Abstract

The primary objective of this paper is to provide a partial summary of olefin unit accident reports, safety related stories, and safety lessons learned. Literature citations are provided when possible for accidents and related safety issues. The primary goal in developing this paper was to provide a general reference document for use during a HAZOP or similar process safety review of an olefin unit.

Introduction

A critical issue in doing a HAZOP or similar process safety review is past industry experiences in similar processing units. Through information sharing and reviewing our industry history we should be able to prevent, or at least minimize some accident risks. Although not a specific legal requirement, recent US government guidelines strongly suggest that general industry experience be considered during a safety review instead of only considering experiences in one plant location or process unit.

A classic view point of process safety published (1,2) by Mr. Trevor Kletz is that:

a. organizations have a short memory
b. similar accidents occur at other locations
c. a past incident is frequently the cause of a future accident

In the preface of one book (3) Mr. Trevor Kletz states: "The purpose here is to show what has gone wrong in the past and to suggest how similar incidents might be prevented in the future. Unfortunately, the history of the process industries shows that many incidents are repeated after a lapse of a few years."

As people involved in older safety incidents retire or change employment the reasons for some operating instructions and/or design preferences are being lost. In Europe and the United States many olefin units are more than twenty years old. The generation of men who followed many of these units through construction, commissioning, and initial operation have retired, advanced into upper management or left the olefin industry. The frequent rotation of process engineering staff and operations management within a plant complex, or to other plant locations reduces the time available to learn concepts that are specific to an olefin unit. Some people perceive little or no incentive to learn process or unit details not required for the next assignment.

Accident and Incident Information

A majority of the accidents and many of the incidents summarized in this paper have previously been published or shared to some extent within the ethylene community. When possible, I have added background data and follow-up information not initially published. Literature citations have been added at times to provide potential explanations and background theory.

Permission to publish accident related stories is sometimes very difficult to obtain due to potential legal issues or the embarrassment of plant staff. As plants change owners and as staff changes occur some of the recorded history of a process unit may also be lost. A few people see no company or personnel benefit to the review and sharing of an older incident report.

Some anonymous descriptions and stories are included in this paper to provide a greater picture of industry experiences. In some cases the current process engineering staff of a plant may have no knowledge of an accident that occurred more than ten years ago at their plant site. The anonymous stories presented in this paper are frequently based on firsthand reports or accident investigation team members. These stories are believed to be truthful. Some plant specific items have been omitted to reduce the potential for identification of a specific plant or company.

Sources for Published Information

In recent years, Proceedings of the Ethylene Producers Conference has provided a good source of information on several safety incidents, and accident prevention programs. Recently the US government through the EPA and OSHA has been aggressive in the dissemination of accident investigations and related data. For example, the internet provides general access to the "accident investigation report" produced by the EPA, CEPP, and OSHA for the June 22, 1997, fire at the Shell Chemical Company Olefin Unit located in Deer Park, Texas (4-7).

The ammonia industry through the AIChE has a long history of sharing safety and general maintenance information in a published meeting proceeding book each year. Some of the information related to BFW treating, furnaces, methanators, and steam systems is frequently applicable to olefin units.

The refining industry shares and publishes some safety information and experiences in the yearly NPRA Q&A book and sometimes in API documents. The electric power industry through EPRI is a source of information on corrosion, steam generation, piping, turbines, and utility issues.

The National Board of Boiler and Pressure Vessel Inspectors reported 2,445 accidents occured in 1997. These accidents resulted in 18 fatalities and 75 injuries. Human error was linked to 12 of these 18 fatalities. A low-water condition is the leading human-error-related cause of boiler and pressure-vessel accidents. Only 82 of these accidents occured with unfired pressure vessels.

Historical Background

Public awareness of the potential danger from hazardous chemicals and hydrocarbon processing units has increased over the last 15 years as serious chemical accidents have occurred and have been well covered in the press. The 1984 release of methyl isocyanide in Bhopal, India, which directly killed more than 2,000 people focused public attention on the chemical industry. After a chemical plant incident in West Virginia, sent more than 100 people to the hospital and made Americans aware that such incidents can and do happen in the United States.

Public interest in chemical plant safety greatly increased following the October 23, 1989, explosion and fire at a Phillips polyethylene unit in Pasadena, Texas. This accident killed 23 workers and injured at least 130 workers. Total physical damage was estimated at more than $1 billion dollars. The cause of this accident is reported as "human error". Use of contract maintenance staff, training and operating procedures were cited as factors in this accident.

Increased government regulation of chemical plants became good politics following this accident. OSHA officials indicated that: "there are safety problems in the industry, but that most plants do not have the widespread shortcomings and safety inadequacies found at the Phillips plant".

The worst chemical related accident in American History occurred April 16 through 18 in 1947. The French freighter Grandcamp was docked at Texas City, Texas and had been loaded with 2,300 tons of ammonium nitrate. A fire occurred on the ship. This fire could not be controlled and subsequently the ship cargo exploded. At least 516 people were killed, and over 3,000 were injured. Much of the city was destroyed, including about 1,000 buildings and part of an oil refinery. This ammonium nitrate was being sent to Europe for use in fertilizer, as part of a government aid package.

Accident information related to the manufacture and handling of ammonium nitrate had been published in the 1920s and 1930s. During the war years, ammonium nitrate mixed with TNT had been used in "depth charges" and bombs dropped by aircraft. The preferred military explosive was TNT, but TNT production was limited by the availability of toluene that was also being used for aviation gasoline blending. Ammonium nitrate continues to be used as an explosive in large open pit mines and is a basic ingredient in fertilizer blends.

Political Action

Information present in this section is based on published stories, such as reference 39, and does not relate to a personal or specific company viewpoint. Following the Phillips polymer unit explosion, the Occupational Safety and Health Administration called for new mandatory safety standards in the petrochemical industry. OSHA proposed the new guidelines in a report to President Bush outlining causes of the October 23, 1989, Phillips disaster that killed 23 workers and injured another 130. Although the actions proposed in the OSHA report are based primarily on the investigation of the Phillips accident, the agency also considered previous catastrophes in the petrochemical industry.

These safety standards would require companies to analyze hazards in the workplace, ensure equipment works properly, train and inform employees on hazards and develop emergency response procedures. Accidents such as the one in Pasadena, Texas "can be prevented through better safety management, better training of workers, and better response and accountability procedures," OSHA Assistant Secretary Gerard F. Scannell said in Washington.

The proposed guidelines would affect about 2,300 petrochemical plants nationwide. Today, there are no specific industry wide petrochemical safety standards. Rather, individual plants voluntarily follow "recognized industry safe work practices," an aide to Scannell said.

Phillips Petroleum Co. and Fish Engineering were cited for willful violations under general requirements to provide a safe workplace, not for breaches of specific OSHA standards. Fish Engineering was doing contract maintenance work in the plant. Both companies were cited for willful violations under general requirements to provide a safe workplace, not for breaches of specific OSHA standards.

Mr. Gilbert J. Saulter, regional administrator of the Occupational Safety and Health Administration (OSHA) was reported as saying; "We found that had Phillips provided a safe workplace by following OSHA's standards as well as the custom and practices of the industry standards, then the October 23 explosion and fire would not have occurred". Mr. Saulter also stated that OSHA does not plan to refer the case to the Justice Department for criminal investigation because it is not empowered to do that under federal statutes.

Early EPA Legal Action

A critical issue in the legal actions following the 1994 explosion at Terra's Port Neal, Iowa, ammonium nitrate plant was the amount of "generally known" and published ammonium nitrate safety data. The government's accident report was very critical of Terra plant management for not knowing more about ammonium nitrate safety issues. The report stressed that process operators had little formal training and did not fully understand a new DCS package.

The EPA charged Terra Industries for allegedly violating the Clean Air Act (CAA), the Emergency Planning and Community Right-to-Know Act (EPCRA), and the Comprehensive Environmental Response, Compensation and Liability Act (CERCLA). In the settlement, Terra Industries agreed to pay a civil penalty of $500,000 and spend approximately $100,000 on various supplemental environmental projects beneficial to the local community.

Plant Owner's "General Duty"

The 1994 explosion at Terra's Port Neal, Iowa, ammonium nitrate plant became the EPA's first successful judicial action under the plant owner "General Duty Clause". This accident killed four workers, injured 18 in the plant, and forced evacuation of more than 2,500 residents. The explosion released approximately 4,200 tons of anhydrous ammonia and 100 tons of nitric acid. All violations were uncovered during investigations following the explosion. The EPA enforcement action against Terra Industries Inc. represents the first concluded judicial action under the General Duty Clause.

Government Agencies

In response to this public concern about chemical hazards the EPA created a Chemical Emergency Preparedness Program (CEPP) in 1985. Emergency Planning and Community Right-to-Know Act of 1986, also known as Title III of the Superfund Amendments and Reauthorization Act of 1986 (SARA) added reporting requirements that had been voluntary with CEPP.

The EPA, in 1986 also, established its Chemical Accident Prevention Program, integrating it with the Chemical Emergency Preparedness Program. This was followed by the Accidental Release Information Program (ARIP) to collect data on the causes of accidents and the steps facilities take to prevent recurrences. EPA also developed its Chemical Safety Audit Program to gather and disseminate information on practices at facilities to mitigate and prevent chemical accidents.

In recent years EPA programs have focused on:

a. Prevention and preparations for chemical emergencies.
b. Informing the public about chemical hazards in their community.

Recent EPA efforts through the Chemical Emergency Preparedness and Prevention Office (CEPPO) are based on the premise that while industry bears the primary responsibility for preventing and mitigating chemical accidents that many other groups also have a role to play. This has resulted in government agencies, environmental groups, workers, and others gaining access to process plant data during the planning for potential chemical emergencies, and presentation of these plans to the general public.

Legal Requirements

Accurate P&IDs are a critical issue in meeting OSHA "Process Safety Management Regulations". While the term "up-to-date P&IDs" is not specifically stated in the regulation wording, it is strongly implied. In supporting information provided by OSHA the need for "up-to-date P&IDs" is stated. This means that almost every valve and line should be shown in the P&ID set. If items are not shown on the process area P&ID, it is common practice to reference a "typical detail drawing" for items such as analyzer lines, sample systems, pump seal vent systems, steam tracing and similar secondary items. A "management of change" program is also required to be in place to document any changes to the P&IDs (also procedures, chemicals, operating conditions, etc.) after a unit HAZOP or similar design review has been performed.

Good Engineering Practices

The OSHA Process Safety Management regulations state that good engineering practices should be followed. OSHA refers to ASME, ANSI, API, and similar guidelines and recommendations. Many people assume that "good engineering practices" also includes ASTM, NFPA, Factory Mutual, Industrial Risk Insurers and others.

Legal Requirements

OSHA does not have specific requirements regarding ethylene and propylene production. OSHA has extensive general standards regarding training, worker safety for standard plant operations, maintenance, and construction. The EPA and OSHA have very specific regulations for a few specific industries and specific hazardous chemicals.

Safety guidelines developed for large power generation boilers are not frequently applied to cracking furnaces or small fired process fluid heaters. Use of a "fire eye" flare detection system and a related trip is rare in the olefin industry. Safety issues related to combustion air pre-heating and use of both FD and ID fans are not as common in olefin units as in power plant boilers.

Production of high pressure steam in boilers and non-fired heat recovery exchangers is frequently subject to state laws or regulations in addition to OSHA. States typically require that high pressure steam generating equipment be inspected by an independent state certified inspector on a one or two year basis. Some states or local governments require boiler operators to be licensed.

These inspection programs are in part a legacy of a large number boiler accidents and deaths in the 1920s and 1930s as the technology of process control, high temperature alloys, and water treating developed.

HAZOP Review Issues

A hazard and operability (HAZOP) review is an internationally accepted method of examining chemical, gas, and oil processing unit operations that can be illustrated on piping and instrument diagrams (P&IDs). A HAZOP is a rigorous, systematic review of the consequences of process deviations utilizing a team of people with engineering design and operations expertise.

The objective of most HAZOP studies is to critically examine the design of the plant or planned revamp in order to identify any features that would lead to unacceptable personnel safety, operability, equipment damage, business interruption or environmental release consequence. If the design of a specific element is determined to be unacceptable, then one or more recommendations will typically be suggested to mitigate the problem or risk issue.

To make the HAZOP review even more rigorous, a review team may occasionally supplement the basic process review with additional issues such as:

Operability
Mechanical
Safety
Maintenance issues
Instrumentation
Corrosion/erosion

HAZOP Team

The staff (make-up) of a HAZOP team is critical to success of the review process. The review leader must understand the general issues being discussed and know when to terminate a discussion to avoid wasting time or omitting key issues by focusing on trivial matters. Two or more team members should have extensive experience in the type of process being reviewed. A successful safety review frequently includes one or two of the first line operators to share past operating problems, layout issues, and process design concerns.

Successful olefin unit HAZOP reviews have been lead by consultants with refinery and natural gas unit experience instead of olefin plant experience. A person with refinery experience will generally relate well to the olefin unit hot areas. Experience with fired heaters and boilers is critical for both the HAZOP review leader and several members of the review team for a successful cracking furnace area HAZOP review. A person with cryogenic natural gas or LNG experience will generally relate well to the olefin unit cold areas. Experience with dry-out issues, refrigeration, and low temperature distillation is critical for both the HAZOP review leader and several members of the review team for a successful cold area HAZOP review.

HAZOP review team must contain a "critical mass" of people with related industrial experience and basic process knowledge. Sometimes young engineers are successfully used in a meeting "note taking" role, or explaining basic process design data and operating targets. In the case of a company building its first olefin unit, the use of outside consultants and staff training prior to starting a HAZOP review is critical for a productive review process. Observing some or all of a process area review can be a very useful educational experience for engineers and process operators without a formal college degree.

Occasionally a HAZOP review team for a new unit or major revamp will contain one or more people representing the project PMC, local detailed engineering contractor, Bankers, or local government regulators. If the review process includes people with a diverse background, different review objects, or understanding of the chemical industry, then background reference materials are critical to executing an efficient review.

HAZOP Objectives

Members of a HAZOP team must have some critical shared objectives to allow the efficient execution of the process review. A HAZOP review team must be able to rank safety risks and operability issues in order to formulate recommendations for follow-up action. Conducting a HAZOP review of a lump sum process design or a vendor package frequently presents special challenges. The role of a contractor executing a lump sum project is to meet agreed upon specifications and industry standards while making a profit. Client staff frequently wish to make improvements and/or add features for improved operator access, reduced manpower requirements, and to justify spare installed equipment items.

A HAZOP review conducted late in the engineering phase of a new unit project major revamp must consider the philosophy outline in the project "basis of design" documents. Sometimes staff in the HAZOP review meeting have not seen documents outlining a philosophy for blinding, flare size reduction, fireproofing, instrument usage, material of construction, spare relief valves, safety trip selection and similar details. A successful HAZOP review requires that team member agree on basic design principals.

HAZOP Resources

Prior to starting an olefin unit HAZOP review, I recommed that:

a. Team members read reference papers 1 through 6.
b. That copies of these reference papers be in the HAZOP meeting room.

I hope that the olefin related industial accidents discussed in this paper in combination with theory and background data provided by literature citations will aid in conducting future design and safety reviews. I have found that the availability of reference information during the initial discussion or follow-up review of meeting notes improves the team review process and reduces the number of study follow-up items. Tables 1 and 2 provide a summary of olefin related accidents and incidents that are described in the Appendices A and B. Table 3 lists general safety information available in Appendix C.

Published Safety Resources

Table 4 is a listing of safety reference books and accident case histories written or edited by Mr. Tevor Kletz. Mr. Kletz had a long career in the petrochemical division of ICI and was a safety advisor for many years. Books written by Mr. Kletz tend to provide practical information in a straight forward manner to both engineers and process operators.

Tables 5 and 6 list classic safety booklets, I used when learning practical process engineering and plant safety. The 1960s safety booklets listed in Table 5 were developed by an operating company with inputs from many in the chemical and refining industry. These safety booklets were shared with others to promote industry safety. Several of the Table 5 booklets were updated, published, and distributed through the API. Other safety booklets were developed to become part of the API Publication 758, "Safety Digest of Lessons Learned". A listing of API Publication 758 booklets is provided in Table 6. While the booklets shown in Tables 5 and 6 are now "out of print", photocopies are available from several sources. Table 7 lists past EPC papers that could be useful to a HAZOP review team.

Accident Statistics

Accident investigation results presented at the 1994 EPC meeting show that olefin units accounted for 26 of the 170 major hydrocarbon property losses in a 30 year period (27). Olefins unit accidents were 15 percent of the total accidents. Olefins accounted for 19 percent of the economic loss with a total impact of $1.37 billion of the total losses of $7.16 billion dollars. Fire was the initial cause of only 4 of the 26 major olefin unit accidents. A vapor cloud explosion was key in 11 accidents, with explosions being the initial cause of 11 other accidents.

This 1994 paper showed that mechanical failure was the primary issue in 41% of the olefin unit accidents. Operational error accounted for 20% and unknown reasons were cited for 18%.

A 1968 American Insurance Association study of 317 large loss chemical plant explosions and fires in a 20 year period showed the following critical factors (35):

a. Equipment failures were critical in 31% of the cases.
b. Operational failures were key in 17.2% of the accidents.
c. Weak Safety Programs were an issue in 8% of the cases.

Safety Lessons Learned by Others

Past accidents and incidents have influenced design practices of both engineering firms and operation companies. Appendix A and B provides a summary for some of these accidents and incidents. Accidents discussed in Appendix C illustrates similar items in accidents occurring years apart and in different industries.

Information of "vapor cloud explosions" is provided in summaries; A-1, A-3, A-4, A-5, A-7, B-1, B-13, C-1, and C-2. Cold brittle line fractures occurred as part of the incidents discussed in A-1, A-3, and A-4. The accident summarized in A-7 is believed to have been caused by a "sight glass" failure on a cold service vessel.

The accidents summarized in A-2 and B-3 could be related to training or plant safety guidelines. Both of these accidents illustrate that the number of people in near a hydrocarbon leak should be minimized. Human nature causes many people to be interested unusual events. Spectators at an incident or to many people responding to an incident may result in additional injuries or deaths.

Accidents summarized in C-1 and C-2 both relate to maintenance staff experience, training and lack of a detailed task specific procedure. Accident C-1 illustrates that maintenance staff employed by an operating sometimes do not fully understand a repair task when doing work outside of their normal role. Accident C-2 illustrates the issue of using contractor maintenance staff for routine plant actives. In the case of heat exchanger explosions due to NOx, Appendix C-3 shows that this risk was documented well before the cold box explosion at the Shell Berre Olefin Unit summarized in C-4.

Expansion joint failures are presented in stories A-8 and B-14. Incidents A-5 and B-4 relate to large check valves used in compressor systems. Appendix Section C-6 summarizes an EPA/OSHA Press Release about the Accident Investigation Report of the Shell Chemical Company, Deer Park, Texas Explosion and Fire on June 22, 1997. Pump seal related fires in incidents B-3 and B-17 illustrate the value of newer designs that use a double seal with a vent to flare. Incidents B-3 and B-17 occurred in units built before 1980. Incidents B-5 and B-6 related to aging plant equipment and increased failure risk.

Accidents A-1, A-2, A-5, A-6, A-10, A-11, A-12, A-14, C-1, and C-2 illustrate the massive amount of unit damage that can occur from a hydrocarbon leak and fire. Accidents such as A-11, A-12, B-1, and C-2 illustrate the amount of firefighting support sometimes required.

The incident described in Appendix Section A-6 involves an instrument air system problem followed by process operator confusion and a high temperature in a acetylene reactor. The incident described in A-12 relates to an instrument problem in a hydrogenation reactor area.

Incident B-7 describes a major loss of ethylene from a salt dome storage well. Incidents B-8 through B-12 relate to OSBL accidents and risks. Pipeline incidents B-10 and B-11 are very similar, both occurred in the Houston area, and were only 3 years apart.

Facts and Fiction

A key issue in the HAZOP study or similar process safety review is the ability of the review team and/or follow-up team to separate process related facts from fiction. Specific issues such as cold bridle failure risks, furnace decoking, steam drum level control, and hydrogenation reactor high temperature issues are well known to most experienced people in the olefin industry. A few newcomers to the olefin industry believe that highly automated and instrumented plants are safer. Items such as a totally automated furnace decoke system or dryer regeneration system add complexity and instrument maintenance requirements.

The following issues sometimes cause problems during a safety review because the facts versus fiction are not extensively documented or known by people new to the olefin industry:

a. The explosive decomposition of MAPD (a mixture of methyl-acetylene and propadiene) within an olefin unit Depropanizer or C3 Splitter is not a serious risk.
b. Pipeline decomposition of ethylene upon heating alone requires that the ethylene be a super-critical fluid.
c. Vessels and piping exposed to a temperature colder than the low design temperature are not always permanently damaged.
d. Vessels and piping exposed to a temperature higher than design temperature may have a reduced life expectancy and may be permanently damaged.
e. Redundant safety systems are not always the key to safe plant operation.

MAPD Safety

Several olefin units producing polymer gas propylene remove MAPD by distillation instead of hydrogenation. The MAPD is typically recycled with propane to the cracking furnaces. In a few olefin units MAPD is recovered using a solvent such as DMF and exported as a value added product.

MAPD is sold in Canada and the USA in LPG form for metal cutting and welding. MAPD as a liquid has a much lower shipping weight than an equivalent amount of acetylene. MAPD is shipped in cylinders and bullets containing over 1000 gallons. Acetylene is normally shipped dissolved in a solvent such as acetone and shipped in a low pressure cylinder. MAPD is used for underwater cutting and welding because it is much more stable under pressure than acetylene.

Laboratory testing has shown that MAPD mixtures are stable to 100 joules of ignition energy at the extreme storage conditions (68☜C or 154☜F at 220 psig). In this testing, a platinum fuse wire was used as the ignition energy source. MAPD was more stable in mixtures with propylene and propane. The effectiveness of hydrocarbon diluents in stabilization MAPD decreased in the following order: iso-butane > propane > iso-butylene > propylene > butadiene. Like acetylene, methylacetylene and propadiene are stabilized at a specific temperature and pressure by adding inert gas or hydrocarbons that do not decompose under the given conditions.

Within a olefin unit the MAPD concentration is normally below 30 mole percent. Therefore, a MAPD decomposition, by heat alone, would require an external heat source combined with a failure of a pressure relief system. See literature citations 30, 31 and 35 for more information on MAPD safety.

<u>Ethylene Decomposition</u>

The decomposition of ethylene by heating alone and over catalysts has been studied extensively. At least two high pressure ethylene decomposition have occurred in Texas pipelines due to heating by compression. Other incidents have occurred at compressors feeding polymer units, during ethylene drying, dryer regeneration with hot ethylene, ethylene treating over 5A or 13X molecular sieve. See literature citations 7, 8, and 35 for more information on ethylene decomposition and safety related incidents.

<u>Other Decomposition Reactions</u>

Propylene below about 6000 psi does not normally produce an ethylene type decomposition upon heating. Upon heating C4 and higher olefins normally produce polymer (gums, oil, or tar) instead of producing an ethylene type decomposition. I know of only one major C3 hydrogenation incident and this occurred many years ago in a multi-bed vapor phase reactor system.

Papers describing danger and risk of acetylene decomposition have been published extensively. Several acetylene decomposition incidents have occurred due to fires causing heating low pressure acetylene pipelines. Within olefin units that do not extract acetylene for product sale the acetylene concentration is normally well below the explosive limit.

I do not know of any accident specific to acetylene recovery in an olefin unit. After an acetylene hydrogenation reactor accident in Japan, Japanese government policy was to promote the use of acetylene recovery system on the belief that recovery is safer than acetylene hydrogenation.

The decomposition risk of C4 acetylene compounds is well known to those producing a purity butadiene product. An accident caused by C4 acetylene decomposition is described in a series of papers (9, 10 and 11). Within an olefin unit, the concentration of C4 acetylene compounds is normally well below the explosive limit of about 30 mole percent

(35).

Olefin Heating

Heating occurs when olefins such as ethylene, propylene and butene are absorbed on activated carbon, 5A or 13X molecular sieve, and similar materials. The amount of temperature rise is related to the heat of absorption for the material being used and how the olefin is introduced. A "pre-loading" step is commonly used with treating beds in olefin service to minimize the bed temperature rise. Several olefin unit incidents have occurred due to operating error and in one case an operating procedure that did not include a "pre-loading" step. Excessive temperature rises have resulted in absorbent damage, coking, blistering paint on exit piping, and flange leaks.

Most ethylene units use tail gas containing 0.1 to 2 mole percent for regeneration of 3A molecular sieve dryer beds. Over twenty years of experience in numerous plants has shown that provided the regen gas temperature is below 425 degrees F, little coking or sieve damage occurs. In some olefin units, a small amount of carbon dust has been observed in regen gas heaters and downstream piping . Many of these heater used 600 psig or higher pressure steam. In some plants, the steam to these regen gas heaters is 650 to 850 degrees F. These regen gas heaters are typically kept hot to minimize tube sheet leaks related to thermal cycles. Some people believe that rust in these heaters is a catalyst for coke production. One incident of "rust catalyzed ethylene hydrogenation" has been present at an EPC meeting (25).

In remote locations such as salt dome storage wells pure ethylene, in a closed loop, is used for regeneration of 3A molecular sieve dryer beds. Good control of regeneration conditions typically results in a 3A sieve life of 1 to 3 years. As in the olefin unit sieve life is directly related to the number of regeneration cycles. Literature citations 7 and 8 discuss safety issues related to dryer and treater operation.

Laboratory studies have shown that a high temperature 3A, 4A, 5A, and 13X sieve compounds will function in a similar manner to sieve materials used as FCC catalyst. But the sieve crystal matrix suitable for water removal will be damaged during the air burn decoking or regeneration practiced in an FCC unit.

Cold Brittle Failures

All steel contains micro-cracks, in a cold application the critical issue is what occurs at grain boundaries. Cold brittle failures of piping and vessels occur when cracks in the metal's microscopic grain structure propagate into large cracks that may encircle and sever a pipe or create a tear-like opening in a vessel. At ambient temperature, when stress (force) is applied most metals undergo a "plastic deformation". Small cracks within the metal grain structure typically occur during "plastic deformation", but metal strength is not totally lost.

Once vessels and piping operated below the low temperature design point return to the design temperature zone; the risk of a brittle fracture no longer exists provided that stress cracking did not occur at the low temperature. Numerous industry examples exist of piping and vessels, such as an E/P feed drier, that are occasionally exposed to a low temperature with no permanent metal damage. A brittle fracture requires that stress, in the form of internal pressure or weight at pipe supports or similar force be present. Some design codes, such as ASME, specifically address operating piping, vessels and tanks below the normal metal design temperature when the operating at low pressure.

Carbon steel and many of its alloys have a "brittle transition temperature" below which large cracks will occur and progress through a pipe or metal plate. During World War II, some ships built of "low-quality steel" (large grain steel) experienced major hull failures while operating in the cold water and air of the North Atlantic. These ships had no hull failures when operating in the warm air and water of the South Pacific.

Most metals lose some ductility and impact strength as temperature is reduced. In some metals yield and tensile increase as the operating temperature is decreased. Early cryogenic units made extensive use of copper vessels and tubing in heat exchanges because of its ductility and good yield stress to about -300 degrees F. Adding nickel to carbon steel greatly reduces the alloy "brittle transition temperature". Common low nickel steel alloys contain 2.25, 3.5, or 9 percent nickel. Typical USA temperature break points for using these alloys are -75, -150, and -320 degrees F, respectively. The 300 series stainless steels, such as 304, 310, and 316, may be used to -425 degrees with suitable fabrication methods. A 304 steel contains 8 percent nickel and 18 percent chromium and 310 steel contains 20 percent nickel and 25 percent chromium.

A critical issue in use of low temperature alloys is welding and heat treating. The weld metal and welding heat affected zone tend to stress areas where cracks occur. Using the wrong welding rod can cause a 300 series stainless steel weld to experience a brittle failure. Low nickel steel alloys require carefully controlled welding methods as well as a proper "post weld heat treatment" (PWHT). Failure to utilize proper fabrication methods often results catastrophic failures in service or during shop testing. Shop weld failures in low nickel steels is a potential indication of poor welding methods or an off specification base. Reference 36 provides some background on cold brittle failure. Several papers have been presented at EPC meetings on cold service piping and vessel failures, see Table 7 for some references on this topic.

Hot Failures

Failures of furnace radiant and convection section coils due to high temperature operation has been well documented for the olefin and refinery industry. Failures commonly occur due to "creep" a type of plastic like deformation or "stress rupture" as the metal crystal structure changes with time and temperature. The following references provide general information on this topic.

As metal temperature is increased above 600 degrees F the yield stress of many alloys is reduced. Many of the 300 series stainless steels alloys are used to about 1000 degrees F. At high temperature and under pressure a pipe or vessel wall may fail by slowly cracking or fail instantaneously as in a vessel BLEVE (Boiling Liquid Expanding Vapor Explosion) during a fire (38). In general piping life is reduced exponentially with temperature. The amount of time spent at a high temperature is also a critical factor for many alloys. An old training slide summarized this failure risk in the following words; "An elephant has a good memory ... But a furnace tube has a better one! If you let your furnace run 60☜C hotter than design for 6 weeks, you may half the life of the furnace" (38).

In general vessels and piping exposed to a temperature higher than design temperature will have a reduced life expectancy. In some very high temperature exposures the metal structure may be permanently damaged and require replacement.

Redundant Safety Systems

Safety systems such as boiler, cracking furnace, and reactor shutdown (trip) systems are frequently used in process units and power plants to reduce the risk of a major accident. Many older units have operated safely for years without extensive safety trip systems. Ideally a process operator should respond in a timely manner to a process alarm or upset such that no trip occurs.

Automated safety shutdown devices were initially applied to boilers, due to a large number of explosions and fires. At many plant sites, local legal requirements exist for specific trip measurements such as low steam drum level.

In actual operation, many safety shutdowns trade one type of process upset for another that hopefully has a less severe repercussion. Given false inputs to these safety systems can result in equipment damage and/or lost production by creating a process disturbance. Adding voting logic to these trip systems is one way to minimize false trip actions and improve the total trip reliability by providing more than a single field measurement.

Early trip systems used a single air or electronic logic and relay system. The design, check out and maintenance of these systems was occasionally a major problem for operating staff. The "hard wired relay logic" trip systems once through the initial check-out process are very reliable and typically require little maintenance. DCS and PLC based safety shutdown systems are commonly used in modern large process units. These systems generally are lower in cost than a "hard wired relay logic" trip system, easier to design and build using vendor software, and require less field check out time.

PLC Usage

Frequently PLC units used for safety shutdown systems are specified with two of three micro-processors to provide a redundant logic to a system that typically includes multiple inputs and sometimes process measurement voting (2 of 3) logic. Redundant logic is viewed as being critical when a single PLC unit may be used for 4 to 8 cracking furnaces. Redundant logic is also an issue for acetylene reactors, where fast trip action may be required, and when control logic is used to minimize the size of a flare system by applying control actions to numerous distillation towers and several compressors. The number of independent PLC units installed in an olefin unit or similar large plant is frequently a balance between cost and operability.

Problems with PLC Shutdown Systems

I know of two PLC failures in olefin units involving tipple redundant processors. These units were located in different states, had different owners, and used a different PLC vintage. In one plant a second processor developed a problem while a replacement card was on order for another processor. On losing 2 of 3 processors, this PLC activated all its shutdowns resulting in a major unit upset when the acetylene hydrogenation reactors shutdown.

The other incident occurred during the check out of a new PLC just prior to introducing feed to the olefin unit. A PLC vendor representative responding to problems with one processor system installed a software "trouble shooting package". Use of this software package resulted in the short term loss of power to all trip circuits. On loss of signal (power) all trips in this plant were designed to go into fail or trip mode. This PLC shutdown two furnaces on high steam stand-by and vented the acetylene reactor, under nitrogen pressure to the flare header. Had this PLC failure occurred a day later over half of the olefin unit furnace capacity would have tripped off on-line with the potential of furnace coil damage.

PLC input cards and processors are designed for operation in a very limited temperature range and in a dry location. The following incidents have occurred in operating olefin units:

a. Steam leak in HVAC coil results in room heating and water condensation.

b. Ethane/propane rich cracking furnace feed enters control building the HVAC room. A small explosion and fire occurs in the HVAC room. Part of a cinder block wall between the HVAC room and instrument rack area falls down. Some instruments lose power due to wiring damage.

c. Old log reports and computer paper were stacked against the wall in the instrument rack room. Air circulation used IO cabinet cooling was reduced. Random trips occurred and strange DCS process measurements were observed. Modifications were later made to add a fan at the bottom of each cabinet and provide a temperature alarm above the outlet fan on each cabinet.

d. Controller failure results in loss of control and instrument room air conditioning. No manual control by-pass was provided for single large AC unit. Plant staff do not have AC controller spare parts or service manual. Vendor service staff do not have an around the clock "call out" system. Instrument room becomes hot due to heat produced by electronic systems. High temperature alarm sounds in control room. Night shift operators open doors and install "air movers" for cooling. In the early morning, water condensate was observed on DCS and PLC cabinets. The only equipment shutdown caused by water condensate was a PC used to process analyzer data and transfer measurement in engineering units to the DCS.

e. A switch gear explosion occurred in a motor control room resulting in smoke and a minor fire. As designed, HVAC air circulation was stopped to this room based on a smoke alarm. Process operators and later maintenance staff on route to the motor control room repeatedly passed through a room with a UPS unit and instrument input cards. A smoke alarm in the UPS room was activated and stopped HVAC air circulation in the UPS room as designed. After several hours a UPS common trouble alarm occurred. Operation of an electrical bus transfer switch appeared to cause a voltage dip activating several alarms and trips.

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Table 1

Summary of Accidents and Safety Incidents Discussed in Detail

Item	Year	Description
A-1	1975	Explosion in a Naphtha Cracking Unit due to Cold Brittle Piping Failure Followed by Vapor Cloud Explosion at Dutch State Mines, Netherlands
A-2	1990	Flash Fire in Ethane Feed Storage Unit at Indian Petrochemicals (IPCL)
A-3	1965	Explosion and Fire Due to Cold Brittle Flare Line Fracture at PCI Olefin Unit in Lake Charles, La.
A-4	1989	Cold Brittle Line Fracture Results in Gas Leak, Explosion and Fire at Quantum's Morris Illinois Ethane/Propane Cracker
A-5	1997	Cracked Gas Compressor Check Valve Failure Results in Vapor Cloud and Extensive Fire Damage to Shell Chemical Deer Park, Texas, Olefin Unit
A-6	1973	Back-end Acetylene Reactor Incident and Unit Fire at the No. 2 Ethylene Plant of Idemitsu Petrochemical
A-7	1963	Vapor Release and Explosion at Dow Chemical Company's Plaquemine, La. Olefin Unit (Light Hydrocarbon Plant)
A-8	1974	Failure of a Bellows-type Expansion Joint in the Propylene Refrigeration Compressor System at Dow Chemical Co., Plaquemine, La. Olefin Unit
A-9	1996	Ethylene Product Pipeline Flange Leak and Fire Results in the Shutdown Lyondell Petrochemical Company's Two Olefin Units at Channelview
A-10	1994	Fire in Quench Oil Area of Exxon's Baton Rouge Olefin Unit Results in a Major Ethylene Production Outage
A-11	1985	ROW Olefin Unit IV Explosion And Fire is Caused by a Pipe Rupture During Cold Weather Operation
A-12	1985	Fire at Enichem's Priolo, Sicily, Ethylene Plant
A-13	1969	Explosion in Union Carbide Butadiene Recovery Unit Linked to the Decomposition of Vinyl and Ethyl Acetylenes

A-14 1989 Fire Shuts Down Quantum's Morris Illinois Ethane/Propane Cracker

Table 2
Summary of Olefin Unit Accidents and Safety Incidents Referenced

Item	Year	Description
B-1	1977	Vapor Cloud Results in Blast and Fire Damage Brindisl Ethylene Plant
B-2	1985	Fire and Explosions occurred when part of a Wooden Cooling Tower Falls at Esso's Stenungsund Olefin Unit
B-3	1985	Ethylene Product Pump Fire Due to Seal Leakage
B-4	1991	Propane Gas Release in SADAF Olefin Unit
B-5	**	Gasoline Hydrogenation Reactor Wall Failures
	**	This problem has been reported at 3 olefin units.
B-6	1988	Corrosion in a Depentanizer Located Between the First and Second Stage Gasoline Hydrotreating Reactors
B-7	1989	Approximately 7 Million Gallons of Ethylene Escaped from a Salt Dome Storage Well into Adjacent Underground Formation
B-8	1998	Interstate 10 Reopens After Ethylene Tanker Truck Spill
B-9	1998	Fire-fighters Stabilize Trucker's Ethylene Load in Ohio
B-10	1985	Contracted Mowing Weeds Causes Propylene Pipeline Rupture and Fire
B-11	1988	Contracted Mowing Weeds Causes Propane Pipeline Rupture and Fire
B-12	1986	Ethylene Pipeline Fire at Remote Heater
B-13	1988	Shell's Norco Olefins are Shutdown Due to FCCU Blast Damage at Complex
B-14	1966	Flare System Explosion - Monsanto's Chocolate Bayou Olefin Unit
B-15	*	Compressor Deck Lube Oil Fire
B-16	*	Compressor Deck Lube Oil Fire Due to Water in a Steam Header
B-17	*	Pyrolysis Gasoline Fire at a Pump Seal

* Year of incident is unknown.

Table 3

General Accidents and Safety Incidents Referenced

Item	Year	Description
C-1	1980	Vapor Cloud Explosion and Fire Results in the Destruction of an Amoco Chemical Company's Polypropylene Unit
C-2	1989	Vapor Cloud Explosion at Phillips Polyethylene Unit
C-3 *	1962	Hydrogen Recovery Unit - Nitrous Oxide Explosion
C-4	1990	Cold Box Explosion at Shell Berre Due to NOx
C-5	1994	Explosion of Ammonium Nitrate at Terra Industries, Inc. Nitrogen Fertilizer Facility, Port Neal, Iowa
C-6	1998	EPA/OSHA Press Release Accident Investigation Report of the Shell Chemical Company, Deer Park, Texas Explosion and Fire on June 22, 1997

* Accident description and photographs published in 1962.
Date and location of accident is unknown.

Table 4

Safety Reference and Case History Books
By Tevor A. Kletz

Year	Description
1990	Improving Chemical Engineering practices: A New Look at Old Myths of the Chemical Industry
1990	Critical Aspects of Safety and Loss Prevention
1991	Plant Design for Safety: A User-Friendly Approach
1991	An Engineer's View of Human Error
1992	Hazop and Hazan: Identifying and Abscessing Process industry Hazards
1993	Lessons from Disaster - How Organizations Have No Memory and Accidents Recur
1994	Learning from Accidents
1995	Computer Control & Human Error
1996	Dispelling Chemical Engineering Myths
1998	Process Plants: A Handbook for Inherently Safer Design

1998 What Went Wrong? - Case Histories of Process Plant Disasters

Table 5

API Publication 758
Safety Digest of Lessons Learned

Section	Description	Year
1	General Safety Precautions in Refining	1986
2	Safety in Unit Operations	1979
3	Safe Operations of Auxiliaries	1980
4	Safety in Maintenance	1981
5	Safe Operation of Utilities	1981
6	Safe Operation of Storage Facilities	1982
7	Safe Handling of Petroleum Products	1983
8	Environmental Controls	1983
9	Precautions Against Severe Weather	1983

Table 6
Amoco - American Oil Company
Safety Training Series

Book	Edition	Year	Description
1	5	1964	Hazard of Water in Refinery Process Systems
2	5	1964	Hazard of Air (Oxygen) in Refinery Process Systems
3	2	1963	Safe Furnace Firing
4	2	1963	Safe Ups and Downs for Refinery Units
5	2	1962	Hazard of Electricity
6	1	1963	Hazard of Steam
7	2	1964	Safe Handling of Light Ends
8	2	1966	Engineering for Safe Operation
9	1	1964	Safe Operation of Air, Ammonia, and Ammonium Nitrate Plants
10	1	1967	Safe Operation of Refinery Steam Generators and Water Treating Facilities,

Table 7

Some of Incidents and Safety Information Presented
in the Proceedings of the Ethylene Producers' Conference

Volume	Description
7	Pipeline and Salt Dome Storage Safety
	Improving Environmental and Safety Performance of -
	- Atmospheric Relief Valves
	Safety Considerations in Flare System Operation
	Designing for Abnormal Situation Management
	How a Minor Operational Change Can Adversely Affect -
	- Unit Operation and Safety
6	Naturally Occurring Radioactive Material (NORM) -
	- Contamination Encountered During -
	- Propylene Fractionator Modifications
	Catastrophic Piping Failure During Purging Operation
	Safeguarding Olefin Plant Drier Regen Systems
	Pyrophoric and Self Heating Materials in Steam Cracking
	Update on the Activities of NOx Task Group
	NOx in the Cold Part of Ethylene Plants
	Runaway Reactor Survey
	Hydrogen Induced Cracking of Dissimilar Welds -
	- in Low-Temperature Service
	Detection of Corrosion Through Insulation
	Copper Acetylide Formation in CuO Arsine Removal Beds
5	Pygas Hydrogenation Reactor Runaway
	Safety Experience with Light Liquid Hydrocarbon Containment
	A Program for Analyzing the Potential for Low Temperature -
	- Brittle Failure in Equipment
	Dow Chemical's Furnace Safety Interlock System
	Crisis Management During a Major Flood - Cedar Bayou Plant
	Fire Insurance and Ethylene Plants
Year	
1991	Rust Catalyzed Ethylene Hydrogenation Temperature Runaway
1989	A Mercury Induced Aluminum Alloy Piping Failure -
	- in an Ethylene Plant

Appendix A-1
Explosion in a Naphtha Cracking Unit - Dutch State Mines

Summary
Vapor cloud explosion kills 14 people and injures 106 people six of them seriously. Most of the injuries were due flying glass from broken windows. The subsequent explosion involved nearby storage tanks and other parts of the plant as well as 2,310 cases of off-premises damage.

Damage: The naphtha cracking unit was a total loss.

Description
During startup operations on November 7, 1975, a naphtha cracking unit that had recently been overhauled, exploded, killing 14 people and injuring 106. The plant, operated by Dutch State Mines (DSM) since 1966, was lost, as were several storage tanks in a nearby tank farm.

At 9:48 am a cloud was observed, escaping near the depropanizer. Within two minutes the cloud exploded. The ignition took place at one of the furnaces. Based on evidence gained from witnesses, and in particular metal fractures the investigation was concentrated on the depropanizer section. On and around the depropanizer feed-drum. Five piping fractures were found. Three of these fractures were identified by metallurgical inspection as “secondary” ruptures, i.e., caused by the explosion. A fourth fracture could have been a primary rupture, but all the evidence led to the conclusion that the hydrocarbons escaped from a fracture in a 40 mm (1.5 inch) line connection the depropanizer feed drum to its safety valve.

The weld connecting the steel flange to the steel line was broken. The weld connection was made by gas welding. The fracture in the weld turned out to be a brittle one, which indicates a low temperature level. Normally such carbon steels can be used for temperatures as low as -10☜C to -20☜C. In gas-welding, however, crystal growth can occur by aging, causing an increase in the transition temperature up to possibly 0☜C. A low temperature at this point is, however, not observed under normal operating conditions. Normally at this point, the temperature would be about 65☜C.

A failure in the propylene compressor system resulted in the minimum flow valves of the cracked gas compressor were opened with no flow into the deep cooling system. This situation continued for about half an hour. Cold liquid containing a considerable amount of C_2 was present in C_3+ liquid in the feed-drum. Gas flow through a pressure control valve and the pressure build-up in the depropanizer prevented liquid transport from the feed drum onwards. Vapor from the feed drum may have been at about -10☜C. With an atmospheric temperature of only +6☜C it is quite possible to cool the tube connection to the safety valve to 0☜C or lower by heat conduction. This could be below the transition point where a cold brittle fracture can occur leading to rupture.

Reference: A.L.M. van Eijnatten, Dutch State Mines, "Explosion in a Naphtha Cracking Unit"; Chemical Engineering Progress (CEP), September 1977, pages 69-72

Appendix A-2

Flash Fire in Ethane Feed Storage Unit
Indian Petrochemicals Corp. (IPCL)
Nagothane, Western Maharashtra, India

Summary

An ethane feed gas leak led to an flash fire and/or explosion that killed 32 workers. The leak was OSBL of the olefin unit where the ethane gas feed pipeline enters the plant complex. This OSBL unit was not designed by Stone & Webster or commissioned by Stone & Webster.

Damage

The olefin unit (gas cracker) was not damaged by the OSBL blast. Fire destroyed a majority of the ethane feed gas liquification train and damaged the related storage and compression facility.

Outage

The Olefin unit was shutdown for over six months due to feedstock supply and accident investigation issues. The cracker, undamaged by the blast, was operated on ethane gas directly from the pipeline, bypassing the damaged storage unit. Plant operation was limited to 50 percent of capacity, by local government officials, while the OSBL feed system was being rebuilt.

Background

Ethane feed to the olefin unit was supplied as a gas through a 40 km pipeline. At the olefin complex, an ethane feed gas liquification system and low temperature storage tank was used to provide feed surge capacity. No pipeline "trash or iron scale" filters were installed at the olefin complex. No feed driers were installed upstream of the ethane liquification system. Core type heat exchangers each with a small mesh inlet screen were used for ethane feed chilling and condensing in the OSBL liquification system. The ethane feed gas liquification system was designed and built to minimize cost. Core screen cleaning required stopping feed gas flow to the liquification system, since block valves were not installed specifically for screen cleaning. The basis of design for the ethane liquification unit stated that the pipeline feed would be "clean and dry".

Field Modifications

In an attempt to improve the on-stream factor for the ethane liquification system several block valves and bypass valves were added for screen cleaning while feed flow continued. These modifications required welding different pipe alloys that operated below -40 degrees C.

Appendix A-2
(continued)

Description
A leak occurred near a strainer located in front of a core type heat exchanger used for chilling ethane feedstock being routed into the liquefaction unit for storage. Experienced engineers and olefin unit operators responded to the ethane leak and entered the chilling area to determine the leak point. The operators were hoping that a flange leak could be isolated using the new block and by-pass valves without stopping the ethane gas flow. A number of "observers" collected near the ethane feed unit. A fire truck responding to the emergency alarm is believe to have been the ignition source of the flash fire or gas explosion. Most of the "observers" and staff arriving on the fire truck were killed in addition to those working in the leak area.

Published Data
India's largest ethylene production unit has been closed since November following an explosion in an offsite gas feed pipeline that killed more than 20 workers and destroyed the gas storage/compression facility. Indian Petrochemicals Corp. (IPCL, Bombay, India) expects to restart its ethane cracker at Nagothane by the end of March.

The plant was expected back on-stream in June, when repairs to the storage/compression unit are due for completion, but IPCL chairman Hasmukh Shah says that by March the cracker, undamaged by the blast, will operate on gas directly from the pipeline, bypassing the damaged storage unit. That will enable commissioning of downstream plastics units and reduce India’s dependence on imports.

The Western Maharashtra government has given permission for the restart of operations at Indian Petrochemicals Corp. Ltd’s (IPCL) 300,000 tonne/year Nagothane gas cracker for a limited period of three months, pending final environmental clearance. The cracker was closed last November following a hydrocarbon gas leak which led to an explosion and which killed 32 workers.

The temporary clearance allows IPCL to operate the plant at 50 percent capacity, without backup from the off-site battery limit where the explosion occurred. Operations will be closely monitored by the Maharashtra pollution control board, and a technical team from US engineering company Stone & Webster, which licensed the technology for the cracker, will look into the safety and environmental aspects of the restart, official sources said.

Published Data References:
1. Chemical Week, February 6, 1991, page 34.
2. Chemical Week, November 14, 1990, page 14.
3. Platts International Petrochemical Report June 27, 1991, page 7.

Appendix A-3

Explosion and Fire Due to Cold Brittle Flare Line Fracture at PCI Olefin Unit in Lake Charles, La.

Summary

A cold brittle fracture occurred in an 8 inch carbon steel line while -200 degree F gas was flowing through the line.

Damage

Olefin unit was off-line about one month for repair and modification. None of the unit operators were seriously injured. A work force of some 100 PCI personnel plus more than 700 contractor construction workers and engineers had the plant back on stream on October 18.

Description

At 4:31 p.m. on July 13, a plant operator at the PCI Lake Charles, La. Facility spotted gas escaping from a break in a frost covered 8 inch line leading from a demethanizer tower to a flare manifold. A breeze was already carrying the methane-rich mixture toward furnaces only 500 feet away. Though well-trained crews promptly shut off the furnace fuel and fed snuffing steam into the fire boxes, the gas cloud reached the still-glowing furnace at 4:35 (stopped clocks recorded the instant), and rocked the area with explosion and fire.

Several lines were ruptured by adjacent explosions and the fire. Most utilities were lost throughout the plant. A large area of ruptured lines was at a point where the gas flow could not be stopped with the valves. Although operators tried to purge the demethanizer and other light-ends towers with nitrogen, sporadic fires and explosions continued for several days until all light hydrocarbons was burned or boiled away.

The failure that caused the disaster was in an 8 inch carbon steel line: surging in the plant methane system dumped causing low-temperature strain and a break. PCI replaced this entire line, including 24 inch and 30 inch manifolds, with Type 304 stainless steel (this stainless has superior strength and resistance to fracture at low temperatures compared with carbon steel). The company believes that the 18 Cr-8 Ni alloy may not have been required throughout, but it was the most readily available. Since Type 304 has three or four times the coefficient of expansion of carbon steel, thirteen expansion joints had to be included in the new line.

Local Control House

The compressor area control house was demolished. This control house had been constructed with concrete walls and a roof. The replacement was erected with a steel framework as well. The location of this control house was also changed. The old control house was at a second floor level, situated next to a building that houses the compressors and boilers. In terms of making a fast exit from a fire or major leak the old control house's three exits were badly located.

Appendix A-3
(continued)

Safety Driven Modifications
During the repair process, the compressor building was equipped with water sprays to protect compressors. Water-supply lines have been rerouted along the webbing of steel beams and other protective locations; and the main water-control valves are now outside any possible fire area. A single header block valve was added to shut off gas to all the furnaces at once, eliminating the need for an operator going to each furnace individually.

Before the explosion and fire, there were two water monitor nozzles in the plant area. These proved to be inadequate, since they had a range of only 75 to 100 ft. Four more monitors were added. And the monitor valves have been moved back to the battery limits, because during the early hours of the fire it was not possible to get close enough to the monitors to turn them on.

Reference: "Explosion Leads to a Safer Ethylene Plant Design", Chemical Engineering, February 14, 1966, pages 96-97.

Appendix A-4

Cold Brittle Line Fracture Results in Gas Leak,
Explosion and Fire at
Quantum's Morris Illinois Ethane/Propane Cracker

Summary
The explosion occurred in the early morning on Tuesday, September 12, in the acetylene converter area of the facility, causing a fire that raged for most of the day. A back-end style acetylene converter pre-heater failed as a result of inadequate low temperature notch impact resistance during a low temperature excursion that resulted form depressuring the acetylene converter system.

Damage:
Two workers were killed and 17 others were injured. There were seven serious burn cases.

Published Data
Quantum Chemical's ill-fated ethylene plant at Morris, IL was knocked out again last week when a blast ripped through the unit, killing one worker and injuring 17 others. The 940 million lb/year plant had only just been restarted after a fire on June 7, which resulted in $50-million worth of damage, shut it down.

Appendix A-4
(continued)

Accident Description Issued by Morris Plant Staff

Feed to the acetylene conversion system was being controlled by the deethanizer reflux drum overhead control valve. Pressure on the acetylene conversion preheat system was being controlled by control valve to the flare. The automatic block valve which allows flow to the ethylene fractionator was in the closed position. (This valve is opened only when the acetylene conversion system is fully commissioned.) A leak developed on the inlet flange of one of the exchangers in the acetylene conversion preheat system. To eliminate the leak, the overhead control valve of the reflux drum was closed and the system pressure was dropped to flare pressure.

A period of approximately 30 minutes passed from the time the flow to the acetylene conversion preheat system was discontinued until flow as re-initiated. During this time, the overhead control valve allowed a small flow through the acetylene conversion system even though the valve was given the signal to close. Also during this time, the deethanizer reflux drum was found to have a high level reading, in contradiction to the normal level reading being indicated by the level instrumentation. Any liquid which might have carried over into the system could have increased the chilling effect of the depressurization of the acetylene conversion preheat system.

The exchanger which developed the leak was equipped with a bypass and block valves to isolate the exchanger. After the leaking exchanger had been successfully bypassed for repair, the control valve on the outlet of the reflux drum was opened to re-initiate flow to the acetylene conversion system. Shortly thereafter, the first exchanger in the stream from the deethanizer overhead to the acetylene converter preheat system failed in a brittle manner, releasing a large volume of flammable gas. The subsequent conflagration caused major damage to the olefins unit as well as inflicting injuries to a number of individuals, including two fatalities and seven serious burn cases.

The Acetylene Converter Pre-heater failed as a result of inadequate low temperature notch impact resistance during a low temperature excursion that resulted form depressuring the Acetylene Converter System. The heat exchanger shell which failed during re-pressurization of the system was fabricated from carbon steel, ASTM A515 grade 70. Charpy testing on fragments of the failed shell has demonstrated that the brittle transition temperature for the shell material was higher than the design temperature of the exchanger. The original specification did not require normalization of shell plates, stress relief and Charpy test qualification. The shell was nominally one inch thick and had a Charpy “V” notch impact resistance of 15 ft-lb at +57 degrees F.

References:
1. Story by Andrew Wood in Chemical Week, September 10, 1989, page 14.
2. Letter issued by Quantum to EPC members describing the accident.

Appendix A-5

Fire at Shell Chemical Company's Deer Park, Texas Olefin Complex

Introduction

A major fire occurred within Shell's OP-III Olefin Unit on June 22, 1997. This fire resulted in minor process operator injuries, public road closures, and property damage both within the olefin unit and to off site business. EPA and OSHA undertook an investigation of this accident because of its severity, its effects on the public, and "the desire to identify those root causes and contributing factors of the event that may have broad applicability to industry, and the potential to develop recommendations and lessons learned to prevent future accidents of this type". The EPA investigation was conducted in conjunction with an investigation, by OSHA to determine if violations of occupational safety and health laws had occurred.

Accident Outline

At approximately 10:03 am Shell staff working outside of OP-III control room hear a loud "pop" followed by the extremely loud noise of a continuous high-pressure gas release. One person later described the noise as a "jet engine sound". The foreman radios to the control room and informs operators that there has been a gas release and to activate the unit evacuation alarm.

The foreman observes what he later described as a "colorless vapor" originating near the PGC fourth and fifty stage discharge drums and blowing north to south across the pipe alley. He radios the control room again and orders control room operators to "Shut down the PGC [cracked gas compressor] and dump everything to the flare!". He repeats the order three times, but receives no reply.

At approximately 10:07 am, the vapor cloud formed by the gas release has now been generating for several minutes. This vapor reaches an ignition source, causing the vapor to ignite with a blast wave in all directions. As the blast wave moves outward from its origin, it damages and destroys equipment and structures, rips insulation and flashing away from piping, breaks windows, blows down doors, and knocks nearby personnel off their feet and through the air.

The explosion starts a major fire, which is initially fed by the flammable gases still escaping through the original leak, and subsequently from other hydrocarbon lines which rupture when exposed to the intense heat of the blaze. The heat is so intense that it melts steel structural beams, and one entire section of the overhead cooling fans and supporting structure eventually collapses. The fire burns for about ten hours.

At the sound of the explosion, the Shell Deer Park fire crew was activated and, along with OP-III operators already on scene, immediately responded to the fire. Operators outside during the accident activated and positioned fire monitors towards the blaze.

Appendix A-6
(continued)

Shell emergency responders were also able to position a pickup truck-mounted fire monitor to within feet of the center of the fire. Responders drove the portable monitor down the pipe alley from the east directly under the burning pipe rack, positioned the water cannon towards the worst part of the blaze, and abandoned the truck in place to the east of the fire with the water cannon activated.

Later inspection of burn patterns and debris indicated that this single act was probably responsible for substantially mitigating the spread of the fire in that direction. The truck itself, although very near the worst part of the blaze, was protected by the water being continuously sprayed from its portable fire monitor, and suffered relatively little damage. A second truck mounted monitor was positioned to the south of the fire, but responders were not able to place it as close to the fire as the first, and therefore it was somewhat less effective.

Shortly after the explosion, the Shell incident commander contacted the local police department and requested that State Route 225, and Route 8 be closed to traffic passing near the Shell Complex. Police complied with this request and closed sections of these roads adjacent to the complex to non-emergency traffic for approximately three hours. Transportation routes were reopened to public traffic at approximately 1:00 pm, and the fire extinguished at approximately 8:00 pm.

The Clow Model GMZ check valve installed as the PGC [cracked gas compressor] fifty stage suction check valve had an internal diameter of 36 inches and weighed 3.2 tons. The valve had a design limit pressure of 480 psig, and a design limit temperature of 115 degrees F. The JCAIT found no evidence that these limits were exceeded at any time prior to or during the accident.

The investigation report indicates that the purpose of the external shaft keepers was to limit shaft "float" (minor shaft steam piece functions as a drive shaft connects the internal valve disk to an external air-assist cylinder and flapper counterweight assembly. The other stem piece, or idler shaft, simply functions as a hinge for one side of the flapper. The drive shaft penetrates the pressure boundary through a stuffing box. The exterior portion of the drive shaft is connected to the pneumatic piston and counterweight, and the interior portion of the shaft is coupled directly to the valve disk using a cylindrical hardened steel dowel pin and a steel rectangular bar key. This arrangement provides a counter weight to partially balance the weight of the valve disk, and provides the pneumatic power assist to maintain the valve closed as described above.

References: EPA/OSHA Joint Chemical Accident Investigation Report of the Shell Chemical Company's Deer Park, Texas Olefin Complex Fire of June 22, 1997.

EPA Document 550-R-98-005; (This report is available on the internet.)

Appendix A-6

Back-end Acetylene Reactor Incident and Unit Fire at the No. 2 Ethylene Plant of Idemitsu Petrochemical in Japan

Summary
A general unit upset occurred due to a loss of instrument air pressure.
Piping at the outlet of an acetylene reactor became red hot and a gas leak commenced at the flange of the motor valve and ignited. The pipe ruptured at the elbow due to the high temperature and a large quantity of gas ignited, causing the explosion.

Damage:
One operator died in this incident. A fire ball about 60 meter in diameter was observed. About 10 percent of No. 2 Ethylene Plant was damaged. This damage included; 5 Fractionators (towers), 11 receivers (drums), 6 reactors, 23 heat exchangers, 4 pumps, structural steel, piping and instruments. About 500 tons of gas was burnt in the fire.

Plant Capacity: At the time of this incident, was unit ethylene capacity was 200,000 MTA.

Process Design
The No. 2 Ethylene Plant had "Back-end Acetylene Reactor" system consisting of three reactors in a vertical stack. Usually, two of these three reactors were used in series with the reaction being controlled via external cooling between reactors and hydrogen addition.

Under normal conditions, crude ethylene gas from the top of the deethanizer containing 3,000 to 4,000 ppm acetylene is heated to about 60 degrees C and charged to Reactor B. The desired flow of hydrogen to hydrogenate the acetylene in crude ethylene is controlled by computer. The acetylene content of the stream leaving Reactor B is usually about 300 to 500 ppm. This stream is charged to Reactor C after cooling. The acetylene content of the stress leaving Reactor C is less than 2 ppm. The hydrogenation reaction is exothermic, and the unit is controlled to maintain a total temperature rise of 20-30 Deg C in Reactor B, and 5 to 10 Deg C in Reactor C.

Description of Events
The following events (situations) were described in the accident report:

First Stage
At about 18:50 on July 7, 1973, several instruments in the control room of No. 2 ethylene plant started hunting simultaneously, and an alarm buzzer rang. The operators immediately shut down the unit and had the instruments checked out. There was no apparent cause for the incident.

At 18:58 preparations were made to start operation again while further investigations were being made to determine the cause of the previous incident. During the period of abnormal instrument operation, black smoke was observed from the flare stack.

Appendix A-6
(continued)

<u>Second Stage</u>
After a few minutes, the flow of crude ethylene to No. 2 acetylene converter started to decrease, and at the same time the flow of computer-controlled hydrogen decreased too. Flow control was switched from automatic to manual and the flow of crude ethylene was stopped at the same time. Shortly thereafter, the control valve for the unit hydrogen supply was shut manually.

<u>Third Stage</u>
At about 21:23, M_2 temperature point of B Reactor indicated a temperature over 100 Deg C, and crude ethylene from No. 1 Ethylene Plant (capacity 100,000 MTA) was routed to the acetylene converter with the intention of lowering the reactor temperature. Just after this was done the temperature of the catalyst suddenly began to rise, and at about 21:38, all hydrogen to the unit was stopped by abutting the unit block valve.

At that time, the indication on the board mounted temperature recorder was above the scale at over 200☜C. The computer confirmed a temperature of 970☜C at M_2 temperature point and also confirmed that the temperature dropped to 750☜C shortly thereafter.

<u>Fourth Stage</u>
In an attempt to lower the reactor temperature further, the ethylene temperature was reduced by-passing the heat-exchanger at ethylene inlet and, at the same time, outlet gas from the converter was switched to fuel to increase flow through the converter.

a. At a little past 22:00, the piping at the lower outlet of Reactor B became red hot and a gas leak commenced at the flange of the motor valve and ignited.

b. At about 22:15, the pipe ruptured at the elbow due to the high temperature and a large quantity of gas ignited, causing the explosion.

c. An operator who was attempting to extinguish the fire resulting from this gas leak was killed by the explosion.

<u>Fifth Stage</u>
The first spread to the deethanizer, methane splitter, ethylene tower and heat-exchangers, as a fire ball about 60 meter in diameter was observed.

<u>Sixth Stage</u>
Soon after the fire started, fire brigades from Idemitsu, Tokuyama City, and other adjacent companies arrived, but it was not possible to bring the blaze under control due to the explosion. A water curtain was maintained on the neighboring tanks to prevent

temperature rise. Water injection from the fire engines commenced at about 00:00 on July 8 and a nitrogen purge of the towers was attempted to prevent further explosion at about 06:20.

Appendix A-6
(continued)

Situation During this Fire

After the fire commenced, there were two or three explosions, but no windows were damaged at residences 250 meter away and another factory 20 meters away. It was concluded that the intensity of the explosions was not high.

About 500 tons of gas was burnt in the fire. Process gas, principally ethylene, at high pressure, gushed out relatively early with rupture of piping, and is through to have formed a large fireball.

Probable Cause of the Fire

After investigation the process and the damaged plant area, it was concluded that the probable causes of the incident were as follows:

a. The initial cause of the accident was shutting the 4 inch instrument air valve, by mistake, when the operator intended to shut a 2 inch air valve to enable decking of the cracking furnace. During this mistake, the entire instrument (air make-up) function ceased. This occurred at about 18:50 (6:50 pm).

b. The operator who made the mistake, became aware of his error after seeing black smoke coming from the flare stack, and immediately reopened the instrument air valve returning instrument operation to normal. The large volume of fuel gas exhausted due to the emergency shutdown caused the black smoke emitted from the flare stack.

c. In the control room, all instrument operation was abnormal due to the operator's mistakes. After about 8 minutes, the instruments returned to normal situation, and preparations for a startup were made.

d. Supply of ethylene and hydrogen to the converter was initiated. However, the pressure in the deethanizer had dropped during the emergency shut-down, while the pressure in the methane splitter had risen. Since there was a higher pressure level downstream the converter, the flow of ethylene began to decrease, and become zero. The operators switched the controller from automatic to manual, and shut the ethylene inlet control valve. (Time is estimated as 19:02).

e. At this time, the hydrogen control valve was not completely shut and hydrogen was still flowing into the converter. In fact, it is considered that the hydrogen flow was directionally increased due to the supply of ethylene being stopped.
At this point the operators became aware of the continued flow of hydrogen, and shut off the hydrogen control valve. (Time is estimated as 20:08).

Appendix A-6
(continued)

Excess hydrogen flowed in with the ethylene remaining in the converter, and it is considered that rapid hydrogenation of the ethylene commenced. This reaction is exothermic (33.2 Kcal/mol), and the temperature of catalyst began to rise. Investigations after the accident showed temperature point M1 (30 cm from the top of the catalyst layer) to have read 347☜C. Furthermore, local areas of higher temperature were generated, and it is considered there was some catalytic cracking in these areas. At this time, there was only one temperature point indicating and recording at the control rooms (M2 located 1.3 meters from the top of the catalyst layer), and it showed about 100☜C.

It is considered the high temperature some descended gradually in the catalyst layer, since M2 indicated 120☜C at about 21:30. Operators became aware of the temperature rising and started to put in ethylene. As flow of ethylene was insufficient to cool the converter, exit gas was discharged to low pressure fuel gas to increase flow. At the time supply of ethylene was started, hydrogen was switched to automatic, and a hydrogen flow corresponding to the amount of acetylene in the gas was supplied.

f. After starting ethylene flow, gas in the reactor started to move through the reactor causing movement of the high temperature zone. Ethylene which contacted the high temperature some (about 400☜C) was cracked over the Pd catalyst, and temperature began to rise sharply. It is considered further temperature rise was generated by gas-phase thermal cracking or ethylene initiated by the rising high temperature.

The reading of temperature point M2 rose suddenly after starting the flow of ethylene commenced and scaled-out over 200☜C. After about 15 minutes, a temperature of 970☜C was observed by operators, which decreased to 750☜C after 15 minutes. At this time, a temperature of 896☜C was observed at the bottom (1 meter below M2) of the reactor.

The reactor used a palladium based catalyst that has the ability to decompose ethylene at about 400☜C, and this ability is enhanced above 400☜C to about 800☜C. Over 700☜C, it is estimated that non-catalytic thermal decomposition (methane and carbon, or hydrogen and carbon) became violet, and there was conversion to butene, butadiene or propylene and subsequent polymerization to aromatics, polymers or tar. The net result was a continuing rise in temperature to more than 1,000☜C.

An investigation showed much tarry matter and carbon was adhering to the reactor after the accident, which supports the above-mentioned theory.

Appendix A-6
(continued)

g. As the temperature in the reactor rose locally to about 1,000☜C, the exit piping was heated by high temperature gas. The flange near the exit was red hot and after several minutes, crude ethylene leaked from this flange and ignited. After several minutes, the elbow connecting the motor valve ruptured at the weakest point and the fire started. Subsequently neighboring heat exchangers ruptured and the fire became widespread.

   The safety valve was set at 28 Kg/cm2, and was relieving before the elbow was ruptured. However, the pressure in the vessel was much greater than the relief valve setting, and is estimated to have been some 31 Kg/cm2, 15 minutes before the elbow ruptured. This is based on the fact that the pressure of the methane splitter was 30 Kg/Cm2 for about 15 minutes.

<u>References</u>:
The information shown is this appendix is based on an english translation of report issued by the "Accident Investigation Committee". This investigation committee was set up by the Environmental Protection and Safety Bureau of MITI, in order to investigate the fire which occurred in the No. 2 Ethylene Plant at Idemitsu Petrochemical's Tokuyama Factory on
July 7, 1973. This committee carried out their investigation during the period July 14 through July 19.

Appendix A-7

Vapor Release and Explosion at Dow Chemical Company's Plaquemine, La. Olefin Unit (Light Hydrocarbon Plant)

<u>Summary</u>

On April 3, 1963, a vapor release result in at least two explosions and a major fire. It is believed to have been the failure of a top sight glass on a separator on the feed to the dehydrators ahead of the methane distillation column. The true cause of this ethylene plant explosion and fire is unknown.

<u>Damage</u>

This 1963 explosion and fire destroyed the ethylene/propylene plant.
An estimated 250,000 gallons of ethylene fed the fire.
The unit was rebuilt with numerous safety improvements.

<u>Description</u>

A summation of statements taken from all division personnel on duty at the time of the explosion indicates the following:

a. There was a loud hissing noise like steam escaping under high pressure.
b. Approximately 30 seconds after the noise was heard, there was a flash of light followed by a heavy rumble.
c. Two to three minutes later, a second explosion was heard, more muffled than the first, followed by high billowing flames.

Because of the damaging effects of the blast and fire, it is not possible to determine conclusively where the initial vapor release originated.

One possible explanation for the gas release was the D-10 sight glass. The top sight glass was found to be broken and missing. The D-10 separator is on the feed to the dehydrators ahead of the methane distillation column. It operates at 500 to 600 psig. and 60 to 80☜F. The sight glass had been cleaned by removal two days before, and the replacement procedure did not conform to recommended standards. One recording instrument showed a drop in flow and pressure on the methane tower overhead a few seconds before the explosion. A large leak at D-10 could have caused this condition.

The intensity and duration of the fire that followed the explosion were such that it is difficult to separate the extent of damage caused by the explosion and that caused by the fire.

The west (load-bearing) side of the process deck collapsed. The concrete deck, beams, pipes, and vessels under the deck were distorted. Steel H-beams and pipes were found melted near the center of the main structure.

Appendix A-7
(continued)

Two dehydrators and two reactors were shifted from 5 to 7 inches to the north. The four ¾ inch bolts that held each unit in place were sheared off. These vessels were 27 ft. high and weighed 35,000 to 45,000 lb. Each. A solid steel deck surrounded these vessels and extended from the concrete deck level of the process structure. None of the steel deck plates were left in their original locations. Seven pieces of deck plate weighing from 500 to 600 lb. Each were blown to the north between 150 to 250 feet.

Various distillation columns along the west side of the process structure sustained moderate fire damage; however, there were no skirt failures on any of the columns.

Most of the explosion damage outside the light hydrocarbon block but within the plant area consisted of broken and dislocated corrugated asbestos siding, dislocated non-load bearing concrete block walls, broken window glass, and suspended ceilings in some control rooms.

An investigation was conducted by M. G. Zabetakis and H. F. Browne from the Bureau of Mines. They summarized that the force of the explosion was equivalent to about 1 ton of TNT. This same energy can be released by approximately 38,350 cubic feet of stoichiometric ethylene-air mixture or 43,500 cubic feet of stoichiometric methane-air mixture. These mixtures can be formed from less than 200 lb of ethylene or methane.

Fire Water Loss

The initial explosion caused the 8 inch sprinkler feed main to separate from this screwed flange above a two deluge valves.

References:

1. Vapor Release and Explosion in a Light Hydrocarbon Plant
by C. T. Adcock and J. D. Weldon, The Dow Chemical Co.,
Plaquemine, La.; published in Chemical Engineering Progress,
(CEP Vol. 43, No. 8), August 1967, pages 54-57.

Appendix A-8

Failure of a Bellows-type Expansion Joint in the Propylene Refrigeration Compressor System at Dow Chemical Company, Plaquemine, La. Olefin Unit

Summary

A 24-inch bellows-type expansion joint in the propylene refrigeration compressor failed. The propylene vapor cloud traveled about 300 feet the cracking furnace, where ignition occurred. The flashback was a mild rumble sound with a slight vibration.

Damage

The 1974, fire was isolated in Train 2 within minutes; the automatic sprinkler systems either put out or contained the small fires at valve packaging, and leaking flanges. All the electrical, instrument cables, insulation, and painted surfaces in the area of the vapor cloud were damaged by the flash fire. The intensity of the fire under the deck caused damage to the concrete deck, exposing the reinforcing steel in an area around the expansion joint failure. Flames came up around the pipe openings in the deck and damaged the concrete footing, controls, small piping, insulation an painted surfaces.

Background Information

In 1963, ethylene vapor cloud was released in a Dow Chemical light hydrocarbon plant, resulting in an explosion and fire that destroyed the entire facility. The rebuilt plant, incorporating a variety of loss prevention features, was subjected to a similar vapor cloud release and fire 11 years later.

Description

The division experienced a major electrical power interruption that tripped all of the plant's cooling water and furnace quench water pumps. The spare pumps were also made inoperable by the power failure. During the normal shutdown, a 24-inch bellows-type expansion joint in the suction to the interstage of propylene refrigeration compressor failed, allowing an estimated 15,000 gal. Of propylene to escape.

Operators in the area of the rupture heard a loud roar that was similar to a compressor surge. The supervisor and the superintendent ran to the area of the noise and saw a large vapor cloud moving toward the direction of the furnaces. The superintendent immediately gave instructions over the plant page system for all personnel to evacuate the area.

The vapor cloud. Traveled 250 to 300 ft on the north end of the block to the furnace, where ignition occurred. The wind was out of the northwest at approximately 5 miles/hr. Based on the comments of operating personnel, the time estimated for the vapor cloud to reach the furnaces was one to two minutes.

Appendix A-8
(continued)

The flashback was a mild rumble sound with a slight vibration. Flames reached most of the process unit leaving small fires at leaking packing glands and flanges. All 11 sprinkler systems which were flowing almost immediately after the ignition, could have been tripped either by the heat of rise or manual remote trips in the Train 1 control room by the board operator as he evacuated the block.

In 1974, due to the loss of compete water cooling in the plant, the surface condensers began to discharge steam from the surface condenser vacuum relief valve. In the purification section, the steam accidentally set off the sprinklers in that area. This happened two to three minutes before the vapor release. Normal procedure is to trip all sprinkler systems from the remote trips in the control room when there is a spill, but that was not the case. The operators, thinking the power failure was only momentary, proceeded to restart all equipment. When the expansion joint failed, the evacuation announcement was made, and all remote sprinkler trips were tripped. The ignition and tripping of the sprinkler system occurred at about the same time.

References:

1. Vapor Clouds and Fires in a Light Hydrocarbon Plant
by S. A. Saia, Dow Chemical U.S.A., Plaquemine, LA;
published in Chemical Engineering Progress (CEP),
November 1976, pages 56-61

2. Vapor Release and Explosion in a Light Hydrocarbon Plant
by C. T. Adcock and J. D. Weldon, The Dow Chemical Co.,
Plaquemine, La.; published in Chemical Engineering Progress,
(CEP Vol. 43, No. 8), August 1967, pages 54-57.

Appendix A-9

Ethylene Product Pipeline Flange Leak Results in Shutdown of Lyondell Petrochemical Company's Two Olefin Units at Channelview, Texas

Summary
An OSBL fire was caused by an ethylene leak in a 12 inch pipeline.

Damage
No injuries occurred during the blaze that began about 3:45 p.m. on Saturday, July 27, 1996. The fire damaged both the pipeline, which Lyondell uses to transport its petrochemical products out of the plant, and the facility's electrical system. The two olefins trains, with a combined ethylene capacity of 3.8 billion pounds per year, suffered no major damage to the cracking furnaces, during the shutdown.

Description
A flange leak occurred in the high pressure ethylene product export line used by both of the Channelview olefin units. The source of ignition has not been determined. Although the leak was within the Lyondell plant, the pipeline is operated by Arco Pipeline Co. Lyondell plant staff could not access block valves in the Arco Pipeline system. This caused some delay in isolation ethylene from the fire area. The fire continued for less than two hours, until the ethylene burned off.

The fire damaged electrical utility service to the site and all process units were shut down. Lyondell resumed methanol production on Wednesday, July 31. Some secondary process units were on-line by August 5, 1996.

Loss of Earnings
The olefin units resumed operation in just two weeks of down time, compared to the original estimate of two to four weeks, Lyondell Chief Executive Bob Gower said in a statement. The $20 million to $25 million impact on after-tax earnings would be greater than the $15 million the company earned during the second quarter of the year. That figure reflects the loss of production but does not figure in the amount of money the company will spend to make the necessary repairs, a company spokeswoman said.

References:
Houston Chronicle, Sunday, July 28, 1996, page 47A
Houston Chronicle, Tuesday, July 30, 1996, page 2E
Houston Chronicle, Friday, August 16, 1996
Chemical Week, August 7, 1996, page 9
Chemical Week, August 14, 1996, page 12

Appendix A-10

Fire in Quench Oil Area of Exxon's Baton Rouge Olefin Unit Results in a Major Ethylene Production Outage

Summary

A quench oil fire resulted in extensive damage to the larger train of the two-train steam cracking unit. The larger train required several months of repair work.

Damage

Seven contract employees suffered minor injuries as they ran from the explosions and jumped plant fences. Exxon fire fighters contained the blaze to a small area of the chemical plant. Two miles of Interstate 10 were closed to traffic.

Description

The explosions occurred about 8 p.m. Monday (August 8, 1994)in a steam cracking (olefin) unit. The fire was brought under control about midnight, plant officials decided to allow it to burn itself out as it consumes the remaining products in the unit. The fire burned itself out Thursday after about 52 hours.

The two-train steam cracking unit involved in the fire produces 1.9 billion pounds a year of ethylene and 600 million pounds per year of propylene. Exxon uses virgin gas oil and naphtha as the primary feedstocks to the steam cracker involved in the fire.

The fire was limited to, namely to a "sponge tower" and quench oil equipment in the hot fractionation section just downstream of the cracking furnaces. The fire occurred in the larger of the two trains of the steam cracker.

Exxon restarted the smaller train of its ethylene plant that escaped damage in an explosion after about 10 days.

References:

Houston Chronicle, Tuesday, August 9, 1994
Houston Chronicle, Wednesday, August 10, 1994
Houston Chronicle, Friday, August 12, 1994
Houston Chronicle, Tuesday, August 16, 1994

Appendix A-11

ROW Unit IV Explosion And Fire
Follow a Pipe Rupture During Cold Weather Operation

Summary

An explosion And fire partial destroys Rhenische Olefinwerke's ethylene plant at Wesseling in West Germany. Gas release was reported as being due to a pipe rupture following freezing of condensate in the line.

Damage

The fire burned for nine days, primarily because this unit was connected to the flare system and the cold storage boil off area. Because of leaks, these units could not be completely isolated.

Outage

The ethylene plant was shutdown for over 8 months.
An ethylene capacity of 200,000 Ton per year is reported by one source, while a capacity of 250,000 ton per year is given in a follow-up published accident report.

Description

During the first frost period, the temperatures dropped to -18☜C (0☜F) and the pipe diameter expanded, almost to the point of rupture, due to the freezing of condensate in the line. This frost period was followed by a warming trend, until eight days later when a second frost period occurred. The pipe expanded a second time, further thinning the pipe wall and eventually rupturing.

The time interval between the first gas alarm and the explosion was about five minutes. About 4000 m^3/hour (1 million gallons per hour) of water was used to fight the fire. Most of this water was to cool nearby vessels.

Current plant practice now is to keep lines active and to see if any pipes change diameter during cold periods.

References:

1. European Chemical News, May 27, 1985

Appendix A-12

Fire at Enichem's Priolo, Sicily, Ethylene Plant

Summary: A fire damaged the plant and halted production on May 19, 1985.

Damage: The "fire severely damaged the operation".
The ethylene plant was closed for a 10 month shutdown.

Description

Enichem's Priolo, Sicily, ethylene production at the 660,000 metric-tons/yr facility was halted when a fire caused severe damaged. Enichem, the petrochemical sector of Italy's state energy group, Ente Nazionale Idrocarburi (ENI), had major net operating loss of over $137 million after amortization and costs related to the plant fire.

Accident Report

Operations within the ethylene plant were normal until a faulty temperature probe initiated an isolation of the hydrogeneration equipment located within the cold section. While the operators were attempting to regain normal control, the pressure relief system came into operation. About the same time, fire was noted near grade level at the base of the deethanizer column. The source of fuel was believed to have been flange at the deethanizer column reboiler or in the relief system pipe work.

Leaking hydrocarbon, mostly propylene at 375 psig was possibly ignited by hot steam piping. The intense fire rapidly engulfed the adjoining ethylene and propylene distillation columns and spread 180 feet to the storage area. Eventually one tall vertical propane tank exploded, its top section skyrocketing 1,500 feet and missing a gas holder by 30 feet. Two other propylene tanks toppled, one on a pipe rack and the other against an ethylene tank. All were protected by deluge water spry systems which apparently were ineffective under the intense fire exposure. Five of the ethylene and propylene tanks collapsed or exploded. The fire also spread to the API separator and to three floating roof tanks. Pipe racks, motor control centers, pumps, etc., were severely damaged or destroyed.

Within a few minutes after the fire brigade responded, the ethylene column released its 9,300 gallon inventory, destroying one of the plant's two foam trucks. Assisted by outside fire fighting agencies, the plant fire brigade brought the fire under control in 40 hours and finally extinguished it four days after ignition.

References:

Chemical Marketing Reporter, January 20, 1986 p. 3

Appendix A-13

Explosion in Union Carbide Butadiene Recovery Unit Linked to the Decomposition of Vinyl and Ethyl Acetylenes

Summary
An explosion occurred in the reboiler of a distillation tower that had been operated on near total reflux for eight hours. It is believed that the explosion was a decomposition of vinyl-acetylene and ethyl-acetylene which had accumulated to an explosive concentration.

Damage
Extensive damage occurred to the butadiene recovery unit as secondary explosions occurred due to hydrocarbon leakage from damaged equipment.

Description
On October 23, 1969, the 100 foot high refining column in the butadiene unit of a new billion pounds-per-year olefins complex disintegrated with explosive ignition of 540 gallons of liquid hold-up. The unit was operating normally when the stripper make-up compressor was found to be running hot. Crude feed was reduced in preparation for repairing a bad compressor valve. The refining section was put on total reflux for eight hours while compressor repairs were made. It is believed that the explosion was a heat-triggered decomposition of vinyl and ethyl-acetylenes which had accumulated at the tower bottom until an explosive concentration was reached.

The initiator could have been a thermal polymerization assisted by sodium nitrate. This created a deflagration wave that lifted the bottom trays and moved upward in the column. The temperature, pressure, and concentration of vinyl acetylene were high enough at the fourteenth tray to cause the detonation. Sections of metal plate were spread uniformly over a radius of 1,500 feet. One section weighing about 800 pounds traveled 3,000 feet. All five towers in the butadiene section were either felled or heavily damaged.

This Union Carbide butadiene recovery unit is located in Texas City, Texas, less than one hour south of downtown Houston.

References:

1. Butadiene Explosion at Texas City - Part 1
   H. C. Jarvis, Union Carbide Corp., Texas City, Texas
   Chemical Engineering Progress (CEP), June 1971, pages 41-44
2. Butadiene Explosion at Texas City - Part 2
   R. H. Freeman and M. P. McCready
   Union Carbide Corp., South Charleston, WV
   Chemical Engineering Progress (CEP), June 1971, pages 45-50

Appendix A-14

Fire Shuts Down Quantum's Morris Illinois Ethane/Propane Cracker

Summary
A fire occurred in the plant's fractionation unit due to a propylene release. Plant operators were attempting to recover from a power outage when a valve line-up error was made.

Damage
Published damage estimates range from $40-million to $50-million dollars. Approximately 40 acres of this plant were damaged, including the ethylene production area, because of this incident. A Quantum spokesman said two men were injured, but not seriously.

Outage
The entire petrochemical complex was shutdown as a result of the fire which was quickly brought under control. In addition to the cracker, capabilities for 540 million lb/yr low density polyethylene (PE), 250 million lb/yr linear low density PE, 250 polypropylene (PP) 220 million lb/yr ethylene oxide were closed.

Description
After a power outage of the amine system and butane column, plant operators worked to restore normal operating conditions in the ethylene production area. In the process of restoring operations, the vent valves for the depropanizer reflux drum was opened to reduce the pressure in this vessel. The vent line piping was arranged to route the excess product to the flare system or the gas compressor. Since the vent line to the compressor was out-of-service for maintenance, the excess propylene should have been routed to the flare system. However, the propylene was accidentally routed through the 2-inch vent line to the compressor, forming a vapor cloud in the ethylene production area.

While plant personnel attempted to dissipate the vapor cloud with fire water monitors and hose streams, the vapor cloud was ignited. The source of ignition is believed to have been a spark from an incandescent light fixture. The bulb was apparently broken by the cold water of a hose stream or vibrated loose. Approximately 40 acres of this plant were damaged, including the ethylene production area, because of this incident.

References:
1. Platts international Petrochemical Report June 15, 1989.
2. Story by Andrew Wood in Chemical Week, September 10, 1989, page 14.

Appendix B-1
Severe Blast and Fire Damage Brindisl Ethylene Plant

A major gas release in the cold section of a 230,000 metric ton per year ethylene unit, located near Brindisl in Italy, became ignited and caused severe blast and fire damage. Two nearby ethylene units were also damaged. The control building had brick panel walls within a reinforced concrete frame. Blast over-pressures blew out the wall panels and destroyed the controls. Water applied by 40 fire trucks could not be carried off by the sewers, resulting in an 10 inch backup of floating burning liquid and heavy hydrocarbons through the process area.

The fires were controlled in five hours and extinguished three days later.
The initial gas release occurred on December 8, 1977.

Appendix B-2
Fire at Stenungsund Olefin Unit Due to Cooling Water Tower

In 1985, an incident at Esso's Stenungsund, Sweden olefin unit occurred when part of a wooden cooling tower fell to the ground. A fire then occurred that heavily damaged two tanks, a quality control building, and cooling water facilities. Reports indicate that five explosions rocked the site, sending smoke into the area. Residents were evacuated from three neighboring towns. Information about the incident was published in European Chemical News, May 27, 1985.

Appendix B-3
Seal Leak Results in Ethylene Product Pump Fire

This incident occurred in 1985, when a pump with a single seal developed a major leak. This pump was manufactured in the 1970s when a double seal system was considered experimental by many in the petrochemical industry.

Eight workers were injured in a flash fire when the ethylene vapor ignited from leaking ethylene product pump. Reports differ on the men were repairing or isolating the pump when the fire occurred. The plant fire brigade was able to isolate the fire to the pump area shortly after it broke out. Plant damage was described as light.

Seven men were seriously burned and hospitalized. One contractor reported to be in critical condition. One process operator was in guarded condition.

References: Houston Post, 09/28/85, page: 11C
Houston Chronicle, 09/28/85, Section 1, page 6.

Appendix B-4

Propane Gas Release in Saudi Petrochemical Company (SADAF) Olefin Unit

In December 1991, the Saudi Petrochemical Company (SADAF), a chemical plant located in Saudi Arabia and partly owned by Shell Chemical Company, experienced a release of propane gas when a Clow Model GMZ check valve experienced shaft blow-out. Many circumstances in this incident were similar to those in both the June 1997 accident and May 1991 incident. The incident occurred following a process upset in the facility's ethylene plant, where the inadvertent shutdown of a cracked gas compressor resulted in downstream flow instabilities and initiated a 13 hour period of surging in the unit's propane refrigeration compressor. During this period, the Clow Model GMZ check valves installed in the propane refrigeration compression system slammed shut repeatedly.

The shaft of the compressor's third stage discharge valve eventually separated from its disk and was partially ejected from the valve. The shaft was not fully ejected because its path was blocked by an adjacent steam line inches away from the valve, keeping about 70 mm of the shaft's length within the valve body. Propane gas began to leak out of the valve around the gap between the shaft and its stuffing box until operators discovered the leak and shut down the compressor. Operators also discovered that the valve's drive shaft counterweights had broken off of the drive shaft and had been propelled approximately 16 meters from the valve.

The facility was fortunate in this case. An adjacent steam line kept the shaft from being fully ejected from the valve, thus limiting the leak rate and preventing an accident of potentially much greater severity. It was also fortunate that no one was struck by the counterweights when they were propelled from the valve.

A subsequent investigation by SADAF and analysis of the check valve's internal components revealed that the dowel pin which secured the drive shaft to the valve flapper had sheared, and the shaft key had fallen out of its key-way (the same failure mode identified in the 1997 accident at Deer Park).

The SADAF investigation report also revealed that facility maintenance records indicated a long history of problems with the Clow Model GMZ check valves installed there. The valves were installed in 1982, and due to continuing valve malfunctions, underwent repair or modification in 1984, 1986, 1987, 1989, and 1990. These repairs and modifications included replacement of damaged counterweight arms, replacement of seals and gaskets, replacement of dowel pins and internal keys, and installation of external shaft "keepers".

Reference: EPA/OSHA Joint Chemical Accident Investigation Report of the Shell Chemical Company's Deer Park, Texas Olefin Complex Fire of June 22, 1997. EPA Document 550-R-98-005; (This report is available on the internet.)

Appendix B-5

Pyrolysis Gasoline Hydrogenation Reactor Crack
Rupture and Conflagration of a Carbon ½ Mo Steel Vessel
Due to Decarbonization With Age

Accident

In 1988, an olefin unit first stage pyrolysis gasoline hydrogenation reactor developed a crack with an opening of about 560 mm or 22 inches. Leakage of a hot hydrocarbon resulted in a fire that lasted about one hour. The fire was extinguished by stopping feed and allowing hydrocarbon to burn off. No casualties occurred during light off of the fire or during fire fighting. The fire caused extensive damage in an area with a radius of 15 meters.

Age

This olefin unit and reactor when into operation in 1973. The reactor was subjected to about 50 steam and air decoke cycles for catalyst regeneration.

Crack

The crack was vertical with a maximum width of approximately one 10 mm or just under 0.4 inches. Crack location was in the middle of the steel plate, far from any welds and in the bottom of the reactor. The steel plate has a thickness of 29 mm or 1.15 inches. In the area of the fracture the wall had stretched and thinned very regularly at a distance of about 150 mm or 5.9 inches from the rupture.

Failure Mode

The crack was perfectly ductile. This type of a crack could only have been produced with a local overheating of the steel to about 700 degrees C or 1292 degrees F at the service pressure of 40 kg/cm2 or 570 psi or in the case of a reactor starting with a new catalyst. Failure was reported to be due to a high local wall temperature. The incident report stated that: "This rupture was not the result from a metallurgic modification in service" and "it is evident that the type of steel is not to blame. A 1 ¼ Cr-1/2 Mo or 2 ¼ Cr-1 Mo steel would have performed in the same manner as this 0.5 Mo steel (A204 grade C)".

Unit Operation Before the Accident

The catalyst was regenerated before being discharged. An inspection of the wall thickness was made and nothing was abnormal. New nickel catalyst was loaded and operation of the unit was begun after circulation of naphtha following a charge of steam (400 ppm of sulfur over a period of 15 hours (according to the operators).

The reactive feed was placed in the reactor at 4:30 pm. Reactor heat-up begins with an inlet temperature of 40 degrees C and is allowed to rise in temperature by itself. At approximately 3 hours after the introduction of feed, the reactor inlet temperature is at 80 degrees C with an outlet temperature of 170 to 180 degrees C. At 11:30 pm a fire occurs while the reactor outlet temperature is about 210 degrees C.

Appendix B-5
(continued)

Previous Failure

A similar accident occurred in 1978. In this incident the reactor outlet temperature rose to 350 degrees C or 662 degrees F before the vessel wall failed. Accident investigation mechanical testing showed only a very small deterioration of the qualities of the steel and the regular expansion of the area around the crack. This was reported as showing: "that the conditions of the rupture (700☜C at 40 kg/cm2) were reached during normal procedures with a hot point in the reactor".

Another Failure

In 1990, another gasoline hydrotreated first stage reactor wall rupture occurred. This incident occurred approximately 2 days after a reactor restart following a normal steam-air decoke and regeneration cycle.

Upon learning of two similar reactor wall failures this company: "designed a new reactor system for improved process operability, safety and mechanical strength". The new reactor design has the following features:

1. External reactor skin thermocouples connected to an alarm and feed shutdown system.
   Highest temperature measurement is determined using a local microprocessor.
   The highest temperature reading is sent to DCS.
2. Three catalyst beds instead of the two used in the older design.
3. Two inter-bed quenches instead of the one.
4. Shorter catalyst bed to reduce reactor wall stress related to bed support beams.
5. Updated reactor operating procedures.

Appendix B-6

Corrosion in a Depentanizer Located Between the First and Second Stage Gasoline Hydrotreating Reactors

Summary

Severe, localized weld metal corrosion in the heat affected zone (HAZ) was observed in portions of an olefin plant Depentanizer in December, 1988. Investigation indicates that the likely cause is aqueous sulfide corrosion is the responsible corrosion mechanism. Although organic acid corrosion could not be ruled out.

Age and Design

The Depentanizer tower was made of carbon steel. This tower was apparently eight years old and had not been originally stress-relieved. As a result of localized corrosion in the upper section, this tower was cut and a new upper section of carbon steel was welded onto the existing tower. The new section was stress-relieved prior to placing the tower back into operation. Tower stress-relief would be expected to greatly enhance localized corrosion resistance in welded areas in the upper portions of this tower.

Inspection

Internal examination of the Depentanizer tower revealed severe preferential weld metal (HAZ) corrosion in upper areas of this vessel. It is believed that this was the first internal inspection of the tower. This tower had been in intermittent service for approximately eight years. The carbon steel tower is approximately 110 ft. high and operates at a design temperature and pressure of 190 degrees F and 60 psig at the top and 325 degrees F and 70 psig at the bottom. There are 50 trays in this tower. Vessel trays and hardware (valves) were not corroded. These were reportedly Type 410 stainless steel.

Vessel wall sections, internal attachments, and welds were submitted to a testing laboratory. All testing confirmed metal to be carbon steel. All components were examined for possible sulfide stress-corrosion cracking. No such cracking was observed following visual examination or wet fluorescent magnetic particle testing of selected areas.

Corrosion Theory

Carbon steel that has not been stress-relieved can become susceptible to accelerated corrosion around welds (HAZ) and other areas of high residual stress when exposed to acidic media. The pH of deposits found in corroded areas inside the tower were all acidic indicating a low pH corrosion mechanism. Aqueous sulfide and/or weak organic acids could both promote the type of corrosion witnessed. The presence of corrosion at the top of the tower versus the bottom of the tower was believed to be a function of temperature profile. In this tower liquid water could be present at the top tower section as a result of a wet feed stream from tankage or small reboiler steam leak.

Appendix B-6
(continued)

This unit's pyrolysis gasoline and quench water was shown to contain small amounts of organic acid (eg. Acetic acid, butyric acid, propionic acid, etc). A sampling program showed that:

Raw Gasoline Formic acid, 35.4 micrograms/ml
Acetic acid, 63.7 micrograms/ml
Unknown, propionic acid - about 659 mcg/ml
Unknown, pentanoic acid - about 1189 mcg/ml

Appendix B-7

Ethylene Loss from Salt Dome Storage Well

Summary
Ethylene, worth about $6 million before the accident, was lost in 1988 from a salt dome well near Clute, Texas. Following the concern of local residents and at the request of the Railroad Commission a well was drilled at the most likely adjacent location and the ethylene was found. Mr. Guy Grossman, District Director, of the Railroad Commission reported that the ethylene was found on March 19, by the first well drilled. Mr. Grossman said a flare connected to the well will be kept burning until the ethylene is gone. Mr. Grossman also said the agency is satisfied with the recovery process and plans to continue to monitor operations.

Background
The well is owned by Dow Chemical Co. and was leased, at the time of the accident to the South Texas Pipeline Company, a division of Cain Chemical Inc. The storage cavern was leached, or hollowed out, in 1961 and is about one mile northeast of Clute, a city of about 10,000 residents in south Brazoria County. Mr. Sy Bensky Oxy Petrochemical's Director of Environmental Health and Safety was quoted as saying: "I think the plans were to repair it and turn it back to Dow". A later stated said that "the well has repaired" and "the no plans exist to use it again".
The South Texas Pipeline changed its name to Oxy Petrochemical Pipeline, after becoming part of Oxy Petrochemicals. Both companies were owned by Occidental Chemical Petroleum Corp. of Los Angeles at the time ethylene was being flared.

Incident
The ethylene escaped from a pipe casing leading to the cavern in December, 1989. The accident, which may have been caused by movement in the salt dome, was reported to the commission, but not to county officials. The leak is believed to have resulted in more

than 7 million gallons of ethylene escaping about 1,300 feet underground. The ethylene is believed to be below the salt dome "cap rock". Cain officials said that they did not plan a recovery effort because the missing ethylene poses no danger.

Appendix B-7
(continued)

Change in Plans
After the leak was discovered company officials decided not to recover the ethylene because of the cost and its location. They also said the gas was trapped well under the area's water table and the possibility that it would ever surface was minute. After a meeting with the Texas Railroad Commission and the Brazoria County representatives, Cain Chemical officials agreed to drill an exploratory well near the site to try to recover more than 7 million gallons of ethylene that escaped from a salt dome cavern.

Local Reaction
The Houston Chronicle published two stories on the lost ethylene. Commissioner Ronnie Broaddus of Clute and County Judge John Damon have said they too should have been contacted, considering the quantity of ethylene missing. Local reaction changed from concern to relief after an agreement was made to locate the ethylene. Mr. R. Broaddus said; "`I'm glad to see that they're going to drill a well" and "It shows me that they are willing to try to ease our minds a little bit."

References: Houston Chronicle, 04/07/90, Section A, Page: 27.
Houston Chronicle, 09/21/89, Section A, Page: 26.

Appendix B-8

Interstate 10 Reopens After Ethylene Tanker Truck Spill

Interstate 10 between San Antonio and Houston reopened Thursday evening after a total closure of nearly two days. An 18-wheel tanker truck tipped over just after 8 pm Tuesday, spilling highly flammable ethylene. The accident was about 12 miles east of Seguin, Texas.

No one was seriously injured, but the road was closed so crews could burn off the liquid. The road was further damaged as hot traffic idled on the blacktop, said state spokesman David Otwell. Since I-10 has no frontage roads in the area, traffic was detoured about 16 miles
through the town of Kingsbury, for a delay of about one hour. About 20,000 vehicles a day normally use the damaged section of westbound I-10, which will see some lane closures in the next few weeks as permanent repairs are made.

Reference: Houston Chronicle, Friday, 07/31/98, Section A, Page 34.

Appendix B-9

Fire Fighters Stabilize Trucker's Flammable Ethylene Load

The driver of a tractor-trailer hauling a load of pressurized flammable liquid pulled into the southbound rest stop on Ohio Interstate 271 early Monday afternoon because the lot was largely unpopulated and he feared his shipment could explode. The liquid ethylene, transported at a chilly -155 degrees F and at some pressure. While still on the Ohio Turnpike, the driver did a random check of tire inflation and of the tank's pressure level and noticed the pressure had built up to somewhere around 90 pounds per square inch.

The tanker could have vented or exploded when the pressure reached about 100 pounds per square inch, said Richfield Fire Chief Russ English, who was on the scene, along with Bath Fire Department, Richfield Township Police and Ohio State Police, all trying to contain the scene while the tanker's vent relieved the pressure.

"It's very, very flammable," English said. "And if it would have somehow ignited, it would have been a real mess." Two fire-fighters directed a steady stream of water over the vent in order to reduce to fire risk of the escaping flammable compound (ethylene or C2H4). Ethylene is used to promote the ripening of fruit.

Chemical Leaman Tank Lines of Lionville, Pa., employs the driver and owns the Kenworth truck, which was headed to Chicago with ethylene, bought from Sunoco. The driver, who refused to give his name, said as soon as he noticed the pressure level going up, he immediately began looking for an unpopulated area toward which to steer.

Was he shaken in the face of a possible explosion? "It's part of your job, you know?" he said, wiping sweat from his forehead. "But yeah, it's good this turned out the way it did." Sunoco representative Bill Sanicky was on the scene to make sure fire-fighters knew what kind of a chemical with which they were dealing.

"You don't set it on fire and you don't breathe it," he said. "Pretty straightforward." Chief English said once the vented pressure went down, the driver was followed to a facility in Wooster where the remainder of the chemical was burned off.

Reference: Story by Dan Harkins, Staff Writer, Sun Newspapers,
Cleveland, Ohio, September 4, 1998

Appendix B-10

Blast in Baytown Erupts After Man Nicks a Propylene Pipeline

A tractor-mower operator accidentally nicked an 8 inch propylene pipeline Monday morning.
A white cloud of gas from the line ignited, rupturing an adjacent 10-inch ethylene pipeline and causing a second explosion.

No one was injured, but the tractor and pickup truck that the two workers deserted in their dash to safety were destroyed by the intense fire. "It scares me to look at it," Mr. Shannon, pointing to the smoldering hunk of metal that once was his tractor. "I've never seen a fire that could melt a tractor tire down to the rim as if it had never been there. I've been through Vietnam and seen bombs go off, but I've never seen anything this bad."

An acre of brush and trees surrounding the spot also was blackened by the blaze. Mr. Shannon, an employee of Ihrig & Yoder Landscaping, had been contracted by Chevron Pipe Line to mow the shoulder-high weeds covering the pipelines. The underground lines, which cross a small
water canal, feed hydrocarbons from the Houston Ship Channel to a petrochemical plant.
Shannon had already cleared a wide swath over the pipes, near where they surface to cross the canal, and was backing up to make his last cut near the canal when he struck the pipe.
"I felt the blade hit and my tractor started vibrating," he recalled. "It all happened in a matter of seconds. The next thing I knew this white stuff - I couldn't tell if it was rain or snow -
started spewing up like water and I heard my supervisor yell for me to run."

Mr. Shannon and Mr. Laughlin ran along the canal for nearly a mile before stopping near Interstate 10. Thompson Road was blocked to through traffic all day as fire fighters from Baytown, Highlands and McNair fought to contain the fire. Chevron officials shut off valves on either end of the two leaks, and then pumped nitrogen into the lines to force out the hydrocarbons.

Reference: Houston Chronicle, 08/06/85, Section 1, Page 13.

Appendix B-11

Propane Pipeline Blast Injures Two Workers and Spurs Evacuation

Balls of flame boiled out of a propane pipeline bumped by a tractor mower Monday, setting off a series of explosions that injured two workers and forced the evacuation of 50 homes near Friendswood, Texas. Friendswood officials evacuated homes within a one-mile radius of the pipeline blaze, which erupted in a pasture, a corridor for several pipelines, just off FM 528, about four miles east of FM 518.

"All of a sudden, it was like boom. The whole ground just went up in huge flames. Some guy came flying out of there like he had wheels on," said Peter Boesel, who was driving along a nearby road when the first blast occurred at 2 pm. An employee of Cross Timbers Production Co., said he was checking a gas well about 300 yards from the site when he noticed mower operator inching toward a Phillips Petroleum pipeline that he knew crossed the American Canal, a rice irrigation ditch.

"I stood there and hollered at him, `Look out for the pipeline," and then "I heard the mower hit, I heard the leak and I started to run. All I felt was the percussion and then the heat. Within two seconds, the fire spread 500 yards." The tractor driver stayed on the moving tractor several seconds, and then "bailed off and took off running down the canal, his clothing on fire. His hair was gone, his face was burned, he was bad."

The tractor driver who was mowing for the Galveston County Water Authority, was listed in critical but stable condition at John Sealy Hospital in Galveston with burns over 64 percent of his body. Another mower operator was treated at the scene.

Three more explosions occurred over the next four hours. Officials said the blasts were either from nearby pipelines igniting or from bursts of escaping gas. The booms rattled windows for miles and sent emergency crews scurrying. Officials allowed the fire to burn Monday night while attempting to cut off remaining gas supplies. Flames at times shot 100 feet into
the air and created a spectacular orange glow against the night sky. Friendswood Fire Chief Bill Wilcox said Phillips officials shut down three lines in the area.

At least seven pipelines owned by several companies, including Valero, South Texas and Kane Chemical cross the area, but it was not known exactly what was in the other pipelines.
Officials were concerned about ethylene and other highly explosive gases.

Mr. Penny Burke, former President of the Friendswood Volunteer Fire Department, complained that several previous fires have occurred at the pipeline site. "They've had four blowouts in the past several years. I'm curious why they've happened so frequently" said Burke, who lives about a half-mile away.

Reference: Houston Chronicle, 11/29/88, Section A, Page: 13.

Appendix B-12

Ethylene Pipeline Fire Lights Up Texas City Skies

A fire fueled by either ethylene or natural gas sent flames shooting 500 feet in the air in Texas City Monday morning. No injuries were reported, but a small unmanned heating station
owned by Dow Pipeline Co. sustained damage. The facility, located near Texas 146 and FM 519, is used to heat ethylene supplied by the pipeline to Dow by Chevron Pipeline Co., officials said.

About 100 fire fighters from the Texas City and La Marque areas fought to contain the fire for about two hours before officials from Dow shut down the pipeline about 8:30 am.
Fire fighters also poured thousands of gallons of water onto nearby tanks at Tex Tin Corporation, a tin-smelting plant near the heating station, to keep them from igniting.

Fire fighters were called at 6:02 am after a La Marque resident spotted the flames. All city fire units responded to the fire, and minutes later units from La Marque and fire fighters from area refinery fire departments were called in. Fire fighters encountered problems getting enough water to the fire and had to lay about 3,000 feet of hose to a hydrant in La Marque. They also used water from the Tex Tin and Union Carbide plants, and fire fighters from Amoco drafted water from a pond near the Texas 146 overpass. The morning rush-hour traffic on Texas 1765, Texas 146 and FM 591 was diverted to prevent spectators from hampering fire fighters efforts.

Mr. Tim Scott a Dow spokesman, said company investigators believe the fire was ignited when a small tube in the heating station ruptured, causing the release of ethylene and the subsequent fire. He said the fire went out after Dow officials shut down the pipeline.
However, Art Spencer, spokesman for Chevron Pipeline Co., which supplies the ethylene to Dow, said company officials believe the heater caught fire for an undetermined reason and ignited natural gas that powers the heater.

Reference: Houston Post, 03/18/86, Section: Local, Page: 8D
Story by Jim Newkirk a Post Reporter

Appendix B-13

Shell's Norco Olefins are Shutdown Due to FCCU Blast Damage at Complex

General

Site damage resulted in the shutdown of all gasoline and ethylene production at the site. The explosion, occurred at 3:34 am on May 5, 1988.

Olefin Unit Damage

One olefin unit employee was killed by a brick wall that fell as a result of an explosion in the FCCU. This olefin unit is about a block from the FCCU. In the older olefin unit, control room instrument damage occurred when a section of the wall and roof fell. Both of the olefin units were shutdown due to general site damage.

FCCU Damage

A catastrophic explosion and fire occurred in a 90,000 b/d fluid catalytic cracking unit (FCCU) located at Shell Oil Co.'s Norco, La. refinery. Six of the seven Shell employees killed were in or near the FCCU's Control Room. Shell and independent investigations concluded the hydrocarbon vapor release that resulted in the explosion and fire occurred because of a corrosion related piping failure in a gas recovery section of the unit. The resulting fire in the FCCU was allowed to burn itself out. The FCCU unit was about 25 years old and had undergone a scheduled turnaround in April.

Site Damage

Electrical power and water supply to many units was affected by the FCCU explosions. Also, shut down by the explosion was Shell's Norco gas processing plant, which has a capacity of 403,300 gal/day of ethane, 320,700 gal/day propane, 107,900 iso-butane, 128,000 butane, and 167,300 natural gasoline.

Damage Outside the Complex

Outside the FCCU site, most of the damage resulted from blast force to roofs, windows, and walls. The FCCU produced a fireball that could be seen 40 miles away.

Two-thirds of the homes in the riverside community sustained damage in the blast, as did most buildings in its tiny business district near the refinery. A forced evacuation of the town's 4,500 residents occurred for about six hours until the blaze was contained. More than 9,000 claims were filed against Shell and, so far, 5,200 have been settled for $24 million, the company said.

References

Oil & Gas Journal, May 9 and May 16, 1988

Chemical Week, May 18, 1988, Pages 8-9.

Houston Chronicle: 05/06/88, Section 1, Page 2.

Houston Chronicle: 05/07/88, Section: Business, Page 3

Houston Chronicle: 08/04/88, Section: Business, Page 3.

Appendix B-14
Flare System Explosion at Monsanto's Chocolate Bayou Olefin Unit

Summary

In July of 1966, an explosion occurred in Chocolate Bayou plant flare system. Minor damage to the system resulted. There were no staff injuries. Witnesses to the incident observed black smoke, but no flame, at the flare tip and at the base of the flare. A loud report at the time of incident was heard through the plant site.

System Damage

The damage to the system was restricted to the expansion joint and the knockout pot at the base of the flare stack. The expansion joint, for all practical purposes, was completely destroyed. Pieces of the expansion joint were found as much as 30 feet from the knockout pot. Inspection of the fragments of the expansion joint revealed holes in the joint as large as a half inch in diameter. These holes were the result of internal corrosion and had existed prior to the incident.

The investigation also revealed the corrosive action on the joint had been detected and temporarily provisions had been made to prevent leakage of the process gas to the atmosphere. An expansion joint which was compatible with the process environment had been procured and was to be installed in the near future.

Incident Background and Cause

Flare system is provided with a natural gas sweep designed to prevent a flashback from the flare tip in case oxygen contamination occur. The natural gas sweep was discontinued two days prior to the incident. A temporary sweep of nitrogen was substituted. The reason for the change in purge gas revolved around preparation for routine relief valve maintenance on the system. The maintenance to be performed consisted of removal of several relief valves for periodic inspection and testing. The relief valves were to be removed with the flare header in service. Removal of the valves without the release of vapor from the header was not possible. The change of purge gases reduced the hazard related with the possible release of combustible vapor during the removal operation.

The relief valves were removed one day prior to the incident and the openings on the flare system were provided with blind flanges. The relief valves were reinstalled approximately five hours prior to the explosion. The nitrogen sweep was still in operation at the time of the incident.

The basic cause of the explosion was the introduction of air into the flare system. The source of the air was either the holes in the severely corroded expansion joint or the venting of air into the flare system from a distillation column in the startup stage. Examination of the temporary nitrogen purge facilities revealed a significant reduction ion the volume of purge gas.

Reference: Flare System Explosions by J. L. Kilby, Monsanto Co., Alvin, Texas from an AIChE Loss Prevention publication.

Appendix B-15
Compressor Deck Lube Oil Fire

A process operator overfilled the lube oil reservoir serving the C2 and C3 refrigeration compressors. This operator started a pump to transfer oil from a storage tank to the lube oil reservoir and forgot about it. Oil leaked from bearings on compressor deck and found a source of ignition (likely hot steam) resulting in fire which burned wiring on ethylene refrigeration turbine controls resulting in operating without normal compressor controls for about seven hours while new wiring was run.

Appendix B-16
Compressor Deck Lube Oil Fire Due to Water in a Steam Header

An operator error in overfilling a steam drum, prior to a furnace start-up, results in water entering the high pressure steam going to propylene compressor turbine. Steam turbine damage occurs after high vibration, oil leaks around the turbine bearings, and ignites. After this incident, the plant installed a turbine shutdown on low steam temperature using a voting system.

Appendix B-17
Pyrolysis Gasoline Fire at a Pump Seal

A GHU feed pump taking suction from a feed surge drum at about 60 psig and discharging into the reactor heating train developed a seal leak. This pump seal leak is believed to have been the result of a bearing failure. Leaking gasoline was ignited, probably by the hot bearing. The suction valve for pump isolation was within 3 feet of the pump. This was the only isolation valve in the area. An operator had to wear a special "fire suit" to close the suction valve with fire raging. After this incident, a valve was installed near the surge drum so that the feed to pump could be stopped without approaching these high pressure pumps.

Appendix C-1

Vapor Cloud Explosion and Fire Results in the
Destruction of Amoco Chemical Polypropylene Unit

Summary

A propylene vapor cloud explosion resulted in major unit equipment damage. Fires fed by propylene and polypropylene burned for over 10 hours.

Damage

Unit was considered a total loss. Damage estimate was in excess of $45 million dollars. Amoco chose not to rebuild at this site.

Description

On October 21, 1980 at an Amoco Chemical polypropylene unit located near New Castle, Delaware a propylene vapor cloud explosion resulted in major unit damage. A major fire destroyed most of the process unit.

A key issue in this accident was the lack of maintenance staff with experience in the assigned task that night.

This accident occurred at night during a baseball world series game and on the plant bowling league night. The maintenance staff reached by telephone for the unplanned overtime "call out" did not have experience in the specific task being assigned.

Improper maintenance procedures during clearing of a plugged recycle cooling line on a 10,000 gallon capacity polypropylene reactor released hydrocarbons and polymer. Instead of removing only the motor operator of a 4-inch plug valve, the valve itself was removed in error. The release of 12,000 to 16,000 pounds of monomer at about 150 psi produced a 250 by 450 foot vapor cloud which ignited after about 2 minutes.

The vapor cloud explosion broke flammable liquid lines throughout the three process trains and opened polymer lines in the finishing area. The blast also broke fire protection system risers, disrupting all fire water. Fires throughout the polymerization finishing and storage silo areas burned for over 10 hours. A total of twenty-one fire departments responded to this accident including volunteer, professional, and industrial fire brigades.

Two of the three polymer process lines, the control building, and the finishing area were severely damaged. The compressor building, solvent recovery area, finished product warehouse and cooling tower were moderately damaged.

Appendix C-2

Vapor Cloud Explosion at Phillips High Density Polyethylene Unit

Summary:
A vapor cloud explosion resulted in major unit damage and a fire in the unit reactor area. The vapor cloud and fuel for the fire was a mixture of ethylene and iso-butane.

Damage:
Published estimates are that plant damages are in excess of $500,000,000.
Numerous legal actions were filed by works and local property owners.

Description:
Shortly after 1:00 pm, on October 23, 1989, a large flow of ethylene, the reactant, and iso-butane, a catalyst carrier, issued forth under about 700 psig from the reactor loop. The vapor cloud drifter northward toward the center of the high density polyethylene (HDPE) process area before ignition, which is believed to have occurred approximately one minute after the release. Seismograph data from recording stations in the area suggested the blast was equivalent to the detonation of 10 tons of TNT.

Smoke from the plant located in Pasadena, Texas could clearly be seen on the west side of Houston. The accident was extensively cover by television and published reports.

Accident Reports
The Occupational Safety and Health Administration cited Phillips for many problems when it proposed $5.7 million in fines against the company. During its investigation of the Oct. 23 explosion that killed 23 workers, OSHA uncovered internal Phillips documents that called for corrective actions but which were largely ignored, Secretary of Labor Elizabeth Dole said last week. Among the 15,000 Phillips records reviewed by OSHA was a management safety study conducted at the Pasadena plant between 1979 and 1981 by DuPont. "Management has the responsibility for ensuring that production operations are inherently safe or are adequately controlled against inadvertent mis-operation," DuPont safety consultant Jan W. Withrow wrote in a confidential 1980 report. "Management must be sure that personnel will not be exposed to hazards which they are unaware of or unable to control.' Withrow recommended Phillips create a special committee to study potentially dangerous systems at the plant, operations known in the industry as "process hazards.'

A government-sponsored study concluded that: Petrochemical companies that use subcontractors to help cut operating costs may be endangering their workers' lives. The seven-month study, prompted by the Oct. 23 explosion at the Phillips 66 plastics plant in Pasadena, examined the potential dangers inherent in the industry's increasing dependence on subcontractors.

"Some industry efforts aimed solely at cutting costs through a greater reliance upon poorly trained contract employees may ultimately jeopardize safety and health in the work place," said the report by the John Gray Institute, part of the Lamar University System in Beaumont.

"Short-term contractors were often found to be under economic pressure to perform a given task quickly under fixed-cost agreements," the study found. "Safety was frequently cited as a secondary consideration among short-term contract workers.'

Among its findings:

a. Contract workers suffer far more injuries and illnesses than regular plant workers, while some subcontractors actively discourage reporting of injuries.

b. Safety is not a priority of most petrochemical operations when choosing a subcontractor. In fact, many such companies don't even know their subcontractor's injury and illness rates.

c. Subcontractor employees receive far less safety and health training than their counterparts on the permanent work force.
"Pronounced differences between the levels of safety awareness among full-time, permanent employees and contract employees were observed," the report said.

d. "Contract employees were routinely instructed to run in the event of an emergency, leaving proprietary (company) employees to handle such emergency procedures as firefighting, spill control and emergency shutdown.'

The John Gray Institute report provided only preliminary results, with a full report due out in August. In releasing the report, the Occupational Safety and Health Administration announced plans to hold a conference for labor, industry and government officials to discuss the issue.

"I think the John Gray study is a signal to (chemical companies) that the jig is up," said Dick Leonard, special projects director for the Oil, Chemical & Atomic Workers International Union. "I'd be frightened as hell, especially of the private actions that they would be subjected to by contractors, members of the community or even workers themselves following the next calamity.' Kyle Olson, director of safety and plant operations for the Chemical Manufacturers Association, said, "If there are problems - and there seem to be, (according to) this study - as an industry we have to roll up our sleeves and get to work on them.' Phillips officials declined to comment on the report.

John Gray officials received questionnaires from 256 petrochemical operations, which voluntarily responded to a survey. But researchers said they gleaned far more valuable information from in-depth case studies conducted at nine petrochemical plants, including four in Texas. While some of the plants studied were recommended by industry as model operations, others were suggested by labor leaders because of known safety problems.

Receiving input from a national steering committee that included union, industry and medical experts, the study was designed to understand how subcontractors affect injury and accident rates at petrochemical plants.

An outside consultant warned Phillips Petroleum Co. about safety shortfalls at its Pasadena plastics plant nearly a decade before October's deadly explosion there, according to documents obtained by the Houston Chronicle.

In 1981, a recommended process-hazards review committee had not begun operating.

In its report, OSHA alleged Phillips willfully disregarded worker safety by failing to conduct safety audits that included process-hazard reviews.

Phillips spokesman George Minter, however, insisted that Phillips "has maintained an active hazards-review program for a number of years at its Houston Chemical Complex. As a result, all processes at the complex have been reviewed under the program.' In his reports, Withrow also had recommended Phillips analyze each position at the plant, to try to identify all potential hazards an employee would face when performing a job. Such a safety study is known as a "job safety analysis.' Despite his admonitions, Withrow in 1981 found company engineers drafting written instructions for each position without using the job safety analysis technique. "There is an overall resistance to using this technique primarily because of the time it requires," Withrow said in his 1981 report.

OSHA also cited a lack of a job safety analysis when issuing its citations. Phillips spokesman Minter would say only that "job safety is part of (plant) procedures.' In his 1981 report, Withrow stressed the need for Phillips to examine the human factor in accidents, an aspect he said company officials too often overlooked. "Auditors are not concentrating on employees performing their jobs in their normal work environment," Withrow wrote. "For example, very few items (in their audits) related to unsafe acts, unsafe positions or unsafe practices. Most items pertained to equipment, the work environment, or housekeeping... Du Pont's experience is that 96 percent of all injuries are the result of the employees' actions, or their failure to act.' Phillips reportedly is focusing on human error as the likely immediate cause of the Oct. 23 explosion in Pasadena. OSHA also cited the company for failing to conduct a "human-factor analysis.' Finally, in his 1981 report, Withrow recommended Phillips continue its relationship with Du Pont. Nonetheless, after Withrow's report, Phillips ' contract with DuPont expired and was not renewed.

References:
Houston Chronicle, 04/25/90, Section: A, Page 1.

Houston Chronicle, 04/27/90, Section: Business, Page 1
Houston Chronicle, 04/27/90, Section: A, Page: 1

Appendix C-3

Hydrogen Recovery Unit - Nitrous Oxide Explosion

Summary: A heat exchanger was damaged as a result of an internal explosion.

Damage: Heat exchanger and some adjacent equipment required replacement.

Description:
The heat exchanger coils fabricated from 1/4 inch copper pressure tubing burst due to an explosion inside the tubes. This heat exchanger normally operated at about -340 degrees F chilling a hydrogen stream upstream of an absorber tower. The explosion occurred during a warming of this exchanger to vaporize material which had frozen in and partially plugged it. The majority of the tubes were opened by the explosion. Some breaks severed the tube completely, with outward flaring of the tubing at the break. Most of these latter breaks occurred at somewhat regular intervals along the tubing without damage to the sections between the breaks. This type of rupture was described is typical of a gas phase detonation.

The accident investigation team established that the high-pressure hydrogen had reacted with small quantities of nitrous oxide (N2O) which had been frozen out in the heat exchanger tubing. The initiation is unknown but was associated with the warming process. The nitrous oxide concentration in the hydrogen stream was in the 0.5 to 3 ppm range. When it had been recognized as a contaminant, it was possible to take corrective action and monitor the stream so as to be certain that the nitrous oxide had been removed.

Reference: Applied Cryogenic Engineering, Edited by R. W. Vance and M. W. Duke Copyright 1962, by John Wiley & Sons, Library of Congress Catalog Card Number 62-18355

Appendix C-4

Cold Box Explosion at the Shell Berre Olefin unit

Summary:
An explosion occurred within a "cold box" located at the Shell Berre Olefin unit in France.
The accident investigation concluded that NOx and gums in the core exploded during the warming process.

Damage:
The Olefin unit was shutdown for nearly five months. A major government review of FCC off-gas processing at low temperatures occurred. Others in the olefin industry stopped processing FCC off-gas and/or review gas processing as a result of this incident.

Description:
The incident occurred after a major unit upset with extensive flaring from the cracked gas compressor. After about one hour the cold box feed gas temperature had increased to about 25 degrees C, to the lack of a continuous forward gas feed. Both the ethylene and propylene refrigeration compressors went into shutdown mode due to high drum levels. Ethylene chilling of the cracked gas was greatly reduced due to the loss of the ethylene refrigeration compressor. Warm cracked gas entered core type heat exchangers that normally operated below -70 deg C.

The accident investigation concluded that NOx and gums in the core exploded during the warming process. Process simulations showed that during the unit upset butadiene and cyclopentadiene could have entered the cold area cores due to the loss of both the ethylene and propylene refrigeration compressors.

Appendix C-5
Explosion of Ammonium Nitrate at Terra Industries, Inc.
Nitrogen Fertilizer Facility, Port Neal, Iowa

Issues and Recommendations
Chemical Emergency Preparedness and Prevention Office (CEPPO)
The United States Environmental Protection Agency

The investigation team concluded that the conditions that caused the explosion existed primarily because of the lack of safe operating procedures in the Terra Port Neal ammonium nitrate unit. Most of the operating procedures that were used in the plant were not written.

The investigation team further concluded that the lack of written safe operating procedures:

1. Would have made development and evaluation of training programs difficult.
2. Would have made enforcement of operating procedure use difficult.
3. Would have made evaluation of the operating procedures for deficiencies and improvements difficult.

Effective safe operating procedures can only be written and evaluated after completion of a comprehensive process hazard evaluation. The investigation team could find no evidence that Terra had conducted such an evaluation of the ammonium nitrate unit. This resulted in a low pH in the neutralizer after shutdown, the unknown presence of contaminants in the neutralizer, the lack of monitoring when the plant was shut down with the process vessels charged, the lack of flow in the neutralizer, the introduction of high temperatures through the nitric acid spargers, and the introduction of low density zones in the neutralizer.

Terra employees assumed that the DCS in the ammonium nitrate unit was not capable of operating in automatic or cascade mode because of a part shortage. A lack of clear communications between operations, maintenance and engineering caused the unit to operate without a pH probe from November 27 through the time of the explosion. pH probe suppliers indicated that a viable pH probe could have been provided in a few days if one had been ordered.
To avoid the conditions described in Section 9 of this report that resulted in the explosion in the ammonium nitrate plant and to minimize the chance of a similar event occurring again, the team developed the following recommendations for ammonium nitrate manufacturers:

1. The investigation team recommends that engineers and operators conduct a thorough process hazard evaluation of ammonium nitrate plants. This should include a thorough literature search to identify materials and conditions that increase the

hazards of producing AN solutions.

This evaluation should be conducted periodically to ensure that the most recent information is always available to the engineers and operators conducting process hazard evaluations. This activity also requires current piping and instrumentation diagrams, unit drawings, materials of construction, equipment histories, and safe operating procedures. Many of the hazards listed in this literature can be avoided through procedural changes. The engineer responsible for the AN unit should head the evaluation team.

2. The investigation team recommends that engineers and operators establish safe process operating parameters for the ammonium nitrate unit. Operating parameters should include at least pH, temperature and the presence of contaminants. This should include a program to monitor feed streams for the presence of known contaminants on a periodic basis as well as periodically reevaluating operating parameter ranges.

3. The investigation team recommends that engineers and operators develop written, safe operating procedures for the ammonium nitrate unit. Procedures should be developed for activities conducted in the AN plant in all modes of operation, including periods when the unit is shut down and the vessels are charged. These procedures should require that process parameters be monitored and should specify actions to be taken when parameter values deviate from acceptable ranges. Management roles in this process include ensuring that these procedures are used and that procedures are appropriate for conducting tasks safely.

4. The investigation team recommends that engineers and operators complete a management of change procedure for all operating parameter range changes. This should include approval to operate the unit outside of approved parameter ranges by the engineer responsible for the AN unit, and documentation of these activities. The engineer responsible for the AN unit should be included in all changes in the facility that could change feed streams or conditions in the AN unit.

5. The investigation team recommends that maintenance, operations and engineering personnel develop a maintenance program that anticipates problems in the AN unit. This program should include predictive failure analyses and an aggressive preventive maintenance program. The maintenance program should be periodically evaluated by this group by at least utilizing maintenance records and equipment histories.

6. The investigation team recommends that engineers, operators, and maintenance personnel develop and deliver training programs that include complete, written safe operating procedures. The training programs should contain specific performance and knowledge goals for participants and the procedures that will be utilized to evaluate participant competence.

7. The investigation team recommends that plant management ensure that engineers, operators, and maintenance supervisors and managers develop lines of communication to ensure that these recommendations are implemented and maintained.

Appendix C-6

EPA/OSHA Press Release Accident Investigation Report of the Shell Chemical Company, Deer Park, Texas Explosion and Fire on June 22, 1997

EPA and the Occupational Safety and Health Administration (OSHA) released a Joint Chemical Accident Investigation Report of the Shell Chemical Company, Deer Park, Texas facility. An explosion and fire took place at the Shell complex on June 22, 1997, resulting in injuries, public sheltering, closure of transportation routes and property damages both on site and off.

The root causes of the accident included:

a. Lessons learned from prior incidents involving Clow check valves at Shell facilities were not adequately implemented.
b. The Clow Model GMZ check valves installed in the Olefin Plant Number III process gas compression system were not appropriately designed and manufactured for the heavy-duty service with which they were used.
c. The process hazards analysis of the process gas compression system was inadequate.
d. Measures necessary to maintain the mechanical integrity of the check valves were not taken.
e. Operating procedures for the start-up of the process gas compression system were not adequate.

The report makes recommendations to prevent future incidents.

Although EPA will continue to have a role in accident investigation and prevention of chemical accidents, the recently funded Chemical Safety and Hazard Investigation Board is now operational. The Board has responsibilities for chemical accident investigations. However, EPA is committed to completing investigations initiated prior to the funding of the Board.

The report can be accessed on the Internet at: http://www.epa.gov/ceppo/acc-his.html.