

A RISK TOO GREAT

HYDROFLUORIC ACID IN U.S. REFINERIES



Surveillance video from July 19, 2009, fire and explosion at the CITGO Corpus Christi Refinery



ACKNOWLEDGEMENTS

In 2010, the United Steel, Paper and Forestry, Rubber, Manufacturing, Energy, Allied Industrial and Service Workers International Union (USW) initiated the Refinery Alkylation Research Action Project to address the alarming number of fatalities and serious injuries in the U.S. oil refining industry. The project was coordinated through the USW-affiliated Tony Mazzocchi Center for Health, Safety and Environmental Education (TMC). We gratefully acknowledge the contributions of all the local unions who participated, and the members of the Project Team:

Contributors

Gary Beevers¹
Teddy Bender²
Kristin Bradley-Bull³
Jonas Dauber⁴
James Frederick⁵
Diane Heminway⁶
Jim Lefton⁷
Julie Lidstone⁸
Teresa Lewis⁹
Tobi Lippin³
Thomas H. McQuiston¹⁰
Dave Miller¹¹
Kim Nibarger⁵
Jim Savage¹²
Denis Stephano¹³
Casey Wardell¹⁴
Mike Wright⁵

1. USW International Vice President, National Oil Bargaining
2. USW Local 10-1 Alkylation Unit Operator; Philadelphia, Pennsylvania
3. New Perspectives Consulting Group, Inc.; Durham, North Carolina
4. USW Local 10-234 Health and Safety Representative; Trainer, Pennsylvania
5. USW Health, Safety and Environment Department; Pittsburgh, Pennsylvania
6. USW Strategic Campaigns Department; Pittsburgh, Pennsylvania
7. USW Assistant to the Director, District 13
8. USW Administrative Assistant, District 13
9. USW Local 10-234 Alkylation Unit Operator; Trainer, Pennsylvania
10. Tony Mazzocchi Center for Health, Safety and Environmental Education; Pittsburgh, Pennsylvania (Lead author)
11. USW Local 10-901 President, Marcus Hook, Pennsylvania
12. USW Local 10-1 President, Philadelphia, Pennsylvania
13. USW Local 10-234 President, Trainer, Pennsylvania
14. USW Local 12-578 President, Woods Cross, Utah.

This survey and report were funded by grant number U45 ES06175 from the National Institute of Environmental Health Sciences (NIEHS), NIH. Its contents are solely the responsibility of the authors and do not necessarily represent the official views of the NIEHS, NIH.

* New Perspectives provides evaluation consulting services for TMC safety and health programs.

Dedicated to Sylvia Kieding

We dedicate this report as a small measure of appreciation for Sylvia Kieding who long served as a union health and safety leader for workers everywhere and especially refinery workers. A long-time supporter and colleague of Tony Mazzocchi, Sylvia was a devoted staff member in health, safety and the environment for the Oil, Chemical and Atomic Workers International Union (OCAW), the Paper, Allied Industrial, Chemical and Energy Workers Union (PACE) and the United Steelworkers (USW) and its Tony Mazzocchi Center for Health, Safety and Environmental Education (TMC) and in cooperation with Queens College, the Worker Health Protection Program (WHPP).

PREFACE: A CULTURE OF RISK

Risk is a natural and unavoidable part of the oil business. As many as four exploratory wells are dry for every well that actually finds oil. Such wells are increasingly expensive, as the hunt for new reserves moves into deeper water and higher latitudes with more extreme weather. A single well can cost hundreds of millions of dollars, and if the well is dry the investment is a total loss. Yet if the risks are great, so too are the rewards. A new field can generate billions in profits. Oil executives are gamblers. They assess, manipulate and ultimately accept huge financial risks every day. The culture of top management is a culture of risk. The oil business rewards risk takers.

But it is one thing to risk money; quite another to risk lives. No industrial process risks more lives from a single accident than does the subject of this report – alkylation using hydrogen fluoride in oil refining. Fifty American refineries use HF alkylation to improve the octane of gasoline. Many are situated in or close to major cities, including Houston, Philadelphia, Salt Lake City and Memphis. In some cases, more than a million residents live in the danger zone of a single refinery. All in all, more than 26 million Americans are at risk.

It is bad enough that such risks exist, especially when much safer processes are available. But are the risks at least being reduced to the absolute minimum through the best possible safety programs? That is the question this report seeks to answer. The study team included safety experts from inside and outside the United Steelworkers as well as refinery workers themselves. Through a standardized questionnaire and data from OSHA, the U.S. Chemical Safety Board, and the industry, they examined the safety of Steelworker-represented refineries using HF alkylation.

The results are shocking. Over a five-year period, the refineries in the study experienced 131 HF releases or near misses and committed hundreds of violations of the OSHA rule regulating highly hazardous operations. Most alarming, for a risk that demands very effective controls, the vast majority of refineries did not reach that level.

Fortunately, HF alkylation can be entirely eliminated. The industry has the technology and expertise. It certainly has the money. It lacks only the will. And if it cannot find the will voluntarily, it must be forced by government action.

This is truly a risk too great.

Leo W. Gerard
International President, United Steelworkers

Gary Beevers
International Vice President, United Steelworkers

TABLE OF CONTENTS

PREFACE: A CULTURE OF RISK	iii
EXECUTIVE SUMMARY	vi
INTRODUCTION AND BACKGROUND	1
THE USW SURVEY	9
SURVEY FINDINGS	13
SUMMARY AND CONCLUSIONS	21
Recommendations: Seven Steps to Safer Refineries.....	21
 APPENDICES	
APPENDIX A: BACKGROUND INFORMATION	A-1
APPENDIX B: TABLES OF FINDINGS DATA	B-1
APPENDIX C: HF USING REFINERIES AND AT RISK LOCATIONS AND POPULATIONS	C-1
 REFERENCES	R-1

The report is available at:

<http://assets.usw.org/resources/hse/pdf/A-Risk-Too-Great.pdf>

A NOTE ON NOTES: References are at the end of the report, and are designated by numbers. Footnotes, which further explain the text, are on the same page as text to which they refer, and are designated by letters.

A Risk Too Great
Hydrofluoric Acid in U.S. Refineries

April 2013

EXECUTIVE SUMMARY

Background: Fifty U.S. oil refineries use large volumes of highly concentrated hydrofluoric acid (HF) as chemical catalysts in a process called alkylation. Alkylation creates additives that boost the octane of gasoline. On average, these 50 refineries each store 212,000 pounds of HF.^a

If released in the atmosphere, HF rapidly forms dense vapor clouds that hover near land and can travel great distances. Like other powerful acids, HF can cause deep severe burns and damage the eyes, skin, nose, throat and respiratory system. But the fluoride ion is also poisonous. Entering the body through a burn or by the lungs, it can cause internal damage throughout the body. At high enough exposures, HF can kill. The Occupational Safety and Health Administration (OSHA) and the Environmental Protection Agency (EPA) regulate HF as *highly toxic*.

EPA requires companies using or storing highly toxic chemicals to gauge how far a worst case release might travel and how many people might be in harm's way. For HF releases from U.S. refineries, the range is three to 25 miles, depending mostly on the amount stored. Twenty-six million people live within the vulnerable zone, many in urban areas like Philadelphia, Memphis, Salt Lake City, and the Houston – Galveston corridor that would be impossible to evacuate quickly in the event of a major release. No other chemical operation puts as many people at risk.

The Survey: How well are refineries managing the risk of an HF release? To answer this question, a research team from the United Steelworkers, the Tony Mazzocchi Center and the New Perspectives Consulting Group developed a 198 question survey that focused on four key issues: incident prevention; incident and near miss experiences; incident mitigation systems, and emergency preparedness and response. Though not directly addressed in the survey, a fifth issue included in this report is safe staffing.

Workers in 28 of the 50 refineries using HF alkylation are represented by the United Steelworkers. Local unions in 23 of those refineries formed site survey teams and completed the survey, for a response rate of 82 percent. Combined, the 23 study refineries produce 3.3 million barrels of finished petroleum products per day and have over 5.3 million pounds of HF on site. These 23 refineries put approximately 12,000 workers and 13 million community members at risk of exposure from an HF release.

What the survey found:

- Within a recent five-year span, study refineries had 293 violations of OSHA's Process Safety Management (PSM) Standard regulating highly hazardous chemical operations.^b
- Over three-quarters of the site survey teams reported at least one HF-related incident or near miss in the previous three years. These totaled 131 HF-related incidents or near

^a Data gathered at U.S. EPA Headquarters by staff from the Center for Public Integrity in October 2010.

^b This does not include the BP refinery in Texas City that received intense OSHA scrutiny following major catastrophic accidents including the 2005 disaster that killed 15 workers. That site had 593 violations. Texas City is also the refinery that stores the largest amount of HF.

misses. Among 16 sites reporting their most serious or potentially serious HF-related events, all reported the events either *did* or *could have* caused injuries to workers on-site, and half indicated that these events could have caused injuries to people in the community.

- A chemical as lethal as HF demands the most effective safety systems. Yet more than half of the site survey teams reported that 26 out of 32 safety systems were *less than very effective* in three critical areas -- maintaining the integrity of HF alkylation processes, maintaining the integrity of related processes such as storage and transfer, and emergency mitigation. For the remaining six systems examined, a majority rated them as *very effective*.
- Almost two-thirds reported their sites were *less than very prepared* with emergency personal protective equipment for on-site workers who might need it during a release.
- Site survey teams rated preparedness for HF-related emergencies for four groups of workers: on-site emergency responders; off-site emergency responders; on-site nursing and medical personnel, and first receivers (e.g., hospital workers). More than half of the sites rated each worker group *less than very prepared* for an on-site emergency. Sites were assessed to be even less prepared for a larger release spreading into the surrounding community.
- Although the survey did not include questions on staffing, a number of site survey teams commented that staffing levels were too low to ensure the safe operation of alkylation units.

Alternatives to HF: There are other ways to perform alkylation in an oil refinery. Some refineries use a modified form of HF containing a chemical which renders it less volatile. Others use sulfuric acid instead of HF. Both methods have their drawbacks, and both are hazardous, although not as hazardous as alkylation using unmodified HF. Far safer alternatives exist for catalyzing alkylation reactions. They use either solid catalysts or liquid ionic catalysts. Both these safer alkylation catalysts have been demonstrated successful at the pilot stage, and, for liquid ionic, in production. Releases of either of these alternative catalysts would be relatively benign, especially in comparison to HF. Still, no U.S. refinery has yet converted to these alternatives.

Conclusions: There must be fundamental change in the oil industry's use of HF. The long-term solution is to replace HF alkylation with safer systems not requiring the use of so toxic a chemical. In the meantime, existing alkylation units can and must be made safer.

In particular, the industry should:

1. Commit to ending the use of HF alkylation and replacing it with safer alternatives as soon as possible.
2. Develop, build and test pilot alkylation units using safer chemicals and processes, sharing lessons from those operations to speed the transition to full-scale safer alternative alkylation processes across the industry.

3. Work cooperatively with unions and other stakeholders to educate site workers, on- and off-site emergency responders and receivers, and the public about the dangers of HF.
4. Make existing HF alkylation processes systems safer by improving process integrity, mitigation systems, and emergency response, and by converting to the use of modified-HF.
5. Create an open and transparent system for reporting HF-related releases, near misses and process upsets, both within and outside the corporation, so that similar events can be avoided.
6. Work with the USW and other unions to promote effective process safety programs based on rigorous hazard identification and correction.
7. Increase staffing to a level that will be effective in preventing, preparing for, and responding to potential HF alkylation unit emergencies.

The government can facilitate this process through intensive inspections of HF alkylation units under OSHA's Process Safety Standard and the EPA Risk Management Program. HF alkylation as it is currently performed in U.S. refineries is a risk too great, but that risk can be reduced and ultimately eliminated.

A Risk Too Great

Hydrofluoric Acid in U.S. Refineries

INTRODUCTION AND BACKGROUND

Thousands of workers, millions of community members and vast stretches of air, land and water are at risk from oil companies' use of hydrofluoric acid (HF) at 50 U.S. refineries. In several cases, a single HF-using refinery puts hundreds of workers and more than one million community members at risk of devastating injuries and even death. This is a risk too great.

Where It All Begins

Clean-burning gasoline requires a high octane rating. Oil refineries achieve these ratings using additives produced in processes called *alkylation*. These alkylation processes work by using acid catalysts to modify petroleum feed materials to form what are called *alkylates*. Refineries blend these alkylates with other refining products to create gasoline for retail sale.

Alkylation: Extremely Hazardous Chemical Processes

Currently, U.S. refineries use two different processes and chemical catalysts for alkylation. One involves very large volumes of highly concentrated sulfuric acid (H₂SO₄). The other, the subject of this report, uses very large volumes of highly concentrated hydrofluoric acid (HF). Sulfuric acid alkylation processes are hazardous, but not as hazardous as HF alkylation. HF is much more dangerous when released because it readily forms dense, highly toxic vapor clouds that hover near land and can travel great distances. In contrast, sulfuric acid typically remains in a liquid state during upsets and releases.^a And while both acids are highly corrosive, HF is also a systemic poison. Importantly, there are now alkylation catalysts and processes that are much safer than either sulfuric acid or HF. This report will address these innovations in later sections.

^a HF has a boiling point of 67 °F and a vapor pressure of 783 mmHg. By comparison, sulfuric acid has a boiling point of 554 °F and a vapor pressure of 0.01 mmHg.

HF – Extremely Toxic

HF is a fast-acting acid and can cause deep, severe burns. Exposure can occur through inhalation and skin contact. HF can permanently damage the eyes, skin, nose, throat, respiratory system and bones. The fluoride ion can enter the body when HF is inhaled or through a skin burn, where it can interfere with calcium metabolism and cause death by cardiac arrest. (See Appendix A: HF Hazards)

Both the Occupational Safety and Health Administration (OSHA) and the Environmental Protection Agency (EPA) regulate HF as *highly toxic*. The quantities of HF stored in the 50 U.S. refineries that use it for alkylation ranges from 5,200 to 870,000 pounds. The average per refinery is 212,000 pounds; the median, 150,000 pounds.¹

Of special importance to these refineries is the concept of *process safety*. Process safety is the art and science of preventing fires, explosions and major releases of dangerous chemicals from tanks, vessels and piping where they are used or stored. OSHA covers these refineries under its *Process Safety Management of Highly Hazardous Chemicals (PSM)* standard. This standard is designed to protect *workers* from catastrophic releases and exposures. EPA covers these same refineries under its *Risk Management Program (RMP)* rule. EPA's rule is designed to protect *communities* by preventing releases and preparing for emergency responses.

Nevada Test Sites Studies

Scientific tests of HF releases conducted in 1986 in the Nevada desert surprised researchers when 100 percent of the released liquid HF formed dense, rolling clouds of toxic vapor (see sequence of photos in Figure 1). The clouds expanded rapidly and researchers measured dangerous concentrations at distances of three to six miles downwind. The tests showed that unless a refinery HF release is effectively mitigated it could place large numbers of refinery workers and large swaths of the surrounding communities in terrible danger.^{2,3}



Figure 1. August 1986, an industry-sponsored controlled release of anhydrous hydrofluoric acid at a remote area of the Nevada Test Site. The seven minute test release created a hydrofluoric acid cloud over 10 feet high and visible from as far as $\frac{3}{4}$ of a mile.

Guidelines, Mitigation and Modifications Not Enough

The American Petroleum Institute (API), an organization of petroleum companies, has a recommended practice titled Safe Operation of Hydrofluoric Acid Alkylation Units (RP 751).^{4a} The guidelines are useful – if followed. But like all API-recommended practices they are voluntary, although OSHA can sometimes use them to establish a violation of the PSM Standard. In addition, the guidelines were developed without the adequate involvement of key stakeholders such as refinery workers, labor unions or community residents and organizations.

The industry has tested and promoted mitigation systems to lessen the impacts of HF releases. These include water cannons, sprays and rapid systems for transferring HF from a compromised vessel. These systems would help contain a release, but they could fail or be overwhelmed in an emergency. (See Appendix A: HF Process Controls and Modifications.)

A small but growing percentage of HF-using refineries use *modified* HF. Modified HF has chemical additives such as sulfolane^b that are intended to reduce the rate of HF vaporization. Theoretically, modification also reduces the distance that an HF plume would travel. However, modification of HF does not keep it from vaporizing and creating a traveling plume, nor does it reduce the toxicity of HF.^c If the release was accompanied by a fire – and many refinery accidents involve fires – the vaporization of even modified HF would be greatly increased.

Lessons from the History of Chemical Disasters

A characteristic of previous major chemical disasters is that they occurred as the result of failures of multiple safety systems. Further, these disasters typically propagated and cascaded in ways that were not fully anticipated and were beyond the capacities of mitigation and emergency response systems. The Deep Water Horizon disaster that began April 20, 2010, in the Gulf of Mexico is a prime example. It immediately killed 11 workers, ignited a fire visible for dozens of miles, and sank a giant oil platform. BP and its contractors tried to activate the main control device, a blowout preventer, but it failed. It remained in a failed state and the disaster continued to unfold until the leak was stopped 86 days later. The disaster showed that the oil industry's prevention and response plans were completely inadequate.

The report of the National Commission on the BP/Deepwater Horizon Oil Spill and Offshore Drilling⁵ repeated the finding made by the Columbia (Space Shuttle) Accident Investigation Board⁶ in 2003 that “complex systems almost always fail in complex ways.” (p. viii and p. 6 respectively) Further, the Deepwater Horizon Commission report stated, “An unfortunate lesson of the oil spill is that the nation was not well prepared for the possibility of widespread, adverse effects on human health and mental well-being, especially among a particularly vulnerable citizenry” (pp. 191-192).

^a The Recommended Practice addresses hazards management, operating procedures and worker protection, new construction, inspection and maintenance, transportation and inventory control, relief and utility systems, and mitigation options and techniques.

^b Chemical name: tetrahydrothiophene 1,1-dioxide: boiling point 545 °F; 0.026 mmHg. The boiling point of modified HF (i.e., the mixture) has not been determined.

^c The “Potential Health Hazards” sections of HF manufacturer Honeywell’s Material Safety Data Sheets for a) Hydrofluoric Acid, Anhydrous and b) Modified Hydrofluoric acid are identical as are the “Emergency Overviews.”

http://www51.honeywell.com/sm/hfacid/common/documents/AHF_MSDS.pdf; (Last accessed March 12, 2013)

<http://www51.honeywell.com/sm/hfacid/common/documents/Modified-HF.pdf>. (Last accessed March 12, 2013)

U.S. Workers, Communities and the Environment at Risk

Twenty-five oil companies use HF at 50 U.S. refineries. Collectively, these refineries put more than 26 million persons at risk from an HF release. Among these are 19 refineries in or near eight major metropolitan areas that put more than 22 million persons at risk. The USW represents approximately 7,000 workers at 28 of these refineries.

(See Appendix C: Table C1 and C2.)

The EPA, through its RMP rule, requires companies with greater than threshold quantities of specific chemicals to estimate of the size of the population at risk from a release. These estimates are made by drawing a circle on a map with the potential release point at the center. The population within the circle defined by a radius of the *endpoint distance* is that which is vulnerable in the event of a worst case HF release. The size of the circle depends on the amount of chemical, in this case HF, that would be released and how far it might travel in a “worst case” scenario as defined by EPA. Among the HF-using refineries in the United States, the median *endpoint distance*^a for HF toxic worst case release is 15 miles (range of 3 mi. to 25 mi. for the 50 refineries). Forty-two of these refineries have an endpoint distance of greater than 10 miles with nearly half of those having an endpoint distance of greater than 20 miles.^b

A Horrifying Scenario

Following 9/11, in his book [The Edge of Disaster: Rebuilding a Resilient Nation](#), Stephen Flynn argued, “Our top national priority must be to ensure that our society and our infrastructure are resilient enough not to break under the strain of natural disasters or terrorist attacks”^{7c} (p. 110). In an article taken from his book, Flynn develops a disaster scenario at an HF-using refinery in a major metropolitan area. He describes events following an “entirely plausible” fictional attack on the refinery’s HF tanks and a major release:

“Thousands of people are trapped in their cars as the



Figure 2. July 2009 hydrofluoric acid fire, explosion and release at the CITGO Corpus Christi Refinery.

^a The distance beyond which specified harmful effects would no longer be felt.

^b Fourteen of the refineries have an endpoint distance of 25 miles, the maximum of EPA’s lookup tables and RMP*Comp software.

^c Stephen Flynn, Ph.D. is a retired officer from the U.S. Coast Guard and an expert on homeland-security. He is now Professor in the Department of Political Science at Northeastern University and Founding Co-Director, George J. Kostas Research Institute for Homeland Security.

hydrofluoric cloud drifts over them, burning their eyes and eyelids. Soon, their lungs become inflamed and congested, depriving them of oxygen and leading to seizures. Most die within ten hours.”⁸

Variations of this scenario might be applicable at any one of the 50 HF-using refineries in the United States.

In addition to the resiliency Flynn calls for, the nation’s refining infrastructure also needs to be resilient enough not to break under the strain of unplanned and unintended systems failures during the course of normal operations, startups and shut downs. These are far more common than natural disasters and terrorist attacks.

The Record

Catastrophic Chemical Accidents and Process Safety Systems

The underlying or root causes of most chemical process accidents are deficiencies in the management of process safety systems. Management of these safety systems is the foundation for OSHA’s PSM standard, the U.S. EPA’s RMP rule, and internationally, the European Union’s Seveso II Directive. Nonetheless, according to former U.S. Chemical Safety Board member Dr. Irv Rosenthal and others, writing in the journal *Process Safety Progress*, these requirements have been insufficient to stem the tide of accidents.⁹ These risk experts stated, “the less than expected decrease in accident incidence has occurred because the newly adopted regulations have not resulted in the hoped for adoption of ‘effective’ process safety management systems by industry” (p. 136).

Refinery Disasters – Infrequent But Not Rare

The infrequency of major catastrophic accidents in the refining industry can foster the belief that the probability of these events is so low that “it can’t happen.” This has given rise to labeling these types of accidents *low probability–high consequence* (LP–HC). Having done extensive research in this arena, the EPA’s James C. Belke stated:

“From the perspective of the individual facility manager, catastrophic events are so rare that they may appear to be essentially impossible, and the circumstances and causes of an accident at a distant facility in a different industry sector may seem irrelevant”¹⁰ (p. 7).

Thus, while the cumulative risk from dozens of refineries is substantially higher, there is a potential for complacency or overconfidence of management at individual refineries.

In 2000, Belke authored an EPA study using RMP incident data from 1994 to 1999.¹¹ That study documented that oil refineries had nearly twice as many accidents as any other RMP industry. One hundred and one of these were HF incidents. That study also revealed HF ranked third among regulated chemicals in the number of process release incidents.

Industry Reports on Safety – No Assurance

An extensive study of process safety incidents by Michael R. Elliot and others¹² sheds additional light on refinery safety. The study found that there are no strong positive correlations between LP–HC incidents and regularly reported occupation illness and injuries (OII) or OII rates. Nonetheless, the refining industry commonly reports on these data as evidence of refinery safety. In May 2010, Deputy Assistant Secretary for Federal OSHA,

Jordan Barab, addressed this and other issues in a speech before the National Safety Conference of the National Petroleum Refiners Association (NPRRA).¹³ He told the industry, “Stop boasting about your safety record [referring to OII rates] when you’re literally putting out fires. You’re only undermining your credibility.”

Barab also spoke in broad terms about the energy industry’s record on major accidents:

“OSHA is particularly concerned about the recent number of serious incidents at refineries that have scalded, burned or struck down your fellow workers. We are tracking these catastrophes and looking for trends -- including problems resulting from aging facilities.”

In 2007, OSHA instituted a National Emphasis Program (NEP) to “reduce or eliminate workplace hazards associated with the catastrophic release of highly hazardous chemicals at petroleum refineries.”¹⁴ This greatly increased the number of OSHA inspections at refineries that were focused on process safety and its PSM standard. Nonetheless, three years later, OSHA’s Barab was moved to express that he was, “deeply troubled by the significant lack of compliance we are finding in our inspections and with the number of serious refinery problems that continue to occur.”¹³

In April 2011, Dr. Rafael Moure-Eraso, Chairperson of U.S. Chemical Safety Board (CSB) used the one-year anniversary of the 2010 Tesoro refinery disaster in Anacortes, Wash., to assess the status of the U.S. refining industry. He said, “Serious incidents at refineries continue to occur with alarming frequency.”¹⁵ The trail of U.S. refinery disasters and non-compliance with regulations is a potent reminder of the potential for catastrophe. (See Appendix A: Major Oil Industry Incidents, and HF Alkylation Unit Incidents.)

USW Study Confirms Industry Unprepared to Prevent or Respond to Refinery Incidents

Following the 2005 BP Texas City Refinery disaster, the USW conducted a nationwide study titled, *Beyond Texas City: The State of Process Safety In The Unionized U.S. Oil Refining Industry*.¹⁶ This study examined the extent of highly hazardous conditions like those that contributed to the Texas City disaster at 51 unionized refineries. The study found that these highly hazardous conditions continued to be pervasive. Further, it found that these conditions had often resulted in incidents or near misses. Training was found to be insufficient and less than a third said their refineries were reported to be *very prepared* to respond safely to hazardous materials emergencies. The study concluded that the refining industry is ripe for future disasters.

Doing More with Less? Understaffing Is Unsafe

Examination of the BP Texas City Disaster Looks at Refinery Staffing

The 2005 BP Texas City disaster surfaced the critically interconnected issues of refinery understaffing and process safety. The Baker Panel, proposed by the CSB and headed by former White House Chief of Staff, James Baker, studied process safety management at five U.S. BP refineries. The Baker Panel study found that understaffing was a serious safety problem, common for routine operations, and existed for upset conditions and emergencies. Understaffing was identified among maintenance personnel, operators, chief operators and

supervisors and was recognized by both hourly workers and management. The study noted that this understaffing resulted in unsafe performance of jobs at the refineries. Understaffing was also linked to inexperienced supervisors, low morale, poor communication, delayed responses to needs, inability to supervise contractors properly, interference with training, and slowed hazard assessments and investigations.¹⁷

While there are no regulations in the United States for governing staffing levels at refineries, the nuclear industry, one with similar disaster potential to refineries with large quantities of HF, provides some guidance. The U.S. Nuclear Regulatory Commission (NRC) in its *Guidance for Staffing Exemption Requests* provides prescriptive regulations for qualifications and staffing levels (e.g., enumerating specific staffing requirements for senior operators and operators for a given number of operating units).^{18,a} In addition, the NRC recognizes that these prescriptions may not be adequate to address certain design features and operations. As a result, the NRC has more detailed regulations in its *Guidance* that requires a task analysis of “risk-significant human actions; difficult tasks identified through the operating experience review; a range of procedure-guided tasks that are well defined by normal, abnormal, emergency, alarm response, and test procedures” and knowledge-based tasks, human decision-making and interactions, and frequent and infrequent tasks (p. II 3-2).

Circadian, a global leader in providing guidance on 24/7 workplace performance and safety solutions, recently published a white paper on safe staffing levels. In that report Circadian stated, “Understaffing is a major contributor to not only fatigue and human error, but also to the health, safety, performance and quality of life” of employees¹⁹ (p. 15). Accordingly, based on extensive field study, they posited that an overall overtime rate of 20 percent is “arguably unsafe to operate because of the significantly increased risk of human error. This is particularly true with night shifts, rotating schedules and/or long, irregular hours.” (p. 13)

The United Kingdom’s Health and Safety Executive (the counterpart to U.S. OSHA) provides further guidance. It established its Staffing Levels and Task Organization Technical Assistance Guide (TAG 061) in part on deficiencies in staffing and task organization identified at Three Mile Island, Chernobyl, BP Texas City and the Challenger Space Shuttle.²⁰ TAG 061 addresses staffing and task organization of licensed nuclear facilities in accordance with the requirements of the International Atomic Energy Agency (IAEA) Requirements and Guides. (See Appendix A: Technical Assessment Guide (TAG) 061: Staffing Levels and Task Organisation.)

Recently, the oil industry attempted to address staffing through the 2010 American Petroleum Institute Recommended Practice 755, “Fatigue Risk Management System,” developed pursuant to a recommendation from the U.S. Chemical Safety and Hazard Investigation Board. Although the CSB requested that the USW and API work together on the issue, and the API promised a “consensus” process, in the end the API insisted on a process through which the union was consistently outvoted on important issues. The union eventually left the discussions in frustration. Although better than nothing, RP 755 is a weak standard, with numerous loopholes and provisions open to interpretation. Like all API Recommended Practices, it is voluntary. So far, it has had little impact on staffing levels.

^a Minimum Requirements Per Shift for On-Site Staffing of Nuclear Power Units by Operators and Senior Operators Licensed Under 10 CFR Part 55 (with allowance for temporary deviations).

Safer Alternatives

Chemists and engineers have come up with a number of ways to make hazardous chemical operations not just safer, but safer at their core. These approaches are called *inherently safer technologies* (IST). First and foremost among these is replacing the dangerous chemicals or processes in use with ones that are safer. Substitution of a less dangerous chemical for a highly toxic one is a long-held, widely accepted best practice in occupational and environmental health. It is also one promoted by the American Institute of Chemical Engineers (AIChE), and its Center for Chemical Process Safety. AIChE, a largely industry-based professional group, has published and promoted the concept of inherently safer design in chemical process industries like oil refining.^{21, 22} Fortunately, inherently safer technologies exist for alkylation.

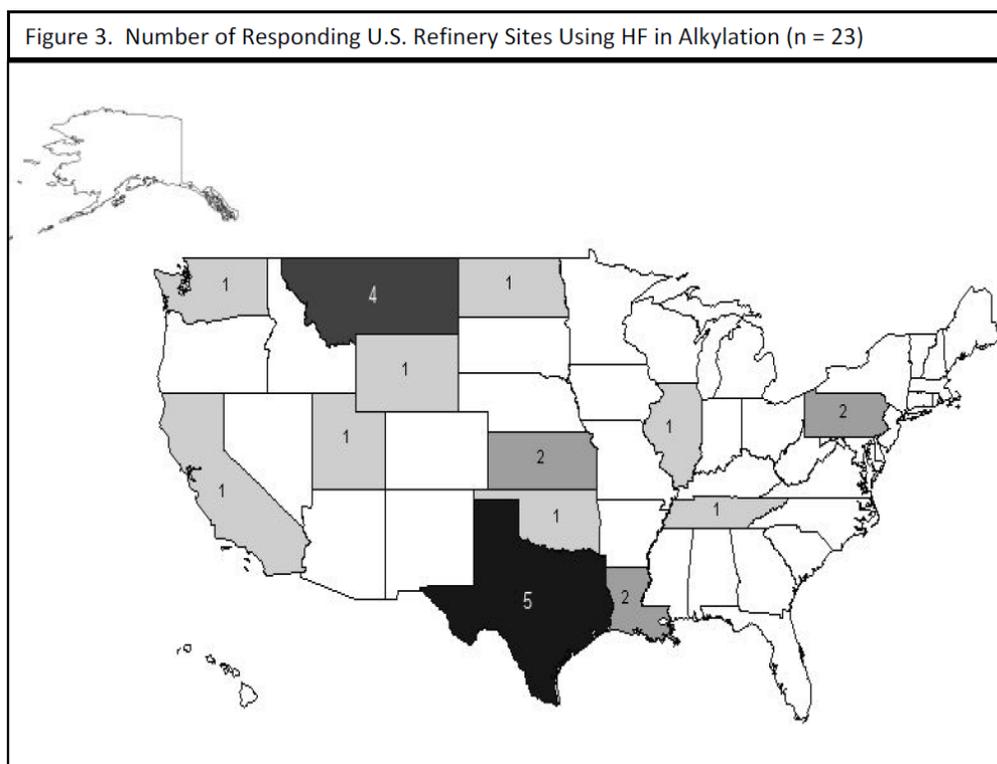
An *ionic liquid alkylation* process has been successfully developed, piloted and put into production. This method is inherently safer than HF alkylation processes. It is also safer than sulfuric alkylation processes. Using ionic liquid alkylation, Chinese refiners²³ have successfully produced alkylates in both pilot and production phases. These alkylates are reported to compare favorably with those produced by HF and sulfuric acid processes. In contrast to alkylates produced with HF and sulfuric acid, these alkylates are produced without the dangers to workers, communities and the environment posed by current processes.²⁴ With ionic liquid alkylation, the large volumes of HF and sulfuric acid would be gone. Also removed would be the risks they pose to the environment, tens of thousands of workers and millions of community members surrounding refineries.

Solid acid catalyst (SAC) alkylation systems are another alternative to HF and sulfuric acid alkylation. In 2004, a consortium of companies announced that they had one and a half years of documented operating performance using a solid acid catalyst (SAC) system. This system also eliminates the use of large quantities of HF and sulfuric acid.

Some have suggested sulfuric acid processes, already widely used in dozens of U.S. refineries, should be considered as a safer alternative to HF alkylation. While sulfuric acid is much safer than HF, it still poses substantial hazards for workers, community members and the environment. (For more see an additional USW report the Sulfuric Acid Alkylation to be released later in 2013.)

THE USW SURVEY

In late 2010, a survey questionnaire was developed by a team of refinery workers, health and safety specialists, and professional survey researchers. The questionnaire was sent to 61 USW refinery local unions with alkylation processes using either hydrofluoric acid (HF) or sulfuric acid in the United States. Twenty-eight of these refineries used HF. Among these, 23 site survey teams returned questionnaires for a response rate of 82 percent. This report is about findings from these 23 refineries. (Findings for the refineries using sulfuric acid for alkylation will be presented in a companion report.) Figure 3 shows the states where the 23 responding HF refineries were located.



The 198-item questionnaire addressed the safe operation HF alkylation units, and the procedures in place to prevent and mitigate releases. Researchers requested that each responding local union create a multi-disciplinary site survey team made up of local union members in six specific roles. These roles included: 1) local union leadership, 2) those with specific health and safety responsibilities, 3) alkylation unit operators, 4) maintenance workers, 5) those on process hazard analysis (PHA) teams, and 6) emergency responders. The range of members participating on each of these 23 site survey teams ranged from 63 percent of those who had served on PHA teams, to 95 percent each for those who were local union leadership or operators, and 100 percent for those with specific health and safety responsibilities. (See Appendix B: Table B1.)

The Study Refineries

Production

Combined, the 23 study refineries with HF alkylation units produced 3.3 million barrels of finished petroleum products per day with an average production of 145,000 barrels per day per refinery.

Quantities of HF

The 23 refineries in this study collectively had over 5 million pounds of HF on site. The quantities of HF per refinery ranged from 5,200 pounds to 870,000 pounds with an average of 233,000 pounds.^a These data were gathered from refining company reports to EPA as part of its Risk Management Program (RMP) rule. Refineries covered under EPA's RMP are required to implement chemical accident prevention and preparedness measures, and to submit summary reports to the government when quantities of listed highly hazardous chemicals, in this case HF, exceed the regulatory threshold. These reports contain information about the quantities of chemicals on site as well as the potential consequences of accident release scenarios.

Additional information is available from OSHA inspection data that identified violations of its Process Safety Management (PSM) Standard (29 CFR 1910.119). The standard is the counterpart to EPA's RMP regulation; it regulates key process safety systems to prevent workers from being injured or made ill at sites with very large quantities of highly hazardous substances.

Potentially Affected Populations

The potentially affected populations for possible worst case releases of HF in the communities surrounding the 23 study refineries range from 20,000 persons to over 3 million persons. In total, over 13 million community members are potentially at risk of exposure to highly toxic HF from the 23 refineries studied.¹

OSHA Violations Found During OSHA Process Safety Management Inspections at Study Refineries

Among the 23 study refineries with HF alkylation units, 21 had OSHA PSM violations within the five years previous to February 2011.^b Among 20 study refineries, there were 293 violations – an average of 21 per refinery, and a range of from 1 to 35 violations. This does not include the BP refinery in Texas City that received intense OSHA scrutiny following major catastrophic accidents including the 2005 disaster. That site, an outlier in terms of data from other refineries, had 593 violations.

Profits Among Companies Operating Study Refineries

One potential obstacle to finding and correcting process safety vulnerabilities or in replacing existing systems and chemicals with safer ones is financial resources. Accordingly, the 2010 gross operating profits for the publicly held corporations operating 18 of the study refineries

^a Data gathered at U.S. EPA Headquarters by staff from the Center for Public Integrity in October 2010.

^b Data extracted from the OSHA's IMIS Database by the staff of the Center for Public Integrity, February, 2011. (<http://www.osha.gov/pls/imis/establishment.html>). PSM violations are from all inspections during the previous five years including, but not limited to OSHA National Emphasis Program (NEP) inspections.

were obtained. These 18 refineries were operated by eight oil companies. In total, these eight companies had gross operating profits in 2011 of approximately \$150 billion.^a

^a Data from Market Watch. <http://www.marketwatch.com>

SURVEY FINDINGS

1. How the Results Are Reported

A major release of HF from a refinery would be catastrophic. Systems whose failures could result in catastrophe demand the highest level of safety. Few airline passengers or government regulators would tolerate airline safety systems that were judged to be *somewhat effective* rather than *very effective*. Likewise, workers, community residents and the natural environment deserve safety systems for refinery processes that are *very effective*. This is especially so when it comes to preventing and responding to potential releases of highly hazardous chemicals like HF. Many of the questions in this survey asked whether refinery safety systems were *very effective*, *somewhat effective*, *somewhat ineffective*, or *very ineffective*. In these cases, *very effective* was the standard we used in this report. Therefore, this report compared safety systems that were judged *very effective* with all those judged to be of lower effectiveness. When making these comparisons we use the phrase “*less than very effective*.” We also use this standard when we assess other measures such as *confidence* and *preparedness*.

2. HF Alkylation Process Safety Systems: Preparedness to Prevent Disaster

The safety of process operations at refineries is governed by what are known as process safety systems. These systems must be in place to operate safely in normal and abnormal conditions and must be able to quickly and effectively mitigate process upsets, leaks, fires and other emergency conditions. The safety of alkylation units depends on the effectiveness of individual component systems within the process unit and their functioning as interdependent parts of an integrated whole. With very large quantities of highly hazardous materials, these systems need to operate at peak performance. The 23 site survey response teams rated 32 process safety systems related to HF alkylation units. These assessments of HF alkylation safety systems are presented in three groups. The first two groups of process safety systems are aimed at prevention:

- A. Effectiveness of safety systems for maintaining the integrity of *HF alkylation processes* (nine systems)
- B. Effectiveness of safety systems for *HF-related processes, storage, and transfer systems, taken as a whole* (11 systems)

These two groups will be discussed in this section. The third group was:

- C. Effectiveness of HF emergency mitigation and response systems (12 systems)

This group will be discussed in the later section — *Prepared to Respond*.

A. Effectiveness of Safety Systems for Maintaining the Integrity of HF Alkylation Processes

Site survey teams rated the nine systems for maintaining the integrity of *HF alkylation processing* as follows:

- For five systems ranked least effective – sewer systems, mechanical integrity of piping, mechanical integrity of pumps valves, seals and vents; maintenance; and integrity of instrumentation – 65 percent to 79 percent of site survey teams rated them

as less than *very effective* (22 percent to 35 percent *very effective*). From 26 percent to 44 percent of sites rated them as ineffective.

- For three process systems – corrosion monitoring, mechanical integrity of pressurized tanks and vessels, and inspection and testing – approximately half (from 52 percent to 56 percent) site survey teams rated them as less than *very effective* (39 percent to 48 percent *very effective*). From 4 percent to 13 percent of sites rated them as ineffective.
- For the only system that fewer than half of the site survey teams rated less than *very effective* was – mechanical integrity of atmospheric tanks – 44 percent rated this system less than *very effective* (56 percent *very effective*). Six percent (6 percent) rated this system ineffective.

(See Appendix B: Table B2.)

B. Effectiveness of Safety Systems for HF-Related Processes, Storage, and Transfer Systems, Taken as a Whole

Site survey teams provided overall ratings for a group of 11 safety systems that focused on process, storage, and transfer systems related to HF alkylation. These ratings follow:

- For three systems ranked least effective – audit programs, maintenance, and health hazard information and education for site personnel *outside* of HF alkylation units – 78 percent to 82 percent of site survey teams rated them as less than *very effective* (9 percent to 22 percent *very effective*). From 26 percent to 39 percent were rated ineffective.
- For six more highly ranked systems – operating manuals and procedures; utility systems; HF unit pre-start-up safety reviews; process hazard analyses (PHAs); leak detection and repair, and strictly controlled access to HF alkylation units key to preventing HF incidents – 57 percent to 69 percent of site survey teams rated them less than *very effective* (26 percent to 43 percent *very effective*). From 9 percent to 35 percent rated them ineffective.^a
- For only two of the safety systems – health hazard information and education for personnel *within* HF alkylation units, and controlled relief and neutralization systems – less than half of the site survey teams (35 percent and 44 percent respectively) rated them as less than *very effective* (65 percent to 52 percent *very effective* respectively).

(See Appendix B: Table B3.)

3. HF Alkylation Unit Incidents and Near Misses

One way to assess the safety of alkylation units is to examine HF-related incident and near miss histories of these processes. The following summarizes site survey team reports of HF-related incidents and near misses.

- Over three-quarters of site survey teams (18 sites or 78 percent) reported at least one HF-related incident or near miss in the previous three years. Five sites (22 percent) reported that they had no HF-related incidents or near misses.

^a For one system, controlled access, 4% said they do not have this. We included this 4% in both “less than *very effective*” and the “ineffective” groupings.

- The 18 sites with HF-related events reported a total of 131 incidents or near misses – 115 events related to HF alkylation processing and 16 events related to HF storage or transfer. This was an average of 7.3 events per site over the three year period, or 2.4 HF-related events per site per year.

Site survey teams provided further details about the most important HF incident or near miss (usually the one that was most serious or potentially serious). Of the 18 sites with events, 89 percent (16 sites) reported incidents as most important and the other two sites reported near misses as most important. Nearly all (17 sites or 94 percent) reported that these events involved alkylation process unit events while 17 percent (3 sites) also involved on-site HF storage, and 11 percent involved both off-loading and on-site transfer of HF (2 sites). Among these events, 83 percent involved spills or releases (15 events) and 17 percent involved fires or explosions (3 events). Site survey teams all reported the events either *did* or *could have* caused injuries to workers on-site. Half (9 sites) indicated that these events could have caused injuries to people in the community. While none reported fatalities related to these events, the number of injuries reported ranged from none to 13. In total, 24 workers were injured. Twenty-two (22) of the injured received first aid and 16 received treatment in emergency rooms. Six were admitted to hospitals for their injuries.

4. Prepared to Respond

A. Effectiveness of HF Emergency Mitigation and Response Systems

A similar picture of deficiency emerged when examining the third set of process safety systems that focused on HF emergency mitigation and response related to potential HF releases. The ratings for these 12 systems follow:

- For the five systems ranked least effective – off-site alarms and notification systems; utility back-up systems; emergency field drills; safe havens for employees needing refuge from HF releases, and diking systems to contain spills – 74 percent to 86 percent rated them less than *very effective* (9 percent to 22 percent *very effective*). From 39 percent to 48 percent rated them *ineffective* or *don't have*.^a
- For four additional mitigation and response systems – chemical neutralization systems; fire suppression systems; remotely operated block valves for isolating HF units, and water curtain and deluge systems – 56 percent to 69 percent of site survey teams rated them less than *very effective* (32 percent to 43 percent *very effective*). From 8 percent to 28 percent rated them *ineffective* or *don't have*.^b
- For only three systems – overall emergency shutdown and isolation systems, on-site alarms, and emergency rapid transfer systems for HF – less than half (40 percent to 43 percent) rated them less than *very effective* (52 percent to 57 percent *very effective*).

(See Appendix B: Table B4.)

^a These include 35 percent *don't have* for off-site alarms, 22 percent for safe havens, 17 percent for utility back-up, and 13 percent for both emergency field drills and for diking. *Don't have* responses are included in *ineffective* and less than *very effective* ratings.

^b These include 23 percent *don't have* for chemical neutralization systems, 9 percent *don't have* for fire suppression systems, 4 percent *don't have* for overall emergency shutdown and isolation systems. *Don't have* responses are included in *ineffective* and less than *very effective* ratings.

An HF release might come about as a result of a fire or explosion. Refinery water supplies need to be sufficient to simultaneously generate fire-fighting foam, cool overheating vessels and piping, (possibly in multiple units) and to operate HF water mitigation systems to suppress HF vapors.

- When asked about adequacy of water supplies for both these purposes, 30 percent reported that their sites *did not have* adequate supplies and 17 percent said *don't know*. A slight majority, 52 percent reported that their sites had adequate water supplies.

B. Emergency Responder Preparedness

Should HF containment systems fail, employees at the site must rapidly perform safe and orderly shutdown, mitigation and evacuation. Accordingly, the survey asked about necessary personal protective equipment (PPE) for every employee who might need it in an HF emergency. Approximately two-thirds of site survey teams (65 percent) reported their sites were less than *very prepared* with PPE (35 percent *very prepared*). More than one in three sites (39 percent) reported that the refinery was unprepared with PPE.

(See Appendix B: Table B5.)

The survey also assessed overall preparedness of four key groups of workers that would need to respond if there was an HF release at a refinery:

- a) The refinery's on-site emergency responders
- b) Local community's off-site emergency responders
- c) On-site nursing and other medical personnel
- d) Local hospitals (or first receivers)

Furthermore, the survey examined this preparedness for three different levels of possible refinery HF releases:

- Releases limited to a work area where fewer than 10 workers may be seriously exposed
- Releases that spread across the whole refinery where dozens of workers may be seriously exposed
- Releases that extend outside the refinery where community members may be seriously exposed

In combination, these four worker groups and these three distinct levels of potential HF releases constituted 12 categories of preparedness. These ratings have added importance when considering that 78 percent of the study refineries reported 131 HF-related incidents or near misses in the previous 36 months. Further, half the site survey teams that reported on their sites' most important incident said the events could have caused injuries to people in the community.

(See Appendix B: Table B6 for the data described below.)^a

^a In reporting of data for each of the work groups, the *don't have* responses are included in the categories of less than *very prepared* and unprepared.

a) Refinery's on-site emergency responders

- For **HF releases limited to a work area**, 57 percent reported that on-site emergency responders were less than *very prepared* (43 percent *very prepared*). More than one in five (22 percent) rated on-site responders unprepared.
- For **HF releases across the refinery**, 79 percent reported that these on-site responders were less than *very prepared* (22 percent *very prepared*). Again, 22 percent rated on-site responders unprepared.
- For **HF releases into the community**, 70 percent rated these responders were less than *very prepared* (22 percent *very prepared*). Nearly half (48 percent) rated them unprepared.

These data show declining levels of preparedness with the increased scope of HF releases. The lowest levels of preparedness were reported for potential releases into the community. This trend of lower levels of preparedness for increasing levels of potential HF releases was reported for the other three key groups of workers: off-site emergency responders, on-site nursing and other medical personnel, and local hospitals' first receivers. These are shown below.

b) Local community's off-site emergency responders

- For **HF releases limited to a work area**, 60 percent reported off-site emergency responders were less than *very prepared* (17 percent *very prepared*). Thirty percent (30 percent) rated them unprepared or *don't have* and 22 percent reported *don't know*.
- For **HF releases across the refinery**, 78 percent reported off-site responders were less than *very prepared* (9 percent *very prepared*). Almost half (48 percent) rated them unprepared or *don't have* and 13 percent reported *don't know*.
- For **HF releases into the community**, 73 percent reported these off-site responders were less than *very prepared* (4 percent *very prepared*). Approximately half (51 percent) rated them unprepared or *don't have* and 22 percent reported *don't know*.

c) On-site nursing and other medical personnel

- For **HF releases limited to a work area**, 69 percent reported on-site medical personnel were less than *very prepared* (30 percent *very prepared*). Thirty percent (30 percent) rated them unprepared or *don't have*.
- For **HF releases across the refinery**, 81 percent reported on-site medical personnel were less than *very prepared* (17 percent *very prepared*). Slightly over half (51 percent) rated these personnel as unprepared or *don't have*.
- For **HF releases into the community**, 78 percent reported on-site medical personnel were less than *very prepared* (13 percent *very prepared*). Over half (61 percent) rated these personnel unprepared or *don't have* and 9 percent reported *don't know*.

d) Local hospitals (or first receivers)

- For **HF releases limited to a work area**, 61 percent reported local hospitals or first receivers were less than *very prepared* (26 percent *very prepared*). About one in three (31 percent) rated first receivers unprepared and 13 percent said *don't know*.
- For **HF releases across the refinery**, 60 percent reported local hospitals or first receivers were less than *very prepared* (17 percent *very prepared*). Forty-three percent (43 percent) rated them unprepared and 22 percent said *don't know*.
- For **HF releases into the community**, 57 percent reported local hospitals or first receivers were less than *very prepared* (13 percent *very prepared*). Forty-four percent (44 percent) rated them unprepared and 30 percent said *don't know*.

5. Emergency Response Training

Prevention and preparedness for HF incidents depend on effective training. To assess prevention and preparedness training, the survey asked site survey teams how confident they were that two groups – the site's hourly work force, and the site's emergency response (ER) teams – had received the ER training they needed to respond safely to an HF release. The survey assessed this confidence for two levels of HF incidents – one in a work area where fewer than 10 workers may be seriously exposed, and one across the whole plant where dozens of workers may be seriously exposed. This assessment was limited to the two worker groups and the two levels of releases about which the site survey team would have information sufficient to make a judgment. (See Appendix B: Table B7.)

The Hourly Workforce

- For **HF releases limited to a work area**, 74 percent were less than *very confident* that the hourly work force had received training they needed to respond safely to an HF release (26 percent *very confident*). Approximately one in four (26 percent) were not confident that this level of training had been achieved.
- For **HF releases across the refinery**, 95 percent were less than *very confident* (4 percent *very confident*). Approximately half (52 percent) were not confident.

Site's Emergency Response Teams

- For **HF releases limited to a work area**, 79 percent were less than *very confident* that the site's team had received the needed training to respond safely to an HF release (22 percent *very confident*). Approximately one in five (18 percent) were not confident that this level of training had been achieved.
- For **HF releases across the refinery**, 82 percent were less than *very confident* (17 percent *very confident*) that the site's ER team had received the needed training. Approximately one-third (34 percent) were not confident.

These data continued the trend noted above with diminished levels of confidence in training when considering an incident affecting the whole refinery as compared to an incident restricted to a single work area.

Need for More Training Related to HF Releases, Fires or Explosions

Large majorities of the site survey teams reported a need at their sites for additional training in both HF-related *prevention* and *emergency response*.

The Hourly Work Force

- For **preventing** HF releases or related fires or explosions, 64 percent reported the hourly work force needed more training.
- For **responding**, 83 percent reported the need for more training.

The Site's Emergency Response Teams

- For **preventing** HF releases or related fires or explosions, 78 percent reported a need for more training.
- For **responding**, 96 percent reported a need for more training.

(See Appendix B: Table B8.)

6. Staffing

The survey did not ask specific questions about staffing levels. Safe staffing is an issue not confined to alkylation units, and it will be dealt with in a future report. However, the survey included an area for comments, and a number of site survey teams wrote that staffing levels were too low to ensure safe operation and effective emergency response. The following quote exemplifies these issues:

Staffing in the alkylation unit is lacking to the point where there are not enough qualified employees to cover the shifts. Training and break-in times have been cut to a minimum to compensate for a lack of staffing. There are only a few employees in the unit with more than a year or two [of] experience.

SUMMARY AND CONCLUSIONS

The potential impact of a large-scale HF release in a heavily populated area is so great that it may be impossible for any refiner or community to be fully prepared. Even highly effective systems sometimes fail. It would take multiple failures to trigger a major release, but the lesson of catastrophic accidents from Bhopal to the Deepwater Horizon is that multiple failures can occur. Roll the dice enough times and even the most unlikely combinations come up. The 50 American refineries using HF roll the dice every day.

Yet if the possibility of an HF disaster cannot be eliminated, it can certainly be reduced. The data presented here show that neither mandatory government regulations nor voluntary industry guidelines have convinced refiners to implement the highly effective safety systems demanded by a chemical as lethal as HF. Numerous accidents have breached one or more lines of defense. The OSHA Process Safety Management Standard is a minimum legal requirement; refineries handling HF should do much more. But OSHA has found violations of the standard in almost every refinery it has inspected. The most compelling data come from the knowledgeable and experienced refinery workers who operate HF alkylation units, or who would be expected to respond to an emergency. Their overwhelming verdict is that the current measures preventing and mitigating a major HF release are simply not good enough.

This survey shows:

- Inadequate systems to safely operate and maintain HF alkylation, storage and transfer units, to respond to emergencies and to mitigate releases.
- Inadequate preparation, training and drills for on-site and off-site first responders and first receivers.
- Diminishing levels of preparedness for increasingly severe accidents.
- Concern over insufficient staff for safe operation.

The only certain way to eliminate the risk of a catastrophic HF release is to eliminate HF. Safer alternatives exist, and are described in the first section of this report. Until that can be done, the safety of existing HF units must be improved.

Recommendations: Seven Steps to Safer Refineries

The USW calls on refining companies using HF to commit to seven steps.

1. **Educate Workers and the Public About the Dangers of HF.** Work with refinery workers, their unions, contract workers, first responders and first receivers, hospitals, municipal, state and federal agencies, and community and environmental groups regarding the health hazards of hydrofluoric acid including the potential consequences of minor and major releases both on- and off-site.
2. **Investigate and Learn about Safer Alternatives to HF.** Work with EPA, Homeland Security, university researchers, and domestic and foreign companies to learn from sites

using safer alternative alkylation processes in order to develop the necessary competencies for transitioning to safer alternatives to HF alkylation.

3. **Commit to Ending HF Use.** Commit to the goal of replacing all HF-using alkylation processes with safer alternatives as soon as possible.
4. **Pilot Test Alternative Solutions.** Each refining company should develop and build a test pilot alkylation reaction section. These pilot operations should use at least one of the existing safer alternative methods in at least one of their refineries. Such methods include solid acid and liquid ionic catalyst processes. They do not include modified HF or sulfuric acid which, although safer, are not safe enough and which need no pilot studies.
5. **Share Lessons to Speed Effective Transition.** Share lessons learned from these pilot operations across the industry with workers, their unions and with surrounding communities. The entire industry is needed to help move development of these alternatives forward across U.S. refining.
6. **Make Existing Operations Much Safer.** Until HF alkylation processes are replaced:
 - a. Work with workers and their unions and apply all necessary corporate resources to ensure that all alkylation unit process and mitigation systems are in optimal working order, regularly inspected and tested, and subjected to rigorous audits and preventative maintenance.
 - b. Work with workers, their unions, fire, emergency response, first receivers, hospitals and community/municipal leaders to engage in an open process for developing, testing and critiquing prevention, preparedness and response capabilities including periodic on-site and off-site drills.
 - c. At least annually, appraise all stakeholders both within and outside refineries with a site-based record of the level of process safety, including significant operational upsets and loss of primary containment incidents, equipment failures, etc.
 - d. Transition existing HF units to modified HF until non-HF units come on line.
7. **Ensure Staffing to Sufficiently Prevent, Prepare and Respond.** As is common practice in other high hazard industries like the nuclear industry, refineries must staff processes with people in sufficient numbers and with qualifications, experience and competencies necessary to ensure optimal safety during all operations including emergencies.

The government can facilitate the transition to safer processes through rigorous enforcement and oversight. Several agencies have a role to play. OSHA can enforce its Process Safety Standard; EPA, its Risk Management Program. HF units could be attractive targets for terrorists. The Department of Homeland Security lacks the authority to require inherently safer processes, but it could at least ensure that site security is adequate. The U.S. Chemical Safety and Hazard Investigation Board could undertake to investigate all HF accidents, even those with only minor injuries, and could initiate a comprehensive study of HF alkylation. Some state and local governments have the authority to address plant safety and emergency response.

No federal agency currently requires industry to consider or adopt inherently safer technology. EPA probably has the authority to do so under Section 112(r)(1) of the Clean Air Act, and a growing coalition of environmental groups, unions and former EPA officials has urged the Agency to act. A similar coalition has lobbied Congress to include a requirement to consider inherently safer technology in the Chemical Facility Anti-Terrorism Standards legislation, so far without success.

Yet it should not take compulsion for the industry to do the right thing. Company profits may vary, but overall the oil companies are the richest in the history of the world. They maintain large research operations. An industry that can design and operate equipment to drill five miles into the earth under more than a mile of seawater can surely design and operate safe alkylolation units. All that is lacking is the will.

A Risk Too Great

Hydrofluoric Acid in U.S. Refineries

The Appendices to the Report of the USW Refinery Research
Action Project

APPENDIX A	BACKGROUND INFORMATION
APPENDIX B	TABLES OF FINDINGS DATA
APPENDIX C	HF USING REFINERIES & AT RISK LOCATIONS AND POPULATIONS



United Steel, Paper and Forestry, Rubber, Manufacturing, Energy, Allied
Industrial and Service Workers International Union

Pittsburgh

April 2013

Appendix A

Background Information

APPENDIX A: BACKGROUND INFORMATION

HF Hazards

HF Toxicity: HF can cause deep tissue burns that may develop over 24 hours, and may initially go unnoticed. Skin coverage with HF of 25 square inches can be fatal. When HF gets into the body, it seeks out and reacts with the body's magnesium and calcium. A chemical antidote, calcium gluconate, can limit damage to health, but a knowledgeable medic or health practitioner must administer it as soon as possible after exposure. This may include skin or respiratory treatments.

HF Exposure Limits: The level of exposure considered immediately dangerous to life and health (IDLH) is 30 parts of HF to one million parts of air (30 ppm).²⁵ The National Institute for Occupational Safety and Health (NIOSH) sets Recommended Exposure Limits (RELs) and the Occupational Safety and Health Administration (OSHA) sets Permissible Exposure Limits (PELs). The NIOSH REL of 3 ppm (2.5 mg/m³) averaged over eight hours is the same as the OSHA PEL. NIOSH also recommends a ceiling exposure of 6 ppm (5 mg/m³) averaged over 15 minutes.

HF Process Controls and Modifications

HF Mitigation Systems: Water sprays may provide partial removal of HF from a vapor cloud release (25 percent to 90 percent found in controlled studies),^a however, efficiencies in actual release conditions cannot be expected to equal those in controlled experiments.^{26, 27, 28} In addition, a release of HF at a high elevation may not be detected by sensors at or near ground level. Water supplies required for these systems can also be problematic. During an HF release at the CITGO, Corpus Christi, Texas, refinery in 2009, the water spray system failed to work properly. Besides requiring huge volumes of water, often times a failure in a refinery processing unit involves multiple events such as a fire or explosion concurrent with a release. These events can disable water delivery systems either with a pumping failure due to loss of electricity or steam or damage to pipes or hydrants. In addition, these water spray systems do not function until activated and delays between releases and activation may allow large quantities of HF to be released without mitigation.^b The 1998 Congressional Report²⁶ said this about water spray systems:

Several facilities are concerned that the mitigation systems pose unworkable design requirements, do not add significantly to the protection of the public, and that the systems have the potential to cause more harm than good. (p. 105)

De-inventory systems are used to remove and neutralize HF and hydrocarbons as quickly as possible following commencement of a release, typically into a large dump tank. These systems do not control or slow the rate of release, but attempt to remove, by transfer, the large volumes that are the source of the release. Further limitations include time to activation

^a There was a series of HF and water spray tests conducted at the Nevada Test Site in 1986 (the Goldfish Test series) and another series in 1988 conducted in a flow chamber (the Hawk Test series).

^b API 751 states, "Early detection is critical in implementing mitigation measures for an HF alkylation unit," though it cannot be guaranteed.

following leak identification, maintenance and reliability issues, and potential failures of the de-inventory systems concurrent with failures that led to the release.

Modeling and related calculations have shown the limited potential of these three safety systems to prevent a release of HF (with or without hydrocarbons) from traveling long distances at high concentrations.²⁹

Major Oil Industry Incidents

The following brief descriptions of oil industry incidents are those that have occurred in the last 10 years that demonstrate the catastrophic consequences of failed prevention and response systems.

- **Deep Water Horizon (Macondo):** As is well-known around the world, the explosions on the Deep Water Horizon on April 20, 2010, began with 126 platform workers, a refining company, an entire industry, and the U.S. government unprepared for an explosion that was to kill 11 workers and dump millions of gallons of crude oil into the Gulf of Mexico. According to the Presidential Commission that studied the disaster, events on the rig could be “traced to a series of identifiable mistakes ... that reveal such systematic failures in risk management that they place in doubt the safety culture of the entire industry.”³⁰ (p. vii) Further, Commissioners determined that the disaster, involved “risks for which neither industry nor government has been adequately prepared, but for which they can and must be prepared in the future.” (p. vii)

While the Deep Water Horizon event has been termed a “one off” event, something that does not have the likelihood to happen again, since April 20, 2010, Chevron has had a leak of similar characteristics off the coast of Brazil potentially releasing up to 3,000 barrels per day.^a Chevron also had a rig burn off the coast of Nigeria for several weeks.^b ConocoPhillips had a well failure in China, polluting over 6,200 square kilometers.^c The website, http://home.versatel.nl/the_sims/rig/index.htm, provides a listing of rig explosions and fires that portrays these oil company events as occurring with an alarming regularity prior to and following the Macondo blowout.

- **Tesoro Anacortes, Wash., Refinery:** On April 2, 2010, an explosion at a Tesoro refinery killed seven workers and caused the refinery to shut down operations for six months and uncovered other deficiencies in the mechanical integrity of equipment. The director of the Washington State Department of Labor and Industry (state OSHA) stated that, “The bottom line is this incident, the explosion and these deaths were preventable.” The state OSHA fined Tesoro \$2.39 million for violation of standards.³¹
- **BP Texas City:** On March 23, 2005, a fiery blast at the BP refinery in Texas City, Texas killed 15 workers, injured 180 others and caused major alarm in the community. According to the U.S. Chemical Safety and Hazard Investigation Board (CSB), the agency charged with investigating and making recommendations for safer operation of facilities using highly hazardous chemicals, the incident led to financial losses exceeding \$1.5 billion.”³² (p. 17) The incident resulted in over 300 citations for OSHA violations resulting in a record fine of \$21 million.³³
- **Self-reported Fires, Multiple Locations:** The USW has tracked industry self-reported fires and collected data from local union reports for the last several years. The refining

^a http://www.alternet.org/rss/breaking_news/734330/chevron_under_fire_over_size_of_brazil_oil_spill/ (Last accessed March 12, 2013)

^b http://www.spill-international.com/news/id731-Rig_Blowout_and_Fire_in_Offshore_Nigeria.html (Last accessed March 12, 2013)

^c http://www.china.org.cn/business/2012-01/25/content_24479642.htm (Last accessed March 12, 2013)

industry self-reported 41 fires in 2008, 45 fires in 2009, 53 fires in 2010, 47 fires in 2011, and 41 in 2012. The number of local union reported fires are substantially higher as often the industry only reports what is required by law or what can be seen outside the fence line. There are numerous smaller fires that have caused lesser amounts of damage, but which carry the potential to have been much more serious.

HF Alkylation Unit Incidents

The following are brief descriptions of U.S. refinery incidents involving hydrofluoric acid.

- **CITGO Corpus Christi, Texas:** On March 5, 2012, an HF release reported as between 300 and 500 pounds took place at a flange that has had leaks reported back as far as September of 2011. The line had been temporarily repaired with clamps on several occasions while CITGO continued to operate.
- **Marathon Canton, Ohio:** On February 28, 2011, equipment failure caused this refinery to leak what the company estimated to be 145 pounds of hydrofluoric acid. Workers were evacuated and one worker was hospitalized. According to FireDirect, "Over the last five years, the Ohio refinery has been cited more often than all but three other refineries using HF for failing to manage hazardous processes."³⁴
- **CITGO Corpus Christi, Texas:** On July 19, 2009, an explosion and fire in the alkylation unit at the CITGO refinery severely injured one worker and burned for two days. Originally CITGO estimated a release of 30 pounds based on ground-level on-site monitoring. According to the CSB, within hours 42,000 pounds of HF was released and the water spray system designed to mitigate or "knock down" the HF vapors was depleted. The refinery had to switch to a supplemental saltwater system from the nearby channel, but transfer piping ruptured and pumps failed. According to the CSB investigation, about 10 percent of the estimated 42,000 pounds of HF released traveled beyond the refinery fence line. Fortunately, due to weather conditions, the plume went into an unpopulated channel. The CSB called for third party safety auditors to examine CITGO's HF alkylation units at its Texas and Illinois refineries.³⁵
- **Sunoco (Delta) Philadelphia, Pa.:** On March 11, 2009, a release of HF sent 13 contract workers to area hospitals because of exposure to a 22 pound release. Four Philadelphia area hazmat crews responded to the incident. OSHA cited the company for four "serious" violations related to the incident.
- **Fire at Giant Industries Refinery, New Mexico:** On April 8, 2004, maintenance workers set out to remove a defective pump in a hydrofluoric acid (HF) alkylation unit at the Ciniza oil refinery in Jamestown, N.M. A shut-off valve was in the open position and a release of flammable gasoline components caught fire. Six employees were injured. Four of these received burns requiring hospitalization. The incident resulted in the evacuation of non-essential employees as well as customers of a nearby commercial enterprise.³⁶
- **Marathon Texas City, Texas:** On October 30, 1987 Marathon in Texas City, Texas, experienced the most potentially dangerous refinery release of HF vapors in U.S. history. A 50-square block area of the community around the refinery was evacuated and over 900 people received medical treatment for injuries. Wind direction prevented the incident from being much more disastrous.

Technical Assessment Guide (TAG) 061: Staffing Levels and Task Organisation³⁷

In its TAG 061, the United Kingdom's Health and Safety Executive defines the Minimum Staff Complement as, "The number of qualified workers who must be present at all times to ensure safe operation of the nuclear facility and to ensure adequate emergency response capability." The TAG requires demonstration of adequate staffing for the licensee "to remain in control of activities that could impact on nuclear safety under all foreseeable circumstances throughout the life cycle of the facility" (p. 2). This means, "The licensee shall make and implement adequate arrangements for dealing with any accident or emergency arising on the site and their effects." (p. 3) As part of its Safety Assessment Principles the TAG states, "An organisation needs adequate human resources, which means having the necessary competences and knowledge in such numbers so as to maintain the capability to manage safety at all times, including during steady state conditions, periods of change and emergency situations." (p. 4) Further, concerning workload, the TAG states, "The workload of personnel required to fulfill safety-related actions should be analyzed and demonstrated to be reasonably achievable," and address the most resource intensive conditions feasible. Finally, the TAG calls for formal staffing assessments for *roles with high potential impact*, for staffing plans and implementation to be detailed and auditable, and for staffing adequacy to be demonstrated through operating experience and emergency exercises.

Appendix B

Tables of Findings Data

List of Tables

Table B1. Types of experience represented on the site survey response teams

Table B2. Effectiveness of safety systems for maintaining the integrity of HF alkylation processes

Table B3. Effectiveness of safety systems for HF-related processes, storage, and transfer systems, taken as a whole

Table B4. Effectiveness of HF emergency mitigation and response systems

Table B5. How prepared is the site regarding emergency personal protective equipment (PPE)

Table B6. How prepared is each group to respond to an HF release. (Scope listed)

Table B7. Confidence that the groups have received the training they need to respond safely to an HF release

Table B8. Need for additional training in HF hazard prevention

APPENDIX B: TABLES OF FINDINGS DATA

Table B1. Type of role/experience on site survey response teams	
Role in Refinery Work or Local Union	Percent
Officers and/or Executive Board members (n=23; 17% missing)	95%
Health and Safety Committee members, Health and Safety Reps., TOP Reps., and/or worker-trainers (n=23; 22% missing)	100%
Operators who work on alkylation unit(s) (n=23; 4% missing)	95%
Maintenance workers who work on alkylation unit(s) (n=23; 35% missing)	73%
Members who have served on a PHA team for alkylation unit(s) (n=23; 30% missing)	63%
Members who are on a refinery emergency response team (HAZMAT, fire brigade, etc.) (n=23; 27% missing)	88%

Table B2. Effectiveness of safety systems for maintaining the integrity of HF alkylation processes

Systems for HF Alkylation Processing	Very effective	Somewhat effective	Somewhat ineffective	Very ineffective	Don't Have	Don't Know
Sewer systems (n=23; 0% missing)	22%	35%	22%	22%	0%	0%
		44% <u>Ineffective</u>				
		79% <u>less than very effective</u>				
Mechanical integrity of piping (n=23; 0% missing)	22%	52%	26%	0%	0%	0%
		26% <u>Ineffective</u>				
		78% <u>less than very effective</u>				
Mechanical integrity of pumps, valves, seals, vents, etc. (n=23; 0% missing)	30%	39%	30%	0%	0%	0%
		30% <u>Ineffective</u>				
		69% <u>less than very effective</u>				
Maintenance (for example, preventative, repair) (n=23; 0% missing)	30%	39%	22%	9%	0%	0%
		31% <u>Ineffective</u>				
		70% <u>less than very effective</u>				
Integrity of instrumentation (n=23; 0% missing)	35%	39%	26%	0%	0%	0%
		26% <u>Ineffective</u>				
		65% <u>less than very effective</u>				
Corrosion monitoring (n=23; 0% missing)	39%	52%	4%	0%	0%	4%
		4% <u>Ineffective</u>				
		56% <u>less than very effective</u>				
Mechanical integrity of <u>pressured</u> tanks, vessels (n=23; 4% missing)	45%	50%	5%	0%	0%	0%
		5% <u>Ineffective</u>				
		55% <u>less than very effective</u>				
Inspection and testing (n=23; 0% missing)	48%	39%	13%	0%	0%	0%
		13% <u>Ineffective</u>				
		52% <u>less than very effective</u>				
Mechanical integrity of <u>atmospheric</u> tanks, vessels* (n=16; 9% missing)	56%	38%	6%	0%	*	0%
		6% <u>Ineffective</u>				
		44% <u>less than very effective</u>				

*Only sites with “atmospheric tanks, vessels” are included; 22% said they *don't have* atmospheric tanks, vessels. Note: Percents may not add up to 100% due to rounding

Table B3. Effectiveness of safety systems for HF-related processes, storage, and transfer systems, taken as a whole						
Processes, Storage and Transfer Systems, Taken as a Whole	Very effective	Somewhat effective	Somewhat <u>ineffective</u>	Very <u>ineffective</u>	Don't Have	Don't Know
Audit programs (n=23; 0% missing)	9%	52%	13%	17%	0%	9%
			30% <u>Ineffective</u>			
		82% <u>less than</u> very effective				
Health hazard information and education for non-HF alkylation personnel (n=23; 0% missing)	17%	43%	30%	9%	0%	0%
			39% <u>Ineffective</u>			
		82% <u>less than</u> very effective				
Maintenance (preventative and repair) (n=23; 0% missing)	22%	52%	17%	9%	0%	0%
			26% <u>Ineffective</u>			
		78% <u>less than</u> very effective				
Operating manuals and procedures (n=23; 0% missing)	26%	48%	17%	4%	0%	4%
			21% <u>Ineffective</u>			
		69% <u>less than</u> very effective				
Utility systems (n=23; 0% missing)	35%	52%	4%	9%	0%	0%
			13% <u>Ineffective</u>			
		65% <u>less than</u> very effective				
Alkylation pre-start-up safety reviews (n=23; 0% missing)	35%	57%	0%	9%	0%	0%
			9% <u>Ineffective</u>			
		66% <u>less than</u> very effective				
Process hazard analysis (PHA) (n=23; 0% missing)	39%	43%	13%	4%	9%	0%
			26% <u>Ineffective/Don't have</u>			
		69% <u>less than</u> very effective				
Leak detection and repair (n=23; 0% missing)	39%	48%	9%	4%	0%	0%
			13% <u>Ineffective</u>			
		61% <u>less than</u> very effective				
Strictly controlled access to alkylation units (n=23; 0% missing)	43%	22%	9%	22%	4%	0%
			35% <u>Ineffective/Don't have</u>			
		57% <u>less than</u> very effective				
Controlled relief and neutralization systems (n=23; 0% missing)	52%	35%	0%	9%	0%	4%
			9% <u>Ineffective</u>			
		44% <u>less than</u> very effective				
Health hazard information and education for HF unit workers (n=23; 0% missing)	65%	22%	4%	9%	0%	0%
			13% <u>Ineffective</u>			
		35% <u>less than</u> very effective				

Note: Percents may not add up to 100% due to rounding

Table B4. Effectiveness of HF emergency mitigation and response systems						
Emergency System	Very effective	Somewhat effective	Somewhat ineffective	Very ineffective	Don't Have	Don't Know
Alarms and notification systems – off-site (n=23; 0% missing)	9%	35%	9%	4%	35%	9%
			48% <u>In</u> effective/Don't have			
			83% <u>Less than</u> very effective			
Utility back-up systems (n=23; 0% missing)	13%	39%	13%	17%	17%	0%
			47% <u>In</u> effective/Don't have			
			86% <u>Less than</u> very effective			
Site's emergency field drills in preparing for an HF release up to and including a worst-case (n=23; 0% missing)	17%	30%	4%	26%	13%	9%
			43% <u>In</u> effective/Don't have			
			73% <u>Less than</u> very effective			
Safe havens (n=23; 0% missing)	22%	30%	9%	13%	22%	4%
			44% <u>In</u> effective/Don't have			
			74% <u>Less than</u> very effective			
Diking (n=23; 0% missing)	22%	39%	13%	13%	13%	0%
			39% <u>In</u> effective/Don't have			
			78% <u>Less than</u> very effective			
Chemical neutralization (n=23; 4% missing)	32%	41%	0%	5%	23%	0%
			28% <u>In</u> effective/Don't have			
			69% <u>Less than</u> very effective			
Fire suppression (n=23; 0% missing)	39%	35%	17%	0%	9%	0%
			26% <u>In</u> effective/Don't have			
			61% <u>Less than</u> very effective			
Remotely operated block valves for unit isolation (n=23; 0% missing)	39%	52%	4%	4%	0%	0%
			8% <u>In</u> effective			
			60% <u>Less than</u> very effective			
Water mitigation, curtain /deluge (n=23; 0% missing)	43%	39%	13%	4%	0%	0%
			17% <u>In</u> effective			
			56% <u>Less than</u> very effective			
Overall emergency shutdown and isolation systems (n=23; 0% missing)	52%	35%	4%	4%	0%	4%
			8% <u>In</u> effective			
			43% <u>Less than</u> very effective			

Table B4. Effectiveness of HF emergency mitigation and response systems						
Emergency System	Very effective	Somewhat effective	Somewhat <u>ineffective</u>	Very <u>ineffective</u>	Don't Have	Don't Know
Alarms and notification systems -- on-site (n=23; 0% missing)	57%	30%	9%	4%	0%	0%
			13% <u>Ineffective</u>			
			43% <u>Less than</u> very effective			
Emergency dump (catalyst/HF rapid transfer systems) (n=23; 0% missing)	57%	17%	0%	4%	9%	13%
			13% <u>Ineffective/Don't have</u>			
			40% <u>Less than</u> very effective			

Note: Percents may not add up to 100% due to rounding

Table B5. How prepared is the site regarding emergency personal protective equipment (PPE).

	Very prepared	Somewhat prepared	Somewhat unprepared	Very unprepared	Don't Have	Don't Know
PPE for every site employee who may need it in an HF-related emergency (n=23; 0% missing)	35%	26%	17%	22%	0%	0%
			39% Unprepared			
		65% <u>less than</u> very effective				

Note: Percents may not add up to 100% due to rounding

Table B6. How prepared is each group to respond to an HF release. (Scope listed)

Group	Very prepared	Somewhat prepared	Somewhat unprepared	Very unprepared	Don't Have	Don't Know
In a work area (where fewer than 10 workers may be seriously exposed)						
Local (off-site) emergency responders (n=23; 0% missing)	17%	30%	9%	17%	4%	22%
			30% Unprepared/Don't have			
			60% <u>less than</u> very prepared			
Local hospitals (n=23; 0% missing)	26%	30%	22%	9%	0%	13%
			31% Unprepared			
			61% <u>less than</u> very prepared			
Site's nursing and other medical personnel (n=23; 0% missing)	30%	39%	13%	13%	4%	0%
			30% Unprepared/Don't have			
			69% <u>less than</u> very prepared			
Site's emergency response team, hazmat team, or fire brigade (n=23; 0% missing)	43%	35%	13%	9%	0%	0%
			22% Unprepared			
			57% <u>less than</u> very prepared			
Across the whole plant site (where dozens of workers may be seriously exposed)						
Local (off-site) emergency responders (n=23; 0% missing)	9%	30%	22%	22%	4%	13%
			48% Unprepared/Don't have			
			78% <u>less than</u> very prepared			
Local hospitals (n=23; 0% missing)	17%	17%	30%	13%	0%	22%
			43% Unprepared			
			60% <u>less than</u> very prepared			
Site's nursing and other medical personnel (n=23; 0% missing)	17%	30%	30%	17%	4%	0%
			51% Unprepared/Don't have			
			80% <u>less than</u> very prepared			
Site's emergency response team, hazmat team, or fire brigade (n=23; 0% missing)	22%	57%	9%	13%	0%	0%
			22% Unprepared			
			79% <u>less than</u> very prepared			

Table B6. How prepared is each group to respond to an HF release. (Scope listed)

Group	Very prepared	Somewhat prepared	Somewhat <u>un</u> prepared	Very <u>un</u> prepared	Don't Have	Don't Know
In the community (where dozens of workers and community members may be seriously exposed)						
Local (off-site) emergency responders (n=23; 0% missing)	4%	22%	17%	30%	4%	22%
			51% Unprepared/Don't have			
			73% <u>less than</u> very prepared			
Local hospitals (n=23; 0% missing)	13%	13%	22%	22%	0%	30%
			44% Unprepared			
			57% <u>less than</u> very prepared			
Site's nursing and other medical personnel (n=23; 0% missing)	13%	17%	22%	35%	4%	9%
			61% Unprepared/Don't have			
			78% <u>less than</u> very prepared			
Site's emergency response team, hazmat team, or fire brigade (n=23; 0% missing)	22%	22%	22%	26%	0%	9%
			48% Unprepared			
			70% <u>less than</u> very prepared			

Note: Percents may not add up to 100% due to rounding

Table B7. Confidence that the groups have received the training they need to respond safely to an HF release.

	Very confident	Somewhat confident	Somewhat not confident	Very not confident
In a work area (where fewer than 10 workers may be seriously exposed)				
Hourly workforce (n=23; 0% missing)	26%	48%	17%	9%
		26% Not confident		
		74% <u>Less than</u> very confident		
Site's emergency response team, hazmat team, or fire brigade (n=23; 0% missing)	22%	61%	9%	9%
		18% Not confident		
		79% <u>Less than</u> very confident		
Across the whole plant site (where dozens of workers may be seriously exposed)				
Hourly workforce (n=23; 0% missing)	4%	43%	30%	22%
		52% Not confident		
		95% <u>Less than</u> very confident		
Site's emergency response team, hazmat team, or fire brigade (n=23; 0% missing)	17%	48%	17%	17%
		34% Not confident		
		82% <u>Less than</u> very confident		

Note: Percents may not add up to 100% due to rounding

Table B8. Need for additional training in HF hazard prevention

	Yes	No
Hourly workforce		
Responding to HF releases or related fires or explosions (possibly involving other hazardous chemicals) (n=23; 0% missing)	83%	17%
Preventing HF releases or related fires or explosions (possibly involving other hazardous chemicals) (n=22; 4% missing)	64%	36%
Emergency response team, hazmat team, or fire brigade		
Responding to HF releases or related fires or explosions (possibly involving other hazardous chemicals) (n=23; 0% missing)	96%	4%
Preventing HF releases or related fires or explosions (possibly involving other hazardous chemicals) (n=23; 0% missing)	78%	22%

Note: Percents may not add up to 100% due to rounding

Appendix C:

HF Using Refineries and At Risk Locations and Populations

Table C1. HF-using Refiners and Locations and Size of Populations at Risk*

Table C1. HF-using Refineries in Metropolitan Areas (Over 500,000 at risk)

Table C1.* 50 HF-using Refiners and Locations and Size of Populations at Risk**

Oil Company	No. of HF Refineries		Refinery Locations	Number of persons at risk	
	Total	USW		Workers Represented by USW [†]	Community [‡]
Valero	8	2	Wilmington, CA; Ardmore, OK; Paulsboro, NJ; Memphis, TN _(USW) ; Port Arthur, TX _(USW) ; Texas City, TX; Corpus Christi, TX; Three Rivers, TX	583	5,575,700
Marathon	6	3	Robinson, IL; Catlettsburg, KY _(USW) ; Garyville, LA; St. Paul Park, MN; Canton, OH _(USW) ; Texas City, TX _(USW)	779	4,448,700
ConocoPhillips^{††}	7	5	Belle Chasse, LA _(USW) ; Billings, MT _(USW) ; Ponca City, OK _(USW) ; Trainer, PA _(USW) ; Borger, TX; Sweeny, TX; Ferndale, WA _(USW)	1,069	3,655,800
CITGO	2	2	Lemont, IL _(USW) ; Corpus Christi, TX _(USW)	422	3,320,000
ExxonMobil	4	3	Torrance CA _(USW) ; Channahon, IL; Chalmette, LA _(USW) ; Billings, MT _(USW)	750	2,414,600
Sunoco^{††}	1	1	Philadelphia, PA _(USW)	611	1,308,400
Murphy^{††}	2	1	Meraux, LA _(USW) ; Superior WI	168	1,236,000
ChevronTexaco	1	1	Salt Lake City, UT _(USW)	115	1,100,000
Houston Refining	1	1	Pasadena, TX _(USW)	476	650,000
BP	1	1	Texas City, TX _(USW)	896	550,000
Placid Refining Co. LLC-Port Allen Refinery	1	0	Port Allen, LA	††	440,200
Flying J	1	1	North Salt Lake, UT _(USW)	95	376,000
Flint Hills Resources, LP-CC West Refinery	1	0	Corpus Christi, TX;	††	349,900
Holly/Frontier	3	3	El Dorado, KS _(USW) ; Woods Cross, UT _(USW) ; Cheyenne, WY _(USW)	465	308,100
CHS Laurel Refinery	1	1	Laurel, MT _(USW)	163	85,000
Connacher Oil/ Montana Refining Co. Inc.	1	1	Great Falls, MT _(USW)	48	69,000
Tesoro	1	1	Mandan, ND _(USW)	132	68,000
Coffeyville Resources (CVR Energy)	1	0	Coffeyville, KS	††	40,700
Wynnewood Refining Company	1	0	Wynnewood, OK	††	40,000
Alon	1	0	Big Spring, TX	††	38,000
Navajo Refining Company	1	0	Artesia, NM	††	16,000
National Cooperative	1	1	McPherson, KS _(USW)	132	20,100
Countrymark Co-op LLP	1	0	Mt. Vernon, IN	††	8,000
Gallup Refinery	1	0	Jamestown, NM	††	4,800
Wyoming Refining Company	1	0	Newcastle, WY	††	3,100
Totals	50	28		6,904	26,126,100

*Data is in part from the Center for Public Integrity. **Ranked by number of community members at risk. _{USW} indicates workers at the site are represented by USW. † Additional thousands of others non-represented employees are at risk. ‡ Reported by refining companies to EPA. †† Not USW, not available. †† Since data was collected the Conoco refinery in Trainer, PA was purchased by Delta Airlines and will be operated by a subsidiary, Monroe Energy; the Sonoco refinery has come under the ownership of Philadelphia Energy Solutions, a joint venture of the Carlyle Group and Sunoco; Calumet Lubricants purchased the Murphy Oil, Superior, WI refinery; and Valero Energy Corporation purchased the Murphy Oil, Meraux, LA refinery.

Table C2.* HF-using Refineries in Metropolitan Areas (Over 500,000 at risk)*

City/Area	Number of Refineries	Refinery Locations	No of community members at risk [†]	Refining Companies
Philadelphia[†]	3	Paulsboro, NJ; Philadelphia, PA (USW); Trainer, PA (USW)	6,878,400	Valero, Sunoco, ^{††} Conoco ^{††}
Chicago	2	Channahon, IL; Lemont, IL (USW)	4,075,900	Exxon, CITGO
New Orleans	4	Belle Chasse (USW), LA; Chalmette, LA; Garyville, LA; Meraux, LA (USW)	3,346,200	Conoco, Exxon, Marathon, Murphy ^{††}
Texas City	4	Texas City, TX (USW); Pasadena, TX (USW)	2,280,000	Crown, BP, Marathon, Valero
Minneapolis	1	St. Paul Park	2,200,000	Marathon
Salt Lake City	3	Salt Lake City, UT (USW); North Salt Lake, UT (USW); Woods Cross, UT (USW)	1,692,300	Chevron, Flying J, Holly/Frontier
Canton, OH	1	Canton, OH (USW)	940,000	Marathon
Memphis	1	Memphis, TN (USW)	792,000	Valero
Totals	19		22,204,800	

*Data is in part from the Center for Public Integrity. **Ranked by number of community members at risk. [†] Reported by Refining Companies to EPA. ^{††} Since data was collected the Conoco refinery in Trainer, PA was purchased by Delta Airlines and will be operated by a subsidiary, Monroe Energy; the Sonoco refinery has come under the ownership of Philadelphia Energy Solutions, a joint venture of the Carlyle Group and Sunoco; and Valero Energy Corporation purchased the Murphy Oil, Meraux, LA refinery.

REFERENCES

- ¹ Center for Public Integrity. 2010. Data gathered in October 2010 at U.S. EPA Headquarters by Center for Public Integrity staff.
- ² Stratford Engineering. 2011. Safety Issues in Alkylation Units. <http://stratfordengineering.com/articles/safety-issues-in-alkylation-units>. (Last accessed March 12, 2013).
- ³ Blewitt DN, Yohn JF, Koopman RP, and Brown TC. 1987. Conduct of Anhydrous Hydrofluoric Acid Spill Experiments. Presented at the International Conference on Vapor Cloud Modeling, Boston, MA. Nov. 2-4. Amoco Corporation Chicago, IL and Lawrence Livermore National Laboratory, Livermore, CA.
- ⁴ American Petroleum Institute. 2007. Safe Operation of Hydrofluoric Acid Alkylation Units: Recommended Practice (RP) 751, 3rd Ed. Washington, D.C.: API Publishing Services.
- ⁵ National Commission on the BP Deepwater Horizon Oil Spill and Offshore Drilling. 2011. Deep Water The Gulf Oil Disaster and the Future of Offshore Drilling Report to the President. <http://www.oilspillcommission.gov/final-report>. (Last accessed March 12, 2013).
- ⁶ Columbia Accident Investigation Board. 2003. Report Volume 1 of the Columbia Accident Investigation Board. http://www.nasa.gov/columbia/home/CAIB_Vol1.html. (Last accessed March 12, 2013).
- ⁷ Flynn S. 2007. The Edge of Disaster. New York: Random House.
- ⁸ Flynn S. 2007. The Next Attack. Washington, D.C.: The Washington Monthly. <http://www.washingtonmonthly.com/features/2007/0703.flynn.html>. (Last accessed March 12, 2013).
- ⁹ Rosenthal I, Kleindorfer PR, and Elliott MR. 2006. Predicting and confirming the effectiveness of systems for managing low-probability chemical process risks. Process Safety Progress. (Vol.25, No.2), 135-155.
- ¹⁰ Belke JC. 1998. Recurring Causes of Recent Chemical Accidents. International Conference on Workshop Reliability and Risk Management, San Antonio TX, 1998 (1996-2009, The Plant Maintenance Resource Center: <http://www.plant-maintenance.com/articles/ccps.shtml>). (Last accessed March 12, 2013).
- ¹¹ Belke J. 2000. Chemical accident risks in U.S. industry: A preliminary analysis of accident risk data from U.S. hazardous facilities, U.S. Environmental Protection Agency, Washington, D. C. <http://www.acusafe.com/Incidents/Statistics/CEPPO-RMPINFO.pdf>. (Last accessed March 12, 2013).
- ¹² Elliott MR, Kleindorfer PR, Dubois J, Wang Y, and Rosenthal I. 2008. Linking OII and RMP*Info Data: Does everyday safety prevent catastrophic loss? International Journal of Risk Assessment and Management. Vol. 10, Nos. 1/2:130-146. http://opim.wharton.upenn.edu/risk/library/2007Elliott,PRK,etal_EverydaySafety.pdf. (Last accessed March 12, 2013).
- ¹³ Barab J. 2010. "Learning From Industry Mistakes." Deputy Assistant Secretary for OSHA, Presentation to the National Petroleum Refiners Association, National Safety Conference. San Antonio, TX, May 19. http://www.osha.gov/pls/oshaweb/owadisp.show_document?p_table=SPEECHES&p_id=2218. (Last accessed March 12, 2013).
- ¹⁴ U.S. Occupational Safety and Health Administration (OSHA). 2007. CPL 03-00-004, Petroleum Refinery Process Safety Management National Emphasis Program. http://www.osha.gov/pls/oshaweb/owadisp.show_document?p_id=3589&p_table=DIRECTIVES. (Last accessed March 12, 2013).
- ¹⁵ U.S. Chemical Safety and Hazard Investigation Board (CSB). News Release. April 1, 2011. http://www.csb.gov/assets/news/document/Tesoro_Anniversary_-_Safety_Message_-_Final.pdf.
- ¹⁶ McQuiston TH, Lippin TM, Bradley-Bull K, Anderson J, Beach J, Beach J, Beevers G, Frederic R, Frederick J, Greene T, Hoffman T, Lefton J, Nibarger K, Renner R, Taylor W, Wright M. 2009. Beyond Texas City: The state of process safety in the unionized U.S. oil refining industry. New Solutions 19(3) 271-288.

-
- ¹⁷ Baker J. et al. 2007. The Report of the BP U.S. Refineries Independent Safety Review Panel (January 30). http://www.bp.com/liveassets/bp_internet/globalbp/globalbp_uk_english/SP/STAGING/local_assets/assets/pdfs/Baker_panel_report.pdf. (Last accessed March 12, 2013).
- ¹⁸ Persensky J, Szabo A, Plott C, Engh T, and Barnes V. 2005. Guidance for Assessing Exemption Requests From the Nuclear Power Plant; Licensed Operator Staffing Requirements Specified in 10 CFR 50.54 (m). U.S. Nuclear Regulatory Commission. <http://www.nrc.gov/reading-rm/doc-collections/nuregs/staff/sr1791/sr-1791.pdf>. (Last accessed March 12, 2013).
- ¹⁹ Siroris AG and Moore-Ede M. 2013. Circadian White Paper: Staffing Levels, A Key to Managing Risk in 24/7 Operations. (1st Ed). Stoneham, MA. <http://www.circadian.com/landing-page/white-paper-staffing-levels.html>
- ²⁰ International Atomic Energy Agency (IAEA). IAEA Safety Guide 'The Operating Organization for Nuclear Power Plants', NS-G-2.4, IAEA, 2008. IAEA Safety Guide 'Conduct of Operations at Nuclear Power Plants', NS-G-2.14, IAEA, 2008. IAEA-TECDOC-1052 NPP Organization and staffing for improved performance – lessons learned, IAEA, 1998.
- ²¹ Kletz T. 1998. Process Plants: A Handbook For Inherently Safer Design. Philadelphia, PA: Taylor and Francis.
- ²² Crowl DA (Ed). 1996. Inherently Safer Chemical Processes: A Life Cycle Approach. New York: American Institute of Chemical Engineers.
- ²³ PetroChina Lanzhou Petrochemical Company.
- ²⁴ Liu Z, Zhang R, Xu C and Xia R. 2006. Ionic liquid alkylation process produces high-quality gasoline. Oil and Gas Journal. October 23: 52-56.
- ²⁵ National Institute for Occupational Safety and Health (NIOSH) Pocket Guide. Hydrogen fluoride. <http://www.cdc.gov/niosh/npg/npgd0334.html>. (Last accessed March 12, 2013).
- ²⁶ Blewitt DN, Yohn JF, Koopman RP, Brown TC, and Hague WJ. 1987. "Effectiveness of Water Sprays on Mitigating Anhydrous Hydrofluoric Acid Releases," Proceedings of International Conference on Vapor Cloud Modeling, CCPS, Cambridge, MA, 2-4 November, pp. 155-180.
- ²⁷ U.S. EPA. 1998. Hydrogen Fluoride Study Report to Congress Section 112(n)(6) Clean Air Act as Amended Final Report. EPA OSWER, Office of Emergency Management. <http://www.epa.gov/osweroe1/docs/chem/hydro.pdf>. (Last accessed July 17, 2012).
- ²⁸ Slavav JP. 1991. HF mitigation by water sprays. BETE Fog Nozzle, Inc. Presentation at the PETRO-SAFE Conference, Houston, TX. http://www.bete.com/pdfs/BETE_HF_mitigation.pdf. (Last accessed March 12, 2013).
- ²⁹ Cornwell JB, Johnson DW. 1995. Effectiveness of mitigation systems in reducing hazards of hydrogen fluoride leaks. First Risk Control Engineering Seminar, Maracaibo, Venezuela. <http://www.questconsult.com/resources/papers/pdf/paper45.pdf>. (Last accessed March 12, 2013).
- ³⁰ National Commission on the BP Deepwater Horizon Oil Spill and Offshore Drilling. 2011. Deep Water: The Gulf Oil Disaster and the Future of Offshore Drilling. Report to the President. www.oilspillcommission.gov. (Last accessed March 12, 2013).
- ³¹ Malik NS. 2010. Tesoro fined \$2.4 million for deadly blast at refinery. Wall Street Journal (October 4). <http://online.wsj.com/article/SB10001424052748704631504575532281314909438.html>. (Last accessed March 12, 2013).
- ³² U.S. Chemical Safety and Hazard Investigation Board (CSB). 2007. Investigation Report: Refinery Explosion and Fire (15 Killed, 180 Injured). BP, Texas City, Texas, March 23, 2005. Washington, D.C.: CSB. March 2007. <http://www.csb.gov/assets/document/CSBFinalReportBP.pdf>. (Last accessed March 12, 2013).
- ³³ U.S. OSHA. 2005. OSHA Fines BP Products North America More Than \$21 Million Following Texas City Explosion. September 22, 2005.

http://www.osha.gov/pls/oshaweb/owadisp.show_document?p_id=11589&p_table=NEWS_RELEASES.
(Last accessed March 12, 2013).

- ³⁴ FireDirect. 2011. equipment failure at refinery leads to toxic HF release (March 3).
<http://www.firedirect.net/index.php/2011/03/equipment-failure-at-refinery-leads-to-toxic-hf-release/>. .
(Last accessed March 12, 2013).
- ³⁵ U.S. CSB. 2009. CSB Issues Urgent Recommendations to CITGO; Finds Inadequate Hydrogen Fluoride Water Mitigation System during Corpus Christi Refinery Fire Last July. December 9.
<http://www.csb.gov/newsroom/detail.aspx?nid=298>. (Last accessed March 12, 2013).
- ³⁶ U.S. CSB. 2005. Case Study: Oil Refinery Fire And Explosion, Giant Industries' Ciniza Oil Refinery.
http://www.csb.gov/assets/document/Giant_Case_Study.pdf. (Last accessed March 12, 2013).
- ³⁷ U.K. Health and Safety Executive. 2010. Technical Assessment Guide (TAG): Staffing Levels and Task Organisation. February 22. This TAG is intended to supplement the guidance in T/AST/065, The Function and Content of the Nuclear Baseline. WENRA Reactor Harmonisation Working Group: Reactor Safety Reference Levels, WENRA, January 2008.
http://www.hse.gov.uk/nuclear/operational/tech_asst_guides/tast061.pdf. (Last accessed March 12, 2013).

The report is available at:
<http://assets.usw.org/resources/hse/pdf/A-Risk-Too-Great.pdf>