Activists and Oil Refiners Square Off Over Hydrofluoric Acid

undark.org/article/hydrofluoric-acid-oil-refining-explosion

By Larry Buhl

Torrance, California is a tidy community of mostly mid-century homes situated between Los Angeles and Long Beach. It boasts a beautiful shoreline, an art museum, and nearly 150,000 residents who, with some bad luck, came very close to a toxic calamity in early 2015. An explosion at one of the sprawling oil refineries in the area sent an 80,000-pound piece of equipment hurtling through the air before it landed just feet from a tank containing a modified version of hydrofluoric acid. It was a close call: Had the acid tank been smashed, a deadly chemical cloud could have devastated this bedroom community.

"The consequences would be worse than probably anything except for a nuclear plant meltdown in terms of the number of people who would be at risk."

Citing a federal investigation into the accident, Vanessa Allen Sutherland, then chairwoman of the U.S. Chemical Safety and Hazard Investigation Board, said it had the "potential to be catastrophic."

It's easy to see why: Under intense pressure, hydrofluoric acid has the potential to form an airborne aerosol cloud when released. Such a noxious vapor can immediately penetrate skin and destroy tissue — and it can travel for miles depending on weather conditions. It's the sort of nightmarish scenario that infamously befell residents of Bhopal, India, where a leak of a different gas, methyl isocyanate, went undetected at a Union Carbide pesticide plant in 1984 — an event that killed thousands of people.

According to the federal Energy Information Administration, as of January 2018, there were 135 petroleum refineries operating in the United States. About 100 of these have "alkylation" units, which produce alkylate, a high-octane blending component that helps gasoline burn cleaner. About half of those 100 refineries use hydrofluoric acid as a catalyst in that alkylation process, while the others use sulfuric acid, which in contrast does not turn into a vapor cloud when released.

The petroleum industry doesn't dispute the well-known dangers of hydrofluoric acid, which is the compound hydrogen fluoride dissolved in water, but it points out that it is a common chemical used to manufacture refrigerants, herbicides, pharmaceuticals, aluminum, plastics, and electrical components, albeit in much lower quantities than a typical refinery alkylation unit. The industry has also argued that retrofitting alkylation units to use the safer legacy chemical, sulfuric acid — which no refinery in the U.S. has done — is unnecessary, because failsafe measures make a large aerosol release of hydrofluoric acid highly improbable. Among the measures it points to: adding a chemical to the hydrofluoric acid to inhibit its ability to form a vapor cloud should a release occur.

To date, no one has ever died as a result of an accidental release of hydrofluoric acid in the United States, and in an email, a spokesperson for the American Petroleum Industry told Undark that refinery units using the chemical "have operated at the highest standard of care for years," and are "subject to strict federal regulations." These include guidelines under the Occupational Safety and Health Administration, the Environmental Protection Agency (EPA), the U.S. Coast Guard, and the Department of Homeland Security.

But these are little comfort to some community activists, and even refinery workers, who argue that when it comes to so-called low-probability, high-consequence industrial accidents, sometimes the consequences are too high. Workers argue that safer alternatives are available, for example, and continued use of hydrofluoric acid is simply unnecessary. Community activists, meanwhile, have argued that the industry's real-world protections against hydrofluoric acid release, including using additives, are based on shaky science — or on no evidence at all.

Community activists and even refinery workers argue that when it comes to so-called low-probability, high-consequence industrial accidents, sometimes the consequences are too high.

As it stands, there have been 12 "willful" violations at U.S. refineries since January 2013 according to OSHA records. (A willful violation is defined by OSHA as a knowing failure to comply with a legal safety requirement.) And between 2012 and 2016, an average of 14 accident reports involving hydrogen fluoride or hydrofluoric acid were made around the country each year, according to the U.S. Coast Guard's National Response Center database. Most of those involve skin injuries to workers who came in contact with the substance.

Such accidents and violations — willful and not — concern Mike Wright, the director of Health, Safety, and Environment for the United Steelworkers (USW), which represents 30,000 refinery workers. In 2013, the union released a report warning refineries that not enough safety procedures were in place to prevent catastrophic releases of hydrofluoric acid, and urged the industry to phase it out. Based on worst-case scenario estimates provided to the EPA by refineries using the chemical, the USW study calculated that 26 million Americans were at risk from a release of hydrofluoric acid.

"We've been saying for years that this is maybe the most intrinsically dangerous thing that American industry does," Wright said. "I don't mean the greatest likelihood of an accident. I mean that the consequences would be worse than probably anything except for a nuclear plant meltdown in terms of the number of people who would be at risk."

The industry has known the dangers of an accidental release of hydrofluoric acid since the mid-1980s. In 1986, Ron Koopman, an applied physicist at Lawrence Livermore National Laboratory, led a team of researchers at the behest of the oil company Amoco to test the volatility of the chemical. That analysis

found that none of the chemical stayed on the ground when released. “So you end up then with part of a volatile aerosol that will drift down,” Koopman said, “and is capable of going for long distances, and it remains airborne.”

“You end up then with part of a volatile aerosol that will drift down, and is capable of going for long distances, and it remains airborne.”

The industry didn’t dispute the team’s findings, and Koopman said Amoco and other oil companies started looking for additives that might keep hydrofluoric acid from going airborne when released. By 1990, a court-approved consent decree required Mobil (now ExxonMobil, then the owner of the Torrance Refinery) to either switch from hydrofluoric to sulfuric acid by the end of 1997, or develop a safe form of hydrofluoric acid — one that would not form an aerosol or dense vapor cloud upon release — by the end of 1994. The company chose option two, and promised that a vapor suppressant additive would prevent hydrofluoric acid from forming a cloud in the unlikely event of release.

That additive is known as sulfolane, and of the roughly 50 U.S. refineries with hydrofluoric acid alkylation units today, four use it to make modified hydrofluoric acid, or MHF, including the Torrance refinery — now called the Torrance Refinery Company, or ToRC. When used in adequate concentrations, sulfolane reduces vapor pressure and causes hydrofluoric acid to fall to the ground as a liquid. The problem, according to local activists in Torrance, is that the quantity of sulfolane used isn’t nearly high enough to prevent the chemical from becoming airborne. Refineries discovered very early on that a high concentration prevented the alkylation units from functioning properly. So, they quietly reduced the amount of additive to lower levels — less than 10 percent in many cases.

That and other information was largely invisible to the public until it wasuncovered by a group of citizen activists who live near the site of the Torrance refinery blast. Sally Hayati, a former department director at the Aerospace Corporation and current president of the Torrance Refinery Action Alliance (TRAA), a citizens’ group that wants to ban hydrofluoric acid, has spent three years researching claims made about MHF and the additive sulfolane. Among the group’s findings: The concentration of sulfolane used by the Torrance refinery is no more than 9 percent, which they argue is far too low to make hydrofluoric acid heavy enough to fall to the ground. She also noted that no scientific studies have ever been conducted on the efficacy of using an additive at such a low concentration.

The 2015 explosion at the refinery in Torrance sent ash, smoke, and mangled equipment into the air. It was sheer luck, local community activists say, that a unit containing potentially dangerous hydrofluoric acid went unscathed.

Visual: Ted Soqui/Corbis via Getty

In an email, Betsy Brien, a spokesperson for ToRC's new owner, New Jersey-based PBF Energy, did not dispute that the company uses less than 10 percent sulfolane. But, she said, independent testing and modeling conducted by a court-appointed safety adviser found the refinery's modified alkylation concoction "minimizes or eliminates aerosol formation at unit operating conditions." Brien also pointed to a Quantitative Risk Assessment (QRA) performed by Mobil in 1994 as part of the consent decree process, which concluded that the hydrofluoric acid units using the modified chemical mixture were "24 times safer than a sulfuric acid unit of the same size."

"I feel very strongly that the problem we discovered, that hydrofluoric acid would flash into an aerosol, would also happen under the conditions that these refineries use."

But Hayati and other activists, citing records obtained through local and regional agencies, have argued that the "testing and modeling" cited by ToRC are inadequate in assessing risk, because the models assume higher concentrations of sulfolane and other baseline conditions that don't apply in a working refinery. Their efforts have encouraged the local Air Quality Monitoring District to investigate the refinery's safety claims and to nudge the EPA to review its risk management plans. The federal Chemical Safety and Hazard Investigation Board (CSB) has also subpoenaed former Torrance owner ExxonMobil for additional information regarding MHF, and U.S. Representatives Maxine Waters and Ted Lieu, whose districts contain portions of Torrance, have both pressed for a federal probe into the 2015 explosion and the refinery's safety claims — partly based on evidence uncovered by the citizen sleuths.

Koopman — now an independent safety consultant working with both the industry and environmental groups — said he's seen much of the TRAA's work and that he finds it credible. He also suggested that any assertion that the concentrations of sulfolane used at ToRC and nearby Valero refineries would prevent a catastrophic aerosol release of hydrofluoric acid are "mere speculation."

“I feel very strongly that the problem we discovered, that hydrofluoric acid would flash into an aerosol, would also happen under the conditions that these refineries use,” Koopman said. “But you need experiments to make sure and those haven’t been done. The industry keeps its work proprietary, but if they had definitive proof that the additive would solve the problem, it would be out there.”

Three other U.S. refineries use MHF, and all but one are located in the middle of major metropolitan areas. Hayati speculated that the industry’s insistence on claiming the safety of MHF, despite the lack of peer-reviewed studies — or any studies — is a matter of necessity. Because activists are strong in southern California, where two of the four U.S. refineries that use MHF are located, they have the potential to force local bans, which could, in turn, be the death knell for the use of hydrofluoric acid nationwide. “The industry considers MHF to be vital in saving hydrofluoric acid from regulation. Any hydrofluoric acid refinery community that demands its elimination is fed the MHF story,” Hayati said. “Maintaining an element of doubt is the only thing standing between them and a ban.”

A 2017 report from the CSB slammed the previous owner of the Torrance facility for numerous safety violations. Under new ownership, workers at the facility say things have greatly improved, though Wright, the United Steelworkers representative, said the continued use of hydrofluoric acid remained an unnecessary risk. “We think that if you have to take a lot of measures to keep an operation safe, you’re better off going to something that really can’t have an accident, instead of taking all kinds of measures to basically mitigate the accident that might happen,” Wright said.

It’s a little disingenuous for the industry to say these [new technologies] are untested, because they ought to be testing them.

For its part, ToRC still insists that migrating to sulfuric acid would make the community less safe — a position that Wright and the United Steelworkers also hold, given that sulfuric acid would come with its own problems, including a need for larger equipment, larger acid volumes, higher greenhouse gas emissions, and much heavier use of truck transport. Still, both the Department of Homeland Security (DHS) and the EPA determined that there is no airborne danger to the community from the release of sulfuric acid. The DHS list of dangerous chemicals identifies hydrofluoric acid, but not sulfuric acid. The few refineries building alkylation units from scratch today are also choosing sulfuric acid over HF/MHF.

In an email, ToRC spokesperson Brien also pointed to an outside study that estimated the cost of converting from MHF to sulfuric acid at ToRC would be nearly $1 billion — $600 million up front, with an additional $300 million needed for an acid regeneration plant. The nonprofit Center for Public Integrity, however, cited an industry paper that estimated the cost of retrofitting a typical hydrofluoric acid alkylation unit to use sulfuric acid to be much less — between $50 million and $150 million for each refinery, depending on the size.

Two alternative technologies — ionic liquids and solid acid catalyst — carry none of the inherent risks of hydrofluoric acid/MHF or sulfuric acid. But only one refinery has committed to retrofit its existing alkylation unit to one of these alternatives: Chevron, which will use ionic liquids technology in its Salt Lake City, Utah refinery. Marketed by UOP, a subsidiary of Honeywell, which invented the hydrofluoric acid processes for refineries more than seven decades ago, the substance is much easier to contain and handle than hydrofluoric acid or sulfuric acid, according to Honeywell UOP spokesperson John Simley. He speculated that the industry will only begin phasing out hydrofluoric acid once newer technologies prove themselves cost-effective.

“There’s going to be a rush to be number two” in adopting new technology, Simley said. “That’s typical of the industry that is risk averse in many ways.”

ToRC’s Brien said that solid acid and ionic liquids processes still “need to be proven commercially viable” from both reliability and scalability perspectives. But Wright says he considers this to be mere foot-dragging. “It’s a little disingenuous for the industry to say these [new technologies] are untested, because they ought to be testing them,” Wright said. “It’s their industry. They’re the ones that are creating the risk, and they’ve got to be looking for alternatives.”

Regulators, so far, have been unwilling to force the industry’s hand by banning hydrofluoric acid outright, and the CSB, while able to make recommendations, has no authority to compel their adoption. To date, the state of California has come closest to outlawing the chemical, and the South Coast Air Quality Management District (AQMD) launched a rule-making effort in 2017 to begin phasing out hydrofluoric acid, but it backed off an eventual ban after a series of public hearings and significant pushback from the industry.

A measure passed in the waning days of the Obama administration does compel companies that use chemicals with a high intrinsic hazard to at least research inherently safer methods. And while the Trump administration attempted to delay the implementation of that measure, a federal court blocked that effort last month. Still, Wright considers the new rules “weak tea,” arguing that petroleum companies are unlikely to come out with studies showing the alternatives are better and cost effective.

Meanwhile, the 2015 Torrance Refinery blast prompted the passage ofthree bills for new safety standards on refineries in California. A fourth bill, which would have banned hydrofluoric acid outright, stalled in the legislature.

Without bans on hydrofluoric acid at the local or state level, those fearful of what could happen in a low-probability, high-consequence event must place their hopes on the industry voluntarily converting to a safer alternative.

Ron Koopman, who is currently consulting for the South Coast AQMD, said that so far, worst-case scenarios have been averted because almost every accidental release of hydrofluoric acid has involved a fire. That’s a good thing from a public safety standpoint, he said. “The fire takes the [hydrofluoric acid] straight up in the air, mixes it with air, and reduces the concentration.

“It’s a lucky break,” he added, “and the industry has a history of lucky breaks.”

Larry Buhl is a writer and radio producer based in Los Angeles. He has produced for the BBC, Marketplace, Free Speech Radio News, and Pacifica radio.

UPDATE: This story has been updated to clarify the position of the United Steelworkers on the conversion of alkylation units from hydrofluoric acid to sulfuric acid, and to provide reasoning for that position.