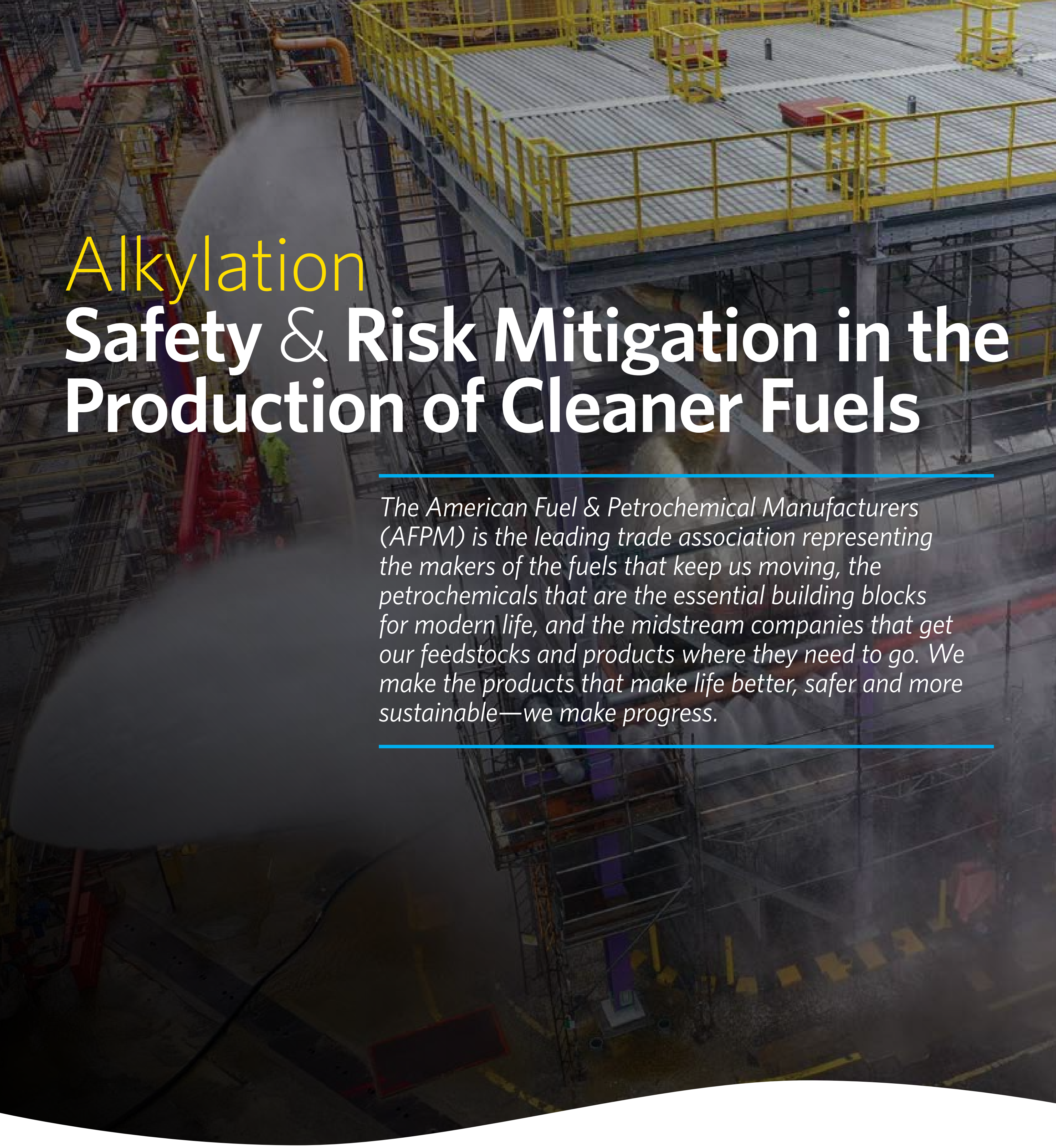

Alkylation
Safety & Risk Mitigation in the Production of Cleaner Fuels

The American Fuel & Petrochemical Manufacturers (AFPM) is the leading trade association representing the makers of the fuels that keep us moving, the petrochemicals that are the essential building blocks for modern life, and the midstream companies that get our feedstocks and products where they need to go. We make the products that make life better, safer and more sustainable—we make progress.

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> *Alkylate is an irreplaceable component of the cleanest petroleum gasoline and aviation gasoline available. This refined product is key to satisfying ultra-low-sulfur fuel standards because it contains ZERO aromatics, such as benzene, no nitrogen and hardly any volatile organics. The availability of alkylate was instrumental in eliminating lead from the U.S. gasoline supply. Producing alkylate requires a catalyst, one of which is hydrofluoric acid.*

An Introduction to Fuel Alkylation & Risk Mitigation

Nothing is more important to U.S. refiners than the safety of our employees, contractors, neighbors and the communities we serve. AFPM members invest significant resources, above and beyond regulatory requirements, to continually improve our safety programs and practices. Nowhere is this more evident than in our alkylation units.

Alkylation units produce alkylate, a necessary blending component for cleaner gasoline and aviation gasoline (avgas). Refiners use alkylate to manufacture fuels with high octane ratings, low Reid Vapor Pressure (RVP) and ultra-low emissions, attributes that help new vehicles operate at their highest efficiency.

Like every industrial process, alkylation poses risks, but they are risks refiners are well-equipped to manage.

The alkylation process is initiated by one of two primary catalysts — hydrofluoric acid (HF) or sulfuric acid. Even though there are slightly fewer HF alkylation units in the United States, both HF and sulfuric acid are used to produce about the same volume of alkylate, roughly 50 percent of U.S. production each.

For both catalyst technologies, refineries use a range of equipment and procedures to safely operate alkylation units.

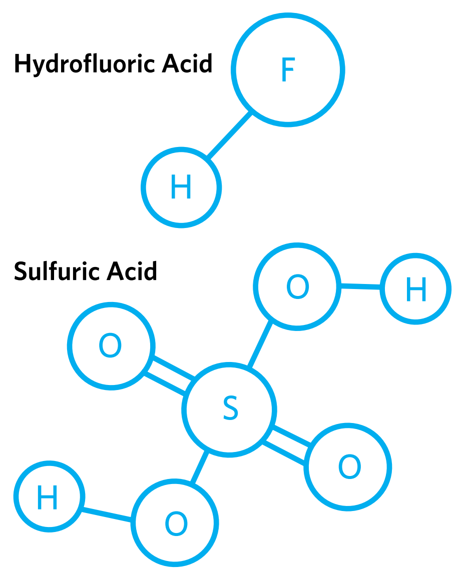
Between the technologies, though, HF often garners the most attention even though it is widely used across industrial manufacturing. In fact, HF is one of the most thoroughly managed and highly regulated industrial chemicals in use today.

> *HF is widely used across industrial manufacturing and is one of the most thoroughly managed and highly regulated chemicals in use today.*

A Long History of HF in Industrial Settings

HF was discovered and first used in manufacturing in the 1700s. Today, it is used to make batteries, hydrogen fuel cell technology for zero emission vehicles, refrigerants, detergents, agricultural products, semiconductors, pharmaceuticals, beer, toothpaste, soap and even treated drinking water. Almost every aluminum can you touch has been etched with HF so that branding and labels can be adhered to the can.

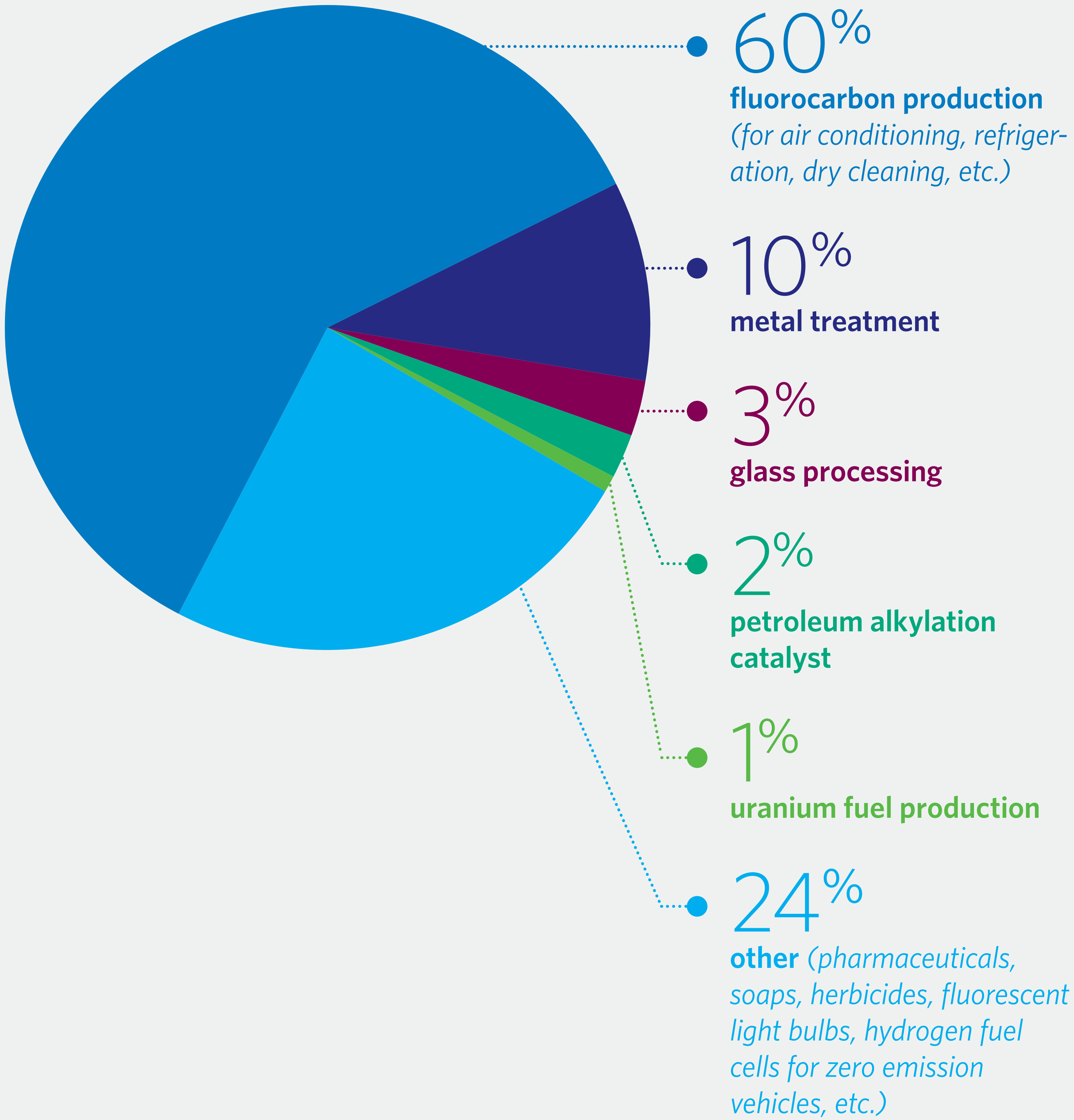
U.S. refiners began using HF as an alkylation catalyst to produce avgas during World War II. Our industry continues to use HF in fuel production, but we are nowhere near the top industrial consumers. Fuel alkylation at refineries is responsible for just two percent of global HF demand. **So even if refiners were to stop using HF, it would still be manufactured, shipped and used around the world in nearly identical quantities.**



The molecular structure of each alkylation catalyst is different, as are the technologies used in their respective process units.

World Consumption of Hydrofluoric Acid—2019

totaling 1.9 million metric tons[1]



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EPA clearly states that RMP planning circles are informational and intended for local emergency response planning. They should not be misinterpreted or misrepresented as predictors of danger.

Regulation & Accountability for HF Across Sectors

In any industrial setting, HF presents operational risks. That's why high volumes of HF stored at any location are highly regulated and subject to federal and state workplace and community safety programs, including:

Risk Management Plans (RMP), *a program of the Environmental Protection Agency (EPA)*

Process Safety Management (PSM), *a program of the Occupational Safety and Health Administration (OSHA)*

Department of Transportation (DOT) *guidelines for moving HF, particularly in high population areas*

The U.S. Coast Guard's ***Maritime Transportation Security Act***

Chemical Facility Anti-Terrorism Standards *from the Department of Homeland Security (DHS)*

Local Emergency Planning Committees (LEPCs), *community-based organizations focused on emergency preparedness*

Managing Risk All Around Us

As part of the Clean Air Act, EPA requires facilities that use or store high volumes of certain chemicals to develop Risk Management Plans (RMPs). These plans aim to prevent accidental releases, but they also establish rapid response protocols and emergency mobilization plans, specific to each site and community, that can be initiated in the rare event of a chemical release. HF is one of nearly 260 chemicals subject to EPA's Risk Management Plan. Among the other RMP-subject chemicals are some very well-known substances, such as ammonia and chlorine.

RMPs require facilities to complete hazard assessments and update them at least every five years. Each assessment details (1) the potential impacts of an unlikely worst-case scenario, including maximum possible reach; and (2) a history of facility incidents over the last five years. Facilities must also evaluate multiple incident scenarios of different scales to ensure every possible risk factor and multiplier is considered for emergency response planning and procedures.

A well-known but frequently misunderstood feature of RMPs are "planning circles." These are literally circular perimeters mapped around RMP facilities that designate the largest possible area that could be impacted by a ***hypothetical*** worst-case scenario. Some surprising assumptions are baked into these hypothetical scenario plans.

First, every RMP worst-case scenario for HF presumes there are zero mitigation technologies that will be deployed in response to an incident. That will never be the case in the United States, since every refinery with an HF alkylation unit is equipped with several forms of mitigation, none of which is "single-point-of-failure," or the only line of defense for a facility or community.

Second, to arrive at a hypothetical worst case, facilities are required to factor in the worst plausible external conditions for an incident and to proceed as though all those conditions will exist simultaneously during an incident. That's just not physically possible. Some of the readings that must be factored into the RMP — such as nighttime wind stability and highest-observed ambient temperature (a daytime reading) — will never happen simultaneously in the real world.

Third, the RMP shows what would happen if an incident occurred while wind was blowing steadily in all directions. This is how we end up with "planning circles" rather than much smaller pie-shaped wedges. In reality, if a release were to occur at a facility, the area potentially affected would not look circular. It would depend on winds speed and wind direction, as well as other geographic factors.

API Recommended Practice 751 (RP 751) is considered the global standard for safely and reliably managing HF alkylation operations at refineries. RP 751 provides comprehensive guidance around these components of HF fuel alkylation:

- *Hazards Management*
- *Operating Procedures and Worker Protections*
- *Materials, Fabrication, Inspection and Maintenance Practices*
- *Transportation and Inventory Control*
- *Pressure Relief, Product Treatment and Utility Systems*
- *Risk Mitigation: Options and Techniques*

The physical impracticality of the "worst-case scenario" model is one reason why EPA is clear that RMP planning circles are intended to aid in emergency response planning by providing "a basis for discussion among the regulated community, emergency planners and responders, and the public, rather than a basis for any specific predictions or actions."[2]

Safe Industry Operations & Risk Management for Hydrofluoric Acid at Refineries

In addition to government regulations and oversight from various boards and agencies, the refining industry maintains recommended practices for the safe, reliable operation of HF alkylation units. These practices—first published in 1992 as API Recommended Practice 751 (RP 751) — are updated roughly every five years based on new data, industry learnings and technologies. A working group of nearly 100 of the top global experts in HF alkylation drives the rigorous revision process. The 5th edition of RP 751, released in August 2021, reflects the work and recommendations of this group carried out over a multi-year review process. Multiple HF alkylation industry forums are also held every year so refiners with HF alkylation units can share their experiences on a variety of issues and topics.

Rigorous adherence to these proven industry practices signals that facilities are going above and beyond the minimum safety standards required by government. RP 751 is recognized by OSHA and the Chemical Safety Board as providing effective guidance for safe operation of HF alkylation units.[3]

RP 751 provides refineries with multiple layers of protection for HF alkylation unit operations, including:

1. *Guidance for HF alkylation unit* ***operating procedures*** *and* ***worker protections,*** *including workforce training and PPE requirements, to ensure that the safety of employees and facility neighbors remains at the forefront.*

2. *Measures to avoid a chemical release, including: routine required* ***hazard and risk assessments;*** *process and* ***mechanical inspections; safe operating limits,*** *which can be thought of as clear lane markers for acceptable flow, temperature and pressure levels in a unit; a* ***material verification program,*** *which includes component checks and positive materials identification, to confirm the different metals and alloys in a unit so corrosion rates can be monitored and appropriate maintenance schedules maintained; and* ***preventive maintenance.***

3. *Measures for* ***immediate leak detection,*** *including acid detecting paint, HF sensors, alarms and remote cameras—tools that identify the source of a leak so that unit personnel can quickly activate acid isolation and other mitigation procedures and equipment.*

4. *Measures to reduce severity and immediately contain a leak if one were to occur, including remote-activated and controlled* ***water mitigation systems*** *and systems to limit the duration of a release, such as* ***rapid acid transfer systems*** *and* ***remote-activated block valves*** *for HF isolation. HF is completely soluble in water, making water mitigation extremely effective. Some facilities also use* ***vapor-suppression additives,*** *though that is not a requirement of RP 751.*

5. *Measures to initiate* ***emergency response*** *in the case of a release, including HF-specific training for emergency response teams and plans covering: protocols for coordinating with local first responders; internal and external communications systems; decision criteria to issue evacuation or shelter-in-place instructions; medical responses to HF exposure; strategies for managing potential fluid runoff; mechanisms for decontaminating equipment, buildings, soil and water.*

API RP 751 goes through a transparent revision process consistent with the American National Standards Institute (ANSI). Every new edition is compiled with due process and consideration is given to comments and input from stakeholders, including government and community participants.

There is no tougher or more comprehensive set of instructions for safely managing HF than RP 751. In fact, no other industry has taken the lead to similarly manage, innovate and drive continuous improvement in process safety.

API RP 751 is comprehensive and rigorous, recommending the best available technologies and proven practices to protect people and the environment. New regional networks of HF alkylation unit operators and experts meet regularly to share practices and learnings from API RP 751 and raise the bar for efficient, responsible refinery operations that may ultimately be considered for the next revision.

Under the guidance of RP 751, HF alkylation operations are getting safer every year. Nationally, there have never been any life-threatening injuries to people in surrounding communities as a result of HF-related incidents. EPA data likewise shows the number of RMP-reportable events has dropped by half in the last decade.

Risk **Relative to What?**

We all assume risk through a number of activities every day: driving, swimming, using electrical appliances, etc. In the United States, we are much more likely to sustain a life-threatening injury from a lightning bolt, bee sting or bicycling accident than an incident involving HF alkylation.

Based on data from the National Safety Council, actual incident reports and mitigation surveys, the theoretical lifetime odds of sustaining a life-threatening injury from HF alkylation in the United States are roughly 1 in 52 million.

By comparison, the lifetime odds of a life-threatening injury to Americans from other causes are much higher. To help visualize the scale, let's say the tiny spec you can barely see below is the one chance in...

1

Families that live in close proximity to HF units certainly have a different risk than those who do not. So, we took this data a step further to be completely clear about concerns specific to our neighbors in local communities. Instead of deriving risk rates from the entire U.S. population, we examined the much smaller population around each refinery with an HF alkylation unit and calculated the risk for individuals among that group.

For those in close proximity to refinery HF units, **the odds of life-threatening injury from HF are just 1 in 144,000 —** still safer than many routine activities.

In the nearly 80 year history of HF alkylation at fuel refineries, there have been no life-threatening injuries caused by HF in the communities surrounding AFPM member refineries. Refinery safety professionals work diligently to analyze industry safety performance and the efficacy of HF mitigation tools so that this record of safe alkylation operations continues.

1 *in* 144,000

chance of life-threatening injury for people living in close proximity to HF alkylation units.

likelihood of life-threatening HF alkylation-related injury 1 *in* 52,000,000

This giant circle, too huge to fit on all the pages of this booklet, represents 52,000,000

1 *in* 107

chance of a dying in a motor vehicle crash

chance of deadly injury from a sharp object

1 *in* 29,000

chance of a life-threatening bicycle wreck

1 *in* 3,825

1 *in* 59,000

chance of death by bee sting

chance of being struck by lightning

1 *in* 138,000

There is No One-Size-Fits All for Risk Mitigation

Every refinery is unique. They are designed with very different configurations and footprints; they have different complexities depending on the types of crude oil they process and the menu and quantities of petroleum products they produce; and they are located in vastly different areas, ranging from rural mountain regions to densely populated cities.

Site-specific considerations like these require every refinery with an HF alkylation unit to develop a customized strategy for risk mitigation, in addition to the facility's participation in the federal RMP program. The right technical mitigation tools for a facility are those that enable the earliest possible detection and fastest possible response to a potential or actual release. Those exact tools differ from site to site.

To conform with API RP 751, each refinery employs some combination of the following technologies and safeguards (a sample of which follows), to prevent, detect and contain HF-related risks:

Prevention

Extensive training and specialized PPE for HF unit operators and emergency responders

Double-sealed pumps

24-hour unit monitoring through video, operator rounds and live-unit diagnostics

Inspection and mechanical integrity programs

Detection

Acid-detecting paint

Multiple individual point sensors and perimeter laser monitors

Multiple targeted, continuously monitored live camera feeds

Integrated unit and facility alarms that cannot be overridden short of incident resolution

Containment

Rapid acid transfer and remote isolation systems

Remotely activated block valves for HF isolation

Water mitigation systems: water cannons; water walls; water curtains; equipment deluges

Modified HF, a vapor suppression additive

External flange and equipment barriers

Additionally, refineries have on-site fire-fighting capabilities that can help apply additional water in the rare event of an HF incident. At some facilities, the refinery firefighters also function as the fire department serving their local community.

Refiners' Uncompromising Commitment to Safety

For 80 years, U.S. refiners have demonstrated that HF alkylation units can be operated safely and responsibly. We are constantly improving and raising expectations for industry. Our hard-earned expertise is reflected in our operating, maintenance, mitigation and design standards for HF alkylation.

The cleanest, most efficient gasoline requires alkylate, and there is no alkylate unless the process to make it is safe. Because nothing matters more than the safety of our workforce, communities and environment, AFPM members invest significant resources, above and beyond minimums set by law, to continually improve the safety of HF alkylation with the goal of zero incidents.

Advantages of HF in Refinery Settings

Most efficient fuel alkylation catalyst, requiring less volume of acid and fewer tank truck shipments

High efficiency process translates to lower consumer costs

Lower volatility than other commonly used industrial chemicals like chlorine or ammonia

Lower boiling point than sulfuric acid, which allows HF catalyst to be regenerated on-site

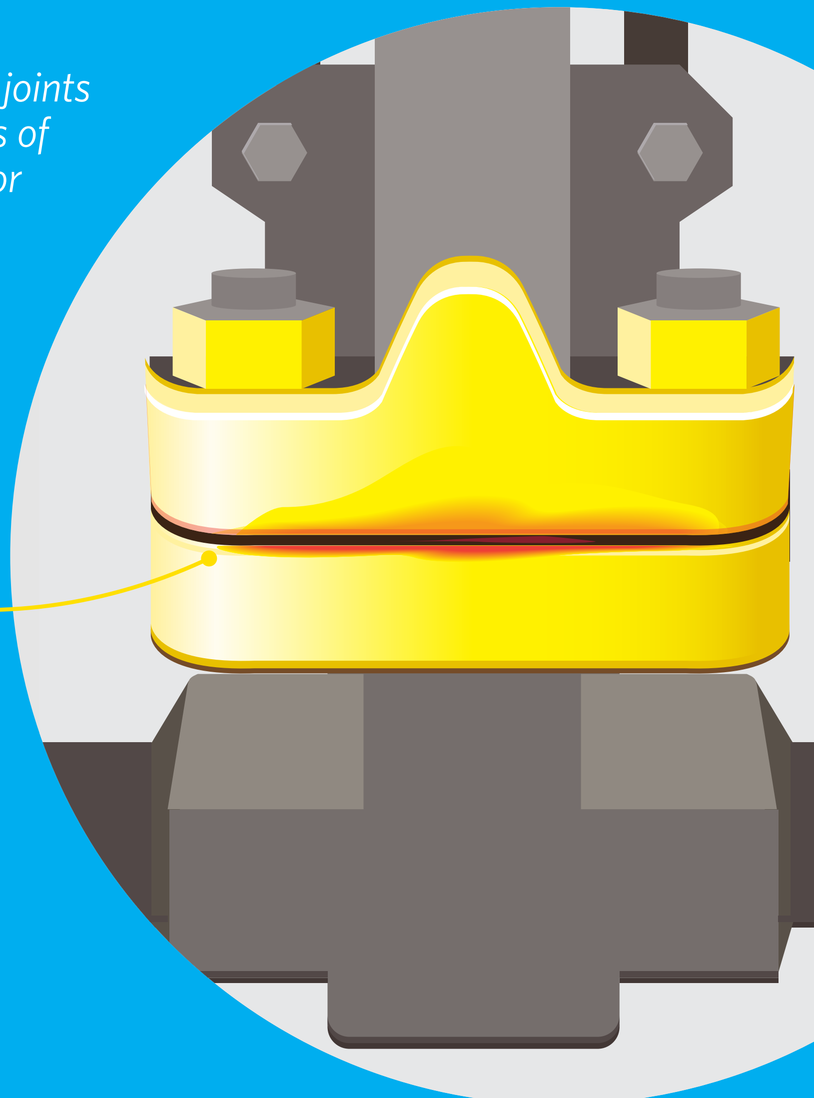
Water soluble, one of the few chemicals able to be mitigated with water

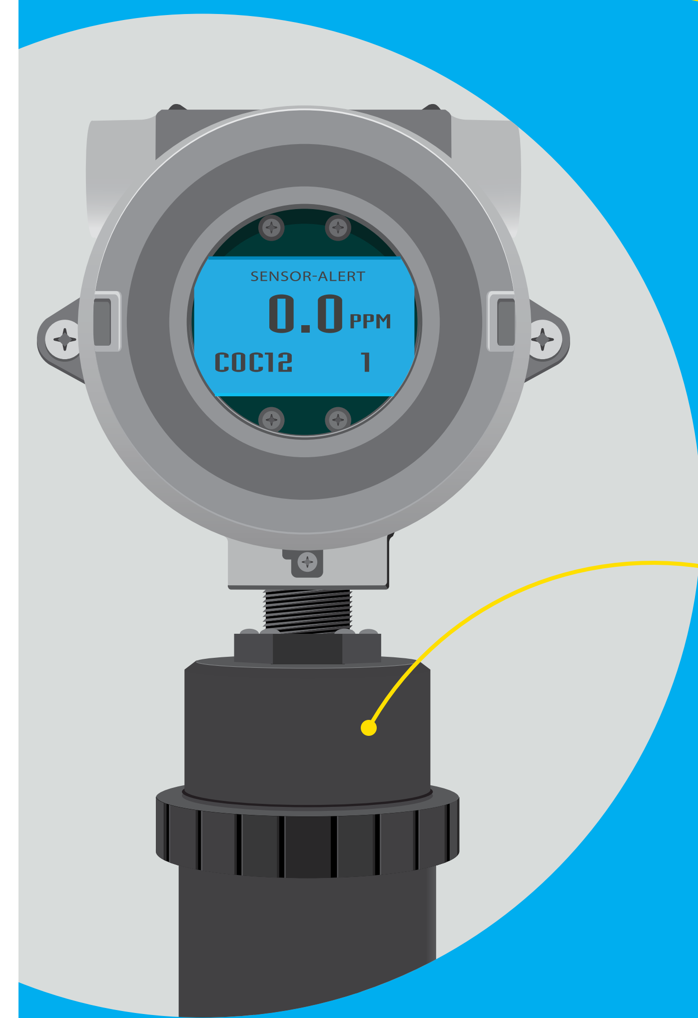
Among the cleanest refinery operating units, with essentially zero fugitive emissions

Essential for avgas production

Early **Detection**

Acid-detecting paint applied to connective joints and flanges in an HF unit provides a means of visual leak detection. Paint will change color from yellow to red at even the slightest presence of HF (down to the parts per billion level, which is too small to technically count as a leak), enabling the earliest possible response from facility personnel.

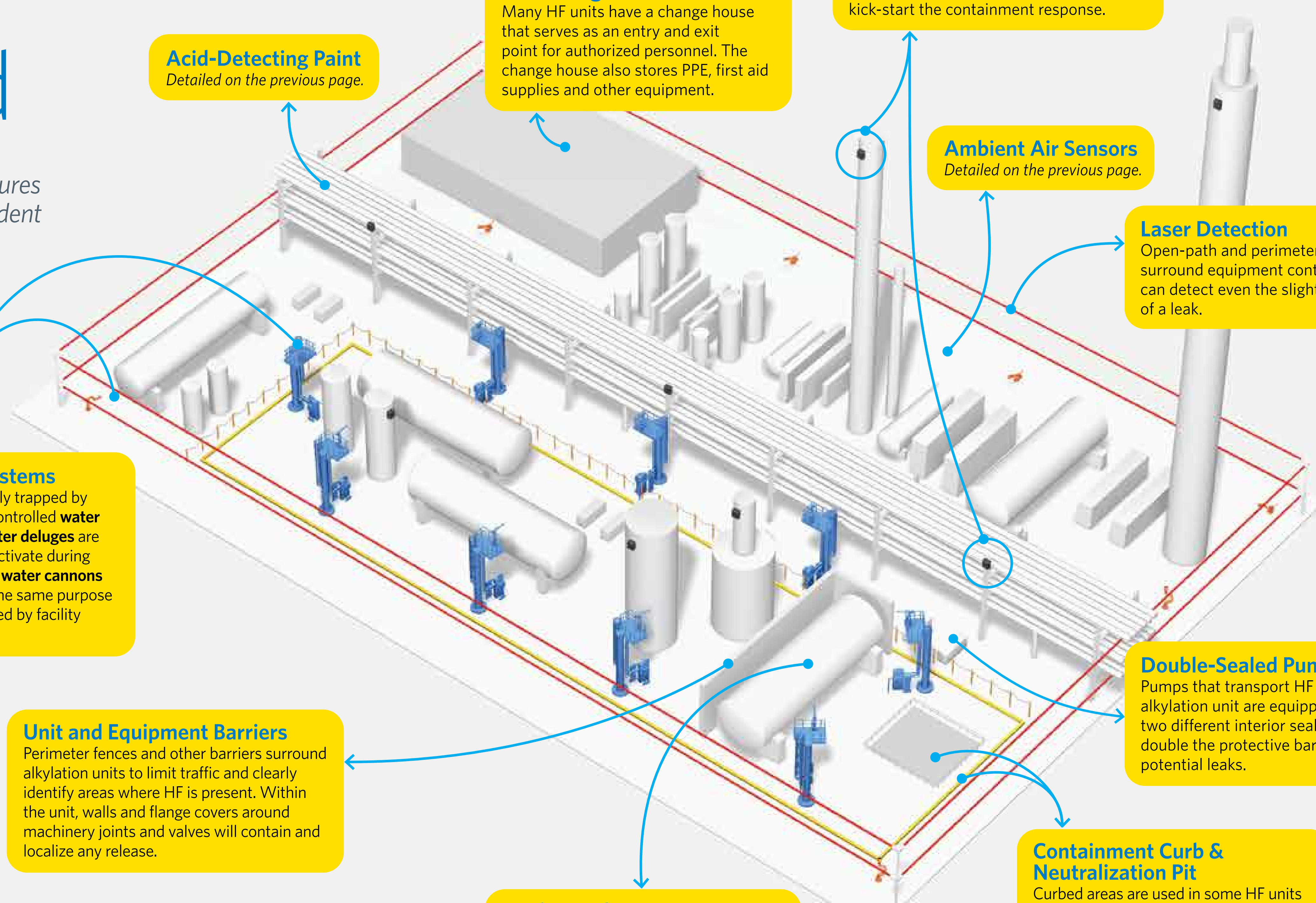




Facilities utilize point sensors, such as lasers, cameras and the chemical spot detector pictured here, to quickly and effectively alert personnel in the event of a possible leak. These reliable sensors are installed around equipment containing HF. Because they can identify trace amounts of HF, point sensors support rapid response, containment and mitigation efforts. Some sensors are programmed to automatically activate other mitigation systems upon alert.

Detection & Containment on the Ground

This sample HF unit diagram depicts some of the features and technologies that may be used by refiners for incident prevention, detection and containment.



Acid-Detecting Paint

Detailed on the previous page.

PPE Change House

Many HF units have a change house that serves as an entry and exit point for authorized personnel. The change house also stores PPE, first aid supplies and other equipment.

Cameras

Closed-circuit video cameras maintain 24/7 visual surveillance within an HF unit to immediately detect a potential leak and kick-start the containment response.

Ambient Air Sensors

Detailed on the previous page.

Laser Detection

Open-path and perimeter lasers surround equipment containing HF and can detect even the slightest presence of a leak.

Water Mitigation Systems

HF is water soluble and easily trapped by water mitigation. Remote-controlled **water towers, water walls** and **water deluges** are designed to automatically activate during releases. **Water turrets** and **water cannons** throughout HF units serve the same purpose but are activated and directed by facility personnel.

Unit and Equipment Barriers

Perimeter fences and other barriers surround alkylation units to limit traffic and clearly identify areas where HF is present. Within the unit, walls and flange covers around machinery joints and valves will contain and localize any release.

Acid Transfer

In the event of an incident, HF acid can be remotely evacuated from the unit into a separate, safe location.

Double-Sealed Pumps

Pumps that transport HF within an alkylation unit are equipped with two different interior seals, providing double the protective barrier against potential leaks.

Containment Curb & Neutralization Pit

Curbed areas are used in some HF units to ensure that water released during mitigation is routed through on-site neutralization and treatment.

AFPM

“Safety is a function of risk awareness and risk management. Where industrial use of HF is concerned, the fuel refining sector has the most exacting guidance for handling and mitigating risks associated with HF catalyst. Recommended practices for HF alkylation are becoming more stringent all the time in response to the latest safety data and real-world experiences.”

Jatin Shah
Managing Director Global Business Development, Senior Principal Consultant Risk Management, Baker Engineering and Risk Consultants

“There are many layers of redundant safety technology for refinery alkylation units. That’s partly because of regulatory requirements, but more importantly it’s because safety is paramount to every refinery employee and our surrounding community. Safety doesn’t stop at our fenceline, the community around the refinery is our home too.”

Sharon Watkins
Vice President, Operations Leader, Monroe Energy

“The extensive personnel training, safety protocols, operating procedures and mitigation mechanisms employed throughout HF alkylation reflect the industry’s commitment to safe, reliable, and environmentally responsible operations.”

Marie Wright
Director of Strategic Planning, PBF Energy

Endnotes:
1 IHS Markit 2019
2 U.S. Environmental Protection Agency
3 U.S. Chemical Safety and Hazard Investigation Board

Cover image: In addition to highly trained personnel, this alkylation unit is equipped with multiple safety systems, including water cannons (shown during testing), monitors, sprays, sensors and laser leak detectors, surveillance cameras and other response technology.