## Chemical Process Safety: Learning from Case Histories

by

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Prepared for Presentation at:

Mary Kay O'Connor Process Safety Symposium

Beyond Regulatory Compliance-Making Safety Second Nature

Texas A& M University

October 26, 1999

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## Chemical Process Safety: Learning from Case Histories with a Focus on Incidents Involving Water & Steam

Water and steam are nearly ever present in most chemical processes. Their physical properties are generally well understood. Periodic process perils are sometimes related to the infamous deeds of water and steam. This paper will review basics on the hazards of water and steam within the chemical and petroleum refinery industries. To the youthful, this chapter can be instructive with eye-opening reality of fundamentals. To more seasoned individuals these case histories can serve as a reminder of the potential hazards of water and steam using vivid examples which were costly in disappointments, dollars, professional reputation and injuries.

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Some years ago, Standard Oil Company (Indiana) published a 70 page booklet entitled <u>Hazards of Water in Refinery Process Equipment</u>. (Reference 1) This booklet appears to be for the bible for hands-on refinery employees and it provides easy-to-understand fundamentals on the hazards. The booklet concludes with these thoughts: "The hazard of water in process units has been present throughout the entire history of petroleum refining. Many persons have been injured or killed because of the uncontrolled mixing of water and hot oil or the heating of bottled-in liquids with no provisions for pressure relief. Stills have ruptured, vessels have exploded violently and exchangers have been blown apart. . . A knowledge of how water reacts, where it can be expected and how to eliminate or control it will make your unit safer and your job easier."

Amoco Oil Company - Refining and Engineering now publishes a 2 inch thick hard bound book entitled <u>Process Safety Booklets</u>. (Reference 2) I highly recommend this book. This Amoco publication is supported with numerous sketches and photos, and incorporates nine previously published, practical booklets: Hazards of Water; Hazards of Air; Safe Furnace Firing; Hazards of Steam; Safe Handling of Lights Ends; and four other topics. It is economically priced at \$ 50 per copy. Copies can be obtained from Mr. Matt L. Smorch, (312) 856 - 7232, or via the mail from Amoco Oil Company, Process Safety Coordinator, Mail Code 1204B, 200 East Randolph Dr., Chicago, IL 60601

Even before refineries, about 100 years ago, poorly designed, constructed, maintained and operated boilers along with water's evil twin - steam were responsible for thousands of boiler explosions. Between 1885 and 1895 there were on average over 200 boiler explosions a year. During the next decade, which spanned the turn of the century, things got worse. (Reference 3)

In the ten year period from 1895 to 1905, there were a reported 3,612 US boiler explosions, an average of one a day. The human suffering was worse. Over 7,600 individuals (or on average 2 people a day) were killed between 1895 and 1905 from boiler explosions. The American Society of Mechanical Engineers (ASME) introduced their first boiler code in 1915 and other major codes followed during the next 11 years. (Reference 3) Over the next half century as technology improved and regulations took effect, US boiler explosions tapered off are now considered a rarity. Equipment damages resulting from problems with water and steam still periodically occur.

The fundamentals of the sometimes destructive nature of water and steam within a chemical plant or petroleum refinery will be discussed and illustrated via case histories. Seven sketches of incidents will be reviewed. An improperly conducted hydrotest creates \$35,000 more unanticipated repairs. An 82 foot (25 m) tall distillation column is accidentally filled with water and while the column is quickly drained, it suddenly collapses and topples. A 73 % caustic soda tank is partially filled with water to clean it

and a steam/caustic mix erupts from the vessel. Steam is improperly is applied to a chlorine cylinder and an ammonia cylinder in separate incidents. A brand new refinery coker is being steamed out in a pre-start up activity and as the steam condenses, the vessel catastrophically collapses. A tragic explosion and fire occurred in a fluid catalytic cracking unit during a startup after a turnaround when superheated oil is allowed into a vessel which had accidentally accumulated water.

## A Hydrotest Goes Awry

On a summer evening in 1996, a Gulf Coast chemical plant had just rejuvenated a recovery tank and was performing the hydrotest when things went wrong. The poorly executed test added \$ 35,000 to the repair costs. Destructive hydraulic forces of mild mannered water were displayed in a classic style. There was embarrassment, but no one was injured. In the previous three weeks this tank had received repairs consisting of a new floor and new walls in the lower section.

The metallic victim was a vertical API 620 tank that is 12 feet (3.66 m) in diameter and 20 feet (6.1 m) high with a 16,900 gallon (64,200 L) capacity. The flat-bottom, domeshaped roof vessel was designed for a 12 psig (83 kPa gauge) maximum allowable working pressure rating. Environmental regulations required a hydrotest at the conclusion of the extensive repairs to ensure fitness for service.

While preparing for the test, two mechanics blinded a six inch (15 cm) pressure relief flanged top mounted nozzle. The craftsman also capped two smaller nozzles on the tank roof with flanges. These smaller nozzles normally were equipped with a pressure gage and a utility hose coupling.

The mechanics connected a fire water hose (1 1/2" diameter and 50 feet long) to the tank to fill it quickly and effectively from a hydrant. The normal firewater system pressure was 135 psig (932 kPa gauge). Next, they opened two 1/2" pipe vents on top for air bleeds. They opened the hydrant, as a strong rain shower began, The crew walked away from the job temporarily.

When the maintenance crew returned to the job site a short time later, they observed a water stream forcefully squirting from the two 1/2" vents. They noticed this normally vertical tank leaning at a slight angle. The bottom bulged upward at the bottom-to-shell joint as much 8 inches (20.3 cm) above the foundation. Anchor nuts ripped through the anchor chairs, and catwalks attached to the tank roof had torn away from welded clips.

# (Four vivid photos of damage to this tank can be found in the Chemical Process Safety book.)

In the past at this section of the plant, chemical process operators (not maintenance mechanics) handled the tank filling step in the hydrotest process. Typically, operators would drape a fire hose into an oversize roof nozzle and fill the tank from the nearest hydrant. In this case, it was reported the two mechanics asked their maintenance supervisor if they could connect the hose to a flanged lower valved nozzle on the tank. The supervisor remembers requesting the mechanics to roll a blind flange at the top for venting purposes if they used the lower nozzle for filling. There must have been poor communication. Obviously the mechanics failed to understand the dynamics of the filling operation, when they chose to open only the two 1/2" top vents.

Two 1/2 inch diameter pipe openings provided only 0.46 square inches of relieving area. These openings were sufficient for the air being expelled, but not for the water that would follow. A Loss Prevention Engineer calculated the flow of fire water from a 135 psig supply through 50 feet of 1 1/2" hose and into the low-pressure tank. During the initial filling as air was being expelled an effective orifice area of only 0.09 square inches was required in order to keep the system pressure below the maximum allowable vessel rating of 12 psig (83 kPa gauge). Once the air was displaced and water was flowing out the tank a relieving area of 2.5 square inches was required. The required relief area was about five times the area of the openings provided.

Total restoration costs were about \$35,000. Foundation repairs including resetting the anchor bolts and other support work cost about \$5,000. An additional \$30,000 was spent to lift the tank, fabricate and install a new tank bottom, reinstall and reconnect the pipe the vessel.

## Afterthoughts on Hydrotest Incident

The mechanics in this area wanted to do a good job and this incident occurred. How can you impress upon the craftsman the weaknesses of low-pressure tanks? The maintenance superintendent in this area wanted practical training to reduce the probability of a repeat. Concerned supervision scheduled 100 mechanics in this section of the plant to a "tender tank" presentation patterned after the Institution of Chemical Engineers Hazard Workshop Module "The Hazards of Under and Over-Pressurizing Vessels". (Reference 3) Procedural changes for hydrotests were also made.

## A Flooded Column Collapses, as Water is being Drained from the System

Late one night, a vacuum created by a fast draining stream of water helped wreck an improperly protected distillation system. Around midnight, during some pre-op steps, operators had determined a leaking water valve had accidentally flooded two idle columns in a distillation system. A destructive vacuum condition was created while draining and pumping water from the system. The vacuum sucked in the lower section of the stripper column walls. As a result, the 82 foot (25 m) tall stainless steel vessel toppled over to a vacant piece of property. It missed other expensive, hard-to-replace, critical equipment including some adjacent tubular reactors and a similar nearby reabsorber. No one was injured; there was no fire or significant release.

This case history has been reproduced with the kind permission of the American Institute of Chemical Engineers. Copyright 1993. It first appeared in "Don't Become Another Victim of Vacuum" Chemical Engineering Progress, 1993. All rights reserved. (Reference 5)

The stainless steel stripper column stood about 82 feet (25 m) tall, which included a column skirt base of about 15 feet (4.6 m) tall. The stripper collapsed in the lower 9-ft

diameter (2.7 m) section just below the conical transition section that tapered down to connect with the upper 5-1/2 ft (1.7 m) diameter section. The vessel was designed to operate about 5 psig (34.5 kPa gauge) and was mechanically rated for about 25 psig (173 kPa gauge).

At the time of the incident, the operating team was preparing to simulate operations by circulating water in the system. Shortly after midnight, operators noticed water coming from the reabsorber vent. Pre-op engineers concluded that water had flooded both the stripper and the reabsorber. They later determined that a leaking the recycle water valve was the culprit which had filled the system. (Reference 5)

The vent line from the stripper was designed to connect to the reabsorber feed line and the reabsorber had an atmospheric vent. When the reabsorber is flooded, the vent line from the stripper could not provide vacuum relief because it was not in the normal gas service. Vacuum relief devices were not originally provided on the stripper.

Figure 1 A Stripper Column Catastrophically Collapses (Courtesy of Guido DeJesus.)

(A sketch of the system containing this 82 foot tall stripper can be found in the Chemical Process Safety book or in Chemical Engineering Progress, September 1993, page 55.)

The crew decided to open the drain valves on the 3-inch (7.6 cm) suction lines from the reabsorber and stripper bottoms pumps. About an hour later, when the level in the reabsorber reached about 75% the crew closed the suction drains valves. They continued by operating the feed stripper bottoms pump creating an even greater partial vacuum. About 10 minutes later at 1:15 a.m., an employee observed the column slowly start tilting, and then toppling from the vertical position. By the time the stripper dropped to a 45° angle, the eye witness reported it was falling very fast.

No one was injured; there was no fire or significant release. After this incident, the operating company had vacuum breakers installed on all of the vessels in this process that

were not designed for full vacuum. In addition, they rerouted the stripper vent line. Operations started up without this stripper and operated for nearly a month while a new column was built in the US on an emergency basis to be air lifted to the Caribbean Island. (Reference 5)

## Water Reacting with Strong Chemicals

The Hazards of Water. . . booklet (Reference 1) reviews the risks of mixing of strong acids and water. In part, it states that the basic chemistry lab maxim: POUR ACID IN WATER - NEVER POUR WATER INTO ACID should be observed. It should even be more important when applied to the large quantities of acids in refineries and chemical plants. Serious overheating or dangerous eruptions of acid can occur if you add water or water solutions to strong acids. And the dilution of some strong acids by water makes the acid more corrosive.

Some operators who have been asked to wash out and prepare vessels for inspection or repairs understand these problems. Energetic reactions are likely with strong sulfuric acid, some salts like calcium chloride and some alkalis. A violent eruption of steam and dilute caustic soda occurred when a preparing 73 % caustic soda storage tank for maintenance. This incident appeared in the British Loss Prevention Bulletin about a decade ago. (Reference 6)

Observant operators discovered a small caustic soda seeping leak at the bottom of 20 foot (6 m) in diameter storage storage/ tank car shipping tank in a somewhat congested spaced tank farm. The tank was oozing 73 % caustic soda at 250 °F (121 °C). Maintenance was promptly scheduled but the tank had to be emptied and cleaned.

To quickly empty the tank, the Shipping Department had intended to load a number of rail tank cars with the hot 73 % caustic soda from the leaking low-pressure, flat-bottom, straight-sided tank. Tank cars were to be loaded during the day and evening shifts. The evening shift chemical process operators were left written instructions to dilute the remaining soda with hot (140 °F or 60 °C) water as the first step in a cleaning and

clearing process. This 73% caustic readily freezes if you do not keep it hot or dilute it during a tank clearing process.

The Shipping Department loaded one less rail tank car than the operations foreman anticipated. Much more caustic soda remained in the tank than the operations supervisor expected when he wrote the tank clearing instructions. There were perhaps 90 tons of 73% caustic soda remaining when operational supervision believed only a small heel would be left.

Operations followed the instructions in the Log Book and started adding hot water to the vessel. It took about 11 hours to increase the tank level by 11 feet (3.4 m) with hot water. The operator completed adding the prescribed amount of water early in the morning approaching 5:45 a.m. About 15 minutes later, the operator opened up compressed air valve to the lance to "roll" or mix the contents within the tank as the Log Book instructions directed. The caustic soda was about 250 °F (121 °C) (well above the boiling point of water) and mixing of water and strong caustic soda solutions is strongly exothermic.

Thirty minutes later, about 6:40 a.m., the tank started making a roaring sound like a jet plane. The vessel buckled upward and a mixture of steam and diluted caustic blew out of the large manway shooting up 25 meters (80 feet) in the air. The explosive release only lasted about 30 seconds, and was followed by non-violent steaming for an additional 30 minutes. (Reference 3)

Violent boiling spewed several tons of caustic soda droplets from an open manway on the roof of the tank. These droplets rained down in the vicinity of the tank and traveled downwind inside the plant. A light wind carried the caustic soda over rail cars on a nearby in-plant railroad spur and further to employee automobiles in the several acre chemical plant's main parking lot. Corrosive chemical fallout was detected over 2 kilometers (1- 1/4 miles) away. The Plant Emergency Brigade used fire hoses to wash down the affected areas. Thirty rail tank cars required a new paint job and some of the employees' cars required cosmetic repairs. Property damages for repainting rail cars and other clean up totaled over \$ 125,000 (US - 1985). Although, there were no serious injuries, a female employee in the parking lot received enough caustic droplets in her hair to require a visit to the beauty parlor. If this incident had occurred about 30 minutes later, the day shift would have been arriving and there would have been a potential for more injuries as the parking lot filled with activity.

## Afterthoughts on Water Wash of a Caustic Soda Tank

After this embarrassing and potentially dangerous incident, management implemented two new procedures.. Precise operating procedures were issued for diluting caustic soda solutions. The procedure required air-rolling to be simultaneously started during any water addition, so only a little material at a time can release the heat of solution.

## Easy-to-Use Steam Heat Can Push Equipment Beyond Safe Design Limits -Chlorine Cylinders

Loss Prevention Engineers and Safety Professionals have repeated stories in Louisiana about the misapplication of steam on one-ton chlorine cylinders. Two similar stories were discussed at inter-plant loss prevention meetings a couple of decades ago. Naturally, the details are now a little vague but the stories were from companies located over 100 miles apart in two separate petro-chemical sections of the state.

Processes that have requirements for low flow rates of chlorine can purchase chlorine in 150 pound and one ton cylinders. These containers are very robust and industries have safety used them for decades. The one-ton cylinders are 2 1/2 feet (0.75 m) in diameter and just under 7 feet (2.1 m) long with extended cylinder walls to protect the valves. Chlorine ton-cylinders are hydrotested at 500 psig (3450 kPa gauge).

Chlorine can be provided from the ton cylinders as a liquid or a gas. The discharge rate depends on the pressure within the cylinder and this is a function of the temperature. In order to withdraw gas, you must vaporize liquid chlorine. Withdrawal tends to reduce

the temperature and hence the vapor pressure and the surrounding air must supply sufficient heat boost the vapor pressure. Typical maximum discharge rate for a one ton chlorine cylinder in a 70 °F environment is about 15 pounds per hour.

When you withdraw chlorine gas from a chlorine cylinder at a rapid rate, the cylinder will cool down. Some companies who need to boost the gaseous chlorine flow rate have placed warm water spray or utility water on the cylinder to add a well-controlled heat input on cool days. However, some individuals were reported to have become more creative and blew live steam via a hose to even further increase the rate of vaporization. That would seem like a good idea, unless you took the time to read the precautions.

Each chlorine ton cylinder has three fusible plugs on each end of the tank to protect it from over temperature. These plugs are designed to melt between 158 °F and 165 °F (70 to 74 °C). They are designed to protect the tank from overpressure if the cylinder is accidentally exposed to fire or other sources of excessive heat. In fact, if you accidentally heat steel containing chlorine to over 483 °F (250 °C), a steel in chlorine fire can be ignited.

The protection philosophy seems to be to protect the cylinder from over pressure by protecting it from over temperature which would vaporize the liquid chlorine. Each of the fusible plugs is in a 3/4 inch threaded plug. If the fuse melts the resulting hole is about 11/32 inch in diameter.

Stories from plant safety professional indicate that live steam was exhausted on the cylinders to make a crude vaporizer to increase chlorine flow. The frightful result was more chlorine, but it was to the atmosphere not to the process. There were no reports of injuries when these memorable stories were told.

Easy-to-Use Steam Heat Can Push Equipment Beyond Safe Design limits -Ammonia Cylinder An ammonia cylinder catastrophically ruptured in a medium sized plant on a summer's evening and two employees required hospitalization. There was no fire and the automatic sprinklers were not triggered into action. There was extensive damage to small pilot plant like operation and the small metal building (approximately 20 feet wide by 30 foot long) that housed the operations. The catastrophic rupture blew most of the metal sheeting from the steel frame on one side of the building. Some structural damage occurred, all glass in windows shattered and engineering estimated the damages to be over \$50,000 a couple of decades ago.

The operation used ammonia from a 150 pound cylinder. For over eight years, this unit used steam to heat the ammonia cylinder. To provide the heat, the unit had a practice of wrapping a length of copper tubing around the cylinder. The tubing was connected to a 15 psig (1 bar) steam supply that flowed around the cylinder and exhausted from the pinched end of the tubing. The cylinder was also loosely wrapped with fiberglass insulation. The purpose of the steam was to ensure a consistent ammonia gas flow with 150 - 200 psig (10 - 13.3 bar) pressure on the upstream side of the regulator. It was seldom necessary to make adjustments to the steam valve in this crude system. None of the plant employees had noticed anything unusual about the cylinder or its installation prior to the incident.

All evidence indicated that the cylinder ruptured due to hydrostatic pressure of expanding liquid ammonia due to excessive heat on the cylinder. Fragments of the cylinder were sent to a testing laboratory for failure analysis. The ruptured cylinder was a full cylinder just put in service. According to the company's literature search, a full cylinder would become hydrostatically full of liquid ammonia at about 130 °F (54.4 °C). If the liquid was further heated tremendous pressures would be developed.

An alternate possibility was that the cylinder was heated to 250 °F (121<sup>o</sup>C) (the steam supply temperature). Raising the temperature that high is unlikely with the crude heating methods and the expected heat losses. However, if the cylinders were heated to a uniform 250 °F (121<sup>o</sup>C) by some method, the internal cylinder pressure could reach

1350 psi (92 bar). This high pressure would generate a very high stress which would closely approach the tensile strength of the cylinder material.

## Heating Water in a Confined System

We have just reviewed the destructive forces created on an ammonia cylinder due to external steam heating. We all need to understand thermal expansion of liquids. I have often heard that heating a completely liquid full container such as piping, a vessel or a heat exchanger will result in tremendous pressures. I always try to ensure that the situation did not happen, by encouraging procedures to avoid the situation or providing over-pressure protection, but did not take the time to calculate the ultimate pressures that could develop.

The *Hazard of Water in Refinery Process Systems* booklet (Reference 1) stated confined water will increase 50 psi (345 kPa) for every each degree (Fahrenheit) in a typical case of moderate temperatures. In short, a piece of piping or a vessel that is completely liquid full at 70 °F and 0 PSIG will rise to 2,500 PSIG if it is warmed to 120 °F. This concept can be better displayed in Table 1 which was adapted from Reference 1, page 4.

Temperature	Pressure
70 ° F	0 PSI
120°F	2500 PSI
170°F	7000 PSI
220°F	13,750 PSI

The Unbelievable Destructive Pressures Developed by Piping that is Completely Full of Water as the Temperatures Increase.

It is difficult to believe these published high pressures from trapped water that has been heated. Perhaps in real life flanged joints yield and drip just enough to prevent sever damages. Overpressure potential of water can be reduced sizing, engineering and installing pressure relief devices for mild mannered chemicals like water. Some companies use expansion bottles to backup administrative controls when addressing more hazardous chemicals such as chlorine, ammonia, and other flammables or toxic handled in liquid form.

## Steam Condenses and a Mega-Vessel is Destroyed During Commissioning

An expanding US petroleum refinery was increasing its petroleum coke production. It has been said that the new corporate owner of this refinery had to drop their plans for a festive formal publicity announcement of the start-up of the unit when a gigantic vessel was destroyed. Project engineers designed, fabricated, installed and were pre-oping four world-class sized coker drums. One of these vessels became a victim of the behavior of water's evil twin steam. A large volume of steam condensed, there were some flaws in design or procedures and the vessel collapsed.

Figure 2 Collapsed Coker Drum in a Refinery. (Courtesy of S. O. Kapenieks)

These gigantic pressure vessels are over 100 feet (30 m) high, 27 feet (8.2 m) in diameter, and the main body was a straight side cylinder 74 feet (23 m) long. The cokers were designed for 55 psig (380 kPa) internal pressure. The coker drum has a dome-shaped top and the lower section is a cone. The lower shell wall thickness was about 0.836 inches (2.1 cm) thick, but the unit was not designed for full vacuum.

The pre-op team steam tested the equipment with up to 50 psig (345 kPa gauge) steam to check for any system leaks. Prior to the steam test, temporary piping 8 inches (20 cm) in diameter was installed to the pre-engineered 24 inch (61 cm) vent to release the steam to the atmosphere. The "A Unit " and the "B Unit" coker shared a common vent line to the atmosphere. Unfortunately, the design of the piping modification created a loop that could collect water as the steam condensed.

The pre-op crew steamed out the "B" Unit first and vented it through the 8 inch steam vent piping. The failure occurred about four days later. An eye witness in the operators' shelter

heard what sounded like a muffled explosion and ran out the back door to see if he could locate fire or smoke. Fortunately, no fire could be seen, but the collapsed coke drum was very visible.

Other witnesses said the coker appeared to be crushed-in like an aluminum beer can being squeezed in the middle. The vessel tore away from levels of decking and was so distorted it was impractical to salvage it.

Further study revealed that the "A Unit" was being steamed-out just after the pre-op crew shut off steam to the "B Unit". The steam in the "B Unit" continued to condense as the unit cooled while steam continued in the "A Unit" for two additional days. The range of the pressure transmitter on the "B Coker Drum" was 0 to 60 psig, therefore it could not indicate a negative pressure.

Evidence indicated that the steam to the "A Unit" was the condensate supply which filled a 27 foot (8.2 m) section of the 24 inch (61 cm) vertical line. The height of the water column is based upon the fact that the internal temperature of the "B Unit" was 144° F.

The investigation team recommended that the vent line be modified to eliminate any possibility of a trap in the vent line. The team also recommended that a low-pressure alarm be engineered and installed to alert the control room operator of low-pressure conditions within the coker drums.

## Afterthoughts on Mega-Vessel Destroyed During Commissioning

Water has the unique ability to expand 1570 times when changing from a liquid to a vapor, and to contract 1570 times when it is condensing. To visualize this dramatic contraction, just think that a typical rail tank car filled with steam at atmospheric pressure could condense to the volume of 10 or 11 gallons of water. (Reference 1) These properties can result in destructive vacuum damage as just shown. The explosive expansion from water to steam can result in a catastrophic incident as the next case history graphically demonstrates.

#### A Tragedy Develops when Hot Oil is Pumped Upon a Layer of Water

An explosion and fire occurred about 11:00 p.m. in a cracking unit on March 3, 1991. Operators were starting-up a world class sized fluid catalytic cracking (FCC) unit after a seven week turnaround for maintenance. During the start-up, a drain valve in the bottom of a pressure vessel was improperly closed, inadvertently allowing water to accumulate in the vessel. When superheated oil was routed into the vessel and it mixed with the water, a steam explosion resulted, catastrophically rupturing the vessel. Oil was propelled from the vessel, was ignited, and the fire engulfed the catalytic cracking unit. After the explosion, plant operators isolated the involved FCC unit and two other similar units at the refinery. The fire burned itself out by about 1:30 a.m. (Reference 3)

Marsh & McLennan's Large Property Damage Losses in the Hydrocarbon- Chemical Industries - A Thirty-Year Review, reported the property damage was \$23,000,000 and the business interruption loss associated with the incident was estimated at \$44,000,000.

A newspaper report stated that one worker saw "a bright flash" shortly before the explosion rocked the area. The article also stated, "The blast rattled windows over a wide portion of South Lake Charles and the fire caused the sky to glow for miles around the Sulphur Plant." (Reference 8) It is tragic that six workers lost their lives and eight other were injured in this incident.

OSHA investigated this incident and applied Process Safety Management (PSM) type standards to the company, despite the fact the PSM Law did not apply to other industries until May 1992. The initial OSHA fine was for about \$8.2 million in proposed penalties and was reduced to a record \$5.8 million for alleged safety violations. The gut wrenching emotions of the company were expressed when a spokesman stated, "You have to understand we are still grieving. The company took the initiative to settle - rather than litigate - because it's time to move forward." (Reference 9)

The settlement also included developing process safety management programs at all of the company's sister facilities and providing OSHA with \$200,000 for industry safety training program. At the time, the \$5.8 million fine was the largest paid in the 20-year history of OSHA. It was also the first major settlement calculated under a seven-fold increase in the maximum civil penalties authorized by the US Congress in November 1990. OSHA cited the refining company for seven violations. Several of the citations were on emergency response procedures & training, but others were on pressure valve inspector training, physical conditions, and written hazard communications program. (Reference 9)

In early July 1991, local newspapers provided detailed accounts of the vessel rupture mechanism. The Vice President of Refining sent a letter each employee and to the local newspapers. The large vertical pressure vessel that catastrophically ruptured was called a F-7 Slurry Drum and its function was to separate heavy oil and catalyst dust. Newspapers explained that the company schedules the three cracking units for periodic maintenance turnarounds once every three years. Furthermore, during these turnarounds the catalytic cracking unit is shut down, oil is drained out and all equipment is cleaned, inspected, and refurbished to be fit for service. A normal startup of a cat cracker is about 48 hours. (Reference 10)

Several local newspaper articles explained that during these start ups, steam is provided to displace any air in the system prior to the introduction of any oil. At the beginning of the startup, temperatures in the unit are cool enough to condense some of the steam into water. Water (steam condensate) collects in the E-1 Fractionator and then pumped into another part of the unit, the F-7 Drum. Under normal startup procedures the operating crew drain all of the water from the F-7 Drum before the hot oil is admitted.

One newspaper quoted the vice president as saying, "For some period of time on March 3 rd, the block valve ... was in the closed position, which prevented water from draining out. As oil began flowing in the reactor and the E-1 fractionator rose to normal operating levels. When the block valve was later opened establishing flow from the bottom of the

F-7 drum, the hot oil . . . came into contact with the water remaining in the bottom of the F-7 drum." The vice president continued, "This water then instantly converted into steam. The enormous and rapid volume expansion of water to steam resulted in an explosive rupture of the F-7 drum, throwing out hot oil which ignited. The drum was equipped with a properly functioning pressure relief valve, but no other pressure relieving device could have relieved the amount of pressure that was suddenly created within the F-7 drum at the time of the explosion." (Reference 11)

When it comes to certain situations like this tragedy, years of excellent operations can be erased with just one case of a superheated oil being routed on to an undetected layer of water. In one of his statements to the press, the vice president stated "This is the first accident of this type in 48 years of operations at the Lake Charles Refinery." (Reference 10)

## Afterthoughts on Steam Explosions

There are many other reports of steam explosions involving hot oil being unintentionally pumped over a hidden layer of water. Water is unique. Many organic chemicals will expand 200 to 300 times when vaporized from a liquid to a vapor at atmospheric pressure. However water has a much higher expansion. Water will expands 1570 times in volume from water to steam at atmospheric conditions. These unique expansion and condensation properties makes it an ideal fluid for steam boiler, steam engines, and steam turbines. However, those same properties can destroy equipment, reputations and lives.

It seems appropriate to conclude this chapter by repeating a quote from *Hazards of Water in Refinery Process Equipment,* (Reference 1) "The hazard of water in process units has been present throughout the entire history of petroleum refining. Many persons have been injured or killed because of the uncontrolled mixing of water and hot oil or the heating of bottled-in liquids with no provisions for pressure relief. Stills have ruptured, vessels have exploded violently and exchangers have been blown apart. . . A knowledge of how water reacts, where it can be expected and how to eliminate or control it will make your unit safer and your job easier."

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