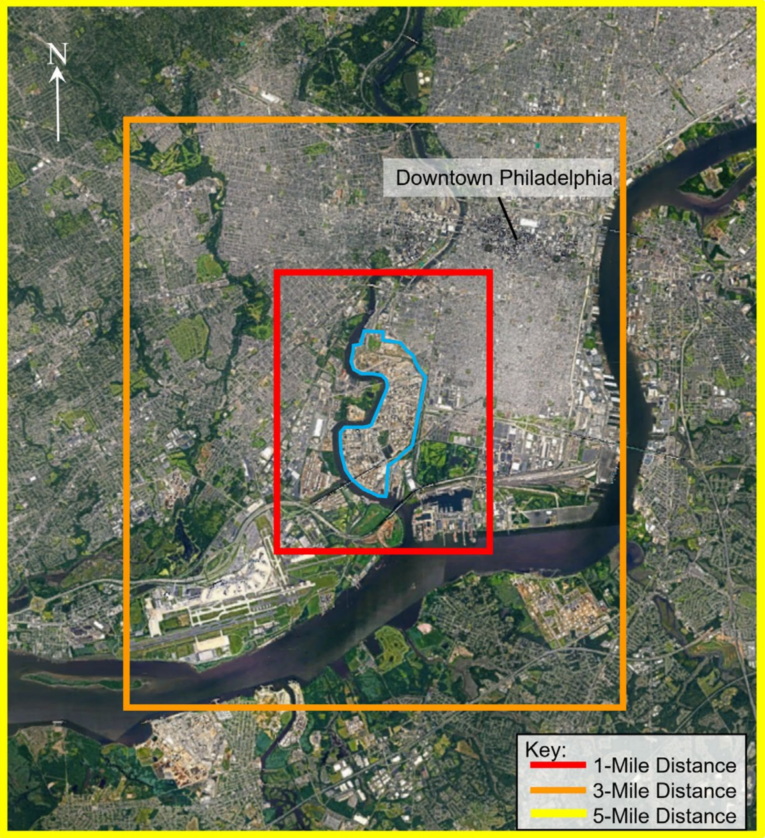

Figure 21. Overhead satellite image of the PES refinery (blue) and the surrounding area. (Credit: Google, annotated by CSB)

Table 2. Summarized Demographic Data for Area Within One Mile of PES Refinery Boundary

Population	Race and Ethnicity	Per Capita Income	Percent Poverty	Number of Housing Units	Types of Housing Units
117,307	• 49% Black • 34% White • 9% Asian • 5% Hispanic • 2% Two+ • < 1% Native • < 1% Islander	$30,962[a]	20%	53,420	• 79% Single Unit • 21% Multi-Unit

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[a] Census Reporter reports that Philadelphia's overall Per Capita Income is $29,644 [107]. The Census Bureau reports that the overall Per Capita Income for the United States $39,052 [108].

2 Incident Analysis

This section discusses the following safety issues the CSB identified in its investigation.

- **Mechanical Integrity.** A steel pipe elbow containing high concentrations of nickel and copper had become severely thin from HF corrosion and ruptured to initiate the incident. Carbon steel with high nickel and copper content is known within the industry to corrode faster from contact with HF than carbon steel with lower nickel and copper content. While the PES pipe elbow had become severely thin from corrosion, adjacent piping components lower in nickel and copper content had not corroded as quickly and were not thin. At the time of the incident, published industry standards and recommended practices did not require refineries to conduct 100% component inspection of carbon steel piping in HF service to identify any piping components corroding and thinning faster than others, which as shown by this incident, can lead to hazardous loss of containment events. After the incident, API RP 751 *Safe Operation of Hydrofluoric Acid Alkylation Units* was revised to include a new requirement for refiners to develop a special emphasis inspection program to inspect all individual carbon steel piping components and welds in identified HF alkylation corrosion zones to identify areas of accelerated corrosion. This new requirement should help prevent future failures of steel piping with high nickel and copper content in HF alkylation units. (Section 2.1)

- **Verifying Safety of Equipment after Changes to RAGAGEP.** The seminal research presented in the 2003 NACE paper 03651 *Specification for Carbon Steel Materials for Hydrofluoric Acid Alkylation Units* directly led to changes in industry guidance quantifying the levels of nickel and copper in steel that could be considered safe for use in HF alkylation units. However, prior to the incident, API RP 751, Sunoco, and PES did not effectively respond to these advancements in industry knowledge by ensuring the safety of existing facilities through requiring all carbon steel piping circuit components to be inspected. Both the OSHA PSM and EPA RMP regulations require companies to determine that their equipment is designed, maintained, inspected, tested, and operating in a safe manner when new safety information is discovered and published in Recognized and Generally Accepted Good Engineering Practice (RAGAGEP) documents. To prevent catastrophic incidents, companies and industry trade groups must take swift action to ensure process safety when new knowledge on hazards is published. These actions must include ensuring that facilities built before the new knowledge was published are still safe to operate. (Section 2.2)

- **Remotely Operated Emergency Isolation Valves.** Based on the thinning of the V-1 vessel steel, the CSB concluded that a jet flame from the ruptured elbow impinged upon the bottom of the V-1 vessel, causing the steel to stretch and thin until the vessel ruptured. The large hydrocarbon sources downstream of the failed elbow could not be remotely or automatically isolated, and therefore PES was unable to stop the jet flame in a timely manner to prevent the V-1 vessel rupture. (Section 2.3)

- **Safeguard Reliability in HF Alkylation Units.** The PES water spray HF mitigation system was damaged during the incident and could not be remotely activated. The damage to the PES water spray HF mitigation system demonstrates that “active” safeguards—or safeguards that require a person or technology to trigger their activation—have the potential to fail in major incidents involving fires and explosions. (Section 2.4)

- **Inherently Safer Design.** Technologies are being developed that could be a safer alternative to HF and sulfuric acid alkylation, including composite ionic liquid catalyst alkylation technology, solid acid catalyst alkylation technology, and the new ionic liquid acid catalyst alkylation technology developed by Chevron, which is now operating at commercial scale at Chevron's Salt Lake City refinery. While EPA has previously issued requirements for companies to evaluate inherently safer technologies, there is currently no Federal regulatory requirement for petroleum refineries to evaluate inherently safer design strategies to reduce the risk of serious accidental releases. (Section 2.5)

The graphical causal analysis (AcciMap) is in **Appendix B**.

2.1 Mechanical Integrity

The CSB metallurgical testing[a] determined that the PES pipe elbow ruptured because it had experienced extensive corrosion that reduced its wall thickness. The ruptured elbow is shown in **Figure 22**. The testing found that the failed steel elbow had a high nickel and copper content, which the industry has found can cause increased corrosion rates in piping in HF service. The failed elbow had corroded at a faster rate in comparison to adjacent piping ***components*** with trace concentrations of nickel and copper.

The original thickness of this piping was 0.322 inch when it was installed in 1973. Thickness measurements of the ruptured elbow show that the piping had a minimum wall thickness of 0.011 inch,[b] which is less than 7% of the PES default retirement thickness of 0.180 inch —the thickness at which PES removes and replaces piping. The ruptured elbow operated at temperatures of around 100°F and HF acid concentrations of around 2.5 weight percent.

Figure 22. The ruptured elbow as found in the PES alkylation unit after the incident (left, outlined in red) and the same rupture during metallurgical testing (right).

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[a] The metallurgical testing report is in **Appendix C**.

[b] 0.011 inch is about half the thickness of a credit card.

2.1.1 Faster Hydrofluoric Acid Corrosion of Steel with High Nickel and Copper Content

Carbon steel is commonly used in HF alkylation units and is known to be susceptible to hydrofluoric acid corrosion [17, p. 16]. In process piping containing some amount of hydrofluoric acid, hydrogen fluoride reacts with iron in the steel to produce iron fluoride. The iron fluoride forms as a film or scale that coats the inside surface of piping and equipment, which acts to protect the steel and slow further corrosion [17, p. 16]. Over time, the corrosion gradually reduces the thickness of equipment and piping. As long as the protective iron fluoride scale remains intact on the inside surface of piping and equipment, corrosion rates of carbon steel piping are typically low [17, p. 47].

However, industry studies have found that high concentrations of copper, nickel, or chromium within the steel, which the literature refers to as ***residual elements*** (REs), can accelerate the corrosion rates of carbon steel exposed to hydrofluoric acid. These studies have found that the iron fluoride film that forms on high-RE steel is less protective than the film that forms on lower-RE steel, likely contributing to the faster corrosion rates experienced in high-RE steel [23, pp. 67-73], [24, p. 7], [25, p. 6], [26].

NACE[a] paper 03651 titled *Specification for Carbon Steel Materials for Hydrofluoric Acid Alkylation Units* (2003) states that to avoid faster corrosion rates in carbon steel in HF service, the recommended composition limits for REs and carbon in base metal are [26, p. 9]:

$$\text{Carbon (C)} > 0.18 \text{ wt.\%}$$

$$\text{Copper (Cu)} + \text{Nickel (Ni)} < 0.15 \text{ wt.\%}$$

As shown in **Table 3** below, post-incident testing found that the ruptured elbow contained nickel and copper content that far exceeded the 2003 NACE technical paper's recommended composition limits, while adjacent piping components did meet these recommended limits and were not thin. The piping locations relative to the ruptured elbow are shown in **Figure 23**.

The CSB concludes that the PES pipe elbow ruptured due to extensive HF corrosion that reduced its wall thickness. The higher concentration of nickel and copper in the PES pipe elbow caused the elbow to corrode faster than other components within the piping circuit. The CSB also concludes that the ruptured elbow's metallurgical composition did not meet the composition limits recommended by NACE paper 03651, which were later adopted by ASTM as supplementary requirements (see Section 2.1.4) and recommended by API RP 751 (see Section 2.1.5). Had the elbow met the composition recommendations, the elbow likely would not have corroded at a significantly faster rate than adjacent piping components and likely would not have failed from excessive thinning.

The PES refinery has shut down and is no longer performing refining operations, so therefore the CSB is not issuing recommendations to PES to correct this metallurgical issue in piping within the HF alkylation unit. The

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[a] NACE was established in 1943, as the "National Association of Corrosion Engineers." It is now an international organization and is known as NACE International [93].

sections below for this safety issue discuss findings and a recommendation to help ensure that this type of metallurgical failure does not occur in HF alkylation units in other refineries.

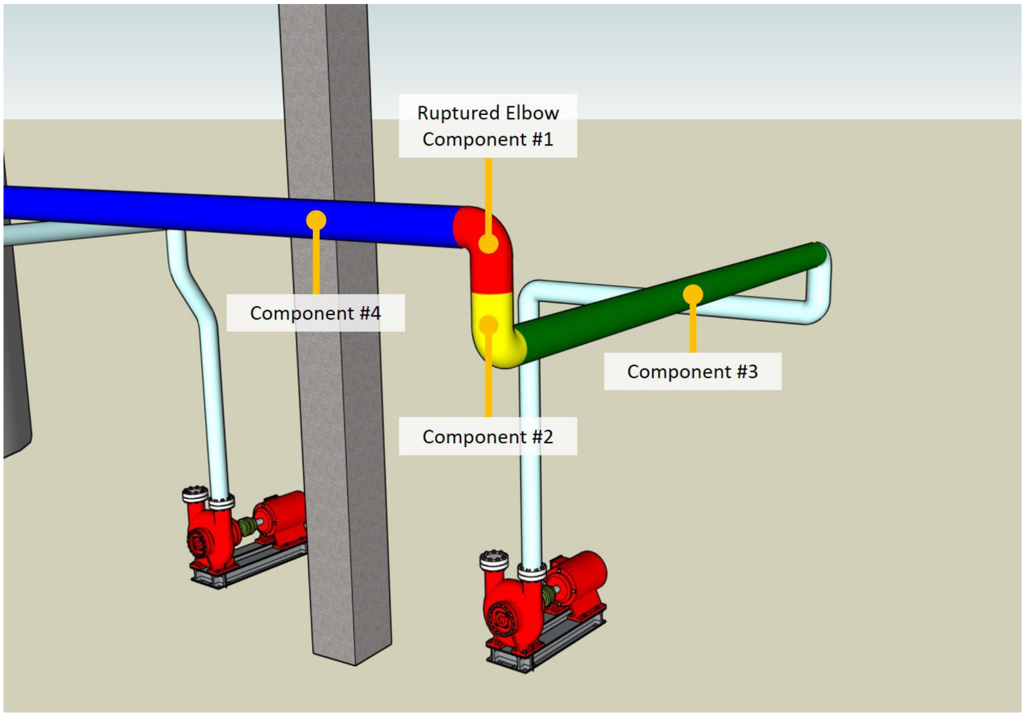

Figure 23. Depiction of the location of the four piping segments discussed in this report. (Credit: CSB).

Table 3. Chemical compositions and wall thicknesses of the ruptured elbow and adjacent piping. Wall thickness measurements are the average values based on several measurements.

Element	(Ruptured Elbow) Component 1 (wt%)	Component 2 (wt%)	Component 3 (wt%)	Component 4 (wt%)
Carbon (C)	0.14	0.24	0.25	0.25
Nickel (Ni)	1.74	≤0.01	<0.01	≤0.01
Copper (Cu)	0.84	0.02	<0.01	<0.01
Cu +Ni	2.58	0.03	0.02	0.02

Average Wall Thickness (inches)	0.011 (Thinnest Measured) 0.113 (Average)	0.306[a]	0.307[b]	0.287[b]

[a] Component 1 (ruptured elbow) and Component 2 are piping elbows. The reported thickness is the average thickness on the outside radius of the bend.

[b] Measured along the circumference of the pipe.

2.1.2 Double Stamping of Elbow as Two Different Steel Specifications

The elbow that ruptured (shown in **Figure 15**) and the other piping components within its circuit were installed around 1973. The original specification[a] for this piping required fittings such as elbows to be constructed of "ASTM A234, Grade WPB, weight to match pipe." ASTM A234 *Standard Specification for Factory-Made Wrought Carbon Steel and Ferritic Alloy Steel Welding Fittings* is an industry standard for pipe fittings, such as elbows. The CSB metallurgical examination of the ruptured elbow confirmed that the pipe elbow was stamped as grade "WPB." The metallurgical examination also identified a faint stamp behind the more prominent "WPB" stamp, which appears to say "YOLOY" (**Figure 24**). YOLOY is a trade name for a particular low-***alloy*** steel put on the market in 1934 by Youngstown Sheet and Tube Company [18, p. 11]. YOLOY is a different specification of steel from ASTM A234 WPB, and its composition matches the specification ASTM A234 WPR, which was established in 1980, after the elbow's installation [19, p. 7].[b]

Table 4 provides the metallurgical composition of the ruptured elbow and the adjacent piping components, and the composition requirements of YOLOY, ASTM A234 WPB (1965), and ASTM A234 WPB (1995–present). The nickel and copper content of the ruptured elbow is much higher than the nickel and copper content of the adjacent components and meets the composition requirements of the YOLOY specification. The elevated nickel and copper content present in the failed elbow indicates that those elements were likely added intentionally to meet the YOLOY specification and were not residual elements.[c] ASTM A234 WPB (1965) did not specify limits on nickel or copper content. Metallurgists the CSB consulted communicated that elements, in this case nickel and copper, could not be intentionally added to the steel and have the material still meet the requirements of a standard in which content requirements for those elements are unspecified. In this view, the re-stamping of a YOLOY component to WPB should not have occurred. However, the 1965 ASTM A234 standard did not explicitly prohibit the addition of unspecified elements to piping component steel. Such language was added in subsequent editions of the standard, as follows:

1. ASTM A234, 1980: "A starting material specification that specifically requires the addition of any element beyond those listed for the materials [in this standard] for the applicable grade of material is not permitted. This does not preclude the use of deoxidizers or the judicious use of elements for grain size control" [19, p. 2].
2. ASTM A234, 1996: "The steel shall not contain any unspecified elements for the ordered grade to the extent that it conforms to the requirements of another grade for which that element is a specified element having a required minimum content" [27, p. 4].

The CSB concludes the following:

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[a] The specification, called Foster Wheeler Specification F (developed in 1972), was for piping containing cold HF acid and hydrocarbon mixtures.

[b] ASTM A234 WPR (1980) specifies the following material composition (in percentages): 0.20 (max) Carbon, 0.40-1.05 Manganese, 0.045 (max) Phosphorus, 0.050 (max) Sulfur, 1.60-2.24 Nickel, and 0.75 – 1.25 Copper.

[c] *Glossary of Metallurgical Terms and Engineering Tables* (1979) defines Residual Elements as "elements present in an alloy in small quantities, but not added intentionally" [94].

- Before the elbow's installation into the HF alkylation unit around 1973, the failed elbow was initially manufactured and stamped as "YOLOY" steel and was later improperly stamped as ASTM A234 WPB steel, a different specification from YOLOY.

- The applicable 1965 edition of ASTM A234 *Standard Specification for Factory-Made Wrought Carbon Steel and Ferritic Alloy Steel Welding Fittings* did not explicitly prohibit the addition of unspecified elements to steel, such as those specified in the YOLOY composition requirements. The lack of prohibitions on the addition of unspecified elements, such as nickel and copper, may have contributed to the double stamping of the failed elbow as both YOLOY and ASTM A234 WPB.

- After the elbow's installation around 1973, language changes to ASTM A234 were made in 1980 and 1996 that make it clear that YOLOY steel cannot be labeled or restamped as ASTM A234 WPB steel. These language changes should prevent future instances of this improper material substitution.

Figure 24. Photo of specification stamps on the failed elbow. "YOLOY," highlighted with red, is faintly visible behind the "WPB" stamp.

Table 4. Chemical compositions of the ruptured elbow and the adjacent piping, and YOLOY and ASTM A234 WPB composition requirements.

Element	Ruptured Elbow Component 1 (wt%)	Component 2 (wt%)	Component 3 (wt%)	Component 4 (wt%)	YOLOY	ASTM A234 WPB (1965) / ASTM A106 B (1972)	ASTM A234 WPB (1995-Present)
Carbon (C)	0.14	0.24	0.25	0.25	0.25 (max)	0.30 (max)	0.30 (max)
Manganese (Mn)	0.80	0.90	0.58	0.57	All other elements are “as normally found in mild steel” [18, p. 13].	0.29 – 1.06	0.29 – 1.06
Phosphorus (P)	≤0.005	0.012	0.007	0.007		0.048 (max)	0.050 (max)
Sulfur (S)	0.010	0.016	0.018	0.015		0.058 (max)	0.058 (max)
Silicon (Si)	0.10	0.24	0.18	0.17		0.10 (min)	0.10 (min)
Nickel (Ni)	**1.74**	≤0.01	<0.01	≤0.01	**2.0 (max)**	**No Specification**	**0.40 (max)**
Copper (Cu)	**0.84**	0.02	<0.01	<0.01	**1.0 (max)**	**No Specification**	**0.40 (max)**

2.1.3 Other Historical Failures of Piping with High Nickel and Copper Content in HF Service

In 1993, a paper was published titled *Effect of Residual Copper, Nickel, and Chromium on the Corrosion Resistance of Carbon Steel in Hydrofluoric Acid Alkylation Service* by H. Hashim and W. Valerioti of Phillips Petroleum Company [24]. The paper analyzed field failures of piping in HF service with elevated copper, nickel, and chromium content over a ten-year period, beginning with the first documented field failure in 1980. These failures are described below:

1. First documented field failure, 1980.

   Components: A six-inch diameter pipe spool consisting of an elbow, long straight piece, and tee. The straight component corroded and failed.

   Service Life: 4 years

   Process: Depropanizer feed consisting of propane, butane, alkylate, isobutane, anhydrous hydrofluoric acid. Temperature: 130°F, Pressure: 300 psig.

   “Examination showed uniform corrosion of the straight pipe, while the adjacent piping showed minimal corrosion loss […]. The straight pipe section was identified as low-temperature steel similar to ASTM A333 Gr. 9. The elbow and tee were plain carbon steel […].”

2. Components: Corroded 24-inch ASTM A105 carbon steel weld neck flange.

   Service Life: 8.5 years

   Process: Vertical outlet piping from main fractionator inner heater reboiler. The piping was insulated except for the flange. The stream contained normal butane, alkylate, some iso-butane, and a small quantity of HF acid. Temperature: 260°F, Pressure: 250 psig.

   "The inside surface of the flange was severely pitted […]. The flange also experienced uniform metal thinning. The adjacent pipe and weld were relatively unaffected. […] Chemical analysis showed the flange met ASTM A 105 requirements, but individual and total copper, nickel, and chromium content(s) were considerably higher than the adjacent pipe […]. "

3. Components: Corroded 3-inch pipe section from acid rerun column overhead line consisting of swaged elbow, straight pipe, and flange.

   Service Life: 18 months

   Process: Alkylate, propane, butane, and iso-butane, saturated with HF acid. Temperature: 130°F, Pressure: 150 psig.

   "The flange and pipe elbow were both severely thinned due to uniform corrosion. […] The compositions were basically the same, except for nickel, copper, and chromium. While meeting the material specification requirements, the residual elements were significantly higher in the corroded pieces versus the non-corroded pipe sections."

4. Components: Ruptured 4-inch diameter pipe from depropanizer charge line.

   Service Life: 9 years

   Process: Depropanizer feed consisting of iso-butane, C5+, propane, normal butane, HF acid, and water. Temperature: 160°F, Pressure: 250 psig.

   "[S]evere metal loss was observed compared to the adjacent pipe sections and butt welds [...]. "

5. Components: Selective corrosion of 3-inch diameter ASTM A234 WPB 90 degree elbow.

   Service life: <1 year

   Process: Iso-butane and hydrofluoric acid. Temperature: 200°F to 250°F, Pressure: 160 psig.

   "In-situ flash radiography showed higher corrosion metal loss in the 90 degree elbow versus adjacent piping […]. In this case, corrosion is expected due to the high operating temperature for carbon steel in HF acid service. In addition, fluid impingement effects certainly were a contributing factor to elbow corrosion, particularly on the outside bend radius. However, it was reported that other 90 degree ASTM A234 carbon steel elbows in this piping system did not show significant metal loss."

The authors also provided possible reasons for the observed differences in steel composition that led to differences in corrosion rates:

> Often [the primary carbon steel grades used in HF alkylation] are specified with controlled chemistry and special steel making practices to avoid welding problems or hydrogen embrittlement in service. Unfortunately, these controlled steels are not always available "off-the-shelf" and have to be bought to ASTM requirements only. Sometimes, the carbon and manganese are restricted, but other elements such as chromium, nickel, or copper are not analyzed or not reported on the material test report (MTR). Substitution with a higher alloy (by a well-intended supplier!) is also sometimes made [24, p. 2].
>
> There are reports of several instances whereby a low alloy steel was substituted for carbon steel due to availability or an occasion where it was thought that the substitution was an upgrade over the carbon steel [24, p. 6].
>
> The increase in [copper, nickel, and chromium] residual elements is the result of expanded use of scrap in steel making as more mini steel mills have come into existence utilizing 100% scrap charge in their electric furnaces and a general decrease in pig iron production for making virgin steel [24, p. 2].

In summary, there is technical literature within the industry documenting that steel piping with high nickel and copper content has experienced faster corrosion rates and failed due to HF corrosion.

2.1.4 Changes to ASTM Piping Specifications

The 1965 version of ASTM A234 *Standard Specification for Factory-Made Wrought Carbon Steel and Ferritic Alloy Steel Welding Fittings*, the applicable version at the time of the pipe installation, required that Grade WPB pipe "permissible raw materials" composition meet the A106 Grade B chemical composition specifications, which is an ASTM standard for straight piping components [28]. The 1972 ASTM A106 standard, which was applicable at the time of the piping installation, did not specify nickel and copper composition requirements [29]. In 1980, ASTM updated A234 and removed the reference to ASTM A106 for chemical composition, instead specifying its own chemical requirements [19]. In 1995, ASTM A234 began specifying nickel and copper composition. The two versions of the ASTM A234 requirements, along with the YOLOY requirement, are shown above in **Table 4**. The CSB concludes that after the 1995 update to ASTM A234 in which limits on copper and nickel composition for WPB steel began to be specified, the PES elbow that ruptured did not meet the new ASTM A234 WPB copper and nickel requirements.

In 1995, ASTM A234 also began specifying "supplementary requirements" that can be specified in an order by the purchaser. One optional supplementary requirement is that the maximum carbon equivalent (C.E.) shall be 0.50, based on the following formula [30]:

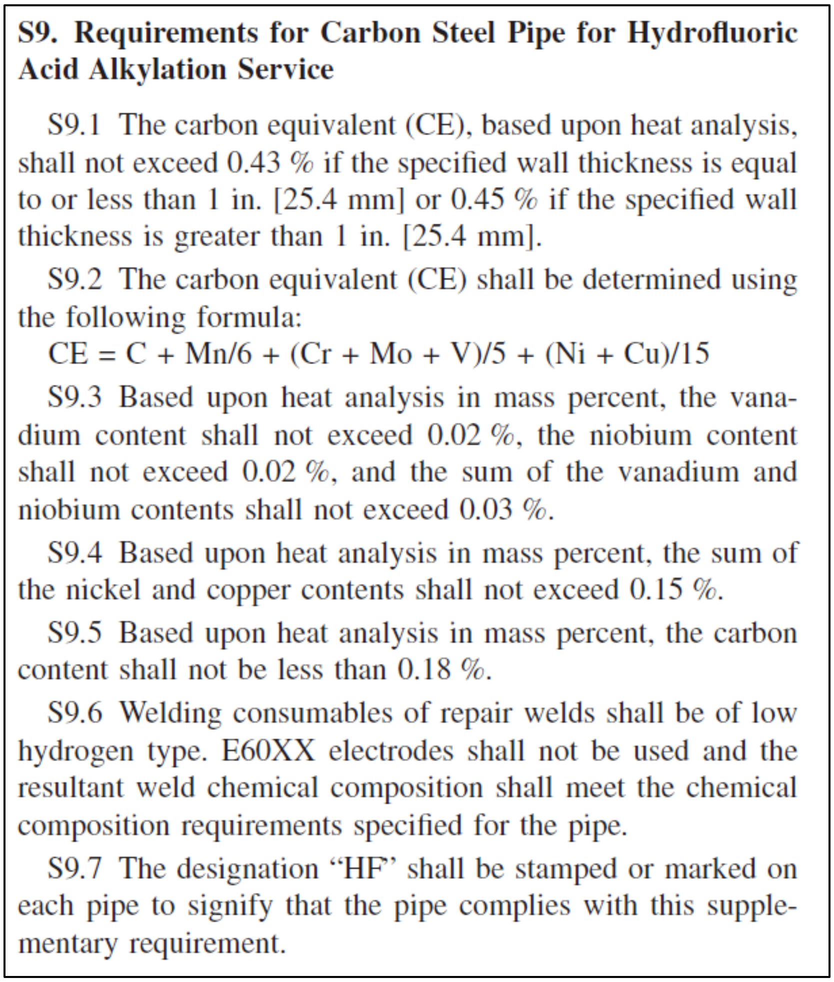
$$\text{C.E.} = \text{C} + \frac{Mn}{6} + \frac{Cr+Mo+V}{5} + \frac{Ni+Cu}{15}$$

where C is carbon, Mn is manganese, Cr is chromium, Mo is molybdenum, V is vanadium, Ni is nickel, and Cu is copper. The incident elbow has a C.E. of 0.49 and meets this requirement.

In 2004, ASTM A106, the standard for straight piping, began providing further supplementary requirements specifically for piping used in HF service [31], incorporating the RE composition recommendations suggested in NACE paper 03651. Current ASTM A106 HF supplementary requirements are shown in **Figure 25**. The CSB concludes that while ASTM A106—the standard for straight piping—has supplementary composition requirements specifically for piping use in HF service incorporating the residual element (RE) composition recommendations in NACE paper 03651, ASTM A234—the standard for fittings—does not include similar supplementary composition requirements.

The CSB also concludes that revisions to the ASTM A234 standard, incorporating the residual element (RE) composition recommendations in NACE paper 03651, can help prevent future installations of equipment that could corrode at varying rates in HF alkylation units.

The CSB recommends to ASTM International to revise ASTM A234 to incorporate supplementary requirements for piping used in HF service, as defined in HF supplementary requirements S9.1 through S9.7 in ASTM A106 version 19a.



S9. Requirements for Carbon Steel Pipe for Hydrofluoric Acid Alkylation Service

S9.1 The carbon equivalent (CE), based upon heat analysis, shall not exceed 0.43 % if the specified wall thickness is equal to or less than 1 in. [25.4 mm] or 0.45 % if the specified wall thickness is greater than 1 in. [25.4 mm].

S9.2 The carbon equivalent (CE) shall be determined using the following formula:

$CE = C + Mn/6 + (Cr + Mo + V)/5 + (Ni + Cu)/15$

S9.3 Based upon heat analysis in mass percent, the vanadium content shall not exceed 0.02 %, the niobium content shall not exceed 0.02 %, and the sum of the vanadium and niobium contents shall not exceed 0.03 %.

S9.4 Based upon heat analysis in mass percent, the sum of the nickel and copper contents shall not exceed 0.15 %.

S9.5 Based upon heat analysis in mass percent, the carbon content shall not be less than 0.18 %.

S9.6 Welding consumables of repair welds shall be of low hydrogen type. E60XX electrodes shall not be used and the resultant weld chemical composition shall meet the chemical composition requirements specified for the pipe.

S9.7 The designation "HF" shall be stamped or marked on each pipe to signify that the pipe complies with this supplementary requirement.

Figure 25. ASTM A106 requirements for carbon steel straight piping for hydrofluoric acid alkylation service. (Credit: ASTM International [32])

2.1.5 American Petroleum Institute (API) Guidance Related to Corrosion, Materials of Construction, and Piping Inspection in HF Alkylation Units

When CMLs were first specified for the PES refinery HF alkylation unit in 1973 (at that time, the refinery was owned by Gulf Oil), the inspection group based the inspection program on the piping being susceptible to a uniform corrosion mechanism and selected representative CMLs to monitor corrosion of the piping. Since 1973, the various refinery owners added additional CMLs. In 2002, the piping circuit containing the failed elbow contained 41 CMLs, and by 2019 the circuit contained 141 CMLs. **Figure 17** shows the portion of the piping circuit that contained the failed elbow, indicating CML locations and the most recent thickness measurements. There was not a CML on the elbow that failed. Described below, at the time of the incident the applicable industry guidance document did not require CMLs on all carbon steel piping components in HF alkylation units.

API RP 751 *Safe Operation of Hydrofluoric Acid Alkylation Units* is the API standard for the industry on operating HF alkylation units, the scope of which is to "communicate[] proven industry practices to support the safe operation of an HF acid alkylation unit" [17, p. 1]. Among other guidance, the standard provides information and guidance on the potential for increased corrosion rates in high-RE steel. Because the PES piping component that failed was likely purposefully manufactured to contain high concentrations of nickel and copper, these elements are in this case not considered "residual elements" (which must be already in the base steel); nevertheless, API guidance relating to varying corrosion rates due to high-RE composition could have led to the identification of the thin elbow. The evolution of API guidance relating to high-RE steel in HF service is discussed below.

API RP 751 (2nd edition, 1999):

This edition introduced the concept of increased corrosion rates in high-RE steel, stating that "it has … been reported that certain residual elements (Cr, Ni, Cu) in carbon steel may contribute to accelerated HF corrosion" [33, p. 7].

API RP 751 (3rd edition, 2007)

This edition of API RP 751 included significantly more information on the potential for localized corrosion in high-RE carbon steel than the previous edition, including an appendix called *Appendix D—Corrosion and Materials Considerations Specific to HF Alkylation*. This new appendix stated:

> The chemistry of the carbon steel has been found to increase the variability of non-uniform corrosion within regions of changing acid strength profile, including the azeotropic concentration of acid with water. A NACE Corrosion 2003, Paper 03651 indicated that the combination of carbon (C) content and residual element content (Cr, Ni, Cu) could increase this non-uniform corrosion by up to 5 fold compared to moderate measured corrosion rates. This same study concluded that non-uniform corrosion would be minimized if: $C > 0.18$ wt% and the $Cu + Ni + Cr < 0.15$ wt% and that the non-uniform corrosion would be maximized if $C < 0.15$ wt.% and $Cu + Ni + Cr > 0.30$ wt%. […] This information

> can assist an operator in focusing their inspection programs for potential localized corrosion due to carbon steel chemistry. There currently is limited technical capability to purchase and validate receipt of this type of low residual element material for a plant. ASTM standards for typical [carbon steel] specifications such as A516, A106, A333, A960, A961 now include supplementary requirements for HF service application [34, p. 38].

API RP 751 (4th edition, 2013, applicable version at time of PES incident)

This edition increased the guidance relating to RE concentrations in carbon steel. When using new carbon steel piping and equipment not meeting ASTM supplementary specifications for HF service, this edition recommended increasing inspection frequency or adding CMLs until a corrosion history of the components could be established. This edition, however, did not clearly guide users on techniques to monitor corrosion rates of carbon steel piping and equipment installed *before* the ASTM supplementary specifications were developed:

> Low RE carbon steel should be used for new piping and equipment in main acid service, trace acid service at elevated temperature or where heating or condensation may take place, and where water may be present with trace HF ("dilute HF" service). If carbon steel meeting the supplementary specifications for low REs is not used or is unavailable, then options that should be reviewed include upgrading the metallurgy to Alloy 400 or increasing the inspection frequency and/or scope, such as increasing condition monitoring locations (CMLs), until a corrosion history can be established to insure the integrity of all components in that particular system [17, p. 16].

In addition, this edition of API RP 751 also stated that localized corrosion due to high-RE composition is a concern at high temperatures, but the circuit containing the elbow that failed operated at about 100 °F, which would not have been considered to be "high temperature." API RP 751 stated:

> In general, carbon steel has demonstrated satisfactory resistance to corrosion in free HF or concentrated HF (such as in reactors and settlers) up to approximately 120 °F and in dissolved HF or vapor phase HF (such as settler effluent and isobutane recycle systems) up to approximately 160 °F. In some cases, carbon steel has shown satisfactory corrosion resistance up to approximately 170 °F in column overhead vapor lines and up to approximately 180 °F in column feed lines where the HF content is well below the solubility limit.… In order to minimize corrosion at these high temperatures, it may also be beneficial to ensure that the residual element (RE) content of the carbon steel meets the recommendations of NACE Paper 03651 and ASTM supplementary requirements for HF service. … Low RE carbon steel should be used for new piping and equipment in main acid service, trace acid service at elevated temperature or where heating or condensation may take place, and where water may be present with trace HF ("dilute HF" service) [17, p. 16].

The language in the various API RP 751 editions did not result in PES or the previous refinery owner Sunoco identifying that the incident elbow had a high nickel and copper content and was corroding faster than other components within the circuit.

API RP 751 (5th edition, 2021)

After the incident, in August 2021, API published the fifth edition of API RP 751 [35]. This new edition now includes a requirement for the development of a special emphasis program to inspect all carbon steel piping in identified HF alkylation corrosion zones to identify components with accelerated corrosion. The new edition of API RP 751 states the following:

> Special emphasis inspection programs to evaluate the condition of all individual components and welds in piping circuits have been conducted by several owner-operators. Most of these programs have identified locations with significant corrosion rate variations and localized thinning of components, welds, and weld [heat affected zones] requiring repairs or replacement. […]
>
> A special emphasis inspection program shall be developed and implemented at least once to inspect all individual carbon steel piping components and welds to identify areas of accelerated corrosion. […]
>
> The special emphasis inspection program shall determine the wall thickness of individual components and welds throughout the unit. […]
>
> After the initial inspection, the CMLs for each piping circuit should include CMLs placed on components that have lower wall thicknesses and/or higher corrosion rates. Successive inspection programs can be implemented to track the findings, to address the impact of operational changes, or to address industry learnings.
>
> Some owner-operators have included PMI for RE as part of their special emphasis inspection program [35, pp. 51-52].

The CSB concludes that:

- PES and the previous owner Sunoco never inspected all carbon steel components within the HF alkylation unit. Such a program was not required in API RP 751 *Safe Operation of Hydrofluoric Acid Alkylation Units*.
- Had PES or Sunoco inspected all carbon steel piping circuit components susceptible to HF corrosion in the HF alkylation unit, they may have identified that the elbow was corroding at a faster rate than adjacent piping components, which could have prevented the incident.
- The new requirements in API RP 751 *Safe Operation of Hydrofluoric Acid Alkylation Units* for refiners to develop a special emphasis inspection program to inspect all individual carbon steel piping components and welds in identified HF alkylation corrosion zones to identify areas of accelerated

corrosion should help prevent future failures of piping components corroding faster due to the presence of significant concentrations of copper and nickel within the steel.

2.2 Verifying Safety of Equipment after Changes to RAGAGEP

The Occupational Safety and Health Administration (OSHA) Process Safety Management of Highly Hazardous Chemicals (PSM) standard, which went into effect in 1992, details safety management requirements that process facilities such as refineries must follow. The PSM standard is divided into 14 required safety management system elements: (1) employee participation, (2) process safety information, (3) process hazard analysis, (4) operating procedures, (5) training, (6) contractors, (7) pre-startup safety review, (8) mechanical integrity, (9) hot work permit, (10) management of change, (11) incident investigation, (12) emergency planning and response, (13) compliance audits, and (14) trade secrets.[a]

Under the process safety information element, the standard states: "For existing equipment designed and constructed in accordance with codes, standards, or practices that are no longer in general use, the employer shall determine and document that the equipment is designed, maintained, inspected, tested, and operating in a safe manner" (emphasis added).[b] An OSHA standard interpretation called ***RAGAGEP** in Process Safety Management Enforcement*, published in 2016, states the following on this PSM requirement:

> Organizations that develop codes and consensus and/or non-consensus documents may update them based on newly identified or recognized hazards; improved understanding of existing hazards; industry operating experience; and/or incidents indicating that more stringent hazard control is needed. If the updated document explicitly provides that new clauses or requirements are retroactive, those updates are relevant to determining whether the employer's practice continues to conform to RAGAGEP. Where RAGAGEP are updated to be more protective but are not explicitly retroactive, PSM does not mandate that employers upgrade their equipment, facilities, or practices to meet current versions of their selected RAGAGEP. However, under 1910.119(d)(3)(iii), employers must determine and document that their equipment is designed, maintained, inspected, tested, and operating in a safe manner. (emphasis added) [2]

The EPA Risk Management Plan (RMP) rule has similar requirements as the OSHA PSM regulation including but not limited to the following requirements:

40 C.F.R. § 68.65(d)(2): "The owner or operator shall document that equipment complies with recognized and generally accepted good engineering practices."

40 C.F.R. § 68.65(d)(3): "For existing equipment designed and constructed in accordance with codes, standards, or practices that are no longer in general use, the owner or operator shall determine and

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[a] 29 C.F.R. § 1910.119

[b] 29 C.F.R. § 1910.119(d)(3)(iii)

> document that the equipment is designed, maintained, inspected, tested, and operating in a safe manner."

EPA has issued guidance with complying with these requirements, as follows:

> EPA expects owners and operators to regularly review new and updated RAGAGEP applicable to their industry to determine where safety gaps exists within their current process. If the updated document explicitly provides that new clauses or requirements are retroactive, those updates are relevant to determining whether the owner or operator's practice continues to conform to RAGAGEP per 40 C.F.R. §68.65(d)(2). Where RAGAGEP are updated to be more protective but are not explicitly retroactive, per 40 §68.65(d)(3), the owner or operator should thoroughly evaluate how their process could still be considered safe amid new industry knowledge. Simply indicating that a process incident at your facility has yet to occur is an inappropriate evaluation for choosing not to adhere to updated RAGAGEP, especially considering changes to RAGAGEP may result from industry accidents, industry operating experience, improved understanding of existing hazards and newly recognized hazards. Oftentimes it will be difficult for the owner or operator to document equipment is designed, maintained, inspected, tested, and operating in a safe manner when there is extensive industry knowledge that indicates aspects of older process operations are no longer safe. Implementation of new industry practices can often relieve compliance issues with process safety information (PSI) requirements under 40 C.F.R. §68.65. [36]

Therefore, while companies are not required by OSHA or EPA to retroactively replace equipment in all cases when new RAGAGEP standards are published, it is the responsibility of companies to determine that their equipment is designed, maintained, inspected, tested, and operating in a safe manner when new safety information is discovered and published, for example in industry standards.

The CSB concludes that the seminal research presented in the 2003 NACE paper 03651 *Specification for Carbon Steel Materials for Hydrofluoric Acid Alkylation Units* directly led to changes in industry guidance quantifying the levels of nickel and copper in steel that could be considered safe for use in HF alkylation units. In 2004, ASTM A106, the standard for straight piping, began providing further supplementary requirements specifically for piping used in HF service [31], incorporating the steel composition recommendations by NACE paper 03651. In 2007, API RP 751 was revised to incorporate the findings presented in NACE paper 03651. These types of status quo "disruptions" in industry, where new knowledge is reported and standards and recommended practices are revised, are crucial moments for the industry to evaluate the hazards of processes that were built *before* this new knowledge was published to ensure they are safe to continue operating. The CSB concludes that API RP 751, Sunoco, and PES did not effectively respond to these advancements in industry knowledge by ensuring the safety of existing facilities through requiring all carbon steel piping circuit components to be inspected.

To prevent catastrophic incidents, companies and industry trade groups must take swift action to ensure process safety when new knowledge on hazards is published. These actions must include ensuring that facilities built before the new knowledge was published are still safe to operate. Ensuring safety can include 100% inspection of all equipment and piping, equipment replacement, and other changes needed to prevent loss of containment events.

2.3 Remotely Operated Emergency Isolation Valves

After the incident, CSB investigators analyzed the V-1 fragments to determine why the vessel ruptured. The investigators observed thinning of the bottom portion of the V-1 fragments, as shown in **Figure 26** and **Figure 27**. Based on the thinning of the V-1 vessel steel, it is reasonable to conclude that a jet flame from the ruptured elbow impinged upon the bottom of V-1 (**Figure 26**). The fire weakened the steel, causing the steel to stretch and thin until the vessel ruptured.

The flame was able to impinge on the bottom of V-1 for a long duration because although there were emergency isolation valves on the suction (inlet) of each of the P-14 pumps, there were no emergency isolation valves downstream of the pumps, between the pumps and columns T-6 and T-7. Those large hydrocarbon sources downstream of the failed elbow could not be remotely or automatically isolated.[a] The CSB concludes that had emergency isolation valves been installed in the PES HF alkylation unit to remotely and automatically isolate the large hydrocarbon sources adjacent to the failed elbow, the duration of the release could have been minimized and the subsequent explosions could have been prevented. The CSB issues a recommendation to the American Petroleum Institute (API) on this subject.

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[a] Following the February 16, 2007 incident at the Valero-McKee Refinery in Sunray, Texas, during which propane feeding a large fire could not be remotely isolated due to the lack of remotely-operated emergency isolation valves within the process, the CSB issued a recommendation to API to update its guidance "so that conformance with [the guidance] includes the design, installation, and use of [remotely-operated emergency isolation valves] and interlocked equipment controls to enable the safe and rapid emergency isolation of process equipment containing highly pressurized flammables [102]." In response to the recommendation, API updated API RP 553 *Refinery Valves and Accessories for Control and Safety Instrumented Systems* with information on Emergency Block Valves, including guidance for the installation and use of emergency block valves for vessels containing light ends (flammables) and toxic materials [103].

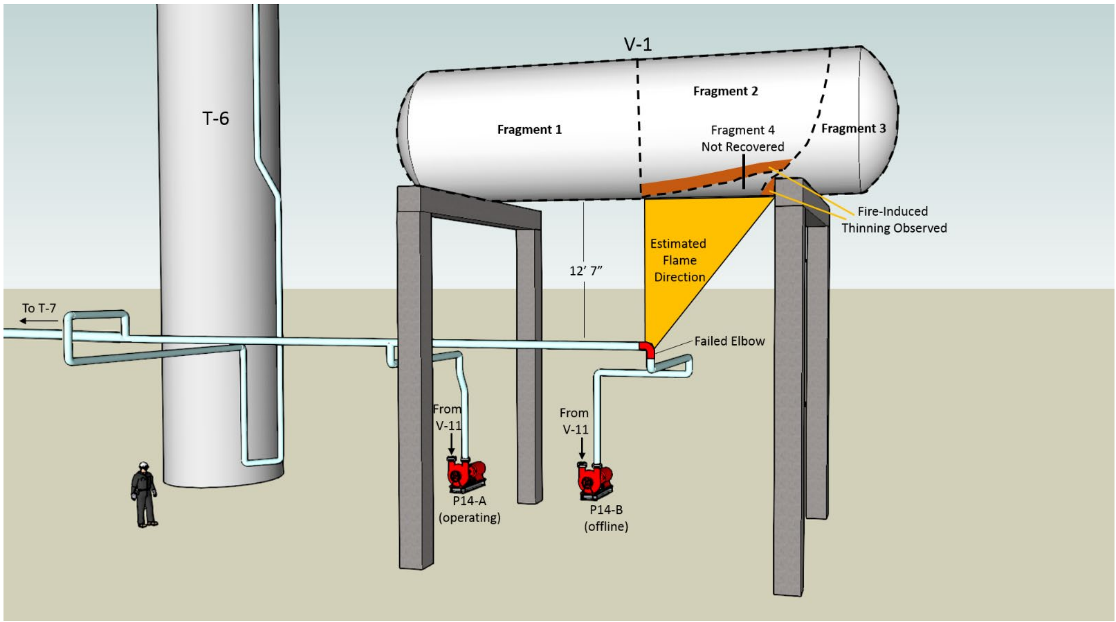

Figure 26. Locations of observed V-1 thinning, and depiction of the estimated flame size originating from the failed elbow, which impinged on the bottom of V-1. (Credit: CSB)

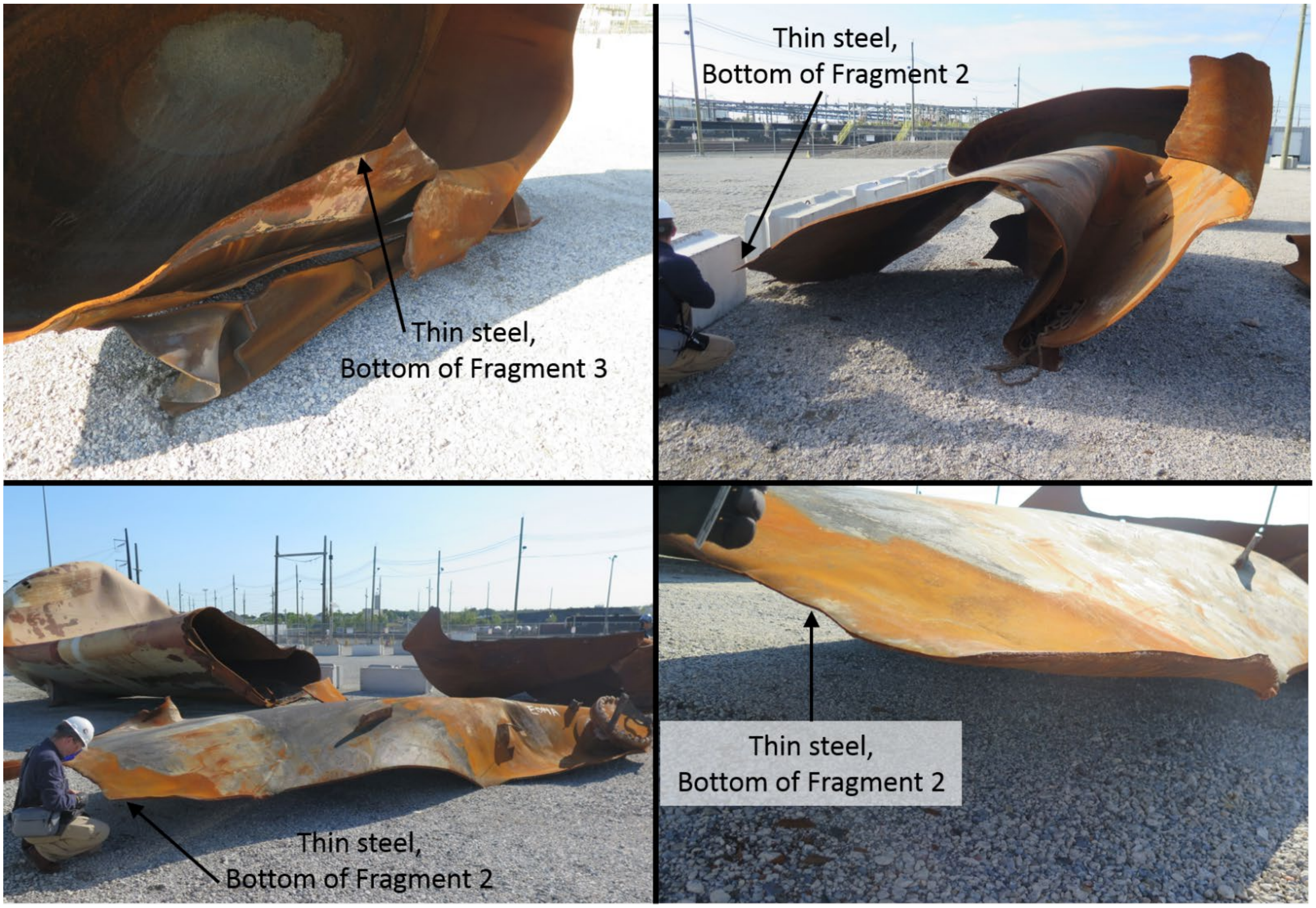

Figure 27. Photos of recovered fragments of V-1. (Credit: CSB)

At the start of the incident, V-1 was about 53% liquid-full of primarily butylene, isobutane, and butane, and the internal pressure was 37 psig.[a] The V-1 pressure indicator's last reading was at 4:02:00 a.m., and then failed at about the time of ignition. The level indicator's last reading was at 4:02:45 a.m. before failing during the fire, last indicating that V-1 was about 25% liquid-full, but this reading may not be reliable due to the fire's effect on the instrumentation.[b] The V-1 pressure and level data are shown in **Figure 28**.

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[a] The pressure relief valve for the V-1 surge drum was set to open at an internal V-1 pressure of 155 psig, designed for an external fire overpressure scenario.

[b] The last liquid level reading measured in V-1 was 25.5 %, at 4:02:45 a.m. This value is not a reliable indication of the liquid level, however, because the data shows the liquid level dropped from about 52% full to 25.5% full in about 15 seconds, which is unlikely. The ongoing fire likely affected this measurement to read an incorrect value.

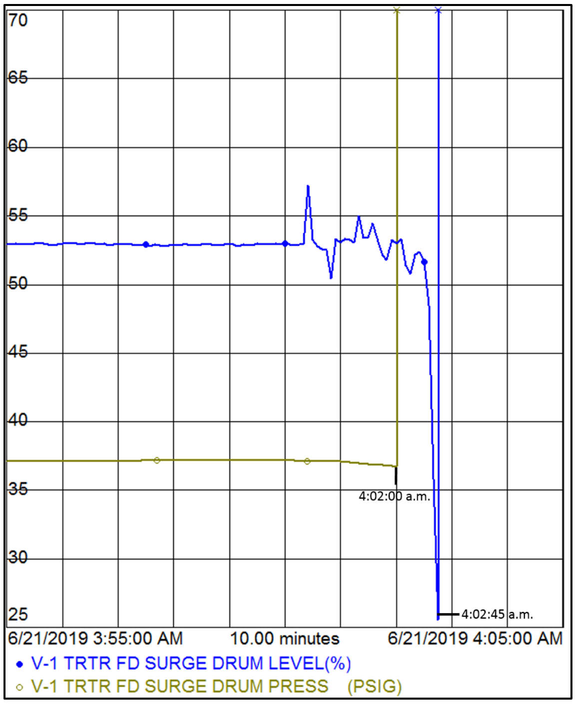

Figure 28. V-1 internal pressure and level before and during the incident. (Credit: CSB)

The rupture of the V-1 vessel appears to have caused a ***boiling liquid expanding vapor explosion*** (BLEVE, pronounced 'blev-ē). A BLEVE is the "sudden loss of containment of a pressure-liquefied gas existing above its normal atmospheric boiling point at the moment of its failure, which results in rapidly expanding vapor and flashing liquid. The release of energy from these processes (expanding vapor and flashing liquid) creates a pressure wave" [1, p. 311]. As required for a BLEVE scenario, the butane/butylene/isobutane mixture in V-1 was above its atmospheric boiling point.[a] Also, the fragmenting of the vessel into multiple pieces, the flattening of Fragment 2 from its original cylindrical shape, and the projecting of the fragments is consistent with a BLEVE scenario [1, p. 314].

This BLEVE event, however, differed from the "typical" BLEVE discussed in the literature. The "typical" BLEVE involves flame impinging on the vapor space of a vessel causing the wall to quickly heat to a high temperature due to the lack of liquid convective heat transfer from the wall [1, p. 318]. The wall weakens and ruptures, causing the BLEVE. At the PES refinery, however, the fire impinged on the bottom of the V-1 vessel, in the liquid space. The CCPS explains that jet fires impinging on the liquid space of a vessel, as is the scenario at PES, can affect the mechanical strength of vessels [1, p. 316] leading to vessel rupture and a BLEVE. Thus, although this was a somewhat atypical BLEVE event, flame impingement on the bottom of V-1 led to the rupture and BLEVE.

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[a] Published normal boiling points: Butane (31°F) [95], Butylene (21°F) [104], Isobutane (11°F) [96].

2.4 Safeguard Reliability in HF Alkylation Units

The PES HF alkylation unit was equipped with a water spray mitigation system. This system was a critical safeguard in the event of an HF release, as it was designed to reduce airborne HF through vapor suppression [a, b], to prevent it from traveling offsite. During the incident, this critical safeguard was damaged. Plant data show that the control system communication to the water pumps had failed at 4:02:06 a.m. (time of ignition) and a backup power system in the unit—the uninterruptible power supply (UPS)—also failed nine seconds later, at 4:02:15. The control system equipment and wiring that sent signals from the control system to the water mitigation pumps were likely damaged when the ignition of the flammable vapor cloud occurred, which produced flame and overpressure. When the control room operator tried to turn on the water pumps that fed the elevated HF mitigation water cannons at 4:12 a.m., the water pumps did not turn on. The system had to be manually turned on in the field by a shift supervisor wearing firefighting protective gear, which occurred at about 4:39 a.m. As described below, there have been multiple incidents or near misses that did or could have released HF from industrial facilities, including refinery HF alkylation units.

2.4.1.1 Notable HF Incidents, Near Misses, and Events

Over the past 30 years, there have been several HF incidents and near misses, as well as multiple industry efforts to study and mitigate the effects of an HF release to the atmosphere. Some of the notable HF incidents, near misses, and events are discussed below in chronological order.

2.4.1.1.1 Goldfish Series (1986)

Before 1986, releases of pressurized, superheated hydrogen fluoride were commonly thought to form liquid pools. Therefore, the industry believed at this time that accidental HF releases could be controlled by using liquid containment dikes [37, p. 35]. In 1986, Amoco, Allied-Signal, DuPont, Mobil, and Lawrence Livermore National Laboratories conducted a series of HF release tests at a Department of Energy test site in Nevada, which was called the “Goldfish” series [37, p. 35]. A major conclusion of these tests was that HF releases did not in fact pool, but instead formed vapor clouds (**Figure 29**) [37, p. 35]. The Goldfish tests also identified that water spray had some positive effect on mitigating HF releases [37, p. 36].

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[a] API RP 751 *Safe Operation of Hydrofluoric Acid Alkylation Units* requires HF alkylation units to be equipped with remotely-activated and remotely-controlled water mitigation systems [17, p. 35].

[b] “[A]pplying high volumes of water to any release of HF will significantly reduce the airborne fraction of the HF released and provide an effective tool for mitigating the effects of an HF release” [17, p. 37].

Figure 29. Photo of a vapor cloud formed when HF was released at a Department of Energy test site in Nevada in 1986. (Credit: Ronald Koopman, Ph.D., P.E.)

2.4.1.1.2 ICHMAP Program (December 1987)

In December 1987, the Industry Cooperative Hydrogen Fluoride Mitigation and Ambient Impact Assessment Program (ICHMAP), with participation by 20 companies, was established. A key objective of the program was to determine how to better design and implement effective mitigation techniques for accidental releases of HF. The program specifically focused on analyzing the effectiveness of water spray and physical vapor barriers (e.g., fences and open-top enclosures) in mitigating an HF release [37, pp. 36-41]. A finding of this program was that "it is imperative that the HF leak be detected as quickly as possible and that large amounts of water be applied as rapidly as possible to provide a high water-to-HF volume ratio"[a] to mitigate an HF release [37, p. 39]. The study of vapor barriers found that the physical barriers (fences, open-top enclosures) were beneficial in reducing HF concentration near-field (e.g., 100 meters downwind of the release point) but had limited benefit to reducing HF concentration far-field (e.g., 500 – 3,000 meters downwind of the release point) [37, p. 42].

2.4.1.1.3 HF Release at Texas City, Texas, Marathon Refinery (October 30, 1987)

On October 30, 1987, hydrofluoric acid was released from the Texas City, Texas Marathon oil refinery (**Figure 30**). During a unit turnaround, a crane was used to lift heavy equipment over a vessel containing hydrofluoric acid. Marathon miscalculated the weight of the equipment and overloaded the crane, causing the crane to tip over. The heavy equipment dropped from the crane and fell onto the HF vessel, severing a 4-inch HF acid loading line and a 2-inch pressure relief line. About 30,000 to 53,000 pounds of HF were released [38, p. 113]. About 4,000 people were evacuated as a result of the hydrofluoric acid release [39]. Over 1,000 residents in the

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[a] Water droplet size is also an important variable in the efficacy of HF water mitigation systems [37].

area went to hospitals with skin burns and irritation to eyes, nose, throat, and lungs [38, p. 113]. The release killed wildlife and vegetation along a 3-mile-long, 0.5-mile-wide path from the refinery.

A sprinkler designed to control a hydrofluoric acid release was damaged by the crane. A siren intended to sound during the emergency was also rendered inoperable when the event knocked out the power for the siren. About 600 people sued Marathon for long-term damage to their health [40]. This incident drew nationwide attention to the use and safety of HF in refineries [38, p. 113].

Figure 30. Video capture of the October 30, 1987, hydrofluoric acid release at the Marathon oil refinery in Texas City, Texas. (Credit: ABC News, 20/20 [40])

2.4.1.1.4 HF Release at Torrance, California, Mobil Oil Refinery (November 24, 1987)

On November 24, 1987, HF was released from the Mobil Oil Refinery in Torrance, California [41]. The 1993 EPA hydrogen fluoride study describes this incident:

> A 165-pound release of HF occurred in 1987 at Mobil Oil's refinery in Torrance, California. The release occurred following an undetected excess flow of HF to the alkylation unit's propane treater. The propane treater uses potassium hydroxide (KOH) to neutralize trace amounts of HF in liquid propane, an alkylation byproduct. An excess of HF was charged to the treater, and was not detected because a series of controllers and alarms was inoperable. The probable cause of the accident, determined by examining the damaged equipment, was that the presence of excess HF resulted in an exothermic reaction and created abnormal pressure, causing the KOH treater to fail. The upstream cooler may have failed as well for the same reason. When the treater failed, it released HF and propane, which exploded and started a large fire [38, p. 114].

2.4.1.2Clean Air Act Amendments of 1990

In 1990, Congress enacted Clean Air Act Amendments. These amendments established, among other things, the CSB [42, p. 2565]. Congress also required that EPA conduct an HF study (discussed below) [42, p. 2560].

2.4.1.3 API RP 751 Safe Operation of Hydrofluoric Acid Alkylation Units First Published (1992)

API RP 751 *Safe Operation of Hydrofluoric Acid Alkylation Units* was first published in 1992, recommending the use of safety systems including:

- hazards management
- operating procedures and worker protection
- materials, maintenance, and inspection
- transportation and inventory control
- relief, utility, and mitigation systems
- appendices covering elements of a comprehensive audit, HF exposure limits, procedures for unloading acid, monitoring and detection systems, water mitigation systems, and emergency isolation of an HF release.

As of the publication date of this report, four successive editions have been published in 1999, 2007, 2013, and 2021.

2.4.1.4EPA HF Study (1993)

Section 112(n)(6) of the Clean Air Act, part of the Clean Air Act Amendments of 1990, states:

> Hydrofluoric Acid – Not later than 2 years after the date of enactment of the Clean Air Act Amendments of 1990, the Administrator shall, for those regions of the country which do not have comprehensive health and safety regulations with respect to hydrofluoric acid, complete a study of the potential hazards of hydrofluoric acid and the uses of hydrofluoric acid in industrial and commercial applications to public health and the environment considering a range of events including worst-case accidental releases and shall make recommendations to the Congress for the reduction of such hazards, if appropriate [42, p. 2560].

EPA complied with this Congressional direction by conducting an HF study and publishing a report to Congress in 1993. The study evaluated:

- the properties and hazards of hydrogen fluoride;
- the hydrogen fluoride industry;
- regulations and initiatives related to hydrogen fluoride;
- hydrogen fluoride industry processes;
- the hazards of hydrogen fluoride processes and industry practices to prevent releases;
- industry practices to detect and mitigate hydrogen fluoride releases;
- the characterization of hydrogen fluoride accidents;
- the modeling of hydrogen fluoride releases; and
- community and facility emergency preparedness and planning.

The study also issued findings and recommendations. The recommendation portion of the report includes the following statement:

> The EPA does not recommend legislative action from the Congress at this time to reduce the hazards associated with HF. The regulations already promulgated, and being developed, [including by] OSHA in the process safety management provisions of the [Clean Air Act Amendments], provide a good framework for the prevention of accidental chemical releases and preparedness in the event that they occur [38, p. 180].

Despite not recommending current legislative changes, the report included another recommendation stating, “EPA should monitor alkylation catalysis and HF additive research for potential process safety improvements” [38, p. 182].

2.4.1.5 Development of Additive to Reduce HF Volatility (Mid-1990's)

In the mid-1990's, an additive chemical was identified that could help reduce the tendency of HF to form a vapor cloud in the event of an HF release to the atmosphere. This additive was first used at the Mobil refinery in Torrance, California, and was then introduced to the Philadelphia Sunoco refinery (the future PES refinery discussed in this report) in 2010.

A 1995 study by Quest Consultants Inc. titled *Effectiveness of Mitigation Systems in Reducing Hazards of Hydrogen Fluoride Leaks* assessed, among other things, the efficacy of such an additive in reducing the amount of HF that vaporized in the event of an HF release. The study analyzed a 50/50 mix by weight of acid/additive in a release scenario. The study found that "[t]he use of an additive to the HF has two effects on the overall behavior of an acid leak. First, the additive reduces the volatility of the acid phase; second, the additive dilutes the acid. The result of these two effects is to release acid at a lower rate than a pure acid release (dilution) and for the acid that is released, a greater percentage falls to the ground (reduced volatility) and does not enter the atmosphere immediately." The study stated that a benefit of using an additive was that it would be "passive" mitigation needing no operator or system response to the leak for the mitigative benefit. The study also pointed out that the additive-to-HF ratio is important, stating "the greater the additive fraction, the greater the dilution, the greater the benefit [43]." As will be discussed in Section 2.4.2.2, the additive used both at PES and at the ExxonMobil Torrance refinery, could result in about half of the released acid vaporizing and forming a vapor cloud in a loss-of-containment event, which is dependent upon the additive fraction used. Active mitigation systems—the RAD and water mitigation systems—would then be needed to reduce the amount of HF released to the atmosphere and to contain released HF.

2.4.1.6 CITGO Corpus Christi Refinery HF Release (July 19, 2009)

On July 19, 2009, a hydrocarbon gas release occurred in the CITGO Corpus Christi East refinery HF alkylation unit, causing a fire that burned for several days. The fire caused multiple failures in the unit, releasing HF to the atmosphere. CITGO reported to the Texas Commission on Environmental Quality that approximately 42,000 pounds of HF released from alkylation unit piping and equipment were captured by the HF water mitigation system, and 30 pounds of HF were not captured by the mitigation system. The CSB, however, disputed these numbers and calculated that about 4,000 pounds of released HF likely were not captured by the HF water mitigation system.

During the incident, CITGO nearly exhausted its stored water supply for fire suppression and HF mitigation on the first day of the multi-day incident response while HF continued to be released. About 11.5 hours after the initial release, before the water supply was completely exhausted, the Refinery Terminal Fire Company began pumping saltwater from the Corpus Christi ship channel into the CITGO fire water system using a barge equipped for firefighting. Multiple failures occurred during the saltwater transfer, including multiple ruptures of the barge-to-shore transfer hoses and two water pump engine failures.

The CSB found that CITGO had never conducted a safety audit of its HF alkylation operations at either of its U.S. refineries equipped with HF alkylation units as recommended by API RP 751 *Safe Operation of Hydrofluoric Acid Alkylation Units*.

The CSB issued urgent recommendations that CITGO ensure adequate water supply to the HF water mitigation system and to conduct third-party audits of all U.S. CITGO HF alkylation units as recommended by API RP 751 [44].

2.4.1.7 South Korea HF Release

On September 27, 2012, over 17,000 pounds of hydrogen fluoride gas released from a chemical plant in South Korea. Five workers were killed, 18 workers were injured, and over 12,000 people from the surrounding area reported injuries. The South Korean government reported that it would pay $33.4 million in compensation to citizens and local businesses [45]. The HF release damaged more than 500 acres of farmland (**Figure 31**) and affected 3,200 livestock animals. The South Korean government designated the area affected by the release as a "special disaster zone" [46].

Figure 31. Photo of damaged crops following September 27, 2012, hydrogen fluoride release in South Korea. (Credit: Yonhap News Agency [47])

2.4.1.8 ExxonMobil Torrance Refinery Explosion (HF Near Miss) (February 18, 2015)

On February 18, 2015, an explosion occurred in the ExxonMobil Torrance, California refinery's electrostatic precipitator (ESP), a pollution control device in the fluid catalytic cracking unit that removes catalyst particles. As a result of this incident, a near-miss event occurred in the modified HF alkylation unit when explosion debris nearly hit tanks in close proximity to the ESP, each containing HF, water, hydrocarbons, and a chemical additive intended to reduce the amount of HF vaporized during a loss of containment event (**Figure 32**). ExxonMobil denied CSB requests for safety information pertaining to the potential release of HF, including a request for "records relating to the documented or asserted degree of HF vapor suppression for modified HF, and industry and/or Mobil/ExxonMobil studies, experiments, modeling of modified HF and its effectiveness in suppressing vapor compared to unmodified HF." The CSB issued subpoenas for this information and pursued enforcement in U.S. federal district court [48].[a] In December 2019, the U.S. Ninth Circuit Court of Appeals ruled that ExxonMobil must produce this information to the CSB [49].[b] ExxonMobil produced this information to the CSB on March 20, 2020. Section 2.4.2.2 discusses the safety information in these documents.

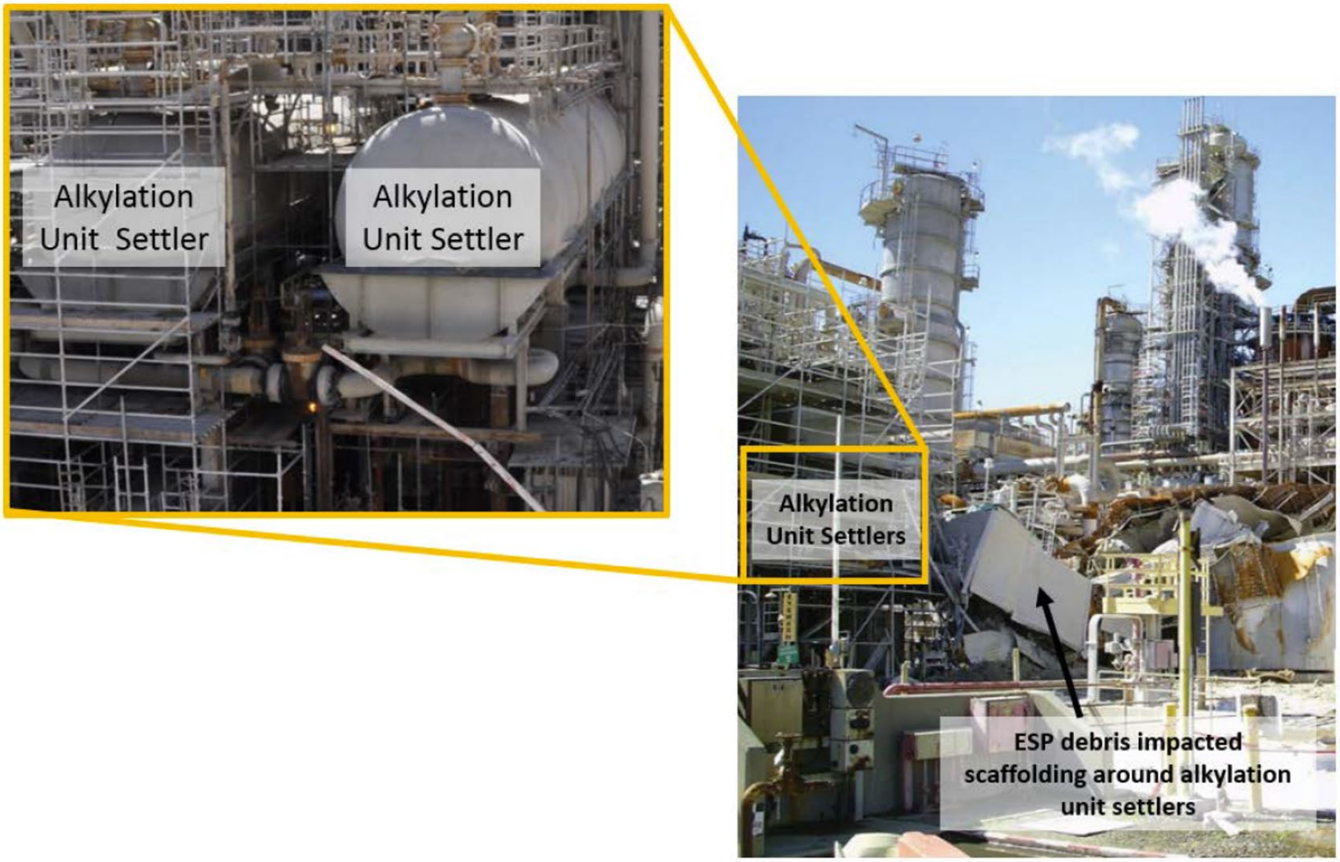

Figure 32. Explosion debris from the February 18, 2015, ExxonMobil Torrance Refinery explosion came in close proximity to the alkylation unit's HF settlers. (Credit: CSB [48]).

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[a] *United States v. Exxon Mobil Corp*., 2017 WL 5153535 (November 3, 2017)

[b] *United States v. Exxon Mobil Corp*., 943 F.3d 1283, 1290 (9th Cir. 2019)

2.4.1.9 Husky Superior Refinery Explosion and Fire (HF Near Miss) (April 26, 2018)

On April 26, 2018, an explosion occurred at the Superior Refinery Company LLC refinery in Superior, Wisconsin ("Husky Superior Refinery") in the refinery's fluid catalytic cracking unit. Debris from the explosion flew about 200 feet, and impacted a large, nearby, aboveground storage tank containing about 50,000 barrels of asphalt, puncturing the side of the steel tank and spilling more than 15,000 barrels of hot asphalt into the refinery (**Figure 33**). This released asphalt ignited about two hours after the explosion, creating a large fire [50].

Figure 33. Post-incident photographs of the leaking asphalt storage tank at the Husky Superior Refinery. (Left photo credit: CSB. Right photo credit: Duluth News Tribune [50])

The Husky Superior Refinery uses hydrofluoric acid in its alkylation unit. The hydrofluoric acid storage tank is located about 150 feet from the equipment that ruptured in the explosion. Neither the hydrofluoric acid tank nor the water curtain equipment surrounding the hydrofluoric acid tank, used to provide water suppression in the event of an acid leak, were impacted by explosion debris, but they were located closer to the ruptured equipment than the asphalt tank that was punctured by the explosion debris [50]. The CSB considers this a near-miss event—it is possible that the hydrofluoric acid equipment could have been punctured by explosion debris.

2.4.1.10 CSB Letter to EPA (April 23, 2019)

Prompted by the recent ExxonMobil Torrance refinery and Husky Energy refinery incidents, on April 23, 2019, CSB's designated interim executive and administrative authority, Dr. Kristen Kulinowski, sent a letter to EPA administrator, Mr. Andrew Wheeler. In the letter, Dr. Kulinowski explained the concerns of community members living near the refineries relating to the potential for a toxic HF release:

> In the last four years, the CSB has investigated two petroleum refinery incidents where an explosion elevated the threat of a possible release of HF or modified

> hydrofluoric acid (MHF). In both investigations, the CSB conducted a public hearing[a, b] in which members of the surrounding communities indicated great concern about the adequacy of the risk management strategies for the use of HF and the effectiveness of community notification procedures in the event of a catastrophic release [51].

Dr. Kulinowski communicated to Mr. Wheeler that the CSB encourages EPA to take action to prevent a catastrophic HF release, stating:

> [T]he CSB strongly encourages the U.S. Environmental Protection Agency (EPA) to initiate a review and update of its 1993 HF study to determine whether refineries' existing risk management plans are sufficient to prevent catastrophic releases; and, to determine whether there are commercially viable, inherently safer alkylation technologies for use in petroleum refineries [51].

2.4.1.11 PES Refinery Fire, Explosions, and HF Release (June 21, 2019)

On June 21, 2019, the PES refinery incident that is the subject of this report occurred. PES estimated that 5,239 pounds of HF released from piping and equipment during the incident. The PES HF water mitigation system was damaged during the incident.

2.4.1.12 EPA Response to CSB Letter (October 8, 2019)

On October 8, 2019, EPA assistant administrator, Mr. Peter Wright, responded to CSB's April 23, 2019, letter. In EPA's response, Mr. Wright communicated that "EPA does not intend to update the Agency's 1993 HF study." Mr. Wright also stated:

> Regarding inherently safer technologies, such determinations are situation-specific. Therefore, the Agency cannot make any general determination that a particular technology—whether used for alkylation or another process—is "commercially viable or inherently safer." EPA continues to believe that the owners and operators of individual facilities are usually in the best position to make such determinations.

2.4.2 HF Mitigation Safeguards and Need for Improvement

In response to the events above, the refining industry developed three main safeguards to minimize the amount of HF vapor that releases to the atmosphere during a release event. These safeguards include (1) rapid acid deinventory (RAD) systems, (2) water spray systems, and (3) the use of an additive in the HF to lower the amount of HF that becomes vapor upon release. All three of these systems are described below. As discussed

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[a] Transcript of CSB public meeting following ExxonMobil Torrance refinery incident [98].

[b] Transcript of CSB public meeting following Husky Energy refinery incident: [99].

above, during the PES incident, refinery workers quickly activated the RAD system, which drained HF from the compromised unit and helped to prevent a catastrophic HF release. It is also important to highlight, however, that the water spray mitigation system was damaged during the incident and could not be remotely activated; a PES employee manually activated the system 40 minutes into the release. This demonstrates that "active" safeguards—or safeguards that require a person or technology to trigger their activation—have the potential to fail in major incidents involving fire or explosions. Refiners operating HF alkylation units need to improve the availability and reliability of active safeguards during incidents involving fire and explosions.

2.4.2.1 RAD and HF Water Spray Systems – "Active" Safeguards That Can Be Subject to Failure

A RAD system is designed to quickly transfer HF from a process unit to an empty vessel in the event of a process loss-of-containment or other incident. The PES refinery had such a system and it functioned as intended on the day of the incident, quickly draining HF from the compromised unit. As seen in this incident, however, the ability to remotely activate the water spray system was compromised by the fire, which is a potential failure mode for RAD systems in fires and explosions. A 1995 paper on HF mitigation systems, written by Quest Consultants, identified the following disadvantages of a RAD system:

1. The system does not reduce the rate at which HF is released.
2. The system does not reduce the fraction of HF released that remains airborne.
3. Because it is an active mitigation system, someone or something must activate the isolation valves that initiate the dump.
4. During the recognition and response time, no acid is removed from the system except for the acid leaking into the atmosphere.
5. If the deinventory rate is small relative to the leak, the benefit derived from the deinventory system may not be significant.
6. Because it is an active mitigation system, maintenance and reliability can be issues.
7. Availability can be an issue. What if the initiating event causing the release of HF from the alkylation unit also damages the deinventorying equipment, thus rendering it inoperable? [43, p. 2]

Water spray systems, such as water cannons or water curtains, are intended to use water spray to absorb HF vapor in the event of a release. The PES refinery had a water spray system, but it was damaged during the incident. The water spray mitigation systems were also damaged or experienced problems in the 1987 Marathon incident and in the 2009 CITGO incident, discussed above. The same 1995 Quest Consultants paper identified the following disadvantages of a water spray system:

1. The system does not reduce the rate at which HF is released.
2. Because it is an active mitigation system, someone or something must activate the water spray curtain before it becomes operational.

3. During the recognition and response time, no acid is removed from the cloud.
4. The efficiency of the curtain is dependent on many factors, such as hole size and location, release orientation, distance between HF release point and water curtain, and the ratio of water mass flow to HF mass release rate.
5. Availability can be an issue. What if the initiating event causing the release of HF from the alkylation unit also damages the water spray curtain equipment, thus rendering it inoperable? [43, pp. 2-3]

At the PES refinery, item number 5 above explains the cause of the water mitigation system damage; the fire and explosions caused the control system communication to the water pumps to fail.

As demonstrated by the PES incident, in a major process safety event involving fire and explosions, active systems can be damaged and may not be available to prevent or mitigate a release of HF.

2.4.2.2 HF Additive at PES and Torrance Refineries

As discussed above, in the mid-1990s an additive chemical was identified that could help prevent HF from forming a vapor cloud in the event of an HF release to the atmosphere. However, public information on the efficacy of the additive in reducing airborne concentration of HF is minimal.[a] The CSB requested information on the efficacy of the additive from ExxonMobil during the CSB's investigation of the 2015 ExxonMobil Torrance refinery incident, but ExxonMobil refused to provide this information. The CSB issued subpoenas for this information and pursued enforcement in U.S. federal district court [48]. The CSB also requested from PES information on the effectiveness of the additive—sulfolane—in reducing HF volatility, but PES communicated to the CSB that it did not possess this information.

In December 2019, the U.S. Ninth Circuit Court of Appeals ruled that ExxonMobil must produce the information the CSB had subpoenaed [49].[b] On March 20, 2020, ExxonMobil produced the documents to the CSB. The documents indicate an anticipated reduction in airborne HF for a specific acid concentration when the sulfolane additive is present, depending on whether there is a physical barrier. Physical barriers considered include flange shrouds and pump barriers, which are locations considered in the documents as "potential acid release points." For a specified HF catalyst mixture containing HF, sulfolane additive, water, and acid-soluble oil, the documents indicate an anticipated airborne reduction factor of 50% for "unbarriered" releases, and an airborne reduction factor of 89% for "barriered" releases, in comparison to releases of pure HF (**Figure 34**). This means, for a release of process fluid containing 20,000 pounds of HF from an "unbarriered" location such as a ruptured pipe or punctured equipment, about 10,000 pounds of HF are anticipated to release to the atmosphere. Modifying HF alkylation units to incorporate the sulfolane chemical additive appears to decrease the potential quantity of HF released during a loss-of-containment event. In large HF release events, however, the formation of toxic HF vapor clouds is still possible, and refineries would rely on other safeguards—including RAD systems and water mitigation systems—which, as shown in this incident, can be compromised in major incidents involving fire or explosions.

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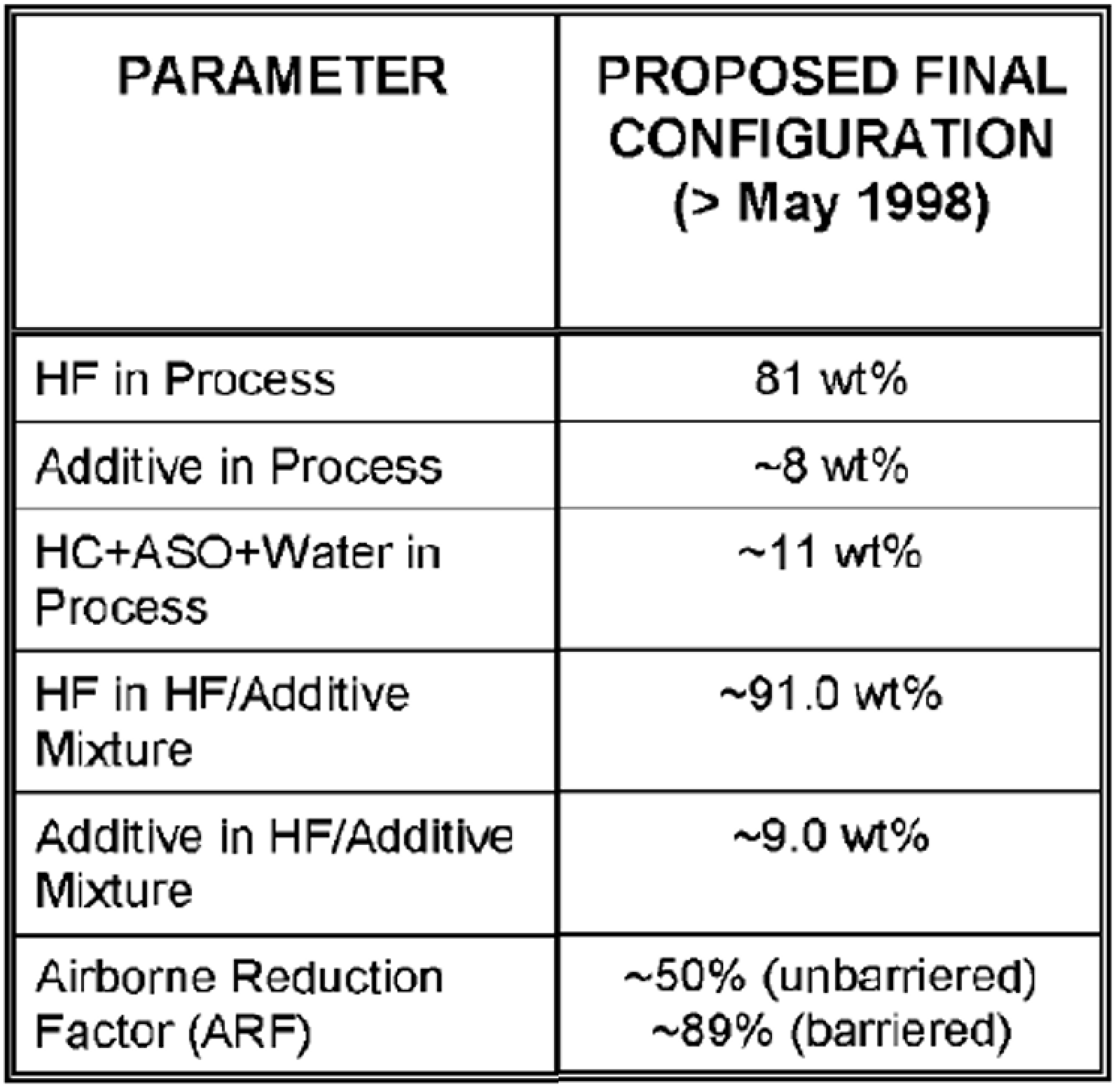
[a] Public information on the efficacy of the additive is limited primarily to a 1992 European patent called Alkylation Catalyst Containing Hydrofluoric Acid and a Sulfone [97]. The proprietor of the patent was Phillips Petroleum Company.

[b] *United States v. Exxon Mobil Corp.*, 943 F.3d 1283, 1290 (9th Cir. 2019)

The information in **Figure 34** does not reflect the current operation at the Torrance refinery, which is now called the PBF Torrance refinery. In addition, the airborne reduction factor indicated in **Figure 34** is dependent on the ratio of the listed chemicals.



PARAMETER	PROPOSED FINAL CONFIGURATION (> May 1998)
HF in Process	81 wt%
Additive in Process	~8 wt%
HC+ASO+Water in Process	~11 wt%
HF in HF/Additive Mixture	~91.0 wt%
Additive in HF/Additive Mixture	~9.0 wt%
Airborne Reduction Factor (ARF)	~50% (unbarriered) ~89% (barriered)

Figure 34. Information contained in a 1999 Torrance Refinery Safety Advisor Project, indicating the Airborne Reduction Factor (ARF) achieved in the HF catalyst mixture containing HF, sulfolane additive, hydrocarbons (HC), water, and acid-soluble oil (ASO), for “unbarriered” and “barriered” releases. (Credit: ExxonMobil)

2.4.2.3 Gaps in Safeguard Requirements in API RP 751

As shown below in **Table 5**, the current, 5th edition of API RP 751 *Safe Operation of Hydrofluoric Acid Alkylation Units*, has gaps that, without correction, could lead to consequences similar to those experienced at PES in the event of a fire or explosion event in an HF alkylation unit.

Table 5. Gaps in API RP 751, 5th edition

Incident Event	API RP 751, 5th edition, 2021 Requirement	Gap
The control system and backup power system failed at the time of ignition.	"A backup power supply shall be provided for the critical electrically powered instruments and unit control systems. Fireproofing of cabling and components *should be considered* [35, p. 23]." (Emphasis added)	As demonstrated by the PES incident, HF control systems and backup power systems can fail in major incidents involving fires and explosions. To prevent knock-on incidents in HF alkylation units, cabling and components for critical safeguards must be protected from fire and explosion damage.
The hydrocarbon release could not be isolated, causing a jet flame to impinge on the V-1 vessel for a long duration. The prolonged jet flame impingement caused the V-1 vessel's rupture and propulsion off-site.	API RP 751 does not require remotely operated emergency isolation valves be installed on large hydrocarbon-containing vessels that could supply the fuel to produce jet flames that can impinge on alkylation unit equipment. And: "The magnitude of an HF release from an HF alkylation unit can be reduced if valves are in place that can quickly isolate the major HF inventories. These remotely activated block valves *should be located* so that large inventories and credible potential leak sources can be safely isolated from each other [35, p. 88]." (Emphasis added)	As demonstrated by the PES incident, jet flames are critically hazardous events in refineries, particularly in high-hazard units such as HF alkylation units. Jet flames can lead to the rupture of equipment, causing major explosions, large projectiles, and the release of hazardous chemicals. To prevent the occurrence of long-duration jet flames and releases of toxic HF, remotely operated emergency isolation valves must be installed on all large hydrocarbon-containing vessels and all large inventories of HF.

The CSB concludes that the 5th edition of API RP 751 *Safe Operation of Hydrofluoric Acid Alkylation Units* contains gaps relating to (1) the protection of control systems and backup power systems from fire and explosion hazards, and (2) the ability to isolate and stop releases from large hydrocarbon-containing vessels and all large inventories of HF using remotely operated emergency isolation valves.

The CSB also concludes that to help prevent future incidents similar to the PES incident, in which control and backup systems were rendered inoperable by fire and large hydrocarbon vessels could not be isolated, API RP 751 should be updated with new safety requirements on these topics.

The CSB recommends to API to revise the RP 751 standard to correct these identified gaps.

2.4.2.4 Recommendation for EPA Compliance Initiative in Refinery HF Alkylation Units

The EPA Risk Management Plan (RMP) rule requires that "[t]he owner or operator shall document that equipment complies with recognized and generally accepted good engineering practices."[a] EPA, which enforces the adherence to industry standards in accordance with its RMP regulation, has an important role in ensuring compliance with industry codes and standards, including API RP 751. EPA currently has an active National Compliance Initiative called Reducing Risks of Accidental Releases at Industrial and Chemical Facilities. The goal of this National Compliance Initiative is:

> [t]o reduce the risk to human health and the environment by decreasing the likelihood of chemical accidents. A successful initiative would reduce communities' risk by having regulated facilities and industry associations work to:
>
> 1. improve safety;
>
> 2. increase compliance with risk management plan and [general duty clause] requirements; and
>
> 3. promote coordination and communication with state and local responders and communities [52].

The CSB concludes that to help ensure that new API RP 751 safety requirements and recommendations are implemented effectively nationwide, EPA should emphasize inspecting refinery HF alkylation units under its National Compliance Initiative called Reducing Risks of Accidental Releases at Industrial and Chemical Facilities to help decrease the likelihood of chemical accidents, and resulting catastrophic consequences, in refinery HF alkylation units.

The CSB issues a recommendation to EPA to focus inspection on refinery HF alkylation units under its National Compliance Initiative.

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[a] 40 C.F.R. § 68.65(d)(2)

2.5 Inherently Safer Design

Of the 155 U.S. petroleum refineries currently in operation as of the date of this report, 46 operate HF alkylation units. HF is a highly toxic chemical that can produce a vapor cloud upon release, and is one of the eight most hazardous chemicals regulated by the EPA Risk Management Program (RMP).[a, b] The other acid catalyst used in refinery alkylation units—sulfuric acid—is not a chemical triggering coverage by the RMP standard, and in the event of a release likely would not produce a vapor cloud that could expose people outside of the refinery to a harmful concentration of the chemical. It too, however, is a hazardous chemical. While it remains a liquid upon release, sulfuric acid is highly corrosive and can cause skin burns and other injuries upon contact [15].

In addition to inherently safer design, facilities can create safer processes is by using the hierarchy of controls when selecting safeguards. The hierarchy of controls is the ranking of safeguards from most to least effective (**Figure 35**). Each control category is defined in the sidebar.

Using a sulfuric acid catalyst or other new alkylation technologies, some of which are discussed later in this section, could prevent off-site human exposure to toxic chemicals in the event of future loss-of-containment events, fires, and explosions in refinery alkylation units. Replacing highly toxic chemicals with less hazardous chemicals is an "inherently safer design" approach.

Hierarchy of Controls

The **"hierarchy of controls"** is a method of identifying and ranking safeguards from most to least effective. Each control category is defined below. These definitions are from the Center for Chemical Process Safety (CCPS) book Inherently Safer Chemical Processes – A Life Cycle Approach [53, pp. 9-10].

Inherently Safer Design—Eliminating the hazard by using materials and process conditions that are non-hazardous; e.g., substituting water for a flammable solvent

Passive Safeguards—Minimizing the hazard through process and equipment design features that reduce either the frequency or consequence of the hazard without the active functioning of any device; e.g., providing a diked wall around a storage tank of flammable liquids

Active Safeguards —Using controls, alarms, safety instrumented systems, and mitigation systems to detect and respond to process deviation from normal operation; e.g., a pump which is shut off by a high-level switch in the downstream tank when the tank is 90% full. These systems are commonly referred to as engineering controls, although human intervention is also an active layer

Procedural Safeguards— Using policies, operating procedures, training, administrative checks, emergency response, and other management approaches to prevent incidents, or to minimize the effects of an incident; e.g., hot work procedures and permits. These approaches are commonly referred to as administrative controls

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[a] The RMP regulation assigns threshold quantities to chemicals that trigger coverage by the regulation. Of the 77 regulated toxic substances, HF is amongst the 8 chemicals with the lowest threshold values triggering coverage. EPA chose threshold quantities "based on a ranking method that considers each substance's toxicity and potential to become airborne and disperse" [100, p. 5104].

[b] The eight most toxic chemicals regulated by EPA RMP based upon threshold quantity (listed in parentheses) are arsine (1,000 lbs), chlorine dioxide (1,000 lbs), chloromethyl ether (1,000 lbs), fluorine (1,000 lbs), hydrogen fluoride / hydrofluoric acid (1,000 lbs), hydrogen selenide (500 lbs), nickel carbonyl (1,000 lbs), and phosgene (500 lbs). See 40 C.F.R. § 68.130.

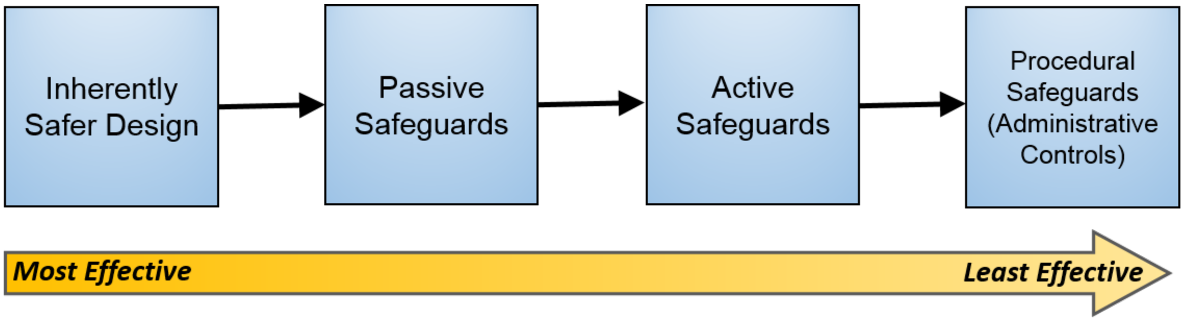

Figure 35. The hierarchy of controls, which ranks safeguards from most to least effective. (Credit: CSB, adapted from CCPS Inherently Safer Chemical Processes—A Life Cycle Approach [53])

2.5.1 CSB Actions on Inherently Safer Design Reviews

The CSB has evaluated and recommended inherently safer design solutions in multiple incident investigations, described below. In all of the described incidents, inherently safer design could have prevented or minimized the incidents' consequences and potential consequences.

2.5.1.1 2008 Bayer CropScience Incident

On August 28, 2008, a runaway chemical reaction occurred inside a 4,500-gallon pressure vessel, causing the vessel to explode violently in the methomyl unit at the Bayer CropScience facility in Institute, West Virginia. The methomyl unit used the highly toxic chemical, methyl isocyanate (MIC), in chemical reactions used to produce methomyl. Flying debris from the explosion struck the protective steel shield blanket surrounding a 6,700-gallon MIC tank but did not damage the tank [54, p. 7].

In 2009, Congress appropriated $600,000 to the CSB and directed that the funds:

> [S]hall be for a study by the National Academy of Sciences [NAS] to examine the use and storage of methyl isocyanate including the feasibility of implementing alternative chemicals or process and an examination of the cost of alternatives at Bayer CropScience facility in Institute, WV [54, p. 90].[a]

The CSB awarded a contract to NAS in September 2010 to meet the Congressional directive [54, pp. 90-91]. In addition to various other subjects covered in the report, the report discussed the multi-attribute utility (MAU) method—one of multiple types of methods companies can employ when evaluating inherently safer design options [55].

2.5.1.2 Tesoro Anacortes Refinery Incident

On April 2, 2010, the Tesoro Refining and Marketing Company LLC ("Tesoro") petroleum refinery in Anacortes, Washington experienced a catastrophic rupture of a heat exchanger in the Catalytic Reformer / Naphtha Hydrotreater unit ("the NHT unit"). The heat exchanger catastrophically ruptured because of High

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[a] Public Law 111-88, 123 Stat. 2949 – 2950

Temperature Hydrogen Attack (HTHA). Highly flammable hydrogen and naphtha at more than 500 degrees Fahrenheit (ºF) were released from the ruptured heat exchanger and ignited, causing an explosion and an intense fire that burned for more than three hours. The rupture fatally injured seven Tesoro employees (one shift supervisor and six operators) who were working in the immediate vicinity of the heat exchanger at the time of the incident [56].

In the Investigation Report, the CSB described how the incident could have been prevented using inherently safer design. The CSB recommended that the Governor and Legislature of the State of Washington augment its process safety management regulations to require companies to:

> Document[] use of inherently safer systems analysis and the hierarchy of controls to the greatest extent feasible in establishing safeguards for identified process hazards. The goal shall be to drive the risk of major accidents to As Low As Reasonably Practicable (ALARP). Include requirements for inherently safer systems analysis to be automatically triggered for all Management of Change and Process Hazard Analysis reviews, prior to the construction of new processes, process unit rebuilds, significant process repairs, and in the development of corrective actions from incident investigation recommendations [56, p. 115].

As of the date of this report, the Governor and Legislature of the State of Washington have not implemented this recommendation [57].

2.5.1.3 Chevron Richmond Refinery Incident

On August 6, 2012, the Chevron Refinery in Richmond, California, experienced a catastrophic pipe failure in a crude unit causing the release of a flammable hydrocarbon process fluid which partially vaporized into a large cloud. Nineteen Chevron employees engulfed by the vapor cloud narrowly escaped avoiding serious injury. The ignition and subsequent continued burning of the hydrocarbon process fluid resulted in a large plume of unknown particulates and vapor. Approximately 15,000 people from the surrounding area sought medical treatment in the weeks following the incident [58, pp. 1-2].

The CSB investigation found that the pipe failure was caused by sulfidation corrosion, a damage mechanism that causes piping walls to thin over time. The CSB also found that the California PSM regulation did not require the use of a recognized methodology for making an objective determination of the effectiveness of safeguards in place to prevent a hazardous consequence from occurring. A more detailed safeguard analysis, which requires sufficient consideration of the principles of inherently safer technology and to driving risks to ALARP could have identified the need to upgrade the metallurgy of the piping to a material less susceptible to sulfidation corrosion.

The CSB issued a recommendation to the California State Legislature, Governor of California to:

> Require the documented use of inherently safer systems analysis and the hierarchy of controls to the greatest extent feasible in establishing safeguards for identified process hazards. The goal shall be to drive the risk of major accidents to As Low As Reasonably Practicable (ALARP). Include requirements for

> inherently safer systems analysis to be automatically triggered for all Management of Change and Process Hazard Analysis reviews, prior to the construction of new process, process unit rebuilds, significant process repairs and in the development of corrective actions from incident investigation recommendations [58, p. 2].

On October 1, 2017, California adopted a new California PSM for Petroleum Refineries regulation (Section 5189.1), which added a new subsection concerning the documented use of inherently safer systems analysis and the hierarchy of controls to the greatest extent feasible in establishing safeguards for identified process hazards. The CSB Board voted to close the recommendation as "Closed-Acceptable Alternative Action [59]."

2.5.2 Significant Potential Off-Site Consequences from Refinery HF Releases

Because HF vaporizes upon release to the air, a large release of HF has the potential to travel off site and expose people, animals, and vegetation to harmful concentrations of the chemical. A 2005 study by the U.S. Public Interest Research Group found that HF releases from refineries could have significant off-site consequences, stating "[s]even petroleum refineries using hydrofluoric acid reported toxic release 'worst-case' scenarios in which more than one million people could be affected." It also found that "15 refineries could place more than 500,000 people in harm's way, and 28 refineries could endanger more than 100,000 people in the event of a worst-case hydrofluoric acid release" [60, p. 5]. The 2012 HF release in South Korea (described above) demonstrates the potential consequences of a large HF release.

Major process incidents at refineries involving fires and explosions that have or that could have caused releases of HF continue to occur with some frequency. Importantly, there have been multiple major incidents in recent years that had the potential to lead to significant HF releases in the U.S., and the PES incident did result in an HF release. As discussed in the next section, there are other alkylation technologies both currently used and in development.

2.5.3 Potential Alternatives to HF Alkylation

The current main alternative to hydrofluoric acid alkylation is sulfuric acid alkylation. Recently, there have been technological advances in developing other, potentially inherently safer alkylation catalysts—catalysts that in the event of a release might not present a major risk to the public or the environment. Some alkylation technological alternatives to HF alkylation are discussed below.[a] The CSB presents the below descriptions based upon publicly available information. The CSB does not endorse any of the technologies presented. Refineries considering any of these technologies must evaluate the technical parameters, hazards, and design factors to determine suitability for their own refinery operations.

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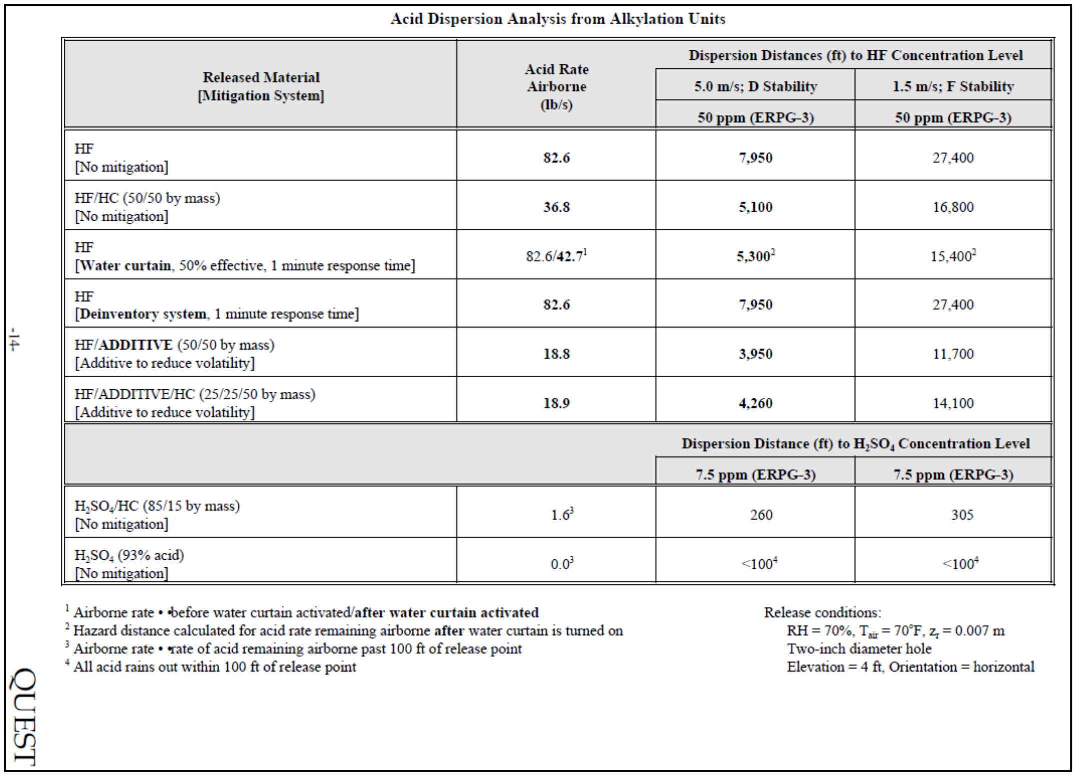
[a] This is not an exhaustive list of all alternative alkylation technologies.

1. Sulfuric Acid Catalyst

Sulfuric acid is the other primary alkylation catalyst used in today’s alkylation units. A 1995 study by Quest Consultants compared the risks associated with HF releases to sulfuric acid releases. The study stated, “Comparisons between releases for HF, both mitigated and unmitigated, and [sulfuric acid] were made. In all cases, the rate of HF that would remain airborne following a release would be larger than the rate of [sulfuric acid] remaining airborne.” The study also stated, “[T]he distances to ERPG-3[a] for HF range from 5.2 miles (8.3 km) to 2.2 miles (3.5 km) under worst-case conditions when various mitigation options and compositions are available [in the releases studied].[b] … None of the [sulfuric acid] releases produced downwind dispersion distances greater than about 300 ft (95 m) from the release point. This is due primarily to the inability of the release to form a significant cloud with [sulfuric acid] in it” [43]. See the tabulation of this information in **Figure 36** below. When comparing the offsite exposure risks associated with sulfuric acid and hydrofluoric acid, sulfuric acid presents the least risk of toxic exposure to populations offsite. For onsite spills, sulfuric acid still presents a hazard to workers and other people in the immediate vicinity of spills. Sulfuric acid is highly corrosive and can cause skin burns and other injuries upon contact [15].



Acid Dispersion Analysis from Alkylation Units

Released Material [Mitigation System]	Acid Rate Airborne (lb/s)	Dispersion Distances (ft) to HF Concentration Level	
		5.0 m/s; D Stability	**1.5 m/s; F Stability**
		50 ppm (ERPG-3)	**50 ppm (ERPG-3)**
HF [No mitigation]	**82.6**	**7,950**	27,400
HF/HC (50/50 by mass) [No mitigation]	**36.8**	**5,100**	16,800
HF [**Water curtain**, 50% effective, 1 minute response time]	82.6/**42.7**[1]	**5,300**[2]	15,400[2]
HF [**Deinventory system**, 1 minute response time]	**82.6**	**7,950**	27,400
HF/**ADDITIVE** (50/50 by mass) [Additive to reduce volatility]	**18.8**	**3,950**	11,700
HF/ADDITIVE/HC (25/25/50 by mass) [Additive to reduce volatility]	**18.9**	**4,260**	14,100
		Dispersion Distance (ft) to H_2SO_4 Concentration Level	
		7.5 ppm (ERPG-3)	**7.5 ppm (ERPG-3)**
H_2SO_4/HC (85/15 by mass) [No mitigation]	1.6[3]	260	305
H_2SO_4 (93% acid) [No mitigation]	0.0[3]	<100[4]	<100[4]

[1] Airborne rate • •before water curtain activated/**after water curtain activated**
[2] Hazard distance calculated for acid rate remaining airborne **after** water curtain is turned on
[3] Airborne rate • •rate of acid remaining airborne past 100 ft of release point
[4] All acid rains out within 100 ft of release point

Release conditions:
RH = 70%, T_{air} = 70°F, z_r = 0.007 m
Two-inch diameter hole
Elevation = 4 ft, Orientation = horizontal

Figure 36. Table showing alkylation unit acid dispersion analysis results from 1995 Quest Consultants study. (Credit: Quest Consultants [43, p. 14])

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[a] Emergency Response Planning Guidelines (ERPGs) are chemical concentration levels used when preparing for and responding to emergencies. They are designed to anticipate the public health effects of exposure to airborne chemicals. ERPG-3 refers to the maximum airborne concentration below which nearly all individuals could be exposed for up to one hour without experiencing or developing life-threatening health effects. ERPG-3 is a worst-case planning level. Exposure to concentrations above the ERPG-3 level will be lethal to some members of the community [101].

[b] Approximately 117,300 people live within one mile of the PES refinery boundary. See Section 1.11 and Appendix D for detailed demographic information of the area surrounding the PES refinery.

2. Ionic Liquid Catalyst

Chevron U.S.A. Inc. developed an ionic liquid acid catalyst, which it has since licensed to Honeywell UOP. The ionic liquid catalyst (called ISOALKY^{TM}) was successfully used for five years in a small unit at the Chevron Salt Lake City refinery. In 2017, Chevron began construction to convert its Salt Lake City refinery's HF alkylation unit to the ISOALKY technology [61]. The commercial-scale unit is now operational [62]. Big West Oil is also converting its HF alkylation unit in North Salt Lake City, Utah to the ISOALKY technology [63]. Regarding the ISOALKY technology, Honeywell UOP stated:

> This new technology uses a non-aqueous liquid salt, or ionic liquid, at temperatures below 100ºC to convert a typical stream from a fluid catalytic cracker into a valuable high-octane blending component that lowers the environmental impact of motor gasoline.
>
> Among the other benefits of this technology, the ionic liquids process can be used in new refineries, as well as existing facilities undergoing capital expansion. It can produce alkylate from a wider range of feedstocks using a lower volume of catalyst. This liquid catalyst has a negligible vapor pressure and can be regenerated on-site, giving it a lower environmental footprint than other technologies. […]
>
> Ionic liquids have strong acid properties, enabling them to perform acid catalysis, but without the volatility of conventional acids. They represent the first new class of liquid alkylation technology since World War II. They are technically a salt in liquid state, comprised largely of ions that convert C4 paraffins and other olefins into an excellent gasoline-range blending product. Due to its low vapor pressure, ionic liquid requires simpler handling procedures than either sulfuric or hydrofluoric acids [61].

3. Solid Acid Catalyst

Lummus Technology, Albemarle Catalysts, and Neste Oil developed technology called AlkyClean, a solid acid catalyst. It is a zeolite catalyst formulation, coupled with a reactor processing methodology, to yield alkylate product. Lummus says of the technology that it "eliminates corrosive liquid acid use and associated safety concerns; is tolerant to feedstock impurities, changes in feedstock olefin composition, and process upsets […]; and lowers maintenance and monitoring requirements [64]." In 2016, AlkyClean Technology was awarded the Presidential Green Chemistry Award from EPA [65].

4. Composite Ionic Liquid Catalyst

Well Resources Inc. developed technology called "ionikylation," which uses a composite ionic liquid as a catalyst for alkylation reactions. Well Resources Inc. states that ionikylation "is a commercially proven, non-hazardous, non-corrosive, and environmentally friendly alkylation process[.]" Well Resources Inc. also communicates that ionikylation technology is currently being used in multiple refineries in China [66].

Some refineries and communities have assessed the costs of switching to other alkylation technologies, as well as the viability of new technologies. For example, a 2016 study by Norton Engineering, which was commissioned by the South Coast Air Quality Management District in California, estimated that the cost of converting a 25,000 barrel per day HF alkylation unit to a sulfuric acid alkylation unit would cost about $110 million [67, pp. 39-41]. The study estimated that a new solid acid catalyst alkylation unit would cost about the same amount [67, p. 39]. The Torrance, California, refinery disputes these numbers and estimates that converting its modified HF alkylation unit to sulfuric acid alkylation would cost about $900 million [68, p. 159]. There are, however, technological designs available to convert from HF alkylation to sulfuric acid alkylation advertised as requiring only 40-60% of the cost of installing a new sulfuric acid alkylation unit [69]. The conversion projects implemented by both Chevron and Big West Oil in Salt Lake City, Utah (described above) can also help inform the industry of costs and commercial viability. The CSB concludes that technologies are being developed that could be safer alternatives to HF and sulfuric acid alkylation, including composite ionic liquid catalyst alkylation technology, solid acid catalyst alkylation technology, and the new ionic liquid acid catalyst alkylation technology developed by Chevron, which is now operating at commercial scale at Chevron's Salt Lake City refinery. The CSB also concludes that the continued development and use of alternative alkylation technologies can prevent future releases of toxic HF from refinery alkylation units.

2.5.4 EPA Inherently Safer Technology Actions

While formally evaluating inherently safer technologies for application at hazardous facilities can help prevent catastrophic incidents, there are currently no Federal regulations or statutes specifically requiring the evaluation of inherently safer technologies available. For example, both the EPA General Duty Clause and the EPA Risk Management Program (RMP) regulation issue safety requirements for facilities handling defined hazardous substances, including HF.[a] Neither require specific action resulting in the formal evaluation of inherently safer technologies. The EPA General Duty Clause found under the Clean Air Act Section 112(r)(1), for example, states the following:

> The owners and operators of stationary sources producing, processing, handling or storing such substances [i.e., a chemical in 40 C.F.R. part 68 or any other extremely hazardous substance] have a general duty [in the same manner and to the same extent as the general duty clause in the Occupational Safety and Health Act (OSHA)] to identify hazards which may result from (such) releases using appropriate hazard assessment techniques, to design and maintain a safe facility taking such steps as are necessary to prevent releases, and to minimize the consequences of accidental releases which do occur [70].

EPA guidance on the implementation of the general duty clause recommends actions that *could* result (but is not specifically required to result) in inherently safer design, as follows:

> Chemicals: The owners and operators should try to substitute less hazardous substances for extremely hazardous substances to minimize inventories when

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[a] 40 C.F.R. § 68.130

> possible. This is usually the most effective way to prevent accidents and should be the priority of a prevention program [71, p. 15].

And

> Equipment: The owners and operators should implement a quality control program to ensure that components and materials meet design specifications and to construct the process equipment as designed. The owners and operators should apply the same standard of care when modifying or repairing the facility. Safety equipment and inherently safer technology can be used to lessen the hazards posed by an extremely hazardous substance. Making vessels containing flammable materials inert, using alternate processes that require lower temperatures or pressures, installing relief systems, determining process siting, installing anti-static devices and other equipment are common mechanisms to lessen the hazards. Owners and operators should consult trade associations, industry consultants (e.g., Center for Chemical Process Safety, others) and safety engineers to determine standards and safety equipment employed at facilities [71, p. 15]. (Emphasis added.)

While the EPA General Duty Clause and its guidance can help spur companies to consider inherently safer design options, more specific and actionable requirements can prompt more robust consideration and evaluation of inherently safer design strategies, ultimately resulting in safer operations.

On August 1, 2013, President Barack Obama issued Executive Order 13650 – Improving Chemical Facility Safety and Security, which required "develop[ing] options for improved chemical facility safety and security that identifies improvements to existing risk management practices through agency programs, private sector initiatives, Government guidance, outreach, standards, and regulations" and required EPA to "determine if the RMP … can and should be expanded to address additional regulated substances and types of hazards" [72], [73]. In response to the Executive Order, on January 13, 2017, EPA published a final rule amending its Risk Management Program (RMP) regulation. In the Summary section of that new rule, EPA communicated:

> The revisions contain several changes to the accident prevention program requirements including an additional analysis of safer technology and alternatives as part of the process hazard analysis for some Program processes, third-party audits and incident investigation root cause analysis for Program 2 and Program 3 processes; enhancements to the emergency preparedness requirements; increased public availability of chemical hazard information; and several other changes to certain regulatory definitions and data elements submitted in risk management plans. These amendments seek to improve chemical process safety, assist local emergency authorities in planning for and responding to accidents, and improve public awareness of chemical hazards at regulated sources [74, p. 4594].

Regarding the requirement for analyzing safer technology and alternatives, the final rule stated:

> The third revision to the prevention program adds an element to the process hazard analysis (PHA), which is updated every five years. Specifically, owners or operators of facilities with Program 3 regulated processes in North American Industrial Classification System (NAICS) codes 322 (paper manufacturing), 324 (petroleum and coal products manufacturing), and 325 (chemical manufacturing) are required to conduct a safer technology and alternatives analysis (STAA) as part of their PHA, and to evaluate the practicability of any inherently safer technology (IST) identified. The current PHA requirements include consideration of active, passive, and procedural measures to control hazards. These revisions support the analysis of those measures and adds consideration of IST alternatives. The provision is intended to reduce the risk of serious accidental releases by requiring facilities in these sectors to conduct a careful examination of potentially safer technology and designs that they could implement in lieu of, or in addition to, their current technologies [74, p. 4595].

Before the new rule's effective date of March 14, 2017, on January 20, 2017, the Assistant to the President and Chief of Staff under President Donald Trump issued "Memorandum for the Heads of Executive Departments and Agencies; Regulatory Freeze Pending Review," stating:

> The President has asked me to communicate to each of you his plan for managing the Federal regulatory process at the outset of his Administration. In order to ensure that the President's appointees or designees have the opportunity to review any new or pending regulations, I ask on behalf of the President that you immediately take the following steps:
>
> […]
>
> With respect to regulations that have been published in the [Federal Register] but have not taken effect, as permitted by applicable law, temporarily postpone their effective date for 60 days from the date of this memorandum […] [75, p. 8346].

In response to the memo, on January 26, 2017 [76], March 16, 2017 [77], and June 14, 2017 [78], the EPA Administrator published rules delaying the publication of the EPA RMP regulation amendments until February 19, 2019. The purpose of the delay was to "allow[] the [EPA] time to consider petitions for reconsideration of the Risk Management Program Amendments and take further regulatory action, as appropriate, which could include proposing and finalizing a rule to revise or rescind these amendments [78, p. 27133]."

On August 17, 2018, the U.S. Court of Appeals for the District of Columbia Circuit determined that EPA's delay of implementing the EPA RMP regulation amendments was "arbitrary and capricious."[a] The Court ordered that the EPA delays be vacated [79]. On September 21, 2018, the Court issued a mandate[b] making the RMP Amendments rule effective. On December 3, 2018, EPA published in the Federal Register that the

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[a] *Air Alliance Houston v. Environmental Protection Agency*, 906 F.3d 1049 (D.C. Cir 2018)

[b] *Air Alliance Houston v. Environmental Protection Agency,* No. 17-1155, Document #1752053 (D.C. Cir 2018)

amendments to the RMP regulation were in effect [80], which included the amendments relating to inherently safer technology.

On December 19, 2019, EPA published a final rule, which, with a few minor exceptions “rescind[ed] all the prevention program related changes in the Amendments rule,” which included the inherently safer technology amendments [81]. As such, the current RMP regulation (as of the date of this report) includes no requirements for facilities to conduct inherently safer technology assessments. The CSB concludes that there is currently no Federal regulatory requirement for petroleum refineries to analyze and implement inherently safer design strategies to reduce the risk of serious accidental releases.

On January 20, 2021, President Joseph Biden issued Executive Order 13990 – Protecting Public Health and the Environment and Restoring Science to Tackle the Climate Crisis, which directed all executive departments and agencies to immediately review and take action to address the promulgation of Federal regulations on topics including improving public health and protecting the environment, ensuring access to clean air and water, and limiting exposure to dangerous chemicals [82]. In response, EPA hosted public listening sessions in June and July 2021 to solicit comments and suggestions from stakeholders pertaining to the RMP regulation [83]. As of the date of this report, EPA’s effort in responding to Executive Order 13990 is ongoing.

Because alternative and safer alkylation technologies exist, as described in this report, the CSB determined that it is critical that petroleum refineries evaluate the applicability of these technologies for implementation in existing HF alkylation units. The CSB concludes that EPA should require petroleum refineries to conduct a safer technology and alternatives analysis (STAA) as part of their PHA, and to evaluate the practicability of any inherently safer technology (IST) identified. The CSB recommends to EPA to take such action.

2.5.5 EPA Prioritization, Risk Evaluation, and Regulation of Chemical Substances and Mixtures

In 2016, Congress amended the Toxic Substances Control Act (TSCA) by enacting the Frank R. Lautenberg Chemical Safety for the 21st Century Act [84]. The 2016 TSCA amendments required EPA to “establish, by rule, a risk-based screening process, including criteria for designating chemical substances as high-priority substances for risk evaluations or low-priority substances for which risk evaluations are not warranted at the time.”[a] For chemicals determined to “present[] an unreasonable risk of injury to health or the environment,” TSCA gives EPA the authority to apply “requirements to such substance or mixture to the extent necessary so that the chemical substance or mixture no longer presents such a risk[.]”[b] As required by the TSCA amendments, EPA issued a final rule, which became effective in September 2017, that “establishes the process and criteria that EPA will use to identify chemical substances as either High-Priority Substances for risk evaluation, or Low-Priority Substances for which risk evaluations are not warranted at the time [85].” **Figure 37** below depicts EPA’s chemical prioritization process. EPA has not yet prioritized hydrofluoric acid or performed a risk evaluation of hydrofluoric acid under the new TSCA requirements [86].

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[a] The Frank R. Lautenberg Chemical Safety for the 21st Century Act, Pub. L. No. 114-182, 130 Stat. 448 (2016), *codified at* 15 U.S.C. § 2605(b)(1)(A)

[b] 15 U.S.C. § 2605(a)

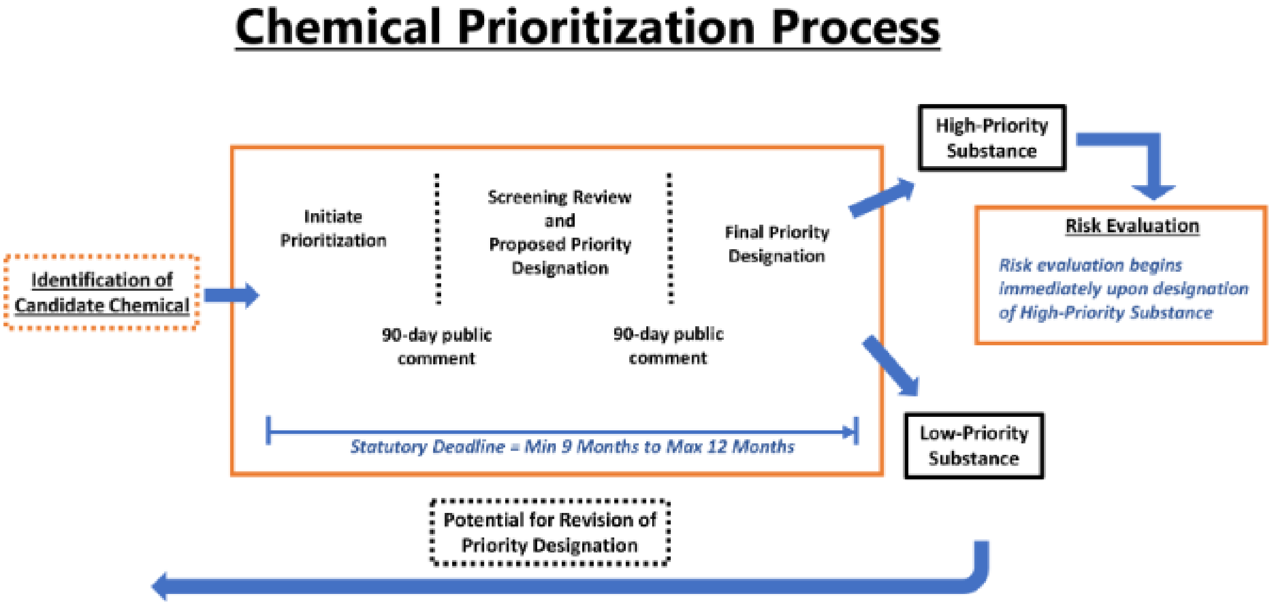

Figure 37. EPA's Chemical Prioritization Process (Credit: EPA [87])

As discussed in Sections 1.2, 2.4, and 2.5 of this report, hydrofluoric acid is a highly toxic chemical that can produce a vapor cloud upon release and is one of the eight most hazardous chemicals regulated by the EPA Risk Management Program (RMP).[a, b] The CSB concludes that EPA should initiate prioritization on hydrofluoric acid, and if hydrofluoric acid is determined to be a High-Priority Substance, conduct a risk evaluation of hydrofluoric acid, and implement any identified corrective actions, as required by the Toxic Substances Control Act. The CSB recommends to EPA to take such action.

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[a] The RMP regulation assigns threshold quantities to chemicals that trigger coverage by the regulation. Of the 77 regulated toxic substances, HF is amongst the 8 chemicals with the lowest threshold values triggering coverage. EPA chose threshold quantities "based on a ranking method that considers each substance's toxicity and potential to become airborne and disperse" [100, p. 5104].

[b] The eight most toxic chemicals regulated by EPA RMP based upon threshold quantity (listed in parentheses) are arsine (1,000 lbs), chlorine dioxide (1,000 lbs), chloromethyl ether (1,000 lbs), fluorine (1,000 lbs), hydrogen fluoride / hydrofluoric acid (1,000 lbs), hydrogen selenide (500 lbs), nickel carbonyl (1,000 lbs), and phosgene (500 lbs). See 40 C.F.R. § 68.130.

3 Conclusions

3.1 Findings

Mechanical Integrity Findings

1. The PES pipe elbow ruptured due to extensive HF corrosion that reduced its wall thickness. The higher concentration of nickel and copper in the PES pipe elbow caused the elbow to corrode faster than other components within the piping circuit.

2. The ruptured elbow's metallurgical composition did not meet the composition limits recommended by NACE paper 03651, which were later adopted by ASTM as supplementary requirements and recommended by API RP 751. Had the elbow met the composition recommendations, the elbow likely would not have corroded at a significantly faster rate than adjacent piping components and likely would not have failed from excessive thinning.

3. Before the elbow's installation into the HF alkylation unit around 1973, the failed elbow was initially manufactured and stamped as "YOLOY" steel and was later improperly stamped as ASTM A234 WPB steel, a different specification from YOLOY.

4. The applicable 1965 edition of ASTM A234 *Standard Specification for Factory-Made Wrought Carbon Steel and Ferritic Alloy Steel Welding Fittings* did not explicitly prohibit the addition of unspecified elements to steel, such as those specified in the YOLOY composition requirements. This 1965 lack of prohibitions on the addition of unspecified elements, such as nickel and copper, may have contributed to the double stamping of the failed elbow as both YOLOY and ASTM A234 WPB.

5. After the elbow's installation around 1973, language changes to ASTM A234 were made in 1980 and 1996 that make it clear that YOLOY steel cannot be labeled or restamped as ASTM A234 WPB steel. These language changes should prevent future instances of this improper material substitution.

6. After the 1995 update to ASTM A234 in which limits on copper and nickel composition for WPB steel began to be specified, the PES elbow that ruptured did not meet the new ASTM A234 WPB copper and nickel requirements.

7. While ASTM A106—the standard for straight piping—has supplementary composition requirements specifically for piping use in HF service incorporating the residual element (RE) composition recommendations in NACE paper 03651, ASTM A234—the standard for fittings—does not include similar supplementary composition requirements.

8. Revisions to the ASTM A234 standard, incorporating the residual element (RE) composition recommendations in NACE paper 03651, can help prevent future installations of equipment that could corrode at varying rates in HF alkylation units.

9. PES and the previous owner Sunoco never inspected all carbon steel components within the HF alkylation unit. Such a program was not required in API RP 751 *Safe Operation of Hydrofluoric Acid Alkylation Units*.

10. Had PES or Sunoco inspected all carbon steel piping circuit components susceptible to HF corrosion in the HF alkylation unit, they may have identified that the elbow was corroding at a faster rate than adjacent piping components, which could have prevented the incident.
11. The new requirements in API RP 751 *Safe Operation of Hydrofluoric Acid Alkylation Units* for refiners to develop a special emphasis inspection program to inspect all individual carbon steel piping components and welds in identified HF alkylation corrosion zones to identify areas of accelerated corrosion should help prevent future failures of piping components corroding faster due to the presence of significant concentrations of copper and nickel within the steel.

Verifying Safety of Equipment After Changes to RAGAGEP Findings

12. The seminal research presented in the 2003 NACE paper 03651 *Specification for Carbon Steel Materials for Hydrofluoric Acid Alkylation Units* directly led to changes in industry guidance quantifying the levels of nickel and copper in steel that could be considered safe for use in HF alkylation units. API RP 751, Sunoco, and PES did not effectively respond to these advancements in industry knowledge by ensuring the safety of existing facilities through requiring all carbon steel piping circuit components to be inspected.

Remotely Operated Emergency Isolation Valves Findings

13. Based on the thinning of the V-1 vessel steel, it is reasonable to conclude that a jet flame from the ruptured elbow impinged upon the bottom of V-1. The fire weakened the steel, causing the steel to stretch and thin until the vessel ruptured.
14. Had emergency isolation valves been installed in the PES HF alkylation unit to remotely and automatically isolate the large hydrocarbon sources adjacent to the failed elbow, the duration of the release could have been minimized and the subsequent explosions could have been prevented.

Safeguard Reliability in HF Alkylation Units Findings

15. The 5th edition of API RP 751 *Safe Operation of Hydrofluoric Acid Alkylation Units* contains gaps relating to (1) the protection of control systems and backup power systems from fire and explosion hazards, and (2) the ability to isolate and stop releases from large hydrocarbon-containing vessels and all large inventories of HF using remotely operated emergency isolation valves.
16. To help prevent future incidents similar to the PES incident, in which control and backup systems were rendered inoperable by fire and large hydrocarbon vessels could not be isolated, API RP 751 should be updated with new safety requirements on these topics.

17. To help ensure that new API RP 751 safety requirements and recommendations are implemented effectively nationwide, EPA should emphasize inspecting refinery HF alkylation units under its National Compliance Initiative called Reducing Risks of Accidental Releases at Industrial and Chemical Facilities to help decrease the likelihood of chemical accidents, and resulting catastrophic consequences, in refinery HF alkylation units.

Inherently Safer Design Findings

18. Technologies are being developed that could be safer alternatives to HF and sulfuric acid alkylation, including composite ionic liquid catalyst alkylation technology, solid acid catalyst alkylation technology, and the new ionic liquid acid catalyst alkylation technology developed by Chevron, which is now operating at commercial scale at Chevron's Salt Lake City refinery.
19. The continued development and use of alternative alkylation technologies can prevent future releases of toxic HF from refinery alkylation units.
20. There is currently no Federal regulatory requirement for petroleum refineries to analyze and implement inherently safer design strategies to reduce the risk of serious accidental releases.
21. EPA should require petroleum refineries to conduct a safer technology and alternatives analysis (STAA) as part of their PHA, and to evaluate the practicability of any inherently safer technology (IST) identified.
22. EPA should initiate prioritization on hydrofluoric acid, and if hydrofluoric acid is determined to be a High-Priority Substance, conduct a risk evaluation of hydrofluoric acid, and implement any identified corrective actions, as required by the Toxic Substances Control Act.

3.2 Cause

The CSB determined the cause of the incident was the rupture of a steel piping component with high nickel and copper content that had corroded from HF and thinned faster than adjacent piping components with lower nickel and copper content. The ruptured pipe released propane and toxic hydrofluoric acid to the atmosphere.

Contributing to the incident was the lack of requirements by the American Petroleum Institute, Sunoco, and PES, to inspect all existing carbon steel piping circuit components to ensure they could safely operate in HF service after the industry began quantifying the levels of nickel and copper in steel that could be considered safe for use in HF alkylation units in 2003.

Contributing to the severity of the incident was the absence of remotely operated emergency isolation valves to isolate large sources of hydrocarbons, and incident-induced damage to the water mitigation system that limited PES's ability to suppress released HF during the incident.

4 Recommendations

To prevent future chemical incidents, and in the interest of driving chemical safety change to protect people and the environment, the CSB makes the following safety recommendations:

4.1 U.S. Environmental Protection Agency

2019-04-I-PA-R1

Develop a program that prioritizes and emphasizes inspections of refinery HF alkylation units, for example under EPA's National Compliance Initiative called Reducing Risks of Accidental Releases at Industrial and Chemical Facilities. As part of this program, verify that HF alkylation units are complying with API RP 751 *Safe Operation of Hydrofluoric Acid Alkylation Units*, including but not limited to the implementation of a special emphasis inspection program to inspect all individual carbon steel piping components and welds to identify areas of accelerated corrosion; the protection of safety-critical safeguards and associated control system components, including but not limited to wiring and cabling for control systems and primary and backup power supplies, from fire and explosion hazards including radiant heat and flying projectiles (per recommendation 2019-04-I-PA-R4); and the installation of remotely-operated emergency isolation valves on the inlet(s) and outlet(s) of all hydrofluoric acid containing vessels, and hydrocarbon containing vessels meeting defined threshold quantities (per recommendation 2019-04-I-PA-R4).

2019-04-I-PA-R2

Revise 40 C.F.R. Part 68 (EPA Risk Management Plan) to require new and existing petroleum refineries with HF alkylation units to conduct a safer technology and alternatives analysis (STAA) and to evaluate the practicability of any inherently safer technology (IST) identified. Require that these evaluations are performed every 5 years as a part of an initial PHA as well as PHA revalidations.

2019-04-I-PA-R3

Per the requirements in EPA Rule *Procedures for Prioritization of Chemicals for Risk Evaluation Under the Toxic Substances Control Act*, initiate prioritization to evaluate whether hydrofluoric acid is a High-Priority Substance for risk evaluation. If it is determined to be a High-Priority Substance, conduct a risk evaluation of hydrofluoric acid to determine whether it presents an unreasonable risk of injury to health or the environment. If it is determined to present an unreasonable risk of injury to health or the environment, apply requirements to hydrofluoric acid to the extent necessary to eliminate or significantly mitigate the risk, for example by using a methodology such as the hierarchy of controls.

4.2 American Petroleum Institute

2019-04-I-PA-R4

Update API RP 751 *Safe Operation of Hydrofluoric Acid Alkylation Units* to require the following:

a. Protection of critical safeguards and associated control system components, including but not limited to wiring and cabling for control systems and primary and backup power supplies, from fire and explosion hazards, including radiant heat and flying projectiles; and

b. Installation of remotely-operated emergency isolation valves on the inlet(s) and outlet(s) of all hydrofluoric acid containing vessels, and hydrocarbon containing vessels meeting defined threshold quantities.

4.3 ASTM International

2019-04-I-PA-R5

Revise ASTM A234 to incorporate supplementary requirements for piping used in HF service, as defined in HF supplementary requirements S9.1 through S9.7 in ASTM A106 version 19a.

5 Key Lessons for the Industry

To prevent future chemical incidents, and in the interest of driving chemical safety change to protect people and the environment, the CSB urges companies to review these key lessons:

1. Carbon steel is commonly used in HF alkylation units and is known to be susceptible to HF corrosion. High concentrations of copper, nickel, or chromium within the steel, which the literature refers to as residual elements (REs), can cause faster corrosion rates of carbon steel exposed to HF. To identify piping components with high RE composition and that are corroding faster than other components, refiners must develop a special emphasis inspection program to inspect all individual carbon steel piping components and welds in identified HF alkylation corrosion zones to identify areas of accelerated corrosion, as required in API RP 751. After the initial inspection, the CMLs for each piping circuit should include CMLs placed on components that have lower wall thicknesses and/or higher corrosion rates.

2. To prevent catastrophic incidents, companies and industry trade groups must take swift action to ensure process safety when new knowledge on hazards is published. These actions must include ensuring that facilities built before the new knowledge was published are still safe to operate. Ensuring safety can include 100% inspection of all equipment and piping, equipment replacement, and other changes needed to prevent loss of containment events.

3. To facilitate quickly stopping hydrocarbon and HF releases in HF alkylation units, refiners should install remotely-operated emergency isolation valves on the inlet(s) and outlet(s) of large capacity hydrocarbon containing vessels and all hydrofluoric acid containing vessels in hydrofluoric acid alkylation units. Quickly stopping hydrocarbon and HF releases through the use of remotely-operated emergency isolation valves can help prevent much larger and catastrophic knock-on events, such as equipment ruptures, propelling of equipment fragments, and large releases of HF to offsite communities.

4. “Active” safeguards—or safeguards that require a person or technology to trigger their activation—have the potential to fail in major incidents involving fires and explosions. If critical safeguards fail within an HF alkylation unit, a release of highly toxic HF can occur. Therefore, it is essential that HF alkylation units be equipped with safeguards that can prevent or mitigate the consequences of an HF release in a catastrophic incident involving fire or explosions. Refiners should protect critical safeguards and associated control system components, including but not limited to wiring and cabling for control systems and primary and backup power supplies, from fire and explosion hazards, including radiant heat and flying projectiles.

5. Technologies are being developed that could be safer alternatives to HF and sulfuric acid alkylation, including composite ionic liquid catalyst alkylation technology, solid acid catalyst alkylation technology, and the new ionic liquid acid catalyst alkylation technology developed by Chevron, which is now operating at commercial scale at Chevron’s Salt Lake City refinery. The continued development and use of alternative alkylation technologies can prevent future releases of toxic HF from refinery alkylation units. Refiners should periodically evaluate these and other emerging alternative technologies for use in their alkylation units.

6 References

[1] Center for Chemical Process Safety (CCPS), Guidelines for Vapor Cloud Explosion, Pressure Vessel Burst, BLEVE, and Flash Fire Hazards, 2nd ed., New York: American Institute of Chemical Engineers and John Wiley & Sons, Inc., 2010.

[2] United States Department of Labor, Occupational Safety and Health Administration, "Standard Interpretations - RAGAGEP in Process Safety Management Enforcement," 11 May 2016. [Online]. Available: https://www.osha.gov/laws-regs/standardinterpretations/2016-05-11. [Accessed 15 May 2020].

[3] Marsh JLT Specialty, "100 Largest Losses in the Hydrocarbon Industry," 26th ed., March 2020. [Online]. Available: https://www.marsh.com/uk/insights/research/100-largest-losses-hydrocarbon-industry.html. [Accessed 23 November 2020].

[4] A. McCormick, "Philadelphia Energy Solutions oil refinery announces plans to close following fire," Associated Press, [Online]. Available: https://6abc.com/business/philadelphia-energy-solutions-refinery-to-close-after-fire/5365632/. [Accessed 26 July 2019].

[5] UPI, "Final approval given to Chevron-Gulf merger," [Online]. Available: https://www.upi.com/Archives/1984/10/24/Final-approval-given-to-Chevron-Gulf-merger/7398467438400/. [Accessed 26 July 2019].

[6] Philadelphia Energy Solutions, "Refining Complex - History," [Online]. Available: https://pes-companies.com/refining-complex/history/. [Accessed 26 July 2019].

[7] U.S. Environmental Protection Agency, "PES Holdings, LLC, et. al. Bankruptcy Renewable Fuel Standard Settlement," [Online]. Available: https://www.epa.gov/enforcement/pes-holdings-llc-et-al-bankruptcy-renewable-fuel-standard-settlement. [Accessed 26 July 2019].

[8] L. Kearney and J. Renshaw, "Philadelphia Energy Solutions files for bankruptcy after refinery fire," Reuters, [Online]. Available: https://www.reuters.com/article/us-pes-bankruptcy/philadelphia-energy-solutions-files-for-bankruptcy-after-refinery-fire-idUSKCN1UH0O9. [Accessed 26 July 2019].

[9] A. Maykuth, "After Last-Minute Negotiations, Judge Picks a Winner in Philadelphia Refinery Auction," The Philadelphia Inquirer, 12 February 2020. [Online]. Available: https://www.inquirer.com/business/energy/pes-hilco-philadelphia-refinery-bankruptcy-auction-winner-20200213.html. [Accessed 28 February 2020].

[10] S. Phillips, "PES Refinery Demolition to Take Four Years, New Owner Hilco Says," WHYY, 4 June 2021. [Online]. Available: https://whyy.org/articles/pes-refinery-demolition-to-take-four-years-new-owner-hilco-says/. [Accessed 21 December 2021].

[11] AFPM, "Alkylation - A Key to Cleaner Gasoline and Better Vehicle Mileage," [Online]. Available: https://www.afpm.org/sites/default/files/issue_resources/AlkylationCleanerFuels%26Efficiency2021.pdf. [Accessed 21 December 2021].

[12] U.S. Energy Information Administration (EIA), "Alkylation is an important source for octane in gasoline," [Online]. Available: https://www.eia.gov/todayinenergy/detail.php?id=9971. [Accessed 21 August 2019].

[13] Centers for Disease Control and Prevention (CDC), The National Institute for Occupational Safety and Health (NIOSH), "Hydrogen Fluoride," [Online]. Available: https://www.cdc.gov/niosh/npg/npgd0334.html. [Accessed 20 August 2019].

[14] UNC Environment, Health & Safety, "Hydrofluoric Acid Chemical Safety Information," [Online]. Available: https://ehs.unc.edu/files/2015/09/hydrofluoricacid.pdf. [Accessed 20 August 2019].

[15] Agency for Toxic Substances and Disease Registry, "Public Health Statement - Sulfur Trioxide and Sulfuric Acid," December 1998. [Online]. Available: https://www.atsdr.cdc.gov/toxprofiles/tp117-c1-b.pdf. [Accessed 21 December 2021].

[16] NBC10 Philadelphia, "The Moment a Refinery Blast Rocked Philly," YouTube, 21 June 2019. [Online]. Available: https://www.youtube.com/watch?v=yCXysi2g61Q. [Accessed 24 October 2019].

[17] American Petroleum Institute (API), API RP 751 - Safe Operation of Hydrofluoric Acid Alkylation Units, 4th ed., 2013.

[18] American Society for Testing Materials, "Symposium on High-Strength Constructional Metals," in *Pittsburgh Regional Meeting*, March 4, 1936.

[19] ASTM, ASTM A234-80a: Standard Specification for Piping Fittings of Wrought Carbon Steel and Alloy Steel for Moderate and Elevated Temperatures, 1980.

[20] American Petroleum Institute (API), API 570 - Piping Inspection Code: In-service Inspection, Rating, Repair, and Alteration of Piping Systems, 3rd ed., 2009.

[21] D. P. Nolan, Handbook of Fire and Explosion Protection Engineering Principles (3rd Edition), Elsevier, 2014.

[22] Weather Underground, "Philadelphia, PA Weather History," 21 June 2019. [Online]. Available: https://www.wunderground.com/history/daily/us/pa/philadelphia/KPHL/date/2019-6-21. [Accessed 2 February 2022].

[23] G. Chirinos, D. J. Marsh, R. Newman and D. J. Palmer, "Materials Specification for HF Alkylation Plants," Capcis, Manchester, 2002.

[24] H. H. Hashim and W. L. Valerioti, "Effect of Residual Copper, Nickel, and Chromium on the Corrosion Resistance of Carbon Steel in Hydrofluoric Acid Alkylation Service," in *Corrosion 93*, 1993.

[25] H. S. Jennings, "Materials for Hydrofluoric Acid Service in the New Millennium," in *Corrosion 2001*, LaPorte, 2001.

[26] A. Gysbers, H. Hashim, D. Clarida, G. Chirinos, J. Marsh and J. Palmer, "Specification for Carbon Steel Materials for Hydrofluoric Acid Alkylation Units, Paper No. 03651," *Corrosion 2003, NACE International,* 2003.

[27] ASTM, ASTM Designation: A234/A 234M - 96b - Standard Specification for Piping Fittings of Wrought Carbon Steel and Alloy Steel for Moderate and High Temperature Service, 1996.

[28] ASTM, Designation: A234-65: Standard Specification for Factory-Made Wrought Carbon Steel and Ferritic Alloy Steel Welding Fittings, 1965.

[29] ASTM, Designation: A106-72a: Standard Specification for Seamless Carbon Steel Pipe for High-Temperature Service, 1972.

[30] ASTM International, Designation: A234/A234M - 18a: Standard Specification for Piping Fittings of Wrought Carbon Steel and Alloy Steel for Monderate and High Temperature Service, 2018.

[31] ASTM International, A106 / A106M - 04: Standard Specification for Seamless Carbon Steel Pipe for High-Temperature Service, 2004.

[32] ASTM International, A106/A106M-19a: Standard Specification for Seamless Carbon Steel Pipe for High-Temperature Service, 2019.

[33] American Petroleum Institute (API), "Recommended Practice for Safe Operation of Hydrofluoric Acid Alkylation Units - API RP 751," American Petroleum Institute (API), 1999.

[34] American Petroleum Institute (API), API RP 751 - Safe Operation of Hydrofluoric Acid Alkylation Units, 3rd ed., 2007.

[35] American Petroleum Institute (API), API RP 751 - Safe Operation of Hydrofluoric Acid Alkylation Units, 5th ed., 2021.

[36] U.S. Environmental Protection Agency, "Complying with process safety information (PSI) resulting from new and updated recognized and generally accepted good engineering practices (RAGAGEP)," [Online]. Available: https://www.epa.gov/rmp/complying-process-safety-information-psi-resulting-new-and-updated-recognized-and-generally. [Accessed 17 March 2022].

[37] R. Diener, "Mitigation of HF Releases," *Journal of Loss Prevention in the Process Industries,* vol. 4, no. 1, pp. 35-43, 1991.

[38] "Hydrogen Fluoride Study: Report to Congress, Section 112(n)(6), Clean Air Act As Amended: Final Report," 1993. [Online]. Available: http://www.documentcloud.org/documents/70516-epa-hydrogen-fluoride-study.html. [Accessed 19 November 2019].

[39] P. Applebome, "Acid Leak in Texas Leaves a Residue of Questions," The New York Times, 20 December 1987. [Online]. Available: https://www.nytimes.com/1987/12/20/us/acid-leak-in-texas-leaves-a-residue-of-questions.html. [Accessed 10 September 2019].

[40] ABC News, "Cloud Over Texas City," *20/20,* 1989.

[41] J. L. Rabin, "Mobil Refinery Explosion Rekindles Safety Debate," 20 December 1987. [Online]. Available: https://www.latimes.com/archives/la-xpm-1987-12-20-me-29996-story.html. [Accessed 19 May 2020].

[42] Public Law 101-549, 101st Congress, "Title I - Provisions for Attainment and Maintenance of National Ambient Air Quality Standards (Clean Air Act Amendments of 1990)," 1990. [Online]. Available: https://www.govinfo.gov/content/pkg/STATUTE-104/pdf/STATUTE-104-Pg2399.pdf. [Accessed 19 November 2019].

[43] J. B. Cornwell and D. W. Johnson, "Effectiveness of Mitigation Systems in Reducing Hazards of Hydrogen Fluoride Leaks," in *First Risk Control Engineering Seminar*, Maracaibo, Venezuela, 1995.

[44] U.S. Chemical Safety and Hazard Investigation Board (CSB), "Urgent Recommendations - CITGO Corpus Christi Refinery Hydrofluoric Acid Release and Fire," 9 December 2009. [Online]. Available: https://www.csb.gov/citgo-refinery-hydrofluoric-acid-release-and-fire/. [Accessed 4 February 2020].

[45] Soo Bin Park, "Alert Over South Korea Toxic Leaks," 2013 February 7. [Online]. Available: https://www.nature.com/news/polopoly_fs/1.12369!/menu/main/topColumns/topLeftColumn/pdf/494015a.pdf?origin=ppub. [Accessed 10 September 2019].

[46] RT News, "South Korea's Silicon Valley Declared 'Disaster Zone' After Chemical Leak," 9 October 2012. [Online]. Available: https://www.rt.com/news/south-korea-disaster-leak-967/. [Accessed 10 September 2019].

[47] "yna.co.kr," 9 October 2012. [Online]. Available: https://www.yna.co.kr/view/AKR20121008204200004. [Accessed 2019 10 September].

[48] U.S. Chemical Safety and Hazard Investigation Report (CSB), "Investigation Report: ExxonMobil Torrance Refinery Electrostatic Precipitator Explosion," May 2017. [Online]. Available: https://www.csb.gov/exxonmobil-refinery-explosion-/. [Accessed 25 November 2019].

[49] U.S. Chemical Safety Board, "Statement from CSB Interim Executive Authority on U.S. Ninth Circuit Court of Appeals Decision in ExxonMobil Case," 10 December 2019. [Online]. Available: https://www.csb.gov/statement-from-csb-interim-executive-authority-on-us-ninth-circuit-court-of-appeals-decision-in-exxonmobil-case/. [Accessed 12 December 2019].

[50] U.S. Chemical Safety and Hazard Investigation Board (CSB), "Factual Investigative Update: April 26, 2018 Husky Superior Refinery Explosion and Fire," August 2018. [Online]. Available: https://www.csb.gov/husky-energy-refinery-explosion-and-fire/. [Accessed 25 November 2019].

[51] K. M. Kulinowski, "Letter from CSB Designated Interim Executive and Administrative Authority to EPA Administrator," 23 April 2019. [Online]. Available: https://www.csb.gov/assets/1/6/letter_to_epa_4.23.2019.pdf. [Accessed 20 November 2019].

[52] United States Environmental Protection Agency, "National Compliance Initiative: Reducing Risks of Accidental Releases at Industrial and Chemical Facilities," [Online]. Available: https://www.epa.gov/enforcement/national-compliance-initiative-reducing-risks-accidental-releases-industrial-and. [Accessed 31 January 2022].

[53] Center for Chemical Process Safety (CCPS), Inherently Safer Chemical Processes - A Life Cycle Approach, 2nd ed., Hoboken, New Jersey: CCPS and John Wiley & Sons, Inc., 2009.

[54] U.S. Chemical Safety and Hazard Investigation Board (CSB), "Investigation Report - Pesticide Chemical Runaway Reaction Pressure Vessel Explosion," January 2011. [Online]. Available: https://www.csb.gov/file.aspx?DocumentId=6089. [Accessed 9 February 2022].

[55] National Research Council of the National Academies, Committee on Inherently Safer Chemical Processes, "The Use and Storage of Methyl Isocyanate (MIC) at Bayer CropScience," 2012. [Online]. Available: https://www.nap.edu/read/13385/chapter/1. [Accessed 9 February 2022].

[56] U.S. Chemical Safety and Hazard Investigation Board (CSB), "Investigation Report - Catastrophic Rupture of Heat Exchanger," May 2014. [Online]. Available: https://www.csb.gov/tesoro-refinery-fatal-explosion-and-fire/. [Accessed 9 February 2022].

[57] U.S. Chemical Safety and Hazard Investigation Board (CSB), "Recommendations - Tesoro Refinery Fatal Explosion and Fire," [Online]. Available: https://www.csb.gov/recommendations/?F_InvestigationId=3572. [Accessed 9 February 2022].

[58] U.S. Chemical Safety Board, "Final Investigation Report - Chevron Richmond Refinery Pipe Rupture and Fire," January 2015. [Online]. Available: https://www.csb.gov/chevron-refinery-fire/. [Accessed 2 February 2022].

[59] U.S. Chemical Safety and Hazard Investigation Board (CSB), "Recommendations Status Change Summary," 30 May 2018. [Online]. Available: https://www.csb.gov/assets/recommendation/status_change_summary_ca_(chevron_r13)_c-aaa.pdf. [Accessed 9 February 2022].

[60] U.S. PIRG Education Fund, "Needless Risk - Oil Refineries and Hazard Reduction," August 2005. [Online]. Available: https://uspirg.org/sites/pirg/files/reports/Needless_Risk_USPIRG.pdf. [Accessed 10 September 2019].

[61] Honewell UOP, "Honeywell UOP Introduces Ionic Liquids Alkylation Technology," 23 September 2016. [Online]. Available: https://www.uop.com/?press_release=honeywell-uop-introduces-ionic-liquids. [Accessed 12 December 2019].

[62] A. Doyle, "Safer and More Efficient Alkylation Process Now at Commercial Scale," The Chemical Engineer, 5 May 2021. [Online]. Available: https://www.thechemicalengineer.com/news/safer-and-more-efficient-alkylation-process-now-at-commercial-scale/. [Accessed 13 December 2021].

[63] R. Brelsford, "Big West Oil Lets Contract For Unit Revamp at Utah Refinery," Oil and Gas Journal, 11 November 2021. [Online]. Available: https://www.ogj.com/refining-processing/refining/optimization/article/14213854/big-west-oil-lets-contract-for-unit-revamp-at-utah-refinery. [Accessed 21 December 2021].

[64] Lummus Technology, "AlkyClean," [Online]. Available: https://www.lummustechnology.com/Process-Technologies/Refining/Clean-Fuels/Gasoline-Alkylate-Production/AlkyClean%C2%AE. [Accessed 18 March 2022].

[65] Environmental Protection Agency (EPA), "Green Chemistry Challenge Winners," [Online]. Available: https://www.epa.gov/greenchemistry/green-chemistry-challenge-winners. [Accessed 12 December 2019].

[66] Well Resources Inc. , "About Ionikylation," [Online]. Available: https://www.wellresources.ca/ionikylation. [Accessed 13 December 2019].

[67] Norton Engineering, "Alkylation Technology Study Final Report," 9 September 2016. [Online]. Available: http://www.aqmd.gov/docs/default-source/permitting/alkylation-technology-study-final-report.pdf?sfvrsn=6. [Accessed 3 January 2020].

[68] Torrance Refining Company, "Setting the Record Straight - The Truth About Torrance Refinery MHF," 16 January 2018. [Online]. Available: https://torrancerefinery.com/wp-content/uploads/2018/03/MHF-MvF-TechDeck-Complete-1.16.18-FINAL.pdf. [Accessed 3 January 2020].

[69] CISION, "DuPont Introduces DuPont ConvEx HF Alkylation Conversion and Expansion Technology," 5 September 2017. [Online]. Available: https://www.prweb.com/releases/dupont-clean-technologies/convex-alkylation-tech/prweb14660203.htm. [Accessed 7 January 2020].

[70] U.S. Environmental Protection Agency, "The General Duty Clause," April 2020. [Online]. Available: https://www.epa.gov/sites/default/files/2013-10/documents/gdc-fact.pdf. [Accessed 9 February 2022].

[71] U.S. EPA, "Guidance for Implementation of the General Duty Clause Clean Air Act Section 112(r)(1)," May 2000. [Online]. Available: https://www.epa.gov/sites/default/files/documents/gendutyclause-rpt.pdf. [Accessed 9 February 2022].

[72] The White House, "Executive Order - Improving Chemical Facility Safety and Security," 1 August 2013. [Online]. Available: https://obamawhitehouse.archives.gov/the-press-office/2013/08/01/executive-order-improving-chemical-facility-safety-and-security. [Accessed 24 January 2022].

[73] Federal Register, "78 FR 48029 - Improving Chemical Facility Safety and Security," 7 August 2013. [Online]. Available: https://www.federalregister.gov/documents/2013/08/07/2013-19220/improving-chemical-facility-safety-and-security. [Accessed 24 January 2022].

[74] Federal Register, "82 FR 4594 - Accidental Release Prevention Requirements: Risk Management Programs Under the Clean Air Act," 13 January 2017. [Online]. Available: https://www.federalregister.gov/documents/2017/01/13/2016-31426/accidental-release-prevention-requirements-risk-management-programs-under-the-clean-air-act. [Accessed 24 January 2022].

[75] Federal Register, "82 FR 8346 - Memorandum for the Heads of Executive Departments and Agencies; Regulatory Freeze Pending Review," 20 January 2017. [Online]. Available: https://www.federalregister.gov/documents/2017/01/24/2017-01766/memorandum-for-the-heads-of-executive-departments-and-agencies-regulatory-freeze-pending-review. [Accessed 24 January 2022].

[76] Federal Register, "82 FR 8499 - Delay of Effective Date for 30 Final Regulations Published by the Environmental Protection Agency Between October 28, 2016 and January 17, 2017," 26 January 2017. [Online]. Available: https://www.federalregister.gov/documents/2017/01/26/2017-01822/delay-of-effective-date-for-30-final-regulations-published-by-the-environmental-protection-agency. [Accessed 24 January 2022].

[77] Federal Register, "82 FR 13968 - Accidental Release Prevention Requirements: Risk Management Programs Under the Clean Air Act; Further Delay of Effective Date," 16 March 2017. [Online]. Available: https://www.federalregister.gov/documents/2017/03/16/2017-05288/accidental-release-prevention-requirements-risk-management-programs-under-the-clean-air-act-further. [Accessed 24 January 2022].

[78] Federal Register, "82 FR 27133 - Accidental Release Prevention Requirements: Risk Management Programs Under the Clean Air Act; Further Delay of Effective Date," 14 June 2017. [Online]. Available: https://www.federalregister.gov/documents/2017/06/14/2017-12340/accidental-release-prevention-requirements-risk-management-programs-under-the-clean-air-act-further. [Accessed 24 January 2022].

[79] United States Court of Appeals for the District of Columbia Circuit, "Petitioners' Joint Motion for Expedited Issuance of the Court's Mandate," 24 August 2018. [Online]. Available: https://oshadefensereport.com/wp-content/uploads/2018/09/pet-motion-for-expedited-issuance-of-mandate.pdf. [Accessed 25 January 2022].

[80] Federal Register, "83 FR 62268 - Accidental Release Prevention Requirements: Risk Management Programs Under the Clean Air Act," 3 December 2018. [Online]. Available: https://www.federalregister.gov/documents/2018/12/03/2018-26224/accidental-release-prevention-requirements-risk-management-programs-under-the-clean-air-act. [Accessed 25 January 2022].

[81] Federal Register, "84 FR 69834 - Accidental Release Prevention Requirements: Risk Management Programs Under the Clean Air Act," 19 December 2019. [Online]. Available: https://www.federalregister.gov/documents/2019/12/19/2019-25974/accidental-release-prevention-requirements-risk-management-programs-under-the-clean-air-act. [Accessed 24 January 2022].

[82] Federal Register, "86 FR 7037 - Executive Order 13990 Protecting Public Health and the Environment and Restoring Science to Tackle the Climate Crisis," 25 January 2021. [Online]. Available: https://www.federalregister.gov/documents/2021/01/25/2021-01765/protecting-public-health-and-the-environment-and-restoring-science-to-tackle-the-climate-crisis. [Accessed 24 January 2022].

[83] Federal Register, "86 FR 28828 - Accidental Release Prevention Requirements: Risk Management Programs Under the Clean Air Act," 28 May 2021. [Online]. Available: https://www.federalregister.gov/documents/2021/05/28/2021-11280/accidental-release-prevention-requirements-risk-management-programs-under-the-clean-air-act. [Accessed 24 January 2022].

[84] U.S. Congress, "H.R.2576 - Frank R. Lautenberg Chemical Safety for the 21st Century Act," [Online]. Available: https://www.congress.gov/bill/114th-congress/house-bill/2576. [Accessed 21 July 2022].

[85] Federal Register, "Procedures for Prioritization of Chemicals for Risk Evaluation Under the Toxic Substances Control Act, 82 Fed. Reg. 33753," codified at 40 C.F.R. Part 702, 20 July 2017. [Online]. Available: https://www.federalregister.gov/documents/2017/07/20/2017-14325/procedures-for-prioritization-of-chemicals-for-risk-evaluation-under-the-toxic-substances-control. [Accessed 21 July 2022].

[86] United States Environmental Protection Agency, "Assessing and Managing Chemicals under TSCA - Chemicals Undergoing Risk Evaluation under TSCA," 30 June 2022. [Online]. Available: https://www.epa.gov/assessing-and-managing-chemicals-under-tsca/chemicals-undergoing-risk-evaluation-under-tsca. [Accessed 21 July 2022].

[87] United States Environmental Protection Agency, "Assessing and Managing Chemicals under TSCA - Prioritizing Existing Chemicals for Risk Evaluation," 16 May 2022. [Online]. Available: https://www.epa.gov/assessing-and-managing-chemicals-under-tsca/prioritizing-existing-chemicals-risk-evaluation. [Accessed 21 July 2022].

[88] U.S. Chemical Safety Board, "Board Order 22: Recommendations Program," [Online]. Available: https://www.csb.gov/assets/record/csb_board_order_022_final_20161.pdf.

[89] U.S. Chemical Safety Board (USCSB), "Board Order 40: Investigation Program," [Online]. Available: https://www.csb.gov/assets/record/board_order_040_approved_2_14_17.pdf.

[90] Occupational Safety and Health Administration, "OSHA Instruction CPL 2-2.45A CH-1," 13 September 1994. [Online]. Available: https://www.osha.gov/OshDoc/Directive_pdf/CPL02-02-045_CH-1_20150901.pdf. [Accessed 24 April 2020].

[91] National Institute for Occupational Safety and Health (NIOSH), "Sulfuric Acid," Centers for Disease Control and Prevention, [Online]. Available: https://www.cdc.gov/niosh/npg/npgd0577.html. [Accessed 21 December 2021].

[92] National Institute for Occupational Safety and Health (NIOSH), "Cumene," Centers for Disease Control and Prevention, [Online]. Available: https://www.cdc.gov/niosh/npg/npgd0159.html. [Accessed 21 December 2021].

[93] OnePetro, "Who is NACE International," [Online]. Available: https://onepetro.org/NACE. [Accessed 23 Deceber 2021].

[94] American Society for Metals, Glossary of Metallurgical Terms and Engineering Tables, Metals Park, OH, 1979.

[95] National Institute for Occupational Safety and Health, "n-Butane," Centers for Disease Control and Prevention, [Online]. Available: https://www.cdc.gov/niosh/npg/npgd0068.html. [Accessed 23 December 2021].

[96] National Institute for Occupational Safety and Health, "Isobutane," Centers for Disease Control and Prevention, [Online]. Available: https://www.cdc.gov/niosh/npg/npgd0350.html. [Accessed 23 December 2021].

[97] M. Chalam, J. Child, K. Del Rossi, A. Huss, R. Kurtas and C. Schatz, "Alkylation Catalyst Containing Hydrofluoric Acid and a Sulfone". Patent EP 0 796 657 B1, 18 June 1992.

[98] "CSB Public Meeting Transcript - ExxonMobil Torrance Refinery Incident," 13 January 2016. [Online]. Available: https://www.csb.gov/assets/1/20/public_meeting_transcript.pdf?15637.

[99] U.S. Chemical Safety Board, "Husky Public Meeting," 12 December 2018. [Online]. Available: https://www.csb.gov/assets/1/20/csb_-_husky_meeting_-_121218_pdf.pdf?16451.

[100] Environmental Protection Agency, Federal Register - 40 CFR Part 68 - List of Regulated Substances and Thresholds for Accidental Release Prevention; Requirements for Petitions under Section 112(r) of the Clean Air Act as Amended, vol. 58 No. 11, January 19, 1993, pp. 5102-5125.

[101] F. Cavender, S. Phillips and M. Holland, "Development of Emergency Response Planning Guidelines (ERPGs)," *Journal of Medical Toxicology,* vol. 4, no. 2, pp. 127-131, June 2008.

[102] U.S. Chemical Safety and Hazard Investigation Board, "Investigation Report - LPG Fire at Valero-McKee Refinery," July 2008. [Online]. Available: https://www.csb.gov/valero-refinery-propane-fire/. [Accessed 14 February 2022].

[103] U.S. Chemical Safety and Hazard Investigation Board, "Recommendations Status Change Summary - Valero Refinery Propane Fire," 13 July 2016. [Online]. Available: https://www.csb.gov/assets/recommendation/status_change_summary_valero_mckee_api_r3_c-aaa.pdf. [Accessed 14 February 2022].

[104] J. Speight, Handbook of Petrochemical Processes, Boca Raton: CRC Press, 2019.

[105] Census Reporter, [Online]. Available: https://censusreporter.org/. [Accessed 16 June 2022].

[106] Census Reporter, "About Census Reporter," [Online]. Available: https://censusreporter.org/about/. [Accessed 16 June 2022].

[107] Census Reporter, "Block Group 2, Philadelphia, PA," [Online]. Available: https://censusreporter.org/profiles/15000US421010036002-block-group-2-philadelphia-pa/. [Accessed 16 June 2022].

[108] United States Census Bureau, "Historical Income Tables: People," [Online]. Available: https://www.census.gov/data/tables/time-series/demo/income-poverty/historical-income-people.html. [Accessed 16 June 2022].

Appendix A—Incident Timeline

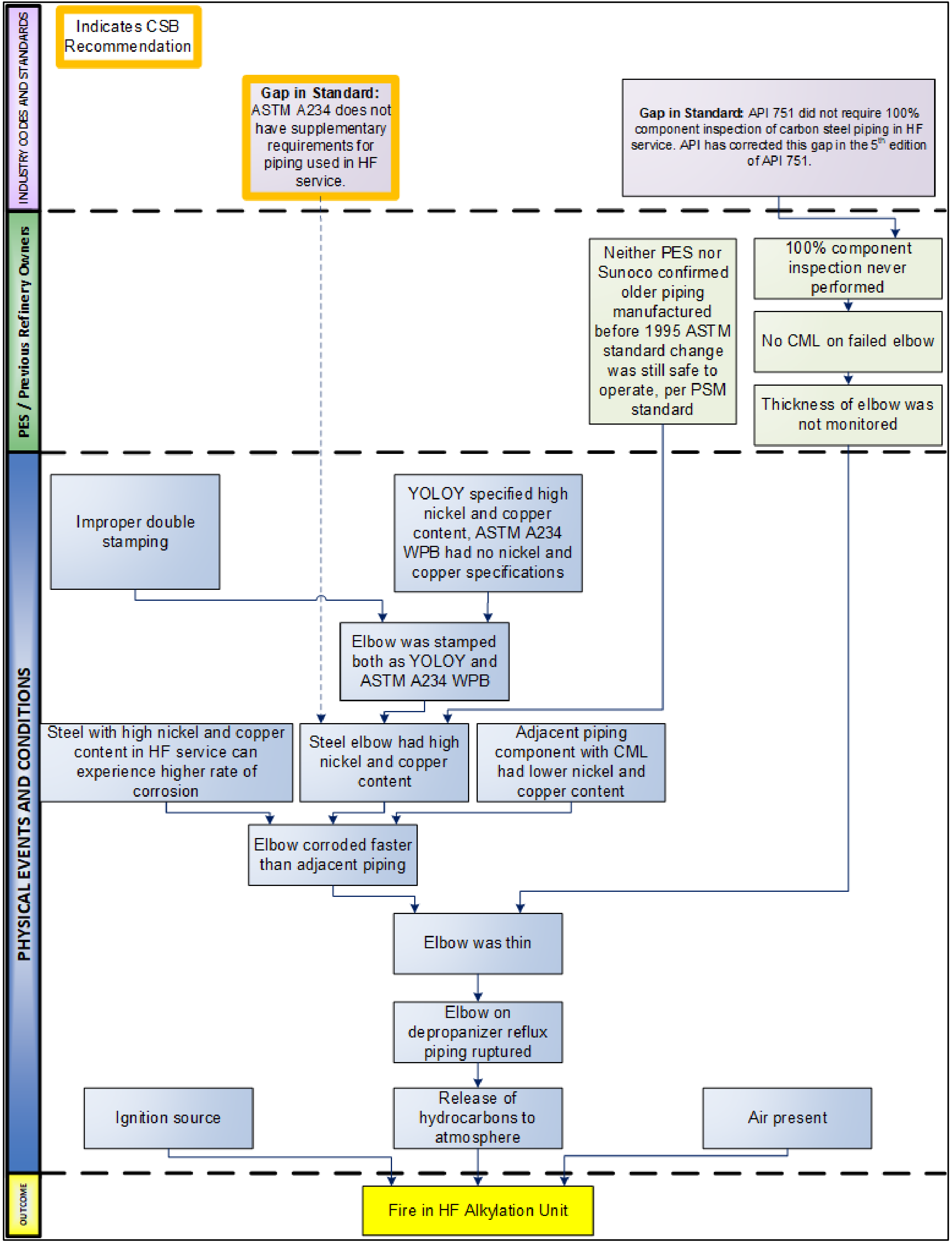
Time	Event
21 Jun 2019 03:34:06.000 a.m.	Control room operator opens valve to send T-7 bottoms product to treatment and storage
21 Jun 2019 03:34:18.000 a.m.	Control room operator closes valve that routed T-7 bottoms product to V-10 as recycle stream
21 Jun 2019 03:55:06.000 a.m.	Operator changes propane stripper feed from 73 to 78 bph
21 Jun 2019 04:00:14.100 a.m.	Operator changes propane stripper feed from 78 to 80 bph
21 Jun 2019 04:00:16.901 a.m.	Pump P14-B (offline pump) High High vibration alarm activates at the moment the pipe elbow ruptures.
21 Jun 2019 04:00:17.000 a.m.	Propane Stripper Feed Low alarm activates
21 Jun 2019 04:00:17.901 a.m.	Pump P-14A (online pump) High High Vibration alarm activates
21 Jun 2019 04:00:21.750 a.m.	HF Detector near V-1 High High alarm activates

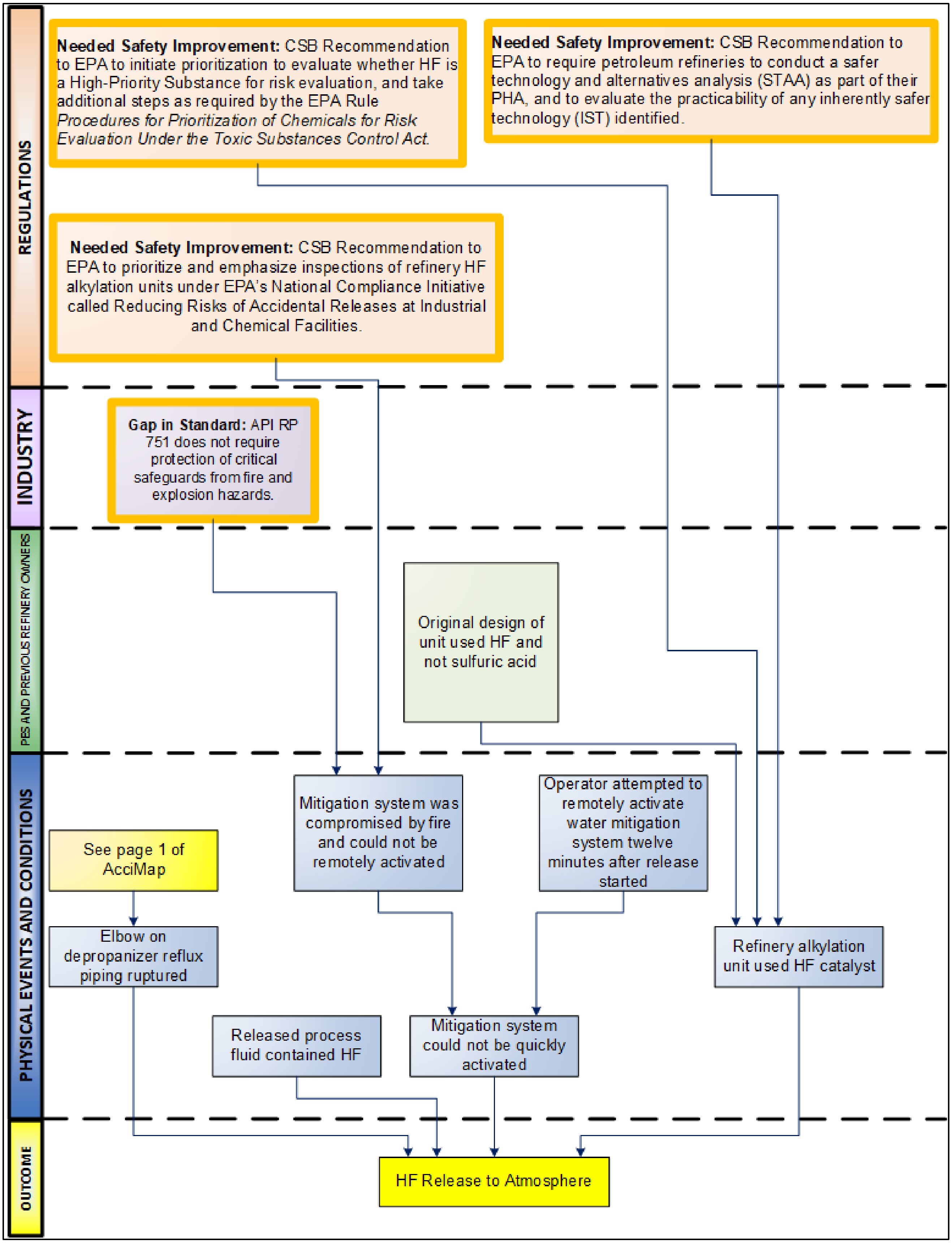
Time	Event
21 Jun 2019 04:00:24.983 a.m.	HF detection alarm in unit activates
21 Jun 2019 04:00:26.233 a.m.	HF detection alarm in unit activates
21 Jan 2019 04:00:30.000 a.m.	V-11 hydrocarbon level begins to decline, from about 66% level reading
21 Jun 2019 04:00:32.873 a.m.	Depropanizer Reflux Low alarm activates
21 Jun 2019 04:00:37.101 a.m.	The HF point sensor near the P14-A and P14-B pumps high alarm activates
21 Jun 2019 04:01:01.100 a.m.	HF Sensor High High alarm activates
21 Jun 2019 04:01:11.505 a.m.	T-6 Temperature High alarm activates
21 Jun 2019 04:01:12.101 a.m.	HF point sensor at the air intake for the local control room High High alarm activates
21 Jun 2019 04:01:13.101 a.m.	HF detection alarm in unit activates
21 Jun 2019 04:01:13.250 a.m.	HF detection alarm in unit activates
21 Jun 2019 04:01:37.101 a.m.	HF point sensor near V-11 high alarm activates

Time	Event
21 Jun 2019 04:01:47.800 a.m.	Control room operator opens valve to route T-7 bottoms back to V-10 to isolate any potential leak from treater section
21 Jun 2019 04:01:53.800 a.m.	Control room operator closes valve from T-7 bottoms to treater section to isolate any potential leak from treater section
21 Jun 2019 04:02:06.000 a.m.	Released hydrocarbons ignite (visible in security footage)
21 Jun 2019 04:02:06.600 a.m.	Control system communication to the water pumps that supplied water to the elevated HF mitigation water cannons fails
21 Jun 2019 04:02:10.601 a.m.	Control room operator closes heater fuel gas emergency shutdown valve
21 Jun 2019 04:02:15.600 a.m.	UPS Failure
21 Jun 2019 04:02:37.700 a.m.	RAD system manually activated from Central Control Room
21 Jun 2019 04:04:31.000 a.m.	PES emergency response personnel arrive at unit (visible in security footage)
21 Jun 2019 04:12:42.101 a.m.	Control room operator attempts to turn on HF water mitigation cannons from control room, but pumps do not activate
21 Jun 2019 04:15:00.000 a.m.	Explosion occurs in alkylation unit (visible in security footage)

Time	Event
21 Jun 2019 04:19:00.000 a.m.	Explosion occurs in alkylation unit (visible in security footage)
21 Jun 2019 04:22:00.000 a.m.	V-1 BLEVE occurs (visible in security footage)
21 Jun 2019 04:39:00.000 a.m.	HF water mitigation pumps manually started and water cannons flow water to unit

Appendix B—Causal Analysis (AcciMap)





Needed Safety Improvement: CSB Recommendation to EPA to initiate prioritization to evaluate whether HF is a High-Priority Substance for risk evaluation, and take additional steps as required by the EPA Rule *Procedures for Prioritization of Chemicals for Risk Evaluation Under the Toxic Substances Control Act.*

Needed Safety Improvement: CSB Recommendation to EPA to require petroleum refineries to conduct a safer technology and alternatives analysis (STAA) as part of their PHA, and to evaluate the practicability of any inherently safer technology (IST) identified.

Needed Safety Improvement: CSB Recommendation to EPA to prioritize and emphasize inspections of refinery HF alkylation units under EPA's National Compliance Initiative called Reducing Risks of Accidental Releases at Industrial and Chemical Facilities.

Gap in Standard: API RP 751 does not require protection of critical safeguards from fire and explosion hazards.

Original design of unit used HF and not sulfuric acid

See page 1 of AcciMap

Elbow on depropanizer reflux piping ruptured

Mitigation system was compromised by fire and could not be remotely activated

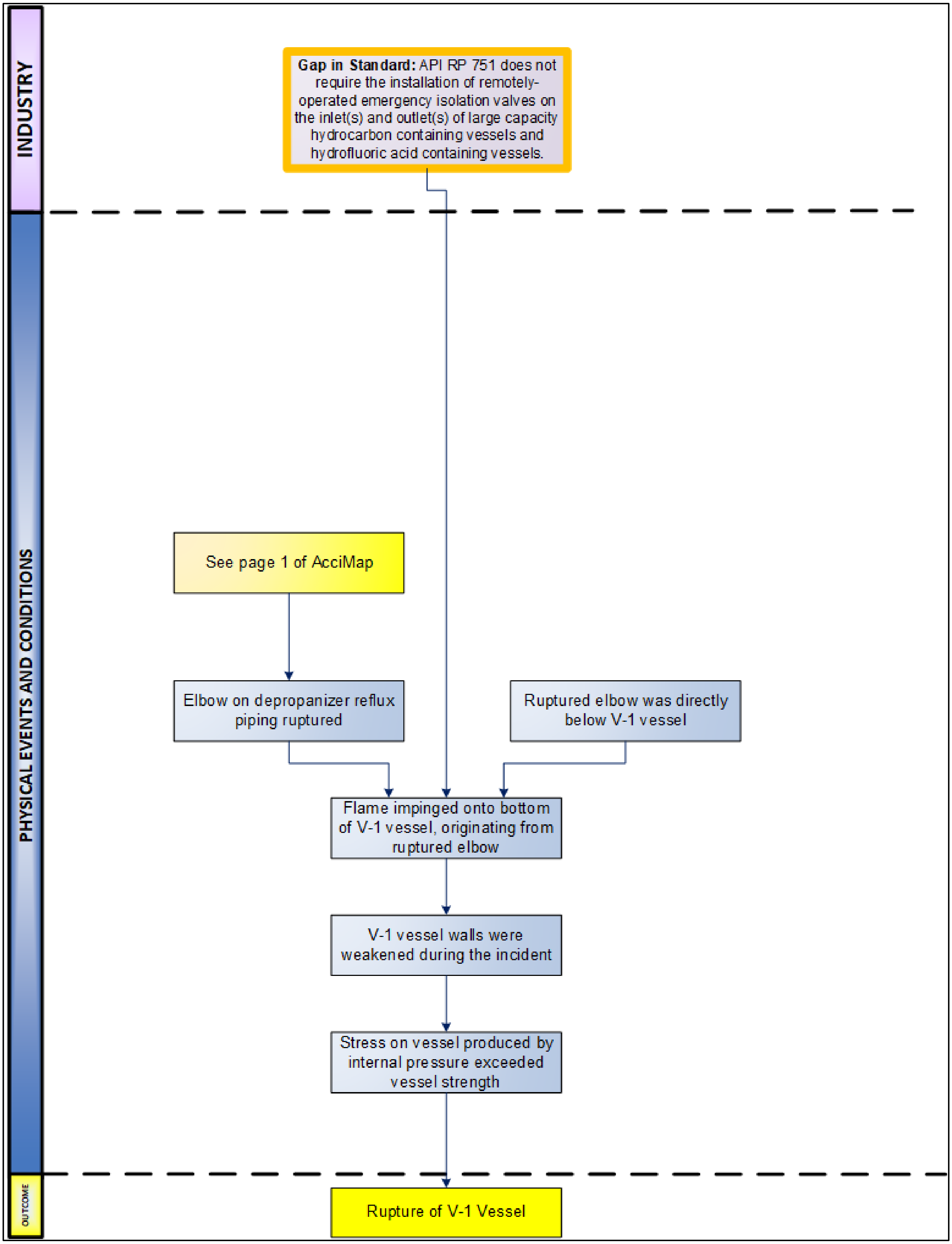
Operator attempted to remotely activate water mitigation system twelve minutes after release started

Refinery alkylation unit used HF catalyst

Released process fluid contained HF

Mitigation system could not be quickly activated

HF Release to Atmosphere


INDUSTRY
PHYSICAL EVENTS AND CONDITIONS
OUTCOME
Gap in Standard: API RP 751 does not require the installation of remotely-operated emergency isolation valves on the inlet(s) and outlet(s) of large capacity hydrocarbon containing vessels and hydrofluoric acid containing vessels.
See page 1 of AcciMap
Elbow on depropanizer reflux piping ruptured
Ruptured elbow was directly below V-1 vessel
Flame impinged onto bottom of V-1 vessel, originating from ruptured elbow
V-1 vessel walls were weakened during the incident
Stress on vessel produced by internal pressure exceeded vessel strength
Rupture of V-1 Vessel

Appendix C—Metallurgical Testing Report

The metallurgical report is located at www.csb.gov on the Philadelphia Energy Solutions investigation page.

Appendix D—Demographic Information for Area Surrounding PES Refinery

The demographic information of the population residing within about 1 mile of the refinery fence line is contained below in **Figure 38** and **Table 6**[a].

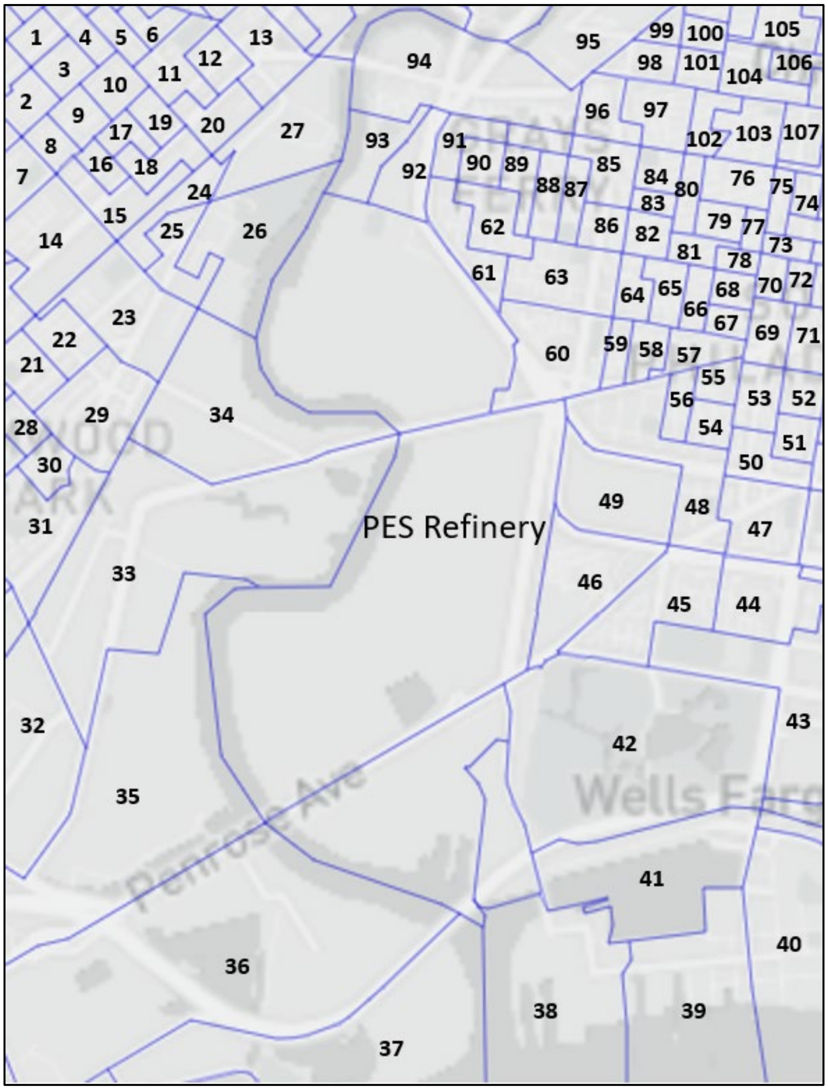


Figure 38. Census blocks in the approximately 1 mile distance from the PES refinery fence line (Credit: Census Reporter with annotations by CSB)

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[a] This information was compiled using 2020 Census data as presented by Census Reporter [105]. "Census Reporter is an independent project to make data from the American Community Survey easier to use. [It is] unaffiliated with the U.S. Census Bureau. A News Challenge grant from the Knight Foundation funded the initial build-out of the site. … Support for [Census Reporter's] 2020 Decennial Census features was provided by the Google News Initiative. … [T]he Medill School of Journalism at Northwestern University, home of the Knight Lab, [] provides in-kind support for some of Census Reporter's ongoing development. Most of [Census Reporter's] server hosting infrastructure is [] provided by the Oregon State University Open Source Lab [106]."

Table 6. Tabulation of Demographic Data for the Populations Within the Census Blocks Shown in **Figure 38**.

Block Number	Population	Median Age	Race and Ethnicity	Per Capita Income	Number of Housing Units	Types of Structures
1	1,347	32.1	80% Black 20% Hispanic	$13,289[a]	342	94% Single Unit 6% Multi-Unit
2	994	31.8	83% Black 7% White 7% Hispanic 3% Native	$18,957	482	100% Single Unit
3	507	59.3	96% Black 4% White	$20,020	371	100% Single Unit
4	844	49.9	98% Black 1% White 1% Hispanic	$19,038	407	98% Single Unit 2% Multi-Unit
5	730	19.9	84% Black 9% White 6% Asian 2% Other	$9,033	340	81% Single Unit 19% Multi-Unit
6	743	34.6	72% Black 9% Asian 8% White 7% Two+ 3% Hispanic	$26,178	339	52% Single Unit 48% Multi-Unit
7	1,052	31.1	100% Black	$16,187	606	86% Single Unit 14% Multi-Unit
8	1,123	31.5	98% Black 2% Asian	$11,490	371	77% Single Unit 23% Multi-Unit
9	1,210	26.5	86% Black 7% White 5% Hispanic 2% Asian	$11,555	445	88% Single Unit 12% Multi-Unit
10	377	61.9	82% Black 18% White	$20,094	250	100% Single Unit
11	1,684	19.6	66% Black 31% Two+ 3% White	$13,573	676	86% Single Unit 14% Multi-Unit
12	1,022	32.5	86% Black 6% Two+ 5% Hispanic 3% White	$14,242	311	100% Single Unit
13	520	48.3	58% Black 29% White 9% Two+ 4% Asian	$34,769	310	75% Single Unit 25% Multi-Unit
14	2,019	23.6	93% Black	$12,643	756	73% Single Unit

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[a] Census Reporter reports that Philadelphia's overall Per Capita Income is $29,644 [107]. The Census Bureau reports that the overall Per Capita Income for the United States $39,052 [108].

Block Number	Population	Median Age	Race and Ethnicity	Per Capita Income	Number of Housing Units	Types of Structures
			4% Hispanic 3% Two+ 1% White			27% Multi-Unit
15	642	36.2	97% Black 3% Islander	$19,320	294	100% Single Unit
16	335	39.8	100% Black	$18,799	167	100% Single Unit
17	327	37.8	88% Black 12% Asian	$19,158	212	92% Single Unit 8% Multi-Unit
18	1,340	35.5	96% Black 2% White 1% Two+	$16,667	546	93% Single Unit 7% Multi-Unit
19	954	40.5	100% Black	$22,402	458	87% Single Unit 13% Multi-Unit
20	623	51.7	96% Black 3% Hispanic 2% White	$41,155	436	53% Single Unit 47% Multi-Unit
21	2,298	28	97% Black 3% White	$15,213	767	88% Single Unit 12% Multi-Unit
22	1,274	28.9	92% Black 5% Asian 3% Hispanic	$17,082	632	77% Single Unit 17% Multi-Unit 5% Mobile Home
23	1,383	31.6	93% Black 4% Native	$18,667	482	88% Single Unit 12% Multi-Unit
24	1,020	31.4	96% Black 4% White	$13,526	378	100% Single Unit
25	769	33.5	89% Black 6% Two+ 3% Asian 2% Hispanic	$15,430	243	95% Single Unit 5% Multi-Unit
26	1,791	15.2	93% Black 4% Hispanic 3% White	$4,947	500	100% Multi-Unit
27	0	N/A	N/A	N/A	N/A	N/A
28	833	35.4	85% Black 8% White 4% Hispanic 2% Asian	$25,437	381	91% Single Unit 9% Multi-Unit
29	2,260	37.4	57% Black 18% Asian 10% Other 10% Two+ 3% White 1% Native	$19,119	1,098	86% Single Unit 12% Multi-Unit 2% Boat, RV, Van, etc.
30	606	37.7	87% Black 13% White	$18,320	294	54% Single Unit 46% Multi-Unit
31	2,170	39.5	89% Black 8% Asian	$20,139	947	95% Single Unit 3% Multi-Unit

Block Number	Population	Median Age	Race and Ethnicity	Per Capita Income	Number of Housing Units	Types of Structures
			3% White			2% Mobile Home
32	0	N/A	N/A	N/A	N/A	N/A
33	0	N/A	N/A	N/A	N/A	N/A
34	0	N/A	N/A	N/A	N/A	N/A
35	0	N/A	N/A	N/A	N/A	N/A
36	0	N/A	N/A	N/A	N/A	N/A
37	0	N/A	N/A	N/A	N/A	N/A
38	0	N/A	N/A	N/A	N/A	N/A
39	0	N/A	N/A	N/A	N/A	N/A
40	0	N/A	N/A	N/A	N/A	N/A
41	0	N/A	N/A	N/A	N/A	N/A
42	1,496	33.5	41% White 36% Hispanic 22% Black 1% Asian	$40,585	792	93% Multi-Unit 7% Single Unit
43	0	N/A	N/A	N/A	N/A	N/A
44	2,115	46.9	92% White 6% Asian 2% Hispanic	$39,524	962	85% Single Unit 15% Multi-Unit
45	1,723	50.1	94% White 4% Hispanic 1% Asian 1% Two+	$50,522	841	80% Single Unit 20% Multi-Unit
46	298	12	65% White 35% Asian	$28,598	138	100% Single Unit
47	2,028	52	97% White 2% Two+ 1% Hispanic	$37,213	937	93% Single Unit 5% Multi-Unit 2% Mobile Home
48	841	59.2	99% White 1% Black	$40,136	472	77% Single Unit 23% Multi-Unit
49	0	N/A	N/A	N/A	N/A	N/A
50	2,019	39.2	93% White 3% Asian 2% Native 2% Two+	$32,724	816	93% Single Unit 7% Multi-Unit
51	1,635	39.6	99% White 1% Asian	$55,200	752	51% Multi-Unit 49% Single Unit
52	1,694	32.4	58% White 30% Black 12% Hispanic 1% Asian	$57,306	892	68% Multi-Unit 32% Single Unit
53	2,024	33.6	88% White 9% Hispanic 3% Asian	$30,644	1,028	59% Single Unit 41% Multi-Unit
54	1,079	43.8	98% White 2% Hispanic	$43,014	407	95% Single Unit 5% Multi-Unit
55	1,185	35.9	81% White	$34,493	455	84% Single Unit

Block Number	Population	Median Age	Race and Ethnicity	Per Capita Income	Number of Housing Units	Types of Structures
			11% Hispanic 7% Asian 1% Black			16% Multi-Unit
56	807	37.3	60% White 23% Asian 10% Two+ 5% Hispanic 2% Black	$32,939	352	94% Single Unit 6% Multi-Unit
57	1,708	32.5	43% Black 28% Asian 22% White 4% Native 2% Two+ 1% Hispanic	$22,153	570	91% Single Unit 9% Multi-Unit
58	1,087	27.8	42% Black 25% White 14% Asian 13% Hispanic 6% Two+	$15,556	522	90% Single Unit 10% Multi-Unit
59	1,127	35.4	53% Black 33% Asian 9% White 3% Two+ 2% Hispanic	$19,345	288	79% Single Unit 21% Multi-Unit
60	2,900	31.2	67% Black 21% White 8% Asian 3% Hispanic	$11,765	1,116	74% Single Unit 26% Multi-Unit
61	2,030	21.2	79% Black 12% White 5% Asian 4% Native	$13,116	576	74% Single Unit 26% Multi-Unit
62	433	51.5	80% Black 11% Asian 9% White	$21,792	346	79% Single Unit 21% Multi-Unit
63	1,746	40.9	50% Asian 47% White 10% Black 4% Two+	$26,103	672	98% Single Unit 2% Multi-Unit
64	1,572	32.9	55% Black 18% Hispanic 17% Asian 4% White 4% Native 2% Two+	$22,571	498	97% Single Unit 3% Multi-Unit
65	1,240	34.3	80% Black 15% White	$25,570	690	100% Single Unit

Block Number	Population	Median Age	Race and Ethnicity	Per Capita Income	Number of Housing Units	Types of Structures
			3% Hispanic 1% Asian			
66	1,259	39.3	40% Asian 28% White 28% Black 5% Hispanic	$19,993	702	87% Single Unit 13% Multi-Unit
67	846	39.5	42% Black 29% Asian 22% White 6% Hispanic	$14,556	390	95% Single Unit 5% Multi-Unit
68	700	63.6	71% Black 23% White 3% Asian 3% Hispanic	$40,933	408	80% Single Unit 20% Multi-Unit
69	1,521	40.1	50% White 30% Asian 13% Black 5% Hispanic 2% Two+	$22,449	793	63% Single Unit 37% Multi-Unit
70	879	39.6	38% Asian 24% White 22% Black 11% Hispanic 5% Two+	$29,659	330	68% Single Unit 31% Multi-Unit
71	1,190	37.3	54% White 31% Asian 13% Hispanic 1% Black 1% Two+	$25,303	464	72% Single Unit 28% Multi-Unit
72	930	31.9	41% Asian 36% White 11% Black 6% Two+ 5% Hispanic	$26,070	511	94% Single Unit 6% Multi-Unit
73	488	49.5	56% Black 22% White 17% Asian 4% Two+	$24,821	241	97% Single Unit 3% Multi-Unit
74	612	32.1	57% Black 30% White 7% Asian 6% Hispanic	$37,169	397	79% Single Unit 21% Multi-Unit
75	505	31.1	40% White 37% Hispanic 12% Black 11% Asian	$38,431	363	89% Single Unit 11% Multi-Unit
76	1,167	29.5	45% Black	$52,784	541	89% Single Unit

Block Number	Population	Median Age	Race and Ethnicity	Per Capita Income	Number of Housing Units	Types of Structures
			39% White 10% Asian 7% Hispanic			11% Multi-Unit
77	365	37.1	49% Black 45% White 6% Hispanic	$53,724	253	99% Single Unit 1% Multi-Unit
78	544	37.5	63% Black 27% Hispanic 9% White	$17,006	192	100% Single Unit
79	1,058	43.3	84% Black 8% White 4% Hispanic 3% Asian 1% Two+	$32,639	590	96% Single Unit 4% Multi-Unit
80	895	31.8	63% Black 28% White 5% Two+ 4% Hispanic	$29,287	442	91% Single Unit 9% Multi-Unit
81	546	47	55% Black 16% White 10% Native 10% Two+ 8% Hispanic	$21,446	363	81% Single Unit 19% Multi-Unit
82	803	38.2	93% Black 4% White 2% Hispanic 1% Asian	$16,913	342	100% Single Unit
83	731	27	61% Black 24% Hispanic 15% White	$19,729	328	95% Single Unit 5% Multi-Unit
84	629	33.5	61% Black 17% White 16% Two+ 5% Asian	$31,935	300	88% Single Unit 9% Multi-Unit 3% Mobile Home
85	683	42	86% Black 13% Hispanic 1% White	$17,567	454	94% Single Unit 6% Multi-Unit
86	230	68.7	75% Black 25% White	$38,840	233	100% Single Unit
87	1,024	29.4	39% Black 34% Asian 15% White 10% Two+ 3% Hispanic	$17,485	386	93% Single Unit 7% Multi-Unit
88	1,944	28.6	54% Black 23% Hispanic 22% White	$14,633	925	95% Single Unit 5% Multi-Unit

Block Number	Population	Median Age	Race and Ethnicity	Per Capita Income	Number of Housing Units	Types of Structures
			2% Asian			
89	1,194	38.4	60% White 22% Hispanic 11% Asian 7% Black	$26,604	539	100% Single Unit
90	552	50.3	49% White 47% Black 3% Asian	$20,374	361	95% Single Unit 5% Multi-Unit
91	409	34.8	84% Black 16% White	$38,392	144	84% Single Unit 16% Multi-Unit
92	0	N/A	N/A	N/A	N/A	N/A
93	0	N/A	N/A	N/A	N/A	N/A
94	1,721	34.7	37% Black 33% White 15% Asian 12% Hispanic 4% Two+	$54,113	750	98% Single Unit 2% Multi-Unit
95	2,179	33.4	74% White 9% Asian 7% Hispanic 6% Black 5% Two+	$71,106	1,064	54% Single Unit 46% Multi-Unit
96	766	53.7	74% Black 19% White 5% Two+ 3% Hispanic	$39,727	550	90% Single Unit 10% Multi-Unit
97	1,116	32.5	50% Black 35% White 10% Asian 3% Two+ 2% Hispanic 1% Native	$40,850	652	93% Single Unit 7% Multi-Unit
98	643	32.8	44% Black 36% White 10% Two+ 9% Asian	$61,833	322	65% Single Unit 35% Multi-Unit
99	1,801	21.9	57% White 41% Black 2% Two+ 1% Hispanic	$28,107	434	80% Single Unit 20% Multi-Unit
100	783	30.6	85% White 15% Black	$53,149	503	76% Single Unit 24% Multi-Unit
101	1,029	29.2	88% White 5% Hispanic 5% Black 2% Two+	$70,020	461	72% Single Unit 28% Multi-Unit
102	756	31.1	68% Black	$29,327	301	90% Single Unit

Block Number	Population	Median Age	Race and Ethnicity	Per Capita Income	Number of Housing Units	Types of Structures
			26% White 4% Hispanic 2% Asian			10% Multi-Unit
103	1,565	35.4	42% Black 42% White 10% Asian 4% Two+ 3% Hispanic	$52,421	783	78% Single Unit 20% Multi-Unit 2% Mobile Home
104	1,597	30.1	67% White 18% Black 6% Asian 4% Hispanic 4% Two+	$73,760	628	82% Single Unit 18% Multi-Unit
105	1,463	33.6	83% White 11% Black 3% Two+ 1% Asian 1% Hispanic	$88,118	788	53% Single Unit 47% Multi-Unit
106	1,250	31.6	52% White 33% Black 11% Hispanic 4% Asian 1% Two+	$58,875	527	70% Single Unit 30% Multi-Unit
107	950	30.6	63% Black 32% White 4% Hispanic 1% Asian	$34,847	510	69% Single Unit 31% Muti-Unit

The percentage of residents living in poverty in the zip codes within about 1 mile of the refinery fence line is contained below in **Figure 39** and **Table 7**.[a]

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[a] This information was compiled using 2020 Census data as presented by Census Reporter.

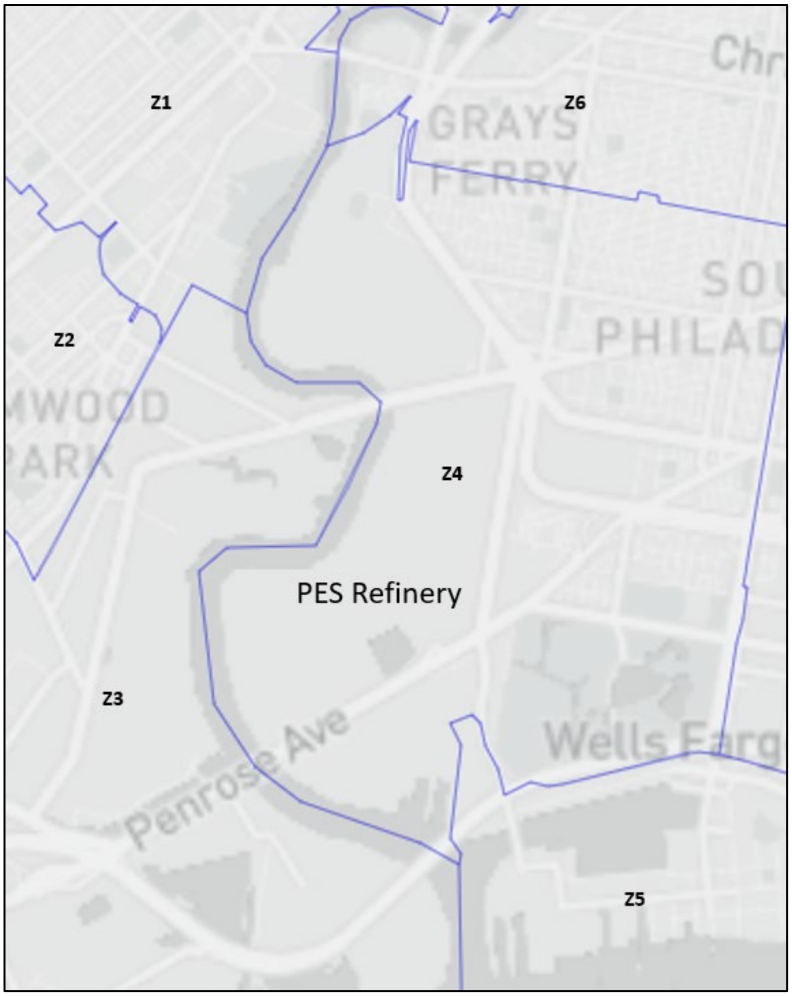

Figure 39. Zip Code boundaries in the approximately 1 mile distance from the PES refinery fence line (Credit: Census Reporter with annotations by CSB)

Table 7. Tabulation of poverty data for the populations within the zip codes shown in **Figure 39**.

Zip Code Label	Zip Code Number	Percentage of Persons Below Poverty Line
Z1	19143	26.9%
Z2	19142	32.4%
Z3	19153	19%
Z4	19145	15.4%
Z5	19112	None (No Residents)
Z6	19146	13.4%

U.S. Chemical Safety and Hazard Investigation Board

Members of the U.S. Chemical Safety and Hazard Investigation Board:

Steve Owens
Interim Executive Authority

Sylvia Johnson, PhD
Member