

Factual Update

October 16, 2019

Incident Summary

- On June 21, 2019, a major process loss of containment caused a fire and explosions at the Philadelphia Energy Solutions Refining and Marketing LLC (PES) Refinery in Philadelphia, Pennsylvania. The PES Refinery is an integrated facility of what were previously two separate refineries, Girard Point and Point Breeze (Figure 1). The incident occurred in the PES Girard Point refinery hydrofluoric acid (HF) alkylation unit.^a



Figure 1. Overhead view of the PES Refinery in Philadelphia, Pennsylvania, showing the Girard Point and Point Breeze refineries. (Credit: Google Earth with modifications by CSB).

- A process flow diagram of the PES hydrofluoric acid alkylation unit is shown in Figure 2. Indicated on the process flow diagram in orange are two equipment failure locations of interest. These identified failures are discussed below.

^a PES uses an additive in its bulk hydrofluoric acid which is intended to reduce the volatility of the hydrofluoric acid in the event of a release.

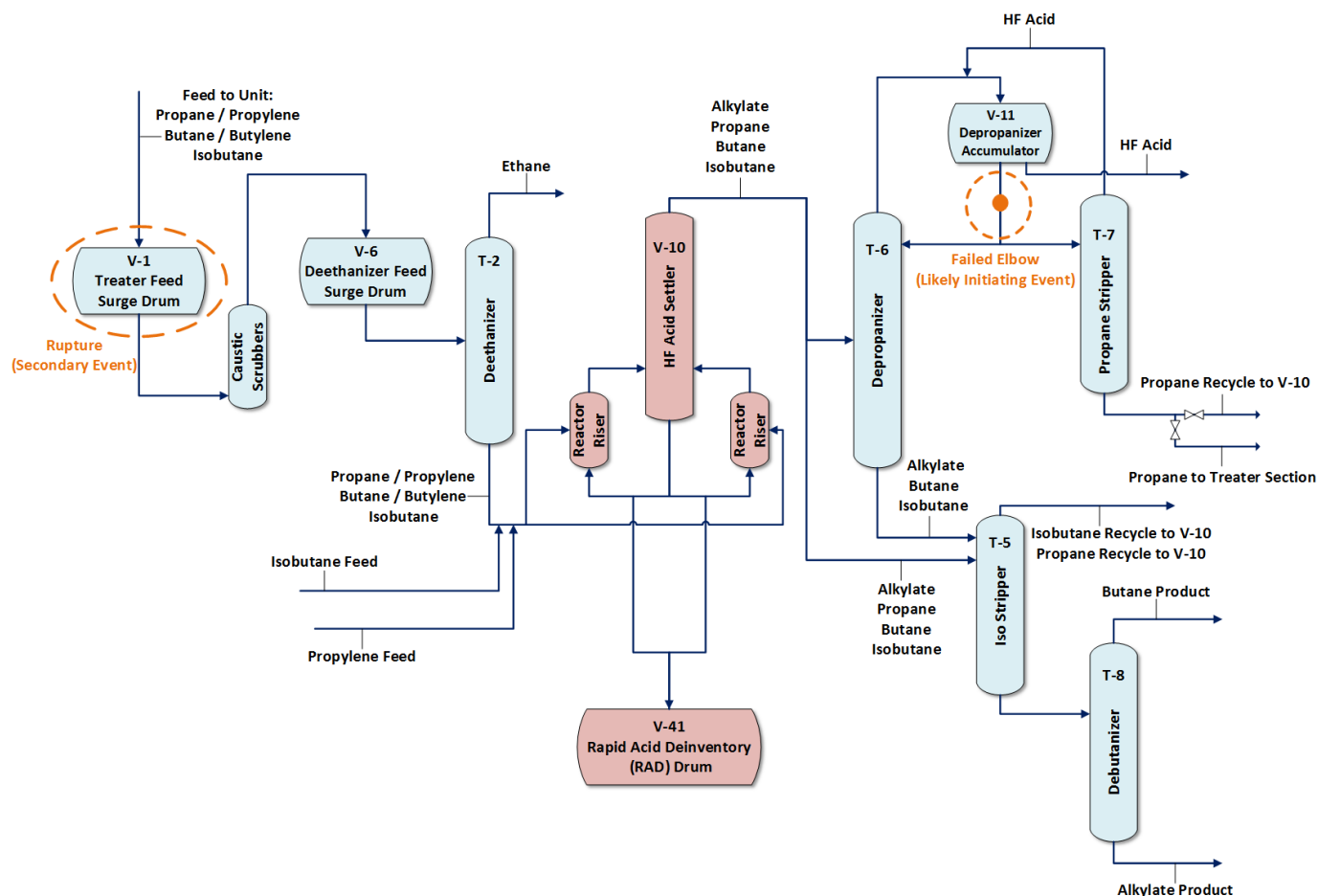


Figure 2. Process flow diagram of PES hydrofluoric acid alkylation unit. The equipment shown in red is the hydrofluoric acid alkylation reaction section and the Rapid Acid Deinventory (RAD) drum, to which the hydrofluoric acid can be routed. (Credit: CSB).

Preliminary Incident Timeline

- During the early hours of Friday, June 21, 2019, the HF alkylation unit was reportedly operating normally.
- At 4:00:16 am, there was a sudden loss of containment causing flammable process fluid containing hydrofluoric acid to release from the PES alkylation unit, forming a ground-hugging vapor cloud (Figure 3).



Figure 3. Security camera footage of leaking process fluid. It formed a large ground-hugging vapor cloud that surrounded some sections of the unit. (Credit: PES).

- At 4:02:06 am, the flammable vapor cloud ignited, causing a large fire in the alkylation unit.
- At 4:02:37 am, the control room operator activated the Rapid Acid Deinventory (RAD) system, which deinventoried bulk hydrofluoric acid^a from the V-10 hydrofluoric acid settler to the RAD drum.
- At 4:15 am, during the ongoing fire, an explosion occurred in the alkylation unit. A second explosion in the unit then occurred at 4:19 am.
- At 4:22 am, a third, and the largest, explosion occurred when the V-1 Treater Feed Surge Drum, containing primarily butylene, isobutane, and butane, violently ruptured (Figure 4, Figure 5). 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 6). This appears to be a secondary event caused by the fire.

^a This bulk acid contained the additive described above.



Figure 4. Video still of V-1 explosion. (Credit: Global News^a).

^a <https://www.youtube.com/watch?v=jo4YAX79U2E>



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. 2019-06-I-PA

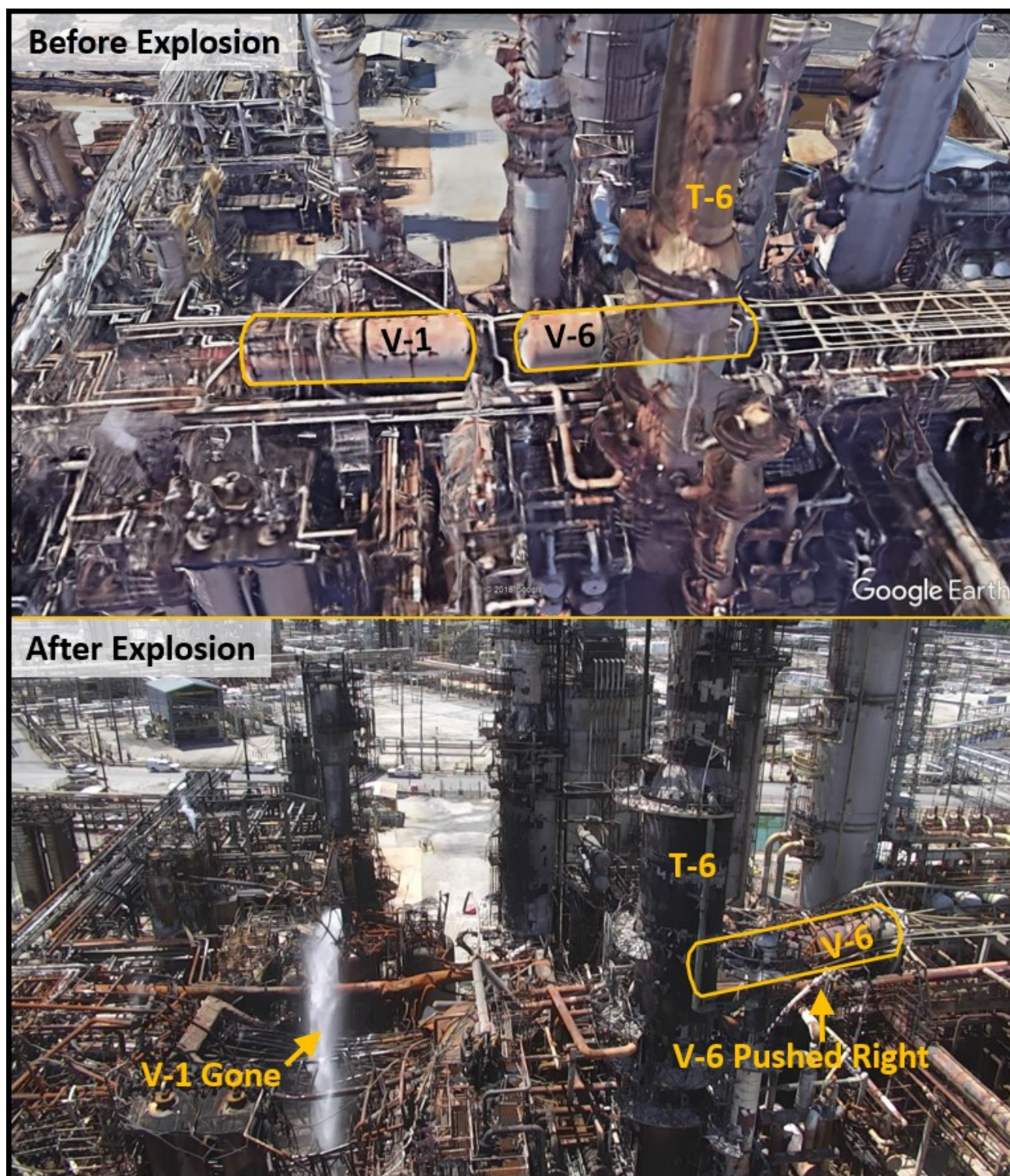


Figure 5. Comparison of incident scene pre-and post-incident. (Top photo credit: Google Earth. Bottom photo credit: PES. Modifications by CSB).

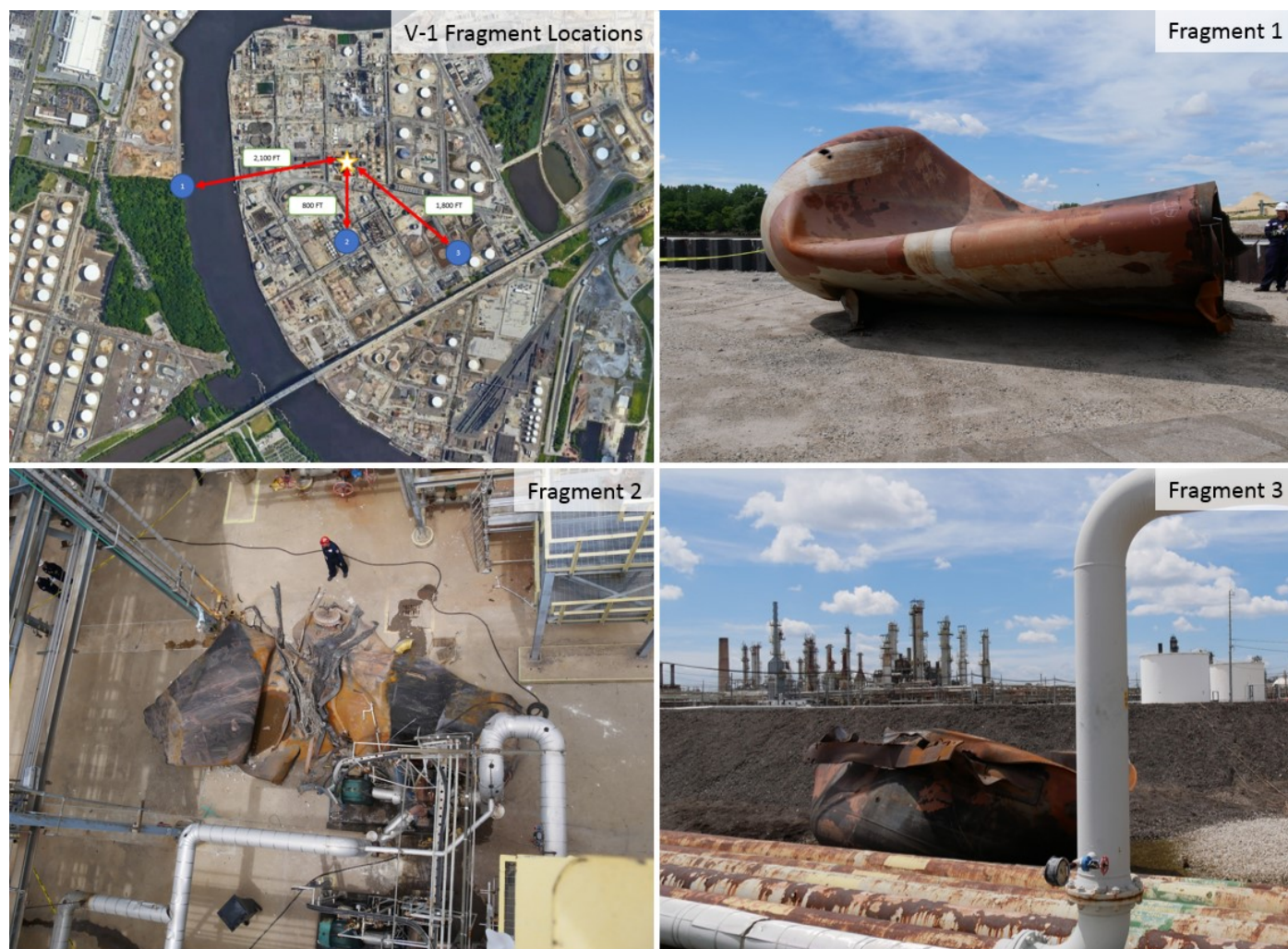


Figure 6. Locations and photos of the post-incident V-1 vessel fragments. The fragment 1 photo was taken after the fragment was recovered from the bank of the river and relocated to the PES refinery. The deformation of fragment 1 was likely caused by impact with the river bank. (Top left photo credit: Google Earth with modifications by CSB. Credit for other photos: CSB).

- The fire was extinguished the following day, on Saturday June 22, at about 8:30 am.

Post-Incident Activities

- After the incident, PES hired a company that specializes in chemically cleaning alkylation units to develop a process to neutralize the hydrofluoric acid contained in the RAD drum. “Neutralization” is the process of reacting an acid (e.g., hydrofluoric acid) with a base (chemical with a high pH) to produce water and a salt.^a The RAD drum neutralization process began on Wednesday August 7, 2019 and was completed on Tuesday August 27, 2019. Additional neutralization and deinventory activities of other equipment in the unit are ongoing.

^a <http://www.phadjustment.com/TArticles/Hydrofluoric-Acid-Neutralization.html>



- PES estimated that about 676,000 pounds of hydrocarbons released during the event, of which an estimated 608,000 pounds were combusted. Low-concentration hydrofluoric acid was also present in some of the process piping and equipment that failed during the incident, causing hydrofluoric acid to release to the atmosphere. Hydrofluoric acid is a highly toxic chemical.^a PES estimated that 5,239 pounds of hydrofluoric acid released from piping and equipment during the incident. It estimated that 1,968 pounds of the released hydrofluoric acid was contained by water spray within the unit and was processed in the refinery wastewater treatment plant, and that 3,271 pounds of hydrofluoric acid released to the atmosphere and was not contained by water spray.
- Five workers experienced minor injuries during the incident and response, requiring first aid treatment. The CSB is unaware of any offsite or onsite health impacts from the hydrofluoric acid release.
- On June 26, 2019, PES announced that the refining complex would be shutting down.^b On July 22, 2019, PES filed for bankruptcy.^c

Ruptured Elbow

- A ruptured pipe elbow was found in the unit post-incident (Figure 7). The rupture of the elbow appears to be the initiating event causing the process fluid release. The elbow was part of the piping between V-11, the depropanizer accumulator, and T-6, the depropanizer distillation column. The elbow was on the discharge (outlet) piping from a pump (one of two pumps in this system) that was not operating at the time of the incident. At the time of the event, this piping was operating at a pressure of about 380 psig and a temperature of about 100 °F. The approximate design composition of process fluid in the piping was:

Material	Weight Percent
Propane	94.7
Hydrofluoric Acid	2.5
Additional Hydrocarbons	2.8

^a Hydrofluoric acid is immediately dangerous to life or health (IDLH) at 30 parts per million (ppm). 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. If inhaled, HF can cause severe lung injury and pulmonary edema—fluid in the lungs—which can result in death. See 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] and UNC Environment, Health & Safety, "Hydrofluoric Acid Chemical Safety Information," [Online]. Available: <https://ehs.unc.edu/files/2015/09/hydrofluoricacid.pdf>. [Accessed 20 August 2019].

^b <https://www.cnn.com/2019/06/26/us/gas-philadelphia-energy-solutions-refinery-shut-down-trnd/index.html>

^c <https://www.reuters.com/article/us-pes-bankruptcy/philadelphia-energy-solutions-files-for-bankruptcy-after-refinery-fire-idUSKCN1UH009>

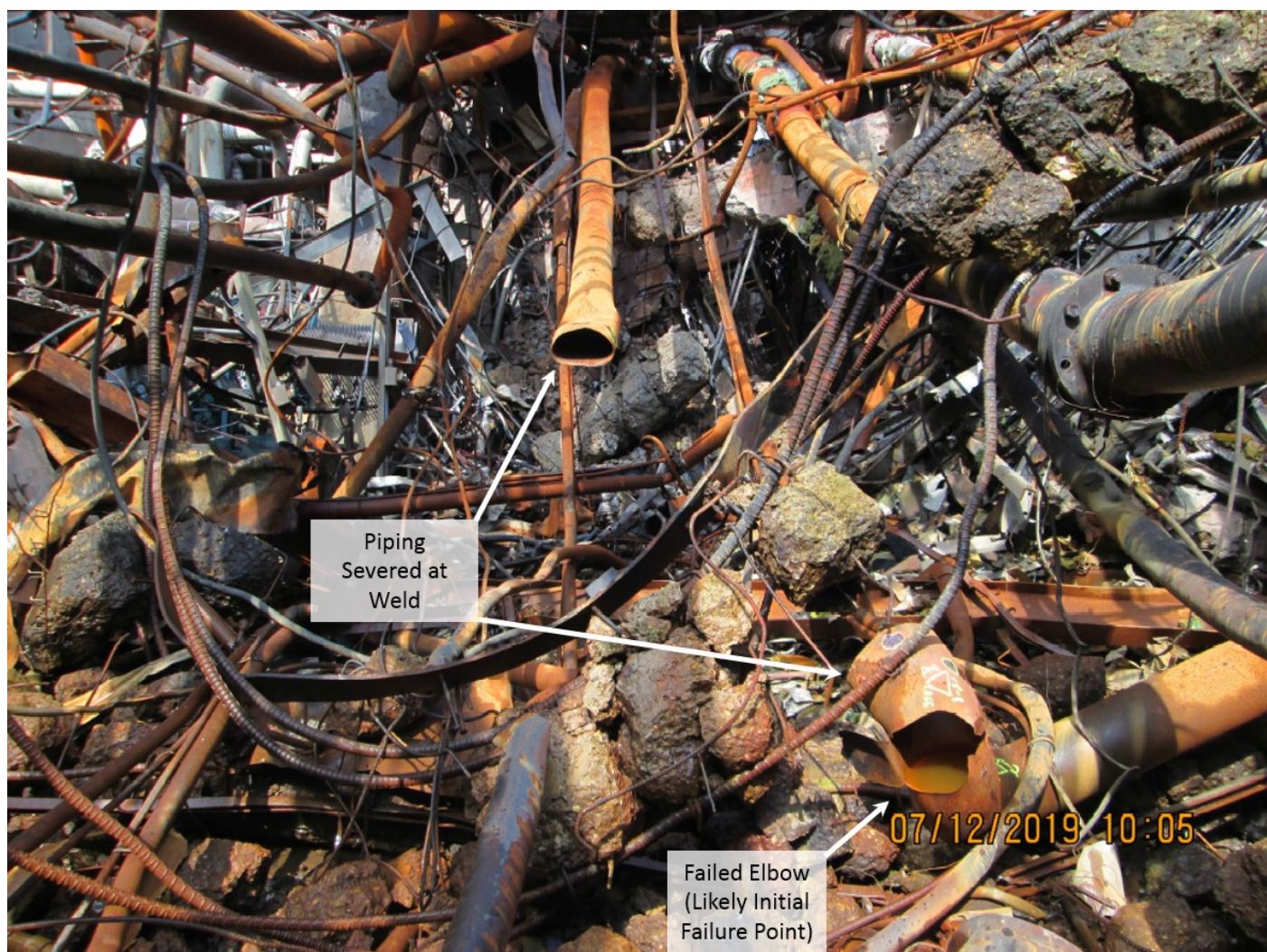


Figure 7. Photo of ruptured pipe elbow found post-incident. (Credit: PES).

- The piping circuit that includes the ruptured elbow was subject to regular ultrasonic thickness measurements at designated condition monitoring locations (CMLs),^a as part of the PES inspection program to monitor the rate of piping metal loss due to corrosion. Locations of CMLs and the most recent thickness measurements are

^a A condition monitoring location (CML) is a designated area where periodic thickness examinations are conducted. Each CML represents as many as four inspection locations located circumferentially around the pipe. 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.

shown in Figure 8. The default retirement thickness^a of this piping in the PES inspection database is 0.180-inch. The most recent CML measurements did not indicate thin pipe.

- A CML was not located on the ruptured elbow, so the thickness of this elbow was not monitored. The thinnest measurement taken of the ruptured elbow post-incident was 0.012 inch.^{b,c} This value is less than 7 % of the PES default retirement thickness.

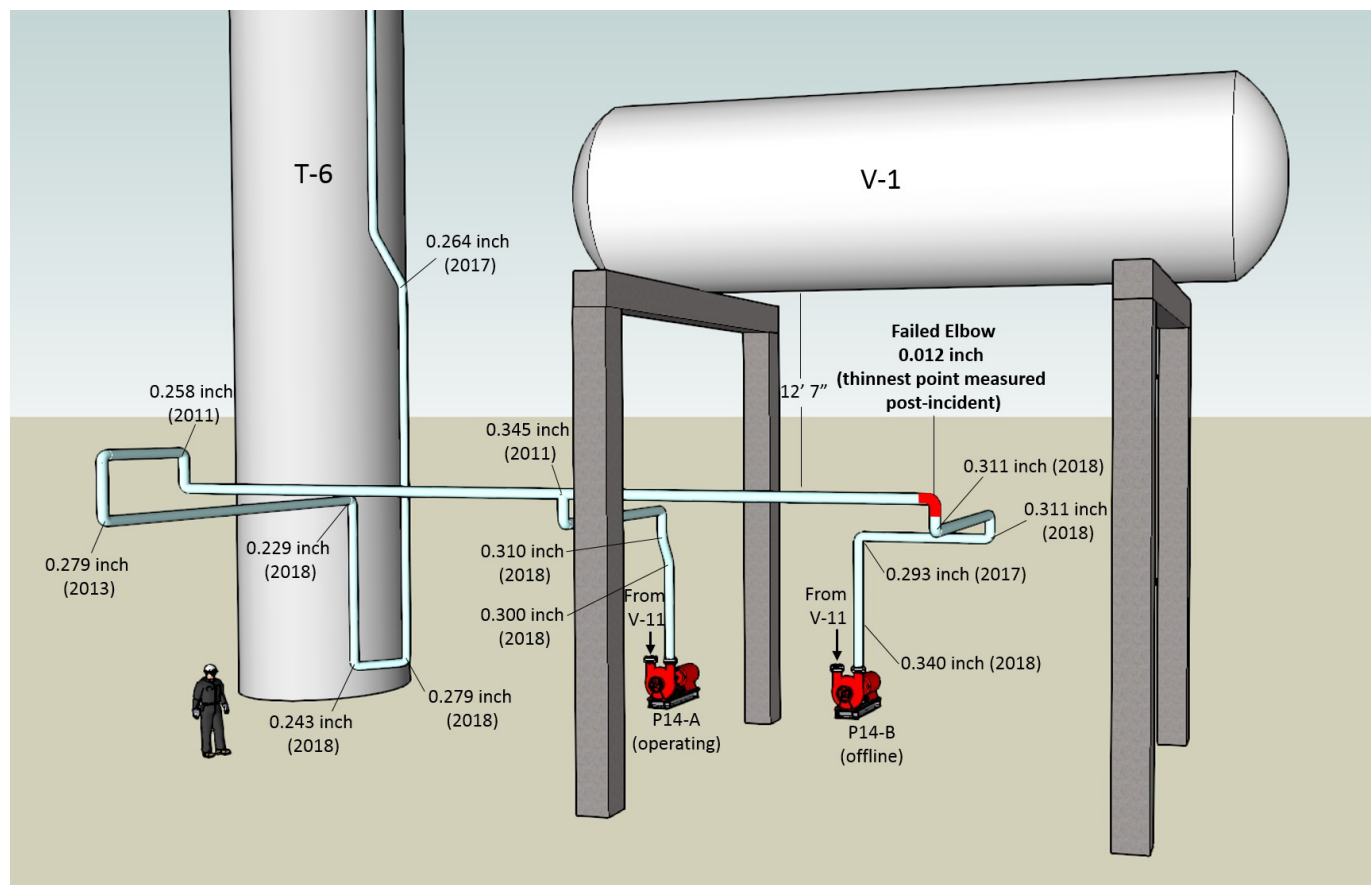


Figure 8. Model of the piping circuit containing the ruptured elbow. The most recent thickness measurements at designated Condition Monitoring Locations (CMLs) are shown. The year of each measurement is shown in parentheses. This figure also illustrates that V-1 was directly above the ruptured elbow. (Credit: CSB).

^a The “retirement thickness” is the piping thickness by which the piping should be replaced.

^b The 2012 Chevron Richmond Refinery fire was caused by the rupture of a piping component that had become extremely thin due to sulfidation corrosion of the piping. The 2009 Silver Eagle refinery fire was also caused by the rupture of a piping component that had become thin from corrosion. See the CSB Final Investigation Report, Chevron Richmond Refinery Pipe Rupture and Fire (<https://www.csb.gov/chevron-refinery-fire/>) and the Exponent Silver Eagle Refinery Metallurgical Analysis Report prepared for the CSB (<https://www.csb.gov/silver-eagle-refinery-flash-fire-and-explosion-and-catastrophic-pipe-explosion/>).

^c 0.012 inch is about half the thickness of a credit card.

- The piping circuit containing the ruptured elbow was installed in about 1973. As of this Factual Update, this piping appears to be the original piping. Both the elbow that failed and the adjacent elbow are stamped “WPB”, indicating they were constructed to meet the ASTM A234 WPB material 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. The 1972 ASTM A106 standard did not specify nickel (Ni) and copper (Cu) composition requirements. In 1995, ASTM A234 began specifying nickel and copper composition, as well as compositions of other elements.^a The WPB composition requirements in 1972 and 1995^b are shown below. The chemical composition of the ruptured elbow and the adjacent elbow are also shown. The nickel and copper content of the ruptured elbow exceeds the updated A234 WPB chemical composition requirements.

Chemical Requirements	A 106 Grade B 1972	A234 WPB 1995 - 2018 (%)	Ruptured Elbow Composition (%)	Adjacent Elbow Composition (%)
Carbon, max %	0.30	0.30	0.14	0.24
Manganese, max %	0.29 to 1.06	0.29 to 1.06	0.80	0.90
Phosphorus, max %	0.048	0.050	≤ 0.005	0.012
Sulfur, max %	0.058	0.058	0.010	0.016
Silicon, min %	0.10	0.10	0.10	0.24
Chromium, max %	No specification	0.40	0.18	0.02
Molybdenum, max %	No specification	0.15	0.06	<0.005
Nickel, max %	No specification	0.40	1.74	≤ 0.01
Copper, max %	No specification	0.40	0.84	0.02
Vanadium, max %	No specification	0.08	<0.005	<0.005

- API RP 751 *Safe Operation of Hydrofluoric Acid Alkylation Units* states: “HF corrosion has been found to be strongly affected by steel composition and localized corrosion rates can be subtly affected by local chemistry differences. NACE Paper 03651 indicated that the combination of carbon (C) content and residual element (RE) content (Cr, Ni, Cu) could increase non-uniform corrosion by up to five-fold compared to baseline measured corrosion rates.”^c
- The investigation is ongoing. At the conclusion of the investigation, the CSB will publish a final investigation report discussing findings, analysis, and issuing recommendations.

^a By 1985, ASTM A234 specified WPB chemical requirements within the standard and did not reference ASTM A106 as was previously done (*ASTM A234/A234M-85a*, 1985). ASTM A106 began specifying the maximum allowable percentage of copper, nickel, and chromium in 1986 (*ASTM A106-86*, 1986). However, ASTM A234 did not begin specifying the maximum allowable percentage of copper, nickel, and chromium for Grade WPB until 1995 (*ASTM A234/A234M-95b*, 1995).

^b The 2018 A234 WPB chemical requirements match the 1995 requirements.

^c American Petroleum Institute (API), API Recommended Practice 751 - Safe Operation of Hydrofluoric Acid Alkylation Units, 4th ed., 2013, p 48.