

**NEEDLESS RISK:  
OIL REFINERIES AND HAZARD REDUCTION**

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## EXECUTIVE SUMMARY

Across the country, petroleum refineries, chemical plants and other industrial facilities use and store large amounts of hazardous chemicals that, if subject to an accident or attack, would release dangerous toxins. Such releases could injure or kill thousands of people that live in communities in close proximity to these facilities. The U.S. Environmental Protection Agency (EPA) warned in 2000 that an accident or terrorist attack at one of 123 chemical facilities could put more than one million individuals at risk of injury or death from toxic chemical exposure. Incidents at another 700 facilities could endanger at least 100,000 people each, and 3,000 facilities could affect more than 10,000 people each.

Many of these facilities, however, present an unnecessary risk to their surrounding communities. Industries often have multiple options for carrying out similar processes, and some of these options are inherently safer than others. Facilities that use fewer or small quantities of hazardous chemicals, or even make changes to storage pressure or other processes, eliminate the possibility of on-site chemical accidents and make themselves less appealing terrorist targets.

Petroleum refineries stand as a stark example of the unnecessary risk posed by such facilities in the event of an attack or accident as well as the opportunity to mitigate this risk by using safer alternatives to toxic chemicals.

Many petroleum refineries use hydrofluoric acid in their processing, which poses a great public safety risk both because of its extreme toxicity to humans as well as its propensity to form a toxic aerosol cloud when released. A catastrophic event at one of these facilities could cause a potentially lethal release of hydrofluoric acid, forming a stable aerosol cloud above the facility and

surrounding neighborhoods. Exposure to hydrofluoric acid results in devastating burns, and pain associated with the exposure may be delayed for up to 24 hours. If the burn is not addressed, tissue destruction may continue for days. Inhalation of fumes can cause symptoms ranging from severe throat irritation to pulmonary edema.

Petroleum refineries using hydrofluoric acid endanger millions of people.

Specifically:

- Of the 153 petroleum refineries in the United States, 50 use hydrofluoric acid in their processing or store it on-site.
- These 50 refineries, using and storing 10.7 million pounds of hydrofluoric acid, endanger more than 15.6 million people living in surrounding communities in 20 different states.
- With 12 refineries using hydrofluoric acid, Texas has more than any state. Louisiana has five oil refineries that currently utilize hydrofluoric acid, and Illinois and Montana have four.
- The five states with refineries using and storing the most hydrofluoric acid include Texas, Louisiana, Illinois, Pennsylvania, and Montana.
- Refineries using hydrofluoric acid in Pennsylvania endanger almost four million people residing in their vulnerability zones, according to conservative estimates. Refineries using hydrofluoric acid in Illinois endanger more than 3.6 million people, ranking the state second. New Jersey ranks third.
- Illinois, Louisiana and Pennsylvania all have two facilities in the list of the ten facilities with the most people residing in their vulnerability zones.

Fortunately, hydrofluoric acid is not the only material oil refineries can use in their refining processes. Many other refineries already use sulfuric acid, a safer alternative, in the alkylation process. This cost-effective switch diminishes the appeal of refineries as a terrorist target and mitigates the public health and safety consequences of an accident. In addition, a new technology, solid acid catalysts, will soon be available for widespread commercial use, offering an even safer option than the use of sulfuric acid.

Petroleum refineries are but one example of the facilities that pose an immediate risk to public health in the event of a terrorist attack or chemical accident. Refineries also are not the only example of facilities that could make cost effective changes to manufacturing processes to reduce or eliminate the use of hazardous chemicals—and therefore the associated threat to public health.

Unfortunately, most industrial facilities have not responded to the increased awareness of terrorism by switching to inherently safer technologies. Instead, industry organizations such as the American Chemistry Council have placed emphasis on increasing physical security measures. Hiring more guards, building higher fences, and placing more lights may all be part of a strong security plan, but this does not actually reduce the threat to the community. Switching chemicals and processes to something less volatile not only reduces the chemical hazard to the community, but also reduces the need for costly add-on security measures and the attractiveness of the facility as a target for attack.

## **CHEMICAL INSECURITY: HAZARDS LEAVE COMMUNITIES EXPOSED**

Across the United States, thousands of industrial facilities use and store hazardous chemicals in large quantities that pose major risks to their neighbors. According to EPA, 123 facilities would each put at least one million people at risk of injury or death in the event of a chemical release. Another 3,000 facilities put at least 10,000 people at risk. Nearly 5,000 facilities store more than 100,000 pounds of at least one EPA-classified “extremely hazardous substance.”<sup>1</sup>

Accidents at chemical and industrial facilities are common. Each year tens of thousands of spills and gas leaks occur as a result of the ongoing use of hazardous chemicals.<sup>2</sup> In Gulfport, Mississippi in February 2003, a cloud of toxic ammonia leaked from a chemical plant after an intruder broke into a fenced compound, attempting to steal the chemical to make illegal drugs. The toxic cloud led to the evacuation of seven hotels and the closure of Gulfport-Biloxi International Airport and a 10-mile stretch of Interstate 10 for seven hours.<sup>3</sup>

Even before September 11, 2001, the Agency for Toxic Substances and Disease Registry (ATSDR) addressed the weak security at chemical facilities. In 1999, ATSDR published a study of chemical site security at two key chemical communities – the Kanahwa Valley in West Virginia and Las Vegas, Nevada. The study found the industry unable to fend off terrorist attacks, noting that industrial chemicals provide terrorists with “effective and readily accessible materials to develop improvised explosives, incendiaries and poisons.”<sup>4</sup>

Since September 11, 2001, it is increasingly apparent that these facilities pose a more sinister threat, as they may become the target of a terrorist attack. A

report by the Army Surgeon General ranked an attack on a chemical plant second only to a widespread biological attack in magnitude of the hazard to the public.<sup>5</sup> On February 12, 2003, the National Infrastructure Protection Center warned, “Al Qa’ida operatives...may attempt to launch conventional attacks against the U.S. nuclear/chemical-industrial infrastructure to cause contamination, disruption, and terror.”<sup>6</sup>

Across the country, select facilities have made major progress by switching to the use of safer chemicals and processes that pose less of a threat to surrounding communities in the event of an accident. Soon after September 11<sup>th</sup>, for example, the Blue Plains Sewage Treatment Plant in Washington, DC switched from using and storing chlorine and sulfur dioxide on-site to using sodium hypochlorite bleach in its processes. For weeks after September 11<sup>th</sup>, workers at Blue Plains removed up to 900 tons of liquid chlorine and sulfur dioxide. Whereas chlorine gas from the Blue Plains facility could have enveloped downtown Washington, DC, Anacostia, Reagan National Airport, and Alexandria in a toxic cloud, sodium hypochlorite bleach is far more benign if accidentally released.<sup>7</sup>

Unfortunately, too few other chemical facilities have followed the lead of the Blue Plains facility, changing the processes and chemicals they use to make their facilities inherently safer. Instead, industry organizations have placed emphasis on increasing physical security measures. The American Chemistry Council, the chemical industry’s lobbying organization, has issued site security guidelines for its member companies and requires these companies take part in its Responsible Care program in order to continue membership in the organization. This set of guidelines, however, focuses only on site security and does not include minimum standards that facilities must follow. For example, it does not require that facilities plan for protection against an armed intruder. In addition,

Responsible Care does not recommend that facilities consider inherently safer technology to reduce the threat these facilities pose to surrounding communities. In fact, the American Chemistry Council instructs third party participants in site security reviews not to even consider safer technologies.

Hiring more guards, building higher fences, and placing more lights may all be part of a good security plan, but this does not actually reduce the threat to the community. Switching chemicals and processes to something less volatile not only reduces the chemical hazard to the community, but also reduces the cost of physical security and the attractiveness of the facility as a target for attack.

Furthermore, some in industry and the government have proposed limiting the public's access to information on the potential impact to public health and safety of chemical hazards. Limitations have been placed on the information any individual can obtain about a chemical facility and its vulnerability zone, and even tighter restrictions have been proposed. Using the argument that such information could provide a "roadmap" for terrorists, EPA and the chemical industry have removed it from the Internet as well. Instead of safeguarding these facilities from terrorists, however, these efforts merely deny public accountability measures that encourage industry reform.

# **HYDROFLUORIC ACID AND THE PETROLEUM INDUSTRY**

Petroleum refineries stand as a stark example of the safety hazards posed by using toxic chemicals in the manufacturing process and the opportunities to switch to safer alternatives.

Petroleum refineries are responsible for nearly 11% of all of the high-risk processes in EPA's Risk Management Program, the agency's primary chemical accident prevention program established under the 1990 Clean Air Act Amendments.<sup>8</sup> Most notably, many of these refineries use hydrofluoric acid, also known as hydrogen fluoride, as a catalyst to produce an additive to gasoline. This additive is then used in turn to increase the octane levels in gasoline, which addresses the problem of engine "knocking." Currently there are 153 petroleum refineries in the United States, 50 of which use hydrofluoric acid as a catalyst to produce alkylate.<sup>9</sup>

## **HYDROFLUORIC ACID: A THREAT TO HEALTH AND SAFETY**

Highly toxic, hydrofluoric acid has many acute consequences for human health, as well as the ability "to kill people on the spot," according to Jonathan Ward, director of toxicology at a University of Texas.<sup>10</sup> Even slight contact with hydrofluoric acid may cause a variety of acute symptoms, including skin burns and deep tissue burns, which may not be felt for up to 24 hours after exposure. In addition, hydrofluoric acid exposure commonly causes eye irritation and can lead to permanent damage. If inhaled, the acid can cause irritation of the nose, throat, and lungs, causing coughing and dyspnea, or shortness of breath. Severe exposure can cause cyanosis, an indicator of hypoxemia, lung injury and a build up of fluid in the lungs, known as pulmonary edema.<sup>11</sup>

Once hydrofluoric acid penetrates body tissue, it can react with the calcium and magnesium in the blood stream, causing abnormally low calcium concentrations and a condition known as hypocalcaemia.<sup>12</sup>

Case studies have shown hydrofluoric acid to be fast acting, reporting instances of respiratory irritation in less than one minute after acute inhalation of 122 parts per million (ppm).<sup>13</sup> Even a concentration as low as 30 ppm of hydrofluoric acid in the air is considered "immediately dangerous to life and health," according to the National Institute for Occupational Health and Safety.<sup>14</sup> General estimates of the lowest lethal concentrations range from 50-250 ppm for a five-minute exposure.<sup>15</sup>

## **USE OF HYDROFLUORIC ACID IN THE PETROLEUM INDUSTRY**

Petroleum refiners use hydrofluoric acid as a catalyst in the alkylation process. With tighter standards on fuel emissions, alkylate has become a key additive in gasoline because it offers a high octane with very low sulfur and nitrogen content.

The production of alkylate requires three primary steps. First, isobutane and light olefins (the feedstock used to create alkylate) must be treated to remove impurities, which would otherwise cause the acid catalyst to quickly become consumed. Next, the feedstock is injected into the reaction chamber of the alkylation unit; upon contact with the acid catalyst, a fast reaction produces both alkylate and excess heat. The heat must be removed to retain the optimum reaction temperature, which varies based on the catalyst used.<sup>16</sup> Third, because some of the acid catalyst leaves the reaction chamber along with the alkylate, further treatment to neutralize the acid is required as well, in order to prevent corrosion further down the production line.

## CHEMICAL ACCIDENTS INVOLVING HYDROFLUORIC ACID

Hydrofluoric acid has a boiling point of 67° F (19.4° C) at atmospheric pressure, and most reactions take place at about 100° F (37.8° C) in petroleum refineries. Therefore, the acid will vaporize whenever the container is penetrated.<sup>17</sup> Furthermore, when the outside temperature is 67° F or greater, the containment unit housing hydrofluoric acid becomes pressurized because of the acid's high volatility. Therefore, if hydrofluoric acid is released from containment, under certain atmospheric conditions it will form a stable aerosol cloud.

Amoco, Mobil, Allied Chemical and DuPont tested the possibility of a release of hydrofluoric acid from one of its refineries then under construction in a Nevada desert in 1986. Under conditions similar to those in an alkylation unit, lethal concentrations of hydrofluoric acid aerosol were present up to 5 miles (8 km) from the release points, at levels much higher than anticipated.<sup>18</sup> The amount of hydrofluoric acid released in the test was relatively small—1,000 gallons in two minutes.<sup>19</sup>

Hydrofluoric acid refineries have long had a history of accidental releases that prove the potentially devastating effects of a release caused by simple human error. The National Response Center's Emergency Response Notification System reported 269 incidents involving hydrofluoric acid from 1992 to 2002.<sup>20</sup> Simple malfunctions, ruptured valves or pipes, or valves accidentally opened often cause significant leaks that can harm both the people and the environment surrounding the refinery.

- On October 30, 1987, a crane at Marathon Oil's Texas City refinery dropped its load on a storage tank, rupturing a pipe and releasing 30,000 pounds, the largest known release, of hydrofluoric acid. The resulting vapor cloud sent 1,037 people to the hospital

suffering from respiratory problems and skin rashes and forced 3,000 residents out of their homes for three days.

“There were houses right up against the fence,” said Ronald Koopman, of Lawrence Livermore. “The only thing that saved people was that the [hydrofluoric acid] plume shot 200 feet up in the air, and it went about 900 meters downwind before it actually came down into the neighborhood. If it had squirted out sideways, it would have killed hundreds, if not thousands.”<sup>21</sup>

- On March 2, 2003, 13 electricians working at the Marathon-Ashland oil refinery in St. Paul Park, Minnesota were hospitalized after being exposed to hydrofluoric acid. They had been hired to repair damage to the facility caused by a fire a few days earlier. While working, a pump leaked one cup of hydrocarbons with trace amounts of hydrofluoric acid, which immediately vaporized and entered their lungs.<sup>22</sup>
- An accidental hydrofluoric acid release in 1991 killed two workers and injured five others at Southwestern Refining Co. in Texas.<sup>23</sup>
- Between 1995 and 1997, four separate one-pound releases of hydrofluoric acid at the Sunoco refinery in Philadelphia injured one worker in each accident.<sup>24</sup>
- On October 2, 2001, 150 pounds of hydrofluoric acid in low concentration leaked within the Valero refinery in Paulsboro, New Jersey. Because the wind was blowing toward neighboring Greenwich Township, a nearby elementary school was forced to secure all the children and staff in the gym by sealing the doors and windows with duct tape and plastic.<sup>25</sup>
- On March 19, 1988, at the Sun Co. refinery in Tulsa, Oklahoma, an accidental release of 210 pounds of

hydrofluoric acid sent a cloud of hydrofluoric acid drifting five miles through downtown. Had the accident occurred on a weekday, more people would have been injured. One resident, living in the downtown area, said “I didn’t realize it was hazardous until I could see it leave orange particles everywhere...And then my eyes burned, my throat burned and my head ached.”<sup>26</sup>

## **HYDROFLUORIC ACID: A TERRORIST TARGET**

According to Neil Livingstone, board chairman of Global Options, a security firm in Washington, DC, hydrofluoric acid is a “known quantity to some terrorists,” particularly those from oil-producing countries where hydrofluoric acid is commonly used.<sup>27</sup> Terrorist attacks over the past ten years have consistently targeted petroleum facilities throughout the world because of their vulnerability, value to economies, and high volumes of toxic chemicals stored onsite. A few examples of coordinated attacks on petroleum facilities over the past ten years include:

- During the Croatian war, Serbian armies attacked a natural gas refinery in eastern Slovenia that stored ethane, propane, and butane with rockets and cluster bombs.<sup>28</sup>
- Serbian forces attacked large fuel storage tanks along the highway from Belgrade to the outskirts of Zagreb and started large fires at Osijek, Sisak, and Karlovak.<sup>29</sup>
- A refinery in Sisak, which produced liquefied petroleum gas (LPG), fuel, petroleum coke, and solvents, was attacked with thousands of Serbian artillery rounds, which hit 38 petroleum storage tanks. If these attacks had destroyed existing stored chemical containers, lethal concentrations of chemicals would have covered a wide area.

- In October 2001, a group of Tamil Sea Tigers attacked and set ablaze the oil tanker MV Silk Pride. It was carrying 225 tons of low-sulfur diesel, 160 tons of kerosene oil, and 275 tons of auto diesel.<sup>30</sup>

An organized attack, similar to the attack on the Sisak refinery by Serbian forces, would be nearly impossible for security guards to prevent.

Furthermore, it is relatively simple for individuals to gain access to chemical plants with the level of security common at refineries. As recently as January 2002, a robber carrying a shotgun made his way into a Citgo Petroleum Corporation facility. Citgo was one of the companies that claimed to have dramatically increased security measures after September 11, 2001.<sup>31</sup> In addition, activists and reporters have breached security at refineries and chemical facilities across the country. Greenpeace activists gained access to Dow Chemical’s Plaquemine, Louisiana, facility in February 2001 by entering the plant through an unlocked gate, and succeeded in gaining access to the control panel that regulates wastewater discharges into the Mississippi River.<sup>32</sup> A reporter in Pennsylvania skirted inadequate security at more than 30 chemical facilities and found that he “could walk or drive right up to tanks, pipes and control rooms considered key targets for terrorists.”<sup>33</sup>

Assuming that onsite security was able to prevent all unauthorized access to a refinery, and water mitigation systems<sup>34</sup> were installed throughout the refinery, it would still not be difficult to release hydrofluoric acid into surrounding communities. According to Carol Coy, a California regulator whose agency pushed for an end to hydrofluoric acid use in southern California, saboteurs could deactivate the mitigation systems simply by shutting off the electricity.<sup>35</sup> Furthermore, munitions fired from an offsite location

could puncture the storage tanks holding hydrofluoric acid.

National security experts recognize that a terrorist attack on chemical facilities and refineries is more likely than an attack with a conventional chemical weapon. Creating chemical weapons is a complex and expensive process, whereas industrial facilities provide relatively easy access to large amounts of chemicals from which a significant chemical release could harm considerable numbers of people. Amy Smithson, director of the Chemical and Biological Weapons Non-Proliferation Project at the Henry L. Stimson Center, testified to this in a House of Representatives committee hearing:

“Although assembling from scratch an unconventional weapons capability that could cause mass casualties is not that elementary, there are tangible routes whereby terrorists could inflict considerable harm with chemical and biological substances. One shortcut involves foul play with industrial chemicals...Logic dictates that if the same result [mass casualties from a chemical release] can be achieved through a less arduous route, terrorists intent on causing mass casualties with chemicals would probably engineer the intentional release of industrial chemicals rather than wrestle with the complexities of making large quantities of the classic chemical warfare agents.”<sup>36</sup>

## REPORT FINDINGS: COMMUNITIES AT RISK

Under the Clean Air Act's chemical accident prevention requirements, industrial plants that use large volumes of certain toxic materials file accident prevention plans that include worst-case accident scenarios. These estimate how far a chemical could travel off-site and still maintain toxic concentrations in certain weather conditions, and report the number of people living within that distance, named the "vulnerability zone."<sup>37</sup>

**TABLE 1. QUANTITY OF HYDROFLUORIC ACID AT PETROLEUM REFINERIES**

State	Quantity (lbs)
Texas	3,053,000
Louisiana	2,491,450
Illinois	1,788,000
Pennsylvania	620,000
Montana	359,000
Kansas	343,000
Utah	264,200
Oklahoma	252,000
New Jersey	240,000
Ohio	238,000
Tennessee	163,000
Kentucky	160,000
Washington	154,734
Wyoming	129,000
North Dakota	107,000
California	101,000
Minnesota	95,000
Wisconsin	81,000
New Mexico	78,900
Indiana	34,900

More than 15.6 million Americans (15,652,142) live inside a vulnerability zone for an oil refinery using hydrofluoric acid

(Table 4).<sup>38</sup> In some cases, the vulnerability zones overlap, posing an even greater danger to people who live and work within the overlapping areas. In Philadelphia, for example, the vulnerability zones of two refineries overlap across the Delaware River, encompassing Philadelphia International Airport, the new sports stadiums, and many city neighborhoods.<sup>39</sup>

Seven petroleum refineries with hydrofluoric acid alkylation facilities have accidental toxic release "worst-case" scenarios where more than one million people could be at risk of exposure to a cloud of toxic hydrofluoric acid gas. Of these seven facilities, four threaten more than two million people, and one threatens more than three million people. Furthermore, 17 refineries could place more than 500,000 people in harms way, and 27 refineries could endanger more than 100,000 people in the event of a worst-case hydrofluoric acid release.

Twenty different states have oil refineries currently operating in its borders that use hydrofluoric acid at a concentration that requires reporting to the Risk Management Program. Texas is home to the most hydrofluoric acid refineries, with twelve, Louisiana is second with five facilities, and Illinois and Montana tie for fourth with four facilities in each state.

**TABLE 2. NUMBER OF REFINERIES USING HYDROFLUORIC ACID AND RANGE OF POPULATION AT RISK**

State	Number of Refineries	Minimum Population	Maximum Population
California	2	230,000	350,000
Illinois	4	83,000	2,500,000
Indiana	1	8,000	8,000
Kansas	2	12,000	27,200
Kentucky	1	240,000	240,000
Louisiana	5	17,402	1,081,649
Minnesota	1	1,700,000	1,700,000
Montana	4	34,000	102,000
North Dakota	1	68,013	68,013
New Jersey	1	2,836,121	2,836,121
New Mexico	2	2,150	24,565
Ohio	1	780,000	780,000
Oklahoma	3	37,000	40,000
Pennsylvania	2	2,200,000	3,900,000
Tennessee	1	791,888	791,888
Texas	12	5,561	650,000
Utah	3	79,615	590,000
Washington	1	120,000	120,000
Wisconsin	1	37,000	37,000
Wyoming	2	3,001	37,240

Based on conservative estimates, refineries in Pennsylvania using hydrofluoric acid endanger the most people, at 3.9 million. Illinois ranks second with more than 3.6 million people at risk, and New Jersey ranks third. (Table 4.)

When individual facilities are analyzed by state, Pennsylvania ranks first as home to the single facility using hydrofluoric acid with the largest population currently residing in its vulnerability zone, at nearly four million. New Jersey ranks second with more than 2.8 million people in the vulnerability zone of one of its facilities, and Illinois ranks third with 2.5 million people at risk from a single facility. Illinois, Louisiana, and Pennsylvania all have two facilities in the list of the ten facilities endangering the most people. (Table 3.)

**TABLE 3. TEN FACILITIES WITH MOST PEOPLE IN VULNERABILITY ZONE**

Refinery	Number of People in Vulnerability Zone
Pennsylvania	3,900,000
New Jersey	2,836,121
Illinois	2,500,000
Pennsylvania	2,200,000
Minnesota	1,700,000
Illinois	1,103,000
Louisiana	1,081,649
Louisiana	830,000
Tennessee	791,888
Ohio	780,000

**TABLE 4. NUMBER OF PEOPLE ENDANGERED BY REFINERIES USING HYDROFLUORIC ACID**

Refinery Location	Number of People in Vulnerability Zone
Pennsylvania	3,900,000
Illinois	3,686,000
New Jersey	2,836,121
Minnesota	1,700,000
Texas	1,660,034
Louisiana	1,099,051
Tennessee	791,888
Ohio	780,000
Utah	590,000
California	580,000
Kentucky	240,000
Montana	169,000
Washington	120,000
Oklahoma	117,000
North Dakota	68,013
Wyoming	40,241
Kansas	39,200
Wisconsin	37,000
New Mexico	26,715
Indiana	8,000
Total U.S. <sup>40</sup>	15,652,142

# HOW POLICYMAKERS AND INDUSTRY SHOULD PROTECT COMMUNITIES

## A PREVENTIVE APPROACH

The actions of American industry—and American regulatory policy—have historically focused on preparing for or managing chemical accidents and releases rather than preventing them. The continuing legacy of chemical accidents in the United States is evidence that this strategy has failed to protect public safety. Furthermore, the events of September 11<sup>th</sup> make plain the need for preventive action. Safety valves may mitigate the effects of an accidental release, and employee training may reduce the chances of an accident, but neither can protect public safety if a terrorist parks a truck bomb at a chemical plant or refinery. Designed to protect only against accidental releases, many accident mitigation technologies could be foiled by a deliberate saboteur.

Reducing or eliminating chemical hazards offers the best strategy to fully protect American communities from both accidents and terrorist attacks involving industrial chemicals. Hazard reduction means making a chemical process *inherently* safer by eliminating the use of highly toxic, volatile, or flammable chemicals or using chemicals in safer quantities or conditions. The concept of inherent safety leads to a hierarchy to guide decisions on the use and management of chemicals:

**First**, reduce or eliminate the *possibility* of a chemical release by choosing inherently safer materials and technologies.

**Second**, reduce the *probability* of a chemical release through secondary prevention measures such as safety valves and double-walled vessels. In preventing terrorism, increasing site security is an additional secondary prevention measure

(although inadequate in the context of modern terrorists' tactics).

**Third**, reduce the *potential severity* of the impacts of a chemical release through mitigation measures (containment dikes, sprinkler systems) or emergency response plans.<sup>41</sup>

Again, the first option—inherent safety—provides the best response to the threat of chemical releases caused by acts of terrorism because it eliminates the potential hazard. Add-on security and mitigation measures could make minor contributions toward preventing an act of terrorism, but traditional tools of terrorists—truck bombs, suicide bombers, and now airplanes—would likely render such measures useless. Site security measures could prevent a terrorist from entering the grounds of a facility, but in the embassy bombings in Africa, the trucks containing bombs were parked near, not inside, facility grounds. Increasing security would have been of little help.

# **INHERENT SAFETY AT REFINERIES: ALTERNATIVES TO HYDROFLUORIC ACID**

There are three options available to petroleum refineries using hydrofluoric acid as a catalyst for alkylates in order to make this process inherently safer.

- Change the alkylation process to use a solid acid catalyst;
- Convert the hydrofluoric acid alkylation unit into a sulfuric acid unit; or
- Add modifiers to the hydrofluoric acid that decrease the gaseous nature of hydrofluoric acid and install mitigation systems.

## **PREVENT THE POSSIBILITY: SOLID ACID CATALYST**

The best option available to oil refineries is switching from using hydrofluoric acid to a solid acid catalyst, which completely eliminates the need to use either hydrofluoric acid or sulfuric acid to produce alkylate. Industry experts report that a variety of solid acid catalysts will be available for use in alkylation facilities within the next four years. Critics, however, insist this technology has been available since the late 1990s, and simple industry inertia has kept solid acid catalysts from becoming the popular choice for refinery alkylation processes.<sup>42</sup>

Solid acid catalysts have tremendous environmental and safety advantages over both hydrofluoric acid and sulfuric acid because they are neither corrosive nor particularly hazardous to people or the environment. Furthermore, in the event that the container housing the catalyst is breached, no further damage would result. Considerable research is being conducted on solid acid catalysts, and two main options currently exist: Akzor Nobel/ABB Lummus AlkyClean™ and UOP Alkylene™.

AlkyClean™ has a demonstration unit currently being tested at Fortum's facilities in Porvoo, Finland. Based on process designs, this new alkylation unit is projected to be cost competitive with installing either a new hydrofluoric acid or sulfuric acid alkylation facility. This solid acid catalyst also can replace existing hydrofluoric acid or sulfuric acid alkylation units, reusing the existing feedstock pretreatment and product distillation/recycle facilities. Converting to a solid acid catalyst would save the facility money over a sulfuric acid plant because this technology does not require refrigeration for the reaction to take place. Furthermore, there is no need to remove acid from the finished product, thereby eliminating yet another step in the process.<sup>43</sup>

The primary difference between the two available processes is how the solid acid is regenerated. The biggest difference is that Alkylene™ does not have the energy savings associated with AlkyClean™. Furthermore, the feedstock does have to be treated to remove impurities. Yet, even with these differences, Alkylene™ is still very cost competitive with hydrofluoric and sulfuric acid facilities, with an estimated cost of \$42.8 million to construct a unit.<sup>44</sup>

## **PREVENT THE SEVERITY: SULFURIC ACID AS AN OPTION**

Sulfuric acid is often used in the alkylation process instead of hydrofluoric acid because when released, it will not readily form a toxic aerosol cloud. Instead, sulfuric acid is released as a liquid form, making it much easier to contain and prevent exposure to those offsite. As a result, sulfuric acid does not pose as much of a threat to life outside of the facility.

Converting a hydrofluoric acid alkylation unit into a sulfuric acid alkylation unit requires several equipment changes. First, a refrigeration process must be added,<sup>a</sup>

because the catalytic reaction using hydrofluoric acid takes place at a higher temperature that does not require refrigeration to maintain.<sup>45</sup> Second, if the hydrofluoric acid facility contains monel—a metal that does not react with hydrofluoric acid—it must be replaced because it does react with sulfuric acid. Finally, an acid regeneration facility also should be constructed onsite so as to decrease the need to frequently transport sulfuric acid, which greatly increases the risk of offsite consequences.

The fundamental difference between using hydrofluoric acid and sulfuric acid in the production of alkylate is in how the acid is regenerated, once the acid becomes too contaminated with impurities. Hydrofluoric acid can be distilled to remove impurities. However, sulfuric acid must go through a series of steps that first break down the acid into sulfur dioxide and then mix the sulfur dioxide with water to create regenerated sulfuric acid.<sup>46</sup> Sulfuric acid catalysts inevitably cost about fifty cents per barrel of alkylate more than hydrofluoric acid catalysts because of the elaborate regeneration process that sulfuric acid requires.<sup>47</sup>

Although sulfuric acid is less hazardous than hydrofluoric acid, direct exposure to sulfuric acid can cause many detrimental health effects at concentrated levels, such as burns or severe irritation to the eyes, skin, and respiratory tract if concentrated fumes are inhaled. Because sulfuric acid is often regenerated offsite, there is an increased risk of an accident involving sulfuric acid due to the increased transportation time. Once onsite, however, it can be regenerated indefinitely if the refinery builds a regeneration facility.

Two options exist to switch the alkylation process from hydrofluoric acid to sulfuric acid: using a conversion system or building a new sulfuric acid alkylation unit. One system for switching from hydrofluoric acid to sulfuric acid is the Alkysafe™ conversion/expansion process, offered by

STRATCO®. Alkysafe™ reuses both the reaction and distillation sections of the alkylation facility.<sup>48</sup> Due to the short downtime and the amount of equipment that is reused, STRATCO claims that Alkysafe™ is cost competitive with mitigation systems being installed on hydrofluoric acid alkylation units. These mitigation systems, on average, will cost a refinery between \$20 million and \$30 million, with costs reaching at most \$50 million.<sup>49</sup>

The cost of building a sulfuric acid alkylation unit varies according to the amount of alkylate the refinery produces each day. As a general rule, a new alkylation unit will cost about \$5,000 per barrel of alkylate produced, per day. Therefore, a new alkylation unit capable of producing 10,000 barrels of alkylate per day would cost about \$50 million. STRATCO's Alkysafe™ process is estimated to cost one-half to two-thirds the cost of installing a new sulfuric acid alkylation unit.<sup>50</sup>

ExxonMobil also offers a sulfuric acid alkylation process that can replace hydrofluoric acid alkylation systems, although the cost of the process is higher than using the STRATCO designs. However, this process also would be competitive with building a new hydrofluoric acid alkylation unit.<sup>51</sup>

#### **REDUCE THE PROBABILITY: HYDROFLUORIC ACID MODIFIERS**

The final option available to decrease the threat of a hydrofluoric acid release is to invest in alkylation modifiers and install active mitigation units, such as water spray systems. This option, however, does not remove the possibility of a terrorist threat, and an adversary could thwart mitigation systems.

Modified hydrofluoric acid reduces the ability of the acid to form an aerosol cloud by a certain percentage, thereby reducing the impact the toxic cloud will have on the surrounding community. UOP and Texaco

estimate the cost of modifying a hydrofluoric acid alkylation refinery using Alkad, a passive mitigation system, at \$7 million. This estimate, however, does not include the cost of active mitigation systems, which would be necessary in order to truly reduce the potential severity of a release.<sup>52</sup> Mitigation systems cost, on average, between \$20 and \$30 million to install.

ConocoPhillips and ExxonMobil have devised their own alkylation modifier under the name ReVAP, which has the ability to reduce hydrofluoric acid aerosol formation when leaked by 60% to 90%. ReVAP is currently being used at the Woods Cross Refinery in Utah and the Torrance Refinery in California.

Earlier this year, public pressure succeeded in persuading the Valero Energy Corporation to switch to modified hydrofluoric acid at its Wilmington, California refinery, near Los Angeles. Since an explosion that caused an accidental release of hydrofluoric acid at a neighboring Torrance refinery in 1987, the local community and government have pushed to shut down two refineries that used hydrofluoric acid and required a third facility to change to modified hydrofluoric acid. The community was able to negotiate an agreement with the South Coast Air Quality

Management District with regards to the Valero facility; Valero will pay a fine up to \$1 million if the renovation is not complete by the end of 2005. The change is expected to cost Valero about \$30 million.<sup>53 54</sup>

Since both modification systems cannot completely reduce the threat of a hydrofluoric acid release, active mitigation units also must be installed. Active mitigation for hydrofluoric acid requires sensors to detect a hydrofluoric acid release; acid pumps to quickly move the acid to remote locations and decrease the amount of acid that is released; and water spray systems that knock the acid to the ground and prevent it from affecting surrounding communities. If the sensors are working properly and detect a leak immediately, water spray systems can knock up to 90% of the hydrofluoric acid to the ground; however, tests have shown that it requires at least forty volumes of water for each volume of hydrofluoric acid released. Effective water spray systems often include water spray curtains and remotely operated water cannons.<sup>55</sup>

**TABLE 5. COMPARISON OF INHERENTLY SAFER TECHNOLOGIES FOR PETROLEUM REFINERIES USING HYDROFLUORIC ACID**

Catalyst	Sulfuric Acid	AlkyClean™ Solid Acid Catalyst	Alkylene™ Solid Acid Catalyst	HF modifier
<b>How Catalyst Regenerated</b>	Decomposed into sulfur dioxide, then regenerated by mixing with water vapor	Frequent regeneration with dissolved hydrogen every two to four weeks.	Catalyst is constantly regenerated using hydrogen, in a separate regeneration chamber.	Distilled
<b>Required Facility Modification</b>	Some versions require a new refrigeration facility and design change and modifications of current equipment; other versions cannot be fitted to existing alkylation processes.	The original multiple reaction chambers can be used, but requires a new regeneration system.	Not designed to retrofit an existing HF alkylation unit. Requires a new alkylation facility.	Additional separation equipment needed to remove leaching acid from alkylate.
<b>Advantage over HF Alkylation unit</b>	Will not form an aerosol cloud and will not pose a threat to life outside the facility.	Does not require removing impurities in alkylate feedstock, and no corrosive acid can leave the reaction chamber. <i>No threat of a chemical spill to anyone.</i>	No corrosive acid can leave the reaction chamber. <i>No threat of a chemical spill to anyone.</i>	Decrease HF aerosol formation from 60% to 90% in the event of a leak, depending on version used.
<b>Additional Mitigation Systems needed</b>	None	None	None	Active mitigation systems needed.
<b>Safety Concerns</b>	Acid spill during transport to the refinery and to the regeneration facility if the regeneration facility is not part of the refinery.	None	None	Active mitigation systems can fail.
<b>Cost of Conversion</b>	Varies depending on the daily output required. Estimated to cost between \$2,500 to \$3,333 per barrel of alkylate produced per day for one version, \$5,000 per barrel for another.	Cost competitive with installing a new hydrofluoric acid or sulfuric acid alkylation unit.	Estimated \$42.8 million to build a new alkylation unit.	Valero is paying an estimated \$30 million to convert its Wilmington, CA refinery; most modifiers cost \$7 million plus the cost of active mitigation systems.

## REDUCING CHEMICAL HAZARDS THROUGH POLICY MEASURES

The possibility that terrorists could turn American industry into weapons that threaten Americans' safety provides policy-makers with a clear imperative to revise existing policy on lethal chemical releases. Furthermore, more action is needed than simply increasing physical security at chemical facilities; more physical security measures do nothing to offset the possibility of terrorists taking extreme measures to orchestrate a chemical release.

### INADEQUACIES OF EXISTING POLICIES

#### *Gap in Security Policy, Industry Cannot Be Left to Voluntary Measures*

Since September 11<sup>th</sup>, 2001, our nation has tightened security in a variety of venues. Airports and airlines have numerous new regulations they must follow; airplanes have routinely patrolled our water supply; our government has even established an entire new governmental department, the Department of Homeland Security, to coordinate security measures. Despite, however, the repeated admission by government officials that the chemical industry poses a significant security threat, no federal regulations exist that require oil refineries or any chemical facility to reduce their hazards when they are able to do so.

Instead, some facilities subscribe to a voluntary industry program known as Responsible Care. Responsible Care was an initiative developed by the Chemical Manufacturers Association (CMA), now the American Chemistry Council (ACC), in 1988 to respond to the public's lack of confidence in the chemical industry. The CMA needed to act to address the poor public image or else, according to John Johnstone, a former chairman of CMA, "end up in worse shape than the atomic industry."<sup>56</sup> Fifteen years

later, the ACC requires all member companies to comply with this voluntary initiative to improve security. This initiative, however, only requires facilities to install physical security guidelines and does not address preventing accidents or terrorist attacks by switching to safer technology.

A former member of the Security Committee of the American Chemistry Council, as well as a former Security Manager for Georgia-Pacific Company, has addressed just how inadequate these voluntary guidelines are. In a letter to Georgia Public Interest Research Group in March 2003, Sal DePasquale claimed the industry's efforts are "nothing more than a process for self assessment," and warned that an individual company can "assess itself and conclude that all is well, when it may not be, and therefore decide to do nothing."<sup>57</sup>

Furthermore, few facilities actually are member organizations of ACC—and therefore do not participate in ACC's voluntary initiative to address chemical security. Oil refineries, for instance, are generally members of the American Petroleum Institute (API), which does not subscribe to the Responsible Care partner program, although API does have a separate voluntary program.

#### *The Emergency Planning and Community Right-to-Know Act*

After the 1984 Union Carbide chemical disaster in Bhopal, India, grassroots pressure convinced Congress to pass the Emergency Planning and Community Right-to-Know Act (EPCRA). This act established a network of Local Emergency Planning Committees (LEPCs) and required facilities to disclose a baseline of important information on chemical risks, including the amount of extremely hazardous materials stored at particular facilities.

Despite some positive results of EPCRA, including the creation of the Toxics Release Inventory and a general decline in

toxic releases, this Act did not address the need to prevent chemical releases before they happen. Instead, it only addressed the need to prepare for and respond to them. The LEPCs that were established lack the authority to mandate hazard reduction, and many are inactive.<sup>58</sup>

### *The Clean Air Act and Risk Management Program*

In response to an explosion at a Phillips chemical facility in Texas that killed 23 workers in 1989, Congress took further action by adding amendments to the Clean Air Act in section 112(r). These amendments established the Risk Management Planning (RMP) program that requires industry to: first, develop a hazard assessment that covers various release scenarios, off-site consequences, and a five-year accident history; second, a prevention program that manages procedural areas such as training and safety audits; and third, an emergency response program.

Therefore, the Risk Management Planning program addresses the management of chemical risks, but not their prevention. If the RMP program were fully implemented as EPA originally intended, the worst-case scenario estimates of off-site impacts of chemical releases would be available in a national database and could reduce chemical hazards, much as the Toxics Release Inventory has. Although originally available to the public online, the RMP plans have been removed from public view and are now difficult for individuals to obtain.

The case study of the voluntary changes at the Valero refinery in California shows that when a community is aware of the threat a local refinery poses to its safety, public pressure may successfully persuade the facility to change its chemicals and processes in order to reduce the threat. In order for the RMP program to be successful, risk management plans must be readily available to the public.

### *EPCRA and RMP Too Specific to Address Threat*

In addition to the limitations addressed above, both EPCRA and the RMP program were not designed to address the threat of a terrorist attack at a chemical facility, and consequently pertain only to certain chemicals, industries, and facilities using quantities of chemicals above certain thresholds.

Smaller quantities of chemicals are easier to manage onsite and therefore pose less of a concern for accidental releases. Terrorists, however, could specifically target smaller quantities of chemicals and still cause significant harm. For example, a single one-ton cylinder of chlorine gas can fall below thresholds for the RMP program. The quantity of chlorine gas in this cylinder, however, could result in toxic concentrations nearly two miles off-site.

### **THE RIGHT-TO-KNOW AS A SAFETY TOOL**

Right-to-know programs that ensure disclosure about chemicals used, stored and released have played a vital role in protecting public safety from toxic hazards. Public access to information about chemical use and releases, and communities' involvement in reducing chemical hazards, should not be limited in the effort to prevent chemical terrorism.

Ensuring a community's right-to-know about chemicals used, stored and released has long been a useful tool in protecting public safety from toxic hazards. In Massachusetts, for example, companies are required to assess and disclose all chemicals used by their facilities as well as complete toxics use reduction plans. Simply by completing these plans, and not necessarily even implementing them, Massachusetts companies have reduced their overall use of toxic chemicals by 41%, the waste generated by 57%, and their environmental releases by 87% between 1990 and 1999. These reductions did not reduce productivity at these facilities at all, as

production rose 52% at the same facilities. Furthermore, these facilities saved a total of \$15 million by reducing their chemical use.<sup>59</sup>

New Jersey has seen similar success with its Pollution Prevention Act, which requires companies to assess and report chemical use. As a result of these reporting requirements and the Toxic Catastrophe Prevention Act, hundreds of drinking water facilities and sewage treatment facilities have stopped using chlorine gas.

Based on these examples, it is likely that if a petroleum refinery completed an assessment of available inherently safer technologies, and was required to disclose the findings to the public, it would change to a safer technology.

#### **PROTECTING COMMUNITIES THROUGH INHERENTLY SAFER TECHNOLOGY**

The most effective means of protecting American communities from the consequence of an act of chemical terrorism is to encourage and mandate hazard reduction that requires facilities to implement inherently safer technologies.

In the case of hydrofluoric acid in alkylation units, inherently safer technology exists and is proven to work. Facilities should change their chemicals and processes to a safer technology as soon as possible, and new facilities should be built using the safest technology available.

Policymakers could require refineries to change their processes as a policy mandate or to conduct a technology options analysis. A technology options analysis is a way to address a range of industries and require them to make a concerted effort to identify inherently safer options in their chemical uses and processes. Furthermore, a technology options analysis provides an opportunity for facilities to adopt technologies with acceptable cost and appropriate performance characteristics and to explain why technically feasible options

were not selected. These technology options analyses should be made public, while protecting legitimate confidential business information, in order to inform communities of safety measures at nearby facilities as well as to disseminate information on innovative technologies.

Oil refineries using hydrofluoric acid on site clearly pose an unnecessary risk to surrounding communities. By requiring facilities to switch to inherently safer technologies, as well as requiring them to publicly disclose plans to protect surrounding communities, oil refineries could greatly reduce their risk. As oil refineries are not the only facilities that pose unnecessary risk to surrounding communities, these same policy changes should apply to a variety of industries and facilities. Future policy must focus on eliminating the risk of terrorist attacks and accidents on site, instead of focusing on mitigating the consequences of a hazardous release.

## METHODOLOGY

The vulnerability zone data in this report were collected from Risk Management Planning reports obtained at Environmental Protection Agency Air Docket Centers throughout the country, in compliance with all rules that currently govern the collection of such data.

To estimate the total number of people living in the vulnerability zones in each state and nationally, we reviewed the geographic location of each facility, as oil refineries are often grouped together only a few miles apart. In order to avoid double counting, we assumed if the vulnerability zones of two or more facilities overlapped that they overlapped entirely. In these instances, we included the highest at-risk population from the facilities in our calculations.

As a result, the reported totals are a conservative estimate of the total population at risk in each state. In addition, the totals do not reflect the fact that many individuals are at a heightened risk because they live within the vulnerability zone of two or more oil refineries using hydrofluoric acid.

## NOTES

<sup>1</sup> James Belke, U.S. Environmental Protection Agency. "Chemical accident risks in U.S. industry – A preliminary analysis of accident risk data from U.S. hazardous facilities," September 25, 2000.

<sup>2</sup> U.S. EPA, "Assessment of the Incentives Created by Public Disclosure of Off-Site Consequence Analysis Information for Reduction in the Risk of Accidental Releases," at 2 (Apr. 18, 2000), available online at [http://yosemite.epa.gov/oswer/ceppoweb.nsf/vwResourcesByFilename/incenAss.PDF/\\$File/incenAss.PDF](http://yosemite.epa.gov/oswer/ceppoweb.nsf/vwResourcesByFilename/incenAss.PDF/$File/incenAss.PDF) (visited Mar. 10, 2003).

<sup>3</sup> U.S. Chemical Safety and Hazard Investigation Board, CIRC Report, "Ammonia leaks rousts tourists from Gulf hotels." Available at <http://www.csb.gov>.

<sup>4</sup> Agency for Toxic Substances and Disease Registry. "Industrial Chemicals and Terrorism: Human Health Treat Analysis Mitigation and Prevention," 1999.

<sup>5</sup> The Army Surgeon General found chemical plant terrorism to be second only to a major bioterror event. See Eric Pianin, "Study Assesses Risk of Attack on Chemical Plant." *Washington Post*, March 12, 2002. Available online at <http://www.washingtonpost.com/ac2/wp-dyn/A10616-2002Mar11> (visited Mar. 3, 2003).

<sup>6</sup> National Infrastructure Protection Center, "Homeland Security Information Update," February 12, 2003.

<sup>7</sup> Carol D. Leonnig and Spence S. Hsu, "Fearing Attack, Blue Plains Ceases Toxic Chemical Use." *Washington Post*, November 10, 2001, Page A01.

<sup>8</sup> James Belke, U.S. Environmental Protection Agency, "Chemical accident risks in U.S. industry – A preliminary analysis of accident risk data from U.S. hazard facilities," September 25, 2000.

<sup>9</sup> Energy Information Association, "International Energy Annual, 2001 Edition," released February 2003. Available at <http://www.eia.doe.gov/emeu/iea/table36.html>.

<sup>10</sup> Adam Fifield, "In the Shadow of Danger: The Chemical Plant Peril How Safe, How Secure?" *Philadelphia Inquirer*. April 20, 2003.

<sup>11</sup> "Hydrofluoric Acid: Chemical Safety Information," Environment Health and Safety at University of North Carolina. Available at <http://ehs.unc.edu/pdf/HydrofluoricAcid.pdf>.

<sup>12</sup> Bruce Scott, "Alkylation Process Hazards Management: Does it Matter Which Acid You

Use?" Presented at the 1991 Alkylation Seminar. May 1991.

<sup>13</sup> "Toxicological Profile for Fluorides, Hydrogen Fluoride, and Fluorine." Agency for Toxic Substances and Disease Registry. Available at <http://www.atsdr.cdc.gov/toxprofiles/tp111.html>.

<sup>14</sup> National Institute for Occupational Safety and Health, "Immediately Dangerous to Life and Health Designation," <http://www.state.nj.us/health/eoh/rtkweb/1014.pdf>.

<sup>15</sup> "Hydrofluoric Acid: Chemical Safety Information," Environment Health and Safety at University of North Carolina. Available at <http://ehs.unc.edu/pdf/HydrofluoricAcid.pdf>.

<sup>16</sup> If sulfuric acid is used, the reaction chamber must be refrigerated to sufficiently remove excess heat; hydrofluoric acid requires water cooling towers to cool the reaction chamber.

<sup>17</sup> Bruce Scott. "Alkylation Process Hazards Management: Does it Matter Which Acid You Use?" Presented at the 1991 Alkylation Seminar. May 1991.

<sup>18</sup> DuPont fact sheet, "H<sub>2</sub>SO<sub>4</sub> vs. HF." Available online at

[www.stratco.dupont.com/alk/alkylation\\_03.html](http://www.stratco.dupont.com/alk/alkylation_03.html)

<sup>19</sup> Fred Millar. "Too Close For Comfort." *Friends of the Earth*. Winter 1991.

<sup>20</sup> Database downloaded by Right-to-Know NET, February 2003. Available at <http://d1.rtknet.org/new/erns/>.

<sup>21</sup> Adam Fifield, "In the Shadow of Danger: The Chemical Plant Peril How Safe, How Secure?" *Philadelphia Inquirer*. April 20, 2003.

<sup>22</sup> United States Chemical Safety and Hazard Investigation Board. Chemical Incident Report Center. "Local Refinery Accident Sends 13 to Hospital." 4 March 2003. Accessed online [www.csb.gov](http://www.csb.gov)

<sup>23</sup> Adam Fifield, "In the Shadow of Danger: The Chemical Plant Peril How Safe, How Secure?" *Philadelphia Inquirer*. April 20, 2003.

<sup>24</sup> Adam Fifield, "In the Shadow of Danger: The Chemical Plant Peril How Safe, How Secure?" *Philadelphia Inquirer*. April 20, 2003.

<sup>25</sup> Adam Fifield, "In the Shadow of Danger: The Chemical Plant Peril How Safe, How Secure?" *Philadelphia Inquirer*. April 20, 2003.

<sup>26</sup> Don Steward and Sandi McDaniel. "Danger Adrift: Chaos reigned after Sun Co. Spill." *Tulsa Tribune*. April 28, 1988.

<sup>27</sup> Adam Fifield, "In the Shadow of Danger: The Chemical Plant Peril How Safe, How Secure?" *Philadelphia Inquirer*. April 20, 2003.

<sup>28</sup> Theodore Karasik, "Toxic Warfare," RAND Project Air Force, 2002.

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<sup>29</sup> Theodore Karasik, "Toxic Warfare," RAND Project Air Force, 2002.

<sup>30</sup> Theodore Karasik, "Toxic Warfare," RAND Project Air Force, 2002.

<sup>31</sup> John Tedesco, "Thief breaks refinery security: Two workers lose wallets," *San Antonio Express-News*, February 16, 2002.

<sup>32</sup> Theodore Karasik, "Toxic Warfare," RAND Project Air Force, 2002.

<sup>33</sup> Carl Prine, "Lax security exposes lethal chemical supplies," *Pittsburgh Tribune-Review*, April 7, 2002, and "Companies respond to infiltration of facilities," *Pittsburgh Tribune-Review*, May 5, 2002.

<sup>34</sup> Water mitigation systems are designed to cool nearby liquid petroleum gas containing vessels and columns to insure their structural integrity and to reduce hydrogen fluoride vapors if a leak were to occur. For water mitigation systems to effectively reduce hydrogen fluoride vapors in the event of a leak, sensors to detect the leak must be installed.

<sup>35</sup> Bill Walsh, "Toxins Make Local Plants Possible Target for Terrorists," *Times-Picayune*, July 6, 2003.

<sup>36</sup> Testimony of Amy E. Smithson, Director, Chemical and Biological Weapons Nonproliferation Project, Henry L. Stimson Center, before the House of Representatives Committee on Transportation and Infrastructure Subcommittee on Water Resources and the Environment, November 8, 2001.

<sup>37</sup> It is important to note that not *all* people living within a vulnerability zone could be affected by a single chemical release; those living downwind during a chemical release are most likely to be affected.

<sup>38</sup> Risk Management Plan, EPA Database, 10 July 2003.

<sup>39</sup> Adam Fifield, "In the Shadow of Danger: The Chemical Plant Peril How Safe, How Secure?" *Philadelphia Inquirer*, April 20, 2003.

<sup>40</sup> This number is not the aggregate of all the state totals, but rather takes into account the possibility of overlapping vulnerability zones. For this reason, this estimate is most likely much lower than the actual population at risk.

<sup>41</sup> Adapted from N.A. Ashford, Gobbel, J.V., Lachman, J., Matthiesen, M., Minzner, A., and R.F. Stone, *The Encouragement of Technological Change for Prevention Chemical Accidents: Moving Firms from Secondary Prevention and Mitigation to Primary Prevention*. Cambridge, Massachusetts: Center for Technology, Policy,

and Industrial Development, Massachusetts Institute of Technology, Boston, 1993

<sup>42</sup> Milton Lapkin and Sanford Lewis. "Boosting the First Line of Defense: Report of the Good Neighbor Project for Sustainable Industries." Available at <http://gnp.enviroweb.org/hfexec.htm>.

<sup>43</sup> E.H. van Broekhoven, "A New Solid Acid Isobutane Alkylation Technology AlkyClean." *Catalysts Courier*, September 2001.

<sup>44</sup> "Alkylene™ Process." Technical Data Sheet. Accessed 14 July 2003. [www.uop.com/refining/](http://www.uop.com/refining/)

<sup>45</sup> The catalytic reaction using hydrofluoric acid takes place around 100° F, which only necessitates the use of water cooling towers to maintain an optimum reaction temperature. The reaction to produce alkylate using sulfuric acid is optimized at 45°-50° F (7°-10° C), requiring refrigeration to maintain the optimum reaction temperature.

<sup>46</sup> "Spent Acid Regeneration: Sulfuric Acid." Fact Sheet provided by *Enviro-Chem Systems a Monsanto Company*. Accessed online 22 July 2003. [www.enviro-chem.com](http://www.enviro-chem.com)

<sup>47</sup> Randy Peterson, Alkylation Division at STRATCO, telephone interview on July 21, 2003.

<sup>48</sup> The distillation section of the alkylation unit neutralizes any acid leaving the reaction chamber with the alkylate.

<sup>49</sup> Randall Peterson, "The STRATCO® Alkysafe™ Process: Low Cost Conversion/Expansion From HF To H<sub>2</sub>SO<sub>4</sub> Alkylation." Available online at [www.stratco.dupont.com](http://www.stratco.dupont.com).

<sup>50</sup> Randy Peterson, Alkylation Division at STRATCO, telephone interview on July 21, 2003.

<sup>51</sup> Steven Ackerman, Girish K. Chitnis, and David S. McCaffery, Jr. "ExxonMobil Sulfuric Acid Alkylation Process." Presented at the 5<sup>th</sup> International Topical Conference on Refinery Processing, 10-14 March 2002

<sup>52</sup> Pam Pryor, "Alkylation Current Events" paper presented at the 2001 Alkylation Seminar in Scottsdale, Arizona, November 2001.

<sup>53</sup> Bill Walsh, "Toxins Make Local Plants Possible Target for Terrorists," *Times-Picayune*, July 6, 2003

<sup>54</sup> South Coast Air Quality Management District, "Highly Toxic Chemical to be Phased Out at Valero Refinery," February 7, 2003, available at <http://www.aqmd.gov/news1/hfvalero.htm>.

<sup>55</sup> Bruce Scott. "Alkylation Process Hazards Management: Does it Matter Which Acid You Use?" Presented at the 1991 Alkylation Seminar., May 1991.

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<sup>56</sup> John Holusha, "Chemical Makers Identify a New Hazard," *New York Times*, August 12, 1991.

<sup>57</sup> Sal DePasquale, Letter to Georgia Public Interest Research Group, March 19, 2003.

<sup>58</sup> Resources for the Future, *The Future of Local Emergency Planning Committees*, 1993.

<sup>59</sup> Toxics Use Reduction Institute, Lowell, Massachusetts, available at <http://www.turi.org/turadata/Success/ResultsToDate.html>.