AMERICAN BHOPALS

The Threat of Catastrophic Refinery Accidents and Sabotage to Hydrofluoric Acid Alkylation Units

By

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OFFICER LEO SADOWSKI rolled up his window to ward off the evening chill. He swung the patrol car off the expressway, through an intersection, and up the pleasant tree-lined suburban street. He glanced at his watch: 10:32 p.m. It was awfully quiet, no cars, no people, not even a cat padding across the road. Nothing was stirring, but a dry wind which rustled the leaves along the sidewalks and set the tree branches swaying. What are you complaining about, he asked himself. Usually the problem is too much action rather than too little.

Lights burned in the windows of many of the modest frame homes, but the neighborhood was cloaked in a eerie silence. Was there some kind of crisis, he wondered, that had everyone glued to their television sets, like the night the war against Iraq had started? Crime was down by more than fifty percent that night, he remembered, as even the muggers and crack dealers couldn't tear themselves away from CNN.

He looked over at his partner, Rita Washington.

"What do you think?" he asked.

"I don't know," replied Washington. "They certainly roll up the sidewalks early around here."

"Yeah," said Sadowski. "I don't know what it is, but there's something strange going on." He made a right onto Cherry Street, his headlights reflecting off a low-lying fog clinging to the road and hanging in the trees. "Let's take a look up here."

Moments later, he slammed on the brakes. "Holy Mother of --"

"What is it?"

He flicked on the car's bright lights. Ahead of them, lying near the edge of the road, were two crumpled bodies. Another was sprawled in the middle of the street. A short distance away was a car smashed into a tree, its door open, the driver's limp body hanging out, half in the car, half on the ground. Sadowski could make out yet another body in the driveway of a two-story row house.

"My God," gasped Washington. "What happened?"

"I don't know," said Sadowski, "Call it in. Quick."

Suddenly a figure materialized out of nowhere in the patrol car's headlights. There was a loud thump and a teenage girl ricocheted off the side of the car and, face contorted and gasping for breath, she staggered over to the curb and collapsed.

Washington was out of the car in an instant and at the girl's side.

Sadowski reached for his radio, a strong vinegary smell momentarily filling his nostrils. "This is car Eleven," he said, pressing down the button and speaking into the mike. "We've got a Code Three. Repeat, a Code Three," he informed the dispatcher, using the police code for an emergency.

His eyes began to burn and he blinked reflexively. The vinegary scent had disappeared; in fact, he couldn't smell anything at all.

"Describe the nature of the emergency," the dispatcher's voice crackled on the radio.

In the background, Sadowski heard an undulating industrial warning siren pierce the quiet. The refinery! It was located on a point near the river, little more than a mile away.

"Bodies," Sadowski panted into the mike. His chest felt tight and he was short of breath. "We've got . . . a number of bodies in the street. We need . . . ambulances . . . hazmat team . . ."

Where was Washington? His vision began to blur and he peered across the empty seat, through the open door, looking in vain for his partner. Sadowski's nose was running and he dabbed at the liquid damming along his upper lip.

"Washington!" he called out, wiping away the tears streaming down his cheeks, trying to focus. Then, slowly, two forms materialized in the misty darkness, slumped over, near the side of the street.

With great effort he leaned over and pulled the door on the passenger side shut, and brought the mike to his bluish lips. "Code Thirty," he gasped: officer needs help, emergency. The windows of the patrol car were becoming cloudy and Sadowski felt as though the world was closing in on him.

"What is your location, number Eleven?" came the dispatcher's voice through the static.

He tried to speak into the mike but began retching and gagging instead, the result of esophageal spasms. A red froth formed at his lips. His vision dimmed and soon disappeared altogether, the last slivers of light receding into the distance like a television set that had been turned off.

"Come in, car Eleven. What is your location? Repeat: What is your location?"

There was no response. Sadowski made a last gasp for air as he drowned in the fluid filling his lungs, and he slumped forward against the steering wheel, causing the car horn to blare out angrily.

THE ABOVE SCENARIO IS FICTIONAL, but it could happen. In fact, it nearly did happen just a few years ago in Texas City, Texas.

On October 30,1987, a crane dropped a piece of equipment, damaging a tank containing 35,700 gallons (289,170 pounds) of hydrofluoric (HF) acid and 6,600 pounds of light hydrocarbons, at the Marathon Petroleum Company refinery in Texas City, releasing a cloud of the extremely corrosive acid into the atmosphere. Nearly 4000 people were evacuated as the knee-high silver-colored cloud drifted through a nearby residential area, affecting an area three miles long and a mile wide. In places, HF concentrations reached 50 parts per million (ppm), although in the nearby residential neighborhood affected by the release, the level, fortunately, was probably only a few parts per million. Some of those evacuated lived just 300 meters (less than three football fields) from the damaged HF tank.

Local authorities were slow to respond to the crisis and many of their actions were totally inappropriate. Most of those evacuated, for example, were directed to a community center in the direct path of the plume, only 1.7 miles downwind. The cloud caught up with them and authorities had to evacuate everyone a second time to a school some 4 miles away.

In addition, many experts believe that the scope of the evacuation fell far short of what it should have been. According to Dr. Fred Millar, "We felt a conservative evacuation would have been 70,000 for the three days, on a par with the care taken by officials in Missassaugua, a suburb of Toronto, who evacuated a quarter-million people for a week under the threat of a potential chlorine tank car release after a derailment."[1]

Local officials respond to criticism of their actions by saying that Marathon Oil Company was slow to react to the crisis and did not immediately inform them of the seriousness of the accident at the plant. They also maintain that the company had not impressed upon them the hazards associated with a toxic gas release, and therefore local emergency response plans only focused on fire and explosion contingencies. In other words, they were completely unprepared for the kind of emergency that occurred.

A Near Disaster

There is little debate about the facts of the incident which are well known. At approximately 5:20 p.m., a crane was lifting a process heater convection section over an alkylation unit when it began to teeter precariously. It weighed 189,760 pounds. But someone had made a grievous math error, and the convection section weighed 12,000 pounds more than the crane's maximum load limit. Because the crane was overloaded, it began to topple over and the operator dropped the convection section, which struck the HF tank, shearing off both a 2-inch pressure relief line and 4-inch loading line at the top of the tank, and releasing a dense vapor cloud that began moving in the direction of a nearby residential area. The HF tank had not been emptied, as should always be done when lifting process equipment over a tank containing extremely hazardous chemicals, nor was there an auxiliary holding tank to drain the acid into in the event of an emergency.

From the moment of the accident, everything that could go wrong, did. When the crane toppled, it struck the self-contained sprinkler system that had been designed to "knock down" an errant HF release, putting it out of action. In addition, it also rendered inoperable one of two siren systems, intended to warn plant workers and nearby residents of an emergency at the Marathon facility. The other siren system had been shut off.

It took 44 hours to plug the damaged tank, and officials estimated that approximately 20 percent of the HF and all of the light hydrocarbons stored in the tank escaped into the atmosphere, most of it in the first two hours.[2] Apparently Marathon officials lacked an effective contingency or crisis management plan for addressing the emergency that arose.

According to one report, the assistant manager at the plant site referred to a Du Pont manual in an effort to figure out what to do. During this time, workers at the plant report that they were not given adequate instructions regarding their own safety or properly appraised as to the toxicity of HF. One worker described the scene at the plant as "chaos." Another, Emmett Brown, said that plant employees were ". . . jumping over the fence like mice. The road was filled with people trying to escape the acid."[3]

More than 900 people were treated at local hospitals for various injuries. Dr. Paul J. Papanek, Jr., Chief of the Toxics Epidemiology Program of the County of Los Angeles, investigated the public health impacts of the Marathon Oil Refinery incident three years later. In 1990, he reviewed 121 cases of illness allegedly connected to the HF release, a large number of which involved individuals who had filed legal actions against Marathon. Among the symptoms reported were eye irritation, nose and throat problems, irritation of the upper airway, wheezing and exacerbation of asthma, skin problems, gastritis, nausea and vomiting, headaches, hypocalcemia (low calcium levels in the bloodstream), and problems with anxiety. Indicative of the toxicity of

HF, all of these symptoms occurred despite the relatively low level of exposure most of the victims were subjected to. Indeed, nearly one quarter of those living in the plume path of the release visited a hospital emergency room.

According to Dr. Papanek's report, lawns in the area affected by the plume were seared brown and trees, especially pine trees, were scorched for a distance of 1.5 to 2 miles.[4] Corrosive damage was reported to many homes and vehicles in the same area, including etched and streaked windows on cars and buildings where dew had collected.[5]

According to some experts, "if the accident had released hydrofluoric acid in its more concentrated liquid form instead of gas, the accident could have killed thousands."[6] In Millar's words, "We would have had a Bhopal at Texas City, Texas."[7]

Industrial Disasters

The near disaster was a ominous reminder of the fact that forty years earlier Texas City was the site of the worst industrial accident in American history. In 1947, a ship loaded with ammonium nitrate fertilizer blew up, triggering an explosion at a nearby styrene plant. The following day, yet another nitrate-laden freighter exploded. When it was all over, 576 were dead and 2000 seriously injured.

The Marathon incident came only three years after 2800 (some say the number exceeded 4000) people were killed, and 200,000 were injured, in one of the worst industrial accidents on record, at Bhopal India. On the night of December 3, 1984, forty-five tons of methyl isocyanate, an extremely lethal chemical used in the manufacture of pesticides, began leaking into the atmosphere at a plant operated by Union Carbide, after the failure of a key valve and the fact that five key safety systems were inoperable. Because of favorable weather conditions, the methyl isocyanate eventually affected a twenty-five square mile area. Some of the victims were permanently blinded, others suffered severe respiratory damage, paralysis, and epileptic seizures. The disaster was particularly devastating to the very young and the very old.

And just two weeks before the Bhopal incident, 452 people had been killed, and another 4248 injured, in the explosion of liquefied natural gas (LNG) at a storage facility in Mexico City.

Not a week, or for that matter a day, goes by without some kind of serious industrial accident in some part of the world. Although the United States is a world leader in occupational and industrial safety, train derailments, plant fires and explosions, barge mishaps, and other industrial disasters are still relatively commonplace, and in fact have been on the rise in recent years. Often such disasters are accorded little attention in the media. When an explosion on May 1, 1991, destroyed a large fertilizer plant in Sterlington, Louisiana, killing two, injuring 120, and leaving 7 missing, it received only a dozen lines in *The Washington Post.* An insecticide plant blast in Mexico City four days later, that sickened 500 people and forced the evacuation of 1600, was accorded only 13 lines in the same paper. And an April 4 refinery fire in Lake Charles, Louisiana, that killed and injured more than a dozen people, was described in only 8 lines.

There are what one authority has called hidden "atomic bombs" in most U.S. cities, dangerous industrial processes that can potentially create disasters of major proportions, if improperly managed or intentionally sabotaged. Many of these industrial processes are dangerous because of the chemical substances they employ. In this connection, there are somewhere between five and six million different chemicals. About 6000 new chemicals are discovered every month. Of this total, between 33,000 and 63,000 are classified as hazardous, and they go by 183,000 different names.

According to recent figures assembled by the U.S. Environmental Protection Agency (EPA), ten chemicals account for nearly half of all industrial accidents involving the release of hazardous substances. Sulfuric acid, because of its extensive use, ranks second on this list, along with such chemicals as PCB, anhydrous ammonia, chlorine, hydrochloric acid, sodium hydroxide (lye), and methyl alcohol (methanol or wood alcohol). Because it is not nearly as widely used as the other chemicals, and therefore does not figure in as many incidents, hydrofluoric acid is not included on the list. Nevertheless, it is potentially far more dangerous than many more common chemicals.

Catastrophic Process-Related Incidents

Emergencies such as those described above are called "catastrophic process-related incidents" by the petroleum and chemical industries, and they have fueled a national debate over the safety of many industrial processes that we take for granted and the siting of key facilities employing dangerous technologies and hazardous chemicals. The vast majority of all catastrophic process-related incidents are caused by accidents, poor maintenance, or incorrect operating procedures. However, as the recent conflict in the Persian Gulf made clear, petroleum systems are among the most vulnerable industrial targets to war and sabotage, and for this reason terrorist incidents directed at the petroleum industry are part of process safety management.

Petroleum refinery operations are especially concerned with process safety management when they deal with highly toxic and dangerous materials such as hydrofluoric acid (HF) and sulfuric acid (H_2SO_4), which are categorized as "strong acids."[5] The ruthless use of one of these acids, was recently confirmed in Iraq, where Iraqi helicopters, under the direction of Saddam Hussein, sprayed Kurdish rebels in Kirkuk with sulfuric acid. Because of the extreme toxicity of such acids, the issue of refinery safety and siting has become a major source of contention in many countries where new facilities, especially those employing HF alkylation technology, have been proposed or are on the drawing boards.

Similarly, in the United States industrial safety engineers, the Occupational Safety and Health Administration (OSHA), the Environmental Protection Agency (EPA), unions, environmental groups, state and local governments, and those living in the vicinity of refineries are showing greater interest than ever before in safety procedures and the potential hazards associated with accidental/intentional releases of hydrofluoric and sulfuric acids. Indicative of this concern, the Clean Air Act Amendments of 1990 called attention, in particular, to the dangers of hydrofluoric acid, and as a result the EPA was ordered to undertake a study within the next two years examining these hazards. The final study is due no later than November, 1992.[8]

Serious concern regarding HF's impact on refinery safety also has been expressed in Mexico, Canada, Germany, the United Kingdom, France, and many other nations. In recognition of the dangers of HF, the Mexican government, together with local officials, declared a 1.6 kilometer (1 mile) belt around Quimica Fluor, a HF plant owned in part by Du Pont, as a "zone of public utilization." No new residences may be built in this zone, and the government is discussing the relocation of people already living there.

Refinery Operations

In order to understand and be able to evaluate the potential hazards resulting from a fugitive acid emission in conjunction with refinery operations, it is first necessary to understand refinery operations.

In the early part of the century, petroleum market demand shifted from heating oil to gasoline because of the internal combustion engine and the growth of the automobile industry. As a result of the increased demand, petroleum engineers and chemists developed what was then regarded as the revolutionary catalytic cracking process. In this process, heavy gas oils are subjected to extreme heat (as high as 1050°F) and moderate pressures (no more than 40-50 psig) in the presence of a dust-like catalyst to obtain more of the "light ends" of the barrel, and therefore more gasoline.

After engineers developed the catalytic cracking process, they next attacked the problem of volume loss of the light ends during the process. In this regard, olefins such as butylene and propylene were too volatile to stay dissolved in the gasoline blends and shrinkages of up to twenty-five percent (25%) were not uncommon. One of the most attractive solutions to this problem was the alkylation process, which decreased the volume loss and maximized the amount of gasoline recovered. Today, alkylation is the key process that is used to enhance the octane of gasoline and reduce its pollution effects.

Alkylation is defined as "a process in which high-octane components for gasoline are obtained from the combination of an isoparaffin and olefins in the presence of a catalyst."[9] The alkylation process was first discovered in 1932 using aluminum chloride as the catalyst. However, shortly thereafter it was discovered that sulfuric acid was a more effective catalyst, and the first sulfuric acid catalyzed alkylation unit was put into operation in the late 1930s. The technology was further refined as the result of a joint development effort between four large oil companies and two engineering firms, whose initial goal – as World War II loomed on the horizon – was the development of high octane aviation fuels. The first HF alkylation unit was completed in 1942.

Today, refineries use one of the two acids as catalysts in the alkylation process, although more H_2SO_4 is required than HF to achieve the same result. At the present time in the United States, there are approximately 140 alkylation units utilizing either of the two acids, with sulfuric acid alkylation accounting for 50 percent of the total market. Total production capacity is approximately 1,053,000 barrels per day (bpd) of alkylate. On the average, H_2SO_4 units are used in larger refineries and have a production capacity twice that of HF units: 7500 barrels per stream day versus 3500 barrels per stream day. Because of the growing demand for high-octane gasoline, environmental concerns, and problems licensing new sites, there is a trend toward larger, or so-called "jumbo," units.

Refining industry chemists generally consider that the two acids function similarly as catalysts, and that both are extremely hazardous, requiring the utmost care in handling. Nevertheless, there are some significant differences between the two acids in the area of safety, health, and physical hazards.

Hydrofluoric Acid (HF)

Hydrofluoric acid (HF) is one of the most common industrial chemicals in the world. An English glassworker is credited as having first discovered the substance sometime around 1720, and until the 1930s was used primarily for etching glass and cleaning sand castings. In the 1940s, shortly after it was first commercially produced, refiners started using it as a catalyst in the alkylation process. In addition to being used in the production of high-octane fuels and the polishing, frosting, and etching of glass, it has a variety of other applications, including dissolving ores, acidizing oil wells, cleaning stone and brick, the pickling of copper and brass, and the manufacture of stainless and other alloy steels. (See Appendix 1 for the daily HF alkylate production in the United States.)

It is a very corrosive acid, and corrodes nearly everything but lead, wax, platinum, and polyethylene. In bulk quantities, HF normally is stored in a liquid state by means of pressurization or refrigeration. Most sources suggest that pressurization is preferable since leaks can more readily be detected and dangerous corrosion identified. Corrosion is a major concern, and in their designs engineers seek to minimize the number of connections and joints in industrial facilities using HF.

HF has a very low boiling point and turns into a vapor at room temperature (19.5 degrees Centigrade or 67.8 degrees Fahrenheit).[10] It is more toxic than chlorine, which was used as a chemical warfare weapon by the Germans during World War I, and about one-sixth as toxic as the methyl isocyanate released at Bophal. Ingestion of as little as 1.5 grams can cause sudden death, and external contact with the acid in liquid or vapor form may result in the total destruction of the eyes.

HF is extremely hazardous to health no matter the route of exposure. Extraordinary precautions must be taken by those working with HF in its liquid state. Those handling HF are required to wear neoprene gloves, full face shields, goggles, and neoprene boots. However, if there is an HF leak, a full air-fed acid suit with self-contained breathing apparatus, such as that worn by firemen, or which is connected to an in-plant breathing system, is required. In this connection, one worker described how a small drop hit his arm, and he watched it "smoke" deeply into his flesh, leaving a nasty burn. Indeed, HF burns customarily are deep burns, which destroy many layers of tissue, often penetrating all the way to and dissolving the bone. As one expert put it, "When flesh is destroyed in an HF burn, it is destroyed forever. It does not grow back."

Those with HF acid burns should receive immediate treatment, since any delay is likely to increase the severity of the burn. According to one safety manual, victims should have their clothing removed and then be placed in a shower to wash away any acid residue. Then they should be immersed in ice baths to reduce blistering and the other effects of the burns. "Should blisters form," says the manual, "complete debridement is necessary; all the white raised tissue should be cut away," and ointment applied to the burned area.[11]

Apparently HF burns beneath the fingernails are particularly excruciating. According to the manual, "They may require special treatment, to relieve the pain as well as to prevent infiltration of the HF into the deeper structures with the resulting destruction of tissues which may proceed to bone involvement. The nails may be split from the distal end of the nail bed to allow free drainage."[12]

HF is even more dangerous in its vaporous state since it readily attacks the body's soft tissues and mucous membranes, and can produce tissue dehydration and necrosis. The eyes, mouth, inside of the nose, pharynx, and lungs are particularly susceptible. When inhaled, it can lead to lung congestion and pulmonary edema.[13] As the lungs fill up with fluid, an untreated victim can, in effect, drown in his own fluids. HF poisoning also can produce cardiac arrest.

HF's odor threshold is at 0.5 ppm (parts per million). It has a very acrid smell; some describe it as "vinegary" in light concentrations. In heavy concentrations it destroys the sense of smell. It is capable of inflicting lung injury at 10 ppm, and its IDLH (Immediately Dangerous to Life and Health) threshold is 20 ppm. According to a paper by G. E. Harris and others, at a level of over 50 ppm the vapor "is intolerably irritating and causes damage to lungs; inhalation may result in serious injury."[14] The lowest published concentration causing toxic effects is 110 ppm, and even short exposure at this level causes serious irritation.[15] "At some point, one breath will kill you," observes Dr. Ronald P. Koopman, in testimony before a subcommittee of the House Government Operations Committee. "As the concentrations go down, it takes, then, many minutes, hours, but there is some taint."[16]

Although there has been no catastrophic accident involving HF in the United States, there have been several near disasters, including the Marathon Oil Company incident in 1987. On the other hand, problems with HF are relatively common, and according to the Environmental Protection Agency (EPA) there are hundreds of accidental HF releases, most of them relatively minor, every year. Among the many incidents in recent years was an HF release at the Mobil Oil Company refinery in Torrance, California, in November, 1987. Three explosions rocked the refinery, followed by a fifteen-hour fire and the escape of one-hundred pounds of HF into the atmosphere. Two people were killed and a dozen were injured. The damage to the plant was estimated at $17 million. According to a confidential Mobil Oil Company memo that was released later, three alarm systems and monitoring devices "designed to warn refinery workers of an unsafe buildup of hydrofluoric acid were not working when the accident occurred."[17]

The accidental release of HF at a Sun Refining and Marketing Company facility in Tulsa, Oklahoma, on March 19, 1988, sent 35 people to the hospital. The toxic cloud of HF from the plant even invaded the local police dispatch office. The Phillips Petroleum Company Woods Cross refinery in West Bountiful, Utah, suffered two releases of HF in the space of less than five months. The first occurred in October, 1988, when 1600 pounds of HF escaped from the alkylation unit. In the second incident, in February, 1989, approximately 300 barrels of HF-contaminated wastewater/oil (slop oil) were inadvertently released from a wastewater storage tank.

On March 6, 1991, a pump was being improperly repaired at a Southwestern Refining Company facility in Corpus Christi, Texas, when it began spraying HF. Two workers were killed in the incident and five others injured. Not surprisingly, following the accident the refinery withdrew from the Federal Occupational Health and Safety Administration's Star Program for companies with exemplary safety records. Two Ashland Oil employees were treated at a local hospital following the release of an estimated 250 pounds of HF from its refinery in Ashland, Kentucky, on June 20, 1991.

Sulfuric Acid

Sulfuric Acid (H_2SO_4) is a heavy, strong, oily, corrosive, liquid mineral acid. In its pure form, it is clear and colorless. Non-flammable, it reacts violently with water. H_2SO_4 is the world's largest volume industrial chemical, with an estimated annual consumption of 140-150 million metric tons. It is one of the most useful chemical substances known to man, with literally dozens of major applications. The great majority of all H_2SO_4, or 67 percent, is used in the manufacture of fertilizers, with the balance reserved for petroleum alkylation, iron and steel pickling, uranium ore processing, copper leaching, and the production of batteries, pulp and paper products, industrial explosives, rayon, film, paints, pigments, ethers, and alcohols.[18]

Like HF, sulfuric acid is an extremely hazardous substance. However, by contrast to HF, workers handling H_2SO_4 generally only wear gloves, goggles, and a face shield. If there is a sulfuric acid leak, they also don boots and a "rain suit." H_2SO_4 can be transported by tank car, tank truck, barge or pipeline in simple steel carbon vessels and tanks. Storage facilities should be surrounded by concrete dikes and containment devices. In the event of a spill, lime and caustic are used as neutralizing agents.

In sulfuric acid alkylation units, H_2SO_4 is always in a liquid state. If there is a spill or accidental release, it almost always will be contained in the immediate area, where it can be collected and pumped into a neutralization facility. No toxic gases are formed or released. While anyone who comes into contact with H_2SO_4 in its liquid state is likely to receive severe burns, which could even be life-threatening if not treated, those at risk generally will be workers at the facility where the accident occurs. Under most circumstances, their risk will be minimized by the fact that they are wearing protective apparel.

Extremely high concentrations of H_2SO_4 fumes do pose a health threat, and are capable of shutting down the body's central nervous system, resulting in paralysis of the body's respiratory centers and subsequent death. However, sulfuric acid will not boil unless heated to 625 degrees Farenheit (329 degrees Centigrade), an extremely rare occurrence. In fact, most fresh sulfuric acid storage tanks are open to the atmosphere.

By contrast, HF fumes strongly and is difficult, if not impossible, to control when it is released into the atmosphere. Thus, it has a significantly larger downwind hazard area than H_2SO_4 and it is capable of threatening large numbers of people living in proximity to sites where HF is utilized.

Far more sulfuric acid is required in the alkylation process than HF, chiefly because of differences in the locations of acid regeneration facilities. According to Mielke and Simpson, "on an equal weight basis, approximately 140 times as much sulfuric acid is consumed than hydrofluoric acid."[19] Traditionally, hydrofluoric acid has been regenerated on site at alkylation units employing HF. Spent sulfuric acid, on the other hand, generally has been transported off-site to regional regeneration centers because of the greater capital costs involved in on-site H_2SO_4 regeneration, versus HF regeneration, and the cost-effectiveness of regional regeneration plants. HF's cost advantage in the area of regeneration, however, is rapidly being eclipsed, as will be noted later, by new technological developments.

In summary, the transport of H_2SO_4, even by pipeline, involves some increased risk of spills, although such incidents would be nowhere near as potentially serious as those connected with HF. As Kurata and Smith conclude, "air dispersion modeling indicated that H_2SO_4 releases during transport or from the storage tank would not be significant since H_2SO_4 would pool on the ground and have neglible evaporative emissions."[20]

Acid Releases

Research on the potential hazards associated with accidental or deliberate acid releases indicates that – for all intents and purposes – only HF has the potential for creating a major catastrophe. An H_2SO_4 spill would, in all probability, have an adverse impact only in the immediate vicinity of the spill itself since the acid would remain in liquid form. Once the liquid was contained with dikes or booms, it could readily be cleaned up. By contrast, HF will vaporize and, depending on the wind speed and ambient weather conditions, toxic clouds of HF could travel many miles down wind and represent a catastrophic threat to an extremely large area. Referring to a fugitive HF release, Conrad V. Chester, of the Oak Ridge National Laboratory concluded:

> "Catastrophic rupture of the [HF] alkylation unit tank could conceivably release the entire contents of the tanks, initially liquid on the ground, but very rapidly vapor in the air. If there were no fire associated with the incident opening the tank, evaporation would cool the hydrogen fluoride vapor which would then be carried downwind close to the ground. On a bright sunny day with strong lapse conditions, the contour of the LD-50 would extend a few hundred meters downwind. If the accident occurred at night with a strong inversion and low wind speed the LD-50 contour could extend tens of kilometers downwind. Using actual historical light shifting wind data from the Oak Ridge area, the area coverage of the LD-50 would range from one tenth to a square kilometer to five square kilometers."[21]

The chief problem is that many refineries employing HF are located in or near densely urbanized areas. A single release could have devastating consequences for those living five miles, and even further, from the refinery. According to Fred Millar, "Recent (1986) toxic gas cloud field research has shown that HF plants are much more dangerous, according to the researchers astonishingly more dangerous, to surrounding populations than was previously thought. This means that many chemical facilities in Texas and in the U.S. may be, to put it mildly, 'inappropriately sited.' "[22]

The toxic gas cloud field research Millar is referring to took place at the Department of Energy test facility in the Nevada desert in 1986. Sponsored by private industry, relatively small amounts of HF were released into the atmosphere, and the results stunned scientists. The tests demonstrated that hydrofluoric acid forms a dense, white, roiling cloud of gas that expands rapidly, depending on the wind and ambient weather conditions. The cloud was so dense and damaging to the eyes that anyone caught outside probably could not find their way out. Nor could they, for all intents and purposes, outrun it.

According to scientists who presented a series of six papers on the tests at a 1986 conference in Boston, the first [of six] tests involved the release of 1000 gallons of HF in two minutes.[23] It was the largest and, visually, most impressive test. Extremely high concentrations of HF existed throughout the width of the cloud as well as vertically. Lethal concentrations of HF were discovered as far as 6.2 miles downwind (10 kilometers) from the spill point. The cloud hugged the ground and moved so rapidly, even in relatively calm wind conditions, that it was stated by a conference participant that "a world-class marathon runner would just barely be able to keep in front of the releases at the Nevada test site."

The results from the other five tests, involving smaller releases over longer duration, were consistent with the first. According to Millar, the tests revealed ". . . that the threat from HF was much worse than expected: the downwind gas cloud concentrations of HF were 10 to 100 times greater than predicted by the previously used air dispersion models."[24]

Prior to the Nevada tests, industry analysts maintained that 80 percent of any HF release would fall to the ground as liquid, instead of remaining in vaporous form. In the six Nevada tests, however, "no liquid was collected on the spill pad. This indicates that practically all released HF became airborne."[25] Thus, the Nevada tests demonstrated conclusively that the problem of HF releases was far more serious than previously believed.

Further evidence of the potentially catastrophic results of an HF release came from a study undertaken by Du Pont. The state of New Jersey ordered Du Pont to project the effects of a total failure of a railroad tank car transporting HF. The study concluded that 186,000 pounds of HF would be released in the first hour, and that toxic levels of HF would be present over a four square mile area.

Refiners using HF have responded with efforts to design water curtains or sprays capable of controlling hydrofluoric acid emissions, together with systems to contain and neutralize the captured acid. The water "knocks down" the HF and keeps it from turning into a toxic vapor cloud. However, follow-up tests in Nevada in 1988 demonstrated that "water sprays must drench the acid in a 40-to-1 ratio of water to acid to reduce toxic fumes by 90% – a comparatively safe level."[26] Even a small leak, therefore, requires an enormous amount of water and, according to some sources, a catastrophic release of HF would take "a virtual Niagara Falls to knock it down." In addition, the mitigation system must completely surround a facility, otherwise wind shifts might permit the HF to escape through gaps in the system. Finally, redundancies are required so that the mitigation system is not disabled by a fire, explosion, sabotage, earthquake, or other cause. In the Marathon Oil Refinery incident, for example, the rudimentary mitigation system that existed at the time was put out of commission by the crane that toppled over.

Many observers wonder if a mitigation system can ever be designed and implemented which effectively will meet all contingencies. Would it not be safer, they ask, to phase out HF in favor of sulfuric acid? There also is the question of whether a 90 percent success rate is sufficient. Even if the mitigation system, under optimal conditions, knocks down 90 percent of an errant HF release, it means that 10 percent of the release will escape downwind and potentially threaten everything in its path.[27] This was the conclusion of a study prepared for the South Coast Air Quality Management District in California. According to the study, "If, on the other hand, it is assumed that emergency control measures are 90% effective the HF release will still result in the IDLH [Immediately Dangerous to Life and Health Level] being exceeded outside the facility."[28] By contrast, the report goes on to conclude that, "In an identical accident involving H_2SO_4, the acid will not volatilize and there are essentially no resultant emissions."[29]

All of the releases in the Nevada tests were relatively minor, simulating small punctures of an HF holding tank.[30] Virtually all would have overwhelmed most existing water spray systems at U.S. refineries. According to research done for the South Coast Air Quality Management District, for example, the Golden West refinery in the Los Angeles basin can handle HF releases no greater than 8 gallons a minute. To put this in perspective, a relatively minor release, such as that which occurred at the Phillips Petroleum Company refinery in Kansas City, Kansas, on February 20, 1976, discharged 1050 gallons of HF in less than an hour when a nipple on a storage tank ruptured, or more than 17 gallons a minute. Many, if not most, refineries outside the United States also lack proper mitigation systems to address corrosive acid leaks or emissions.

Thus, even a proponent of water mitigation systems like Richard W. Prugh is forced to conclude that, "Water sprays can be used to help mitigate accidental toxic and/or flammable gas or vapor releases. However, such systems are often limited in their scope and may not be capable of dealing with catastrophic releases."[31]

The Threat to Populated Areas

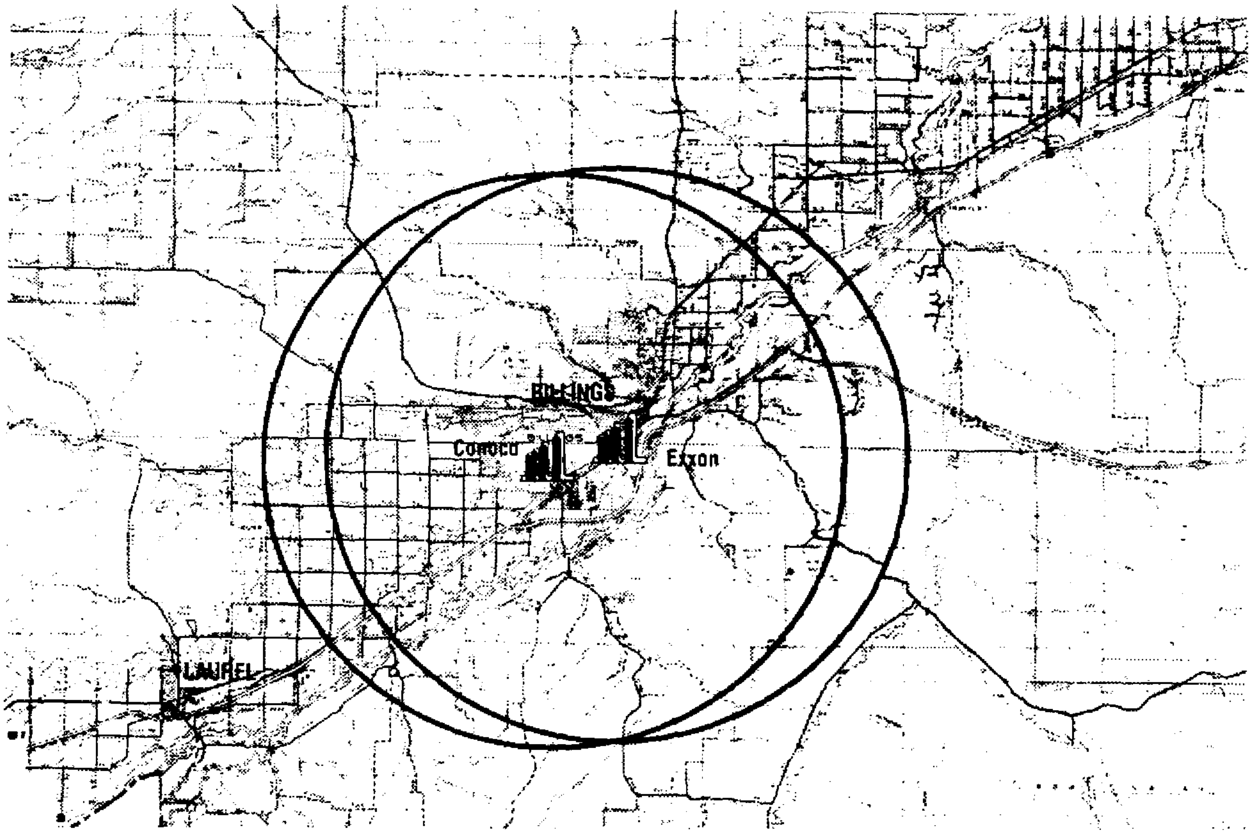
In just 17 metropolitan areas, almost 6 million Americans live within 6.2 miles (10 kilometers) of a refinery with an HF alkylation unit, the distance directly impacted by lethal concentrations of HF in the 1986 Nevada controlled releases. (See Appendix 2 for a list of all HF refineries in the U.S.). Among the metropolitan areas affected are the following:

Metropolitan Region	*Population Living Within 6.2 Miles of HF Refinery*
Los Angeles	1,594,679
Philadelphia	1,059,540
Houston	544,372
New Orleans	532,963
Salt Lake City	337,151
Wichita, Kansas	276,303
Chicago	229,349
Baton Rouge, La.	199,897
St. Paul, Minnesota	155,739
Canton, Ohio	132,813
Port Arthur, Texas	116,751
Corpus Christi, Texas	116,000
Ashland, Kentucky	76,996
St. Louis, Missouri	68,261
Billings, Montana	66,798
Cheyenne, Wyoming	39,852
Duluth, Minnesota	39,852
TOTAL POPULATION IMPACTED =	5,594,747

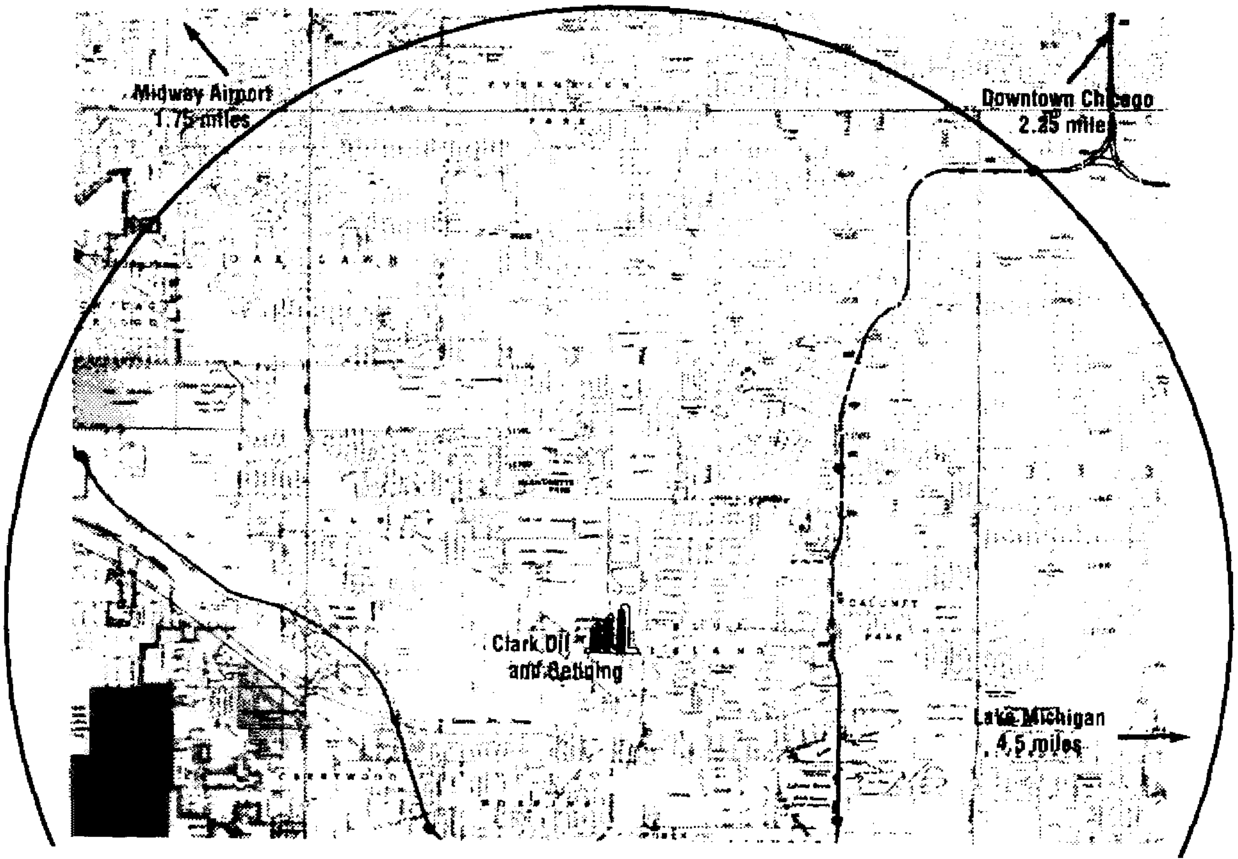
In view of what was learned in the Nevada tests, the populations listed above would be at risk in the event of a major HF release in their respective areas. This is not a matter of speculation, but is predicated on the results of the first test at the Department of Energy test facility in Nevada, in which a relatively small amount – 1000 gallons – of HF was released in two minutes. It also should be noted once again that the six tests in the 1986 series were sponsored, not by opponents of HF, but rather by HF users, manufacturers, and HF alkylation licensors.

Mindful of such considerations, the city of Torrance, California, in the wake of the Mobil refinery explosion, filed suit against Mobil to force it to abandon hydrofluoric acid. The suit was settled out-of-court, with Mobil agreeing to reformulate hydrofluoric acid or, more likely, phase out its use by the end of 1997. Mobil also is required to have a court-mandated special safety master to oversee safety at the refinery.

In a related move, following the incident at the Mobil refinery, the South Coast Air Quality Management District (SCAQMD), in southern



BILLINGS, MONTANA
10 Kilometer potential kill zone (see Nevada tests)



CHICAGO AREA
10 Kilometer potential kill zone (see Nevada tests)