Industrial Accidents Involving Chemical Reactors

A person from one of the major U.S. chemical industries approached AristaTek and asked whether the PEAC tool could help in the assessment of run-away chemical reactions or reactor failure in the synthesis of chemicals. We responded that the PEAC tool was designed primarily for responders to a chemical accident to give information on protective action distances in the case of an accidental release, cleanup, protection of responders and the public, and other safety information, but the PEAC tool is not designed to address the root causes of the chemical accident (failure due to runaway temperature or pressure of a chemical reactor).

This question prompted AristaTek to review industrial accidents investigated by the U.S. Chemical Safety and Hazard Investigation Board and posted on the Internet. Real-world case studies are often the best teacher. Several case studies are examined in this newsletter and matched with PEAC tool information.

U.S. Chemical Safety and Hazard Investigation Board

The U.S. Chemical Safety and Hazard Investigation Board (CSB) is an independent federal agency charged with investigating industrial chemical accidents at fixed facilities. The agency does not issue fines or citations but does make recommendations to the industry involved and to regulatory agencies and labor groups. It is designed to conduct scientific investigations as to the root cause of chemical accidents and is not an enforcement or regulatory body. Most of the Board members and staff have degrees in chemical or mechanical or other engineering disciplines, have PE licenses, have chemical process industry experience, or are health or safety professionals. Congress in establishing CBS specifically stated (see 42 U.S.C. section 7412(r)(6)(G)): "No part of the conclusions, findings, or recommendations of CSB relating to any chemical incident may be admitted as evidence or used in any action or suit for damages arising out of any matter mentioned in an investigation report".

CSB was authorized by the Clean Air Act Amendments of 1990, but did not become operational until 1998. More on the mission statement and history can be found at http://www.csb.gov/index.cfm?folder=Mission_History&page=index .

In 2002, CSB issued a study identifying 167 serious reactive chemical accidents in the United States between 1980 and 2001 that involved more than 100 fatalities collectively. Since 2001, CSB has tracked another two dozen reactive chemical accidents.

A thorough CSB investigation of an industrial accident can take several months, even sometimes over a year because of the complexity of the situation. First responders coming on scene of an accident only have limited information as to what is happening.

Example: April 2004 Toxic Allyl Alcohol Release Dalton Georgia

Information from several CSB Reports, see http://www.csb.gov/index.cfm?folder=news_releases&page=news&NEWS_ID=189 and links.

On 12 April 2004, MFG Chemical, Inc., at their facility in Dalton, Georgia, begin their first-ever production batch of triallyl cyanurate (TAC) in a 2000-gallon chemical reactor. Triallyl cyanurate is an intermediate chemical used in the production of resins, plastics, coatings, and adhesives. The major starting chemical used in the reactor is allyl alcohol. Allyl alcohol reacts with cyanuric chloride in the presence of a catalyst generating TAC and hydrogen chloride. Tests on TAC production had been carried out in the laboratory and small batch reactors, but this was the first time in a large production reactor. The reaction for TAC production generates considerable heat; if the heat is not removed quickly enough from the reactor, the reaction can self-accelerate or "run away". This happened with the production reactor at 9:30PM; operators did not take into account that the heat could not be removed as quickly from the 2000-gallon reactor compared with the small batch reactor. The reactor pressure built up bursting 20 inch diameter manway gasket followed quickly by failure of a rupture disk at 75 psig. The result was allyl alcohol and possibly some hydrogen chloride released as a vapor cloud to the atmosphere. No TAC or cyanuric chloride was released. The MFG crew evacuated and called 911 within minutes. At 14 minutes into the event, residents called in complaining of the odor. After 9 hours into the event, MFG successfully knocked down the escaping vapor cloud using an overhead water spray. At 16.5 hours, the reactor was sealed.

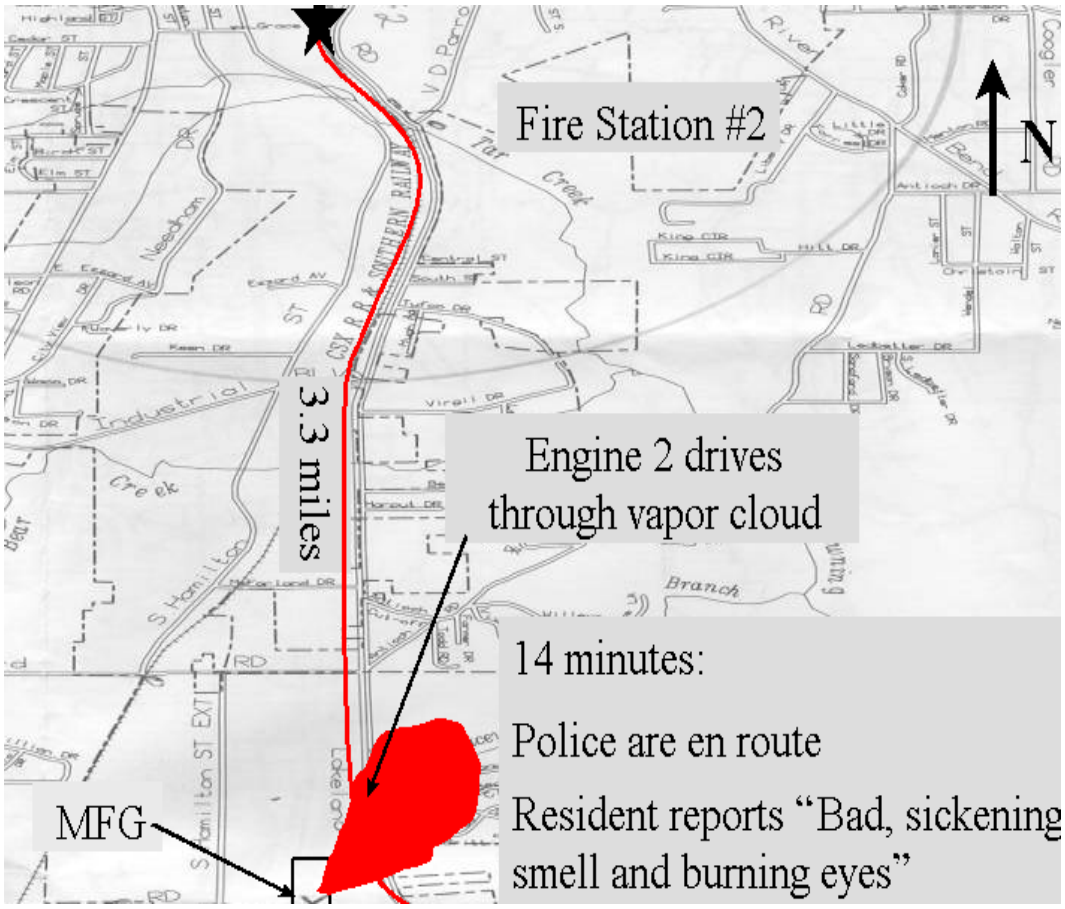
More than 100 families and businesses were evacuated because of the toxic allyl alcohol vapor cloud. Some 154 people were decontaminated and evaluated at a local hospital. Contaminated water runoff from the facility killed fish and other aquatic life in two creeks. Vegetation was chemically burned up to 0.5 miles downwind of the facility.

CSB Chairman Carolyn Merritt said, " This is yet another serious industrial accident that endangered the public and resulted from an uncontrolled chemical reaction. It is vital that chemical operators properly assess the hazards of reactive processes and put appropriate safeguards and emergency plans in place". CSB investigators also noted that the MFG emergency plan for the 31,000 pounds of allyl chloride stored at the site addressed only flammability and not toxicity. Fire and police departments responding to the scene lacked appropriate protective equipment, and 13 police officers were affected by vapors. Another four ambulance crew workers were sickened from exposure forcing withdrawal and inability to treat injured personnel.

The following slides were presented by CSB at a public community meeting held on 16 November 2004 in Dalton, Georgia: The entire slide presentation is available at http://www.csb.gov/completed_investigations/docs/MFG-cmty-mtg-FINAL-posting.html.

Figure 1, top left: 2000 gallon reactor, with roof and walkways

Top, right: rupture disk and manway gasket location as seen from mezzanine floor
Bottom: Projected allyl vapor cloud 14 minutes after release based on resident complaints of odor; emergency responders quickly came to the site but drove through the vapor cloud to get there



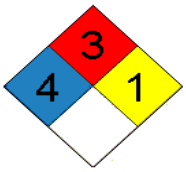
What can the PEAC tool do? The PEAC tool is designed for emergency responders. The PEAC tool does not contain information on run-away chemical reactions which might potentially happen during synthesis. It is still the job of industry to inform emergency responders what chemicals are stored or used on the facilities and provide an off-site consequence analysis of accidents which may potentially happen, and do this ahead of time. Under allyl alcohol, the PEAC tool displays the image shown at the left, below. The user can also model the downwind plume cloud; the PEAC tool asks the user information on the meteorology and amount or container size released and a level of concern, and the PEAC tool calculates a downwind protective action distance (example, below right).

Allyl alcohol

CAS 107-18-6
UN 1098
GUIDE 131 - Flammable liquids - toxic

Colorless liquid with mustard-like odor

NFPA Information



Health (Blue): 4 Deadly
Fire (Red): 3 Flash point < 100°F
Instability (Yellow): 1 Unstable if heated

Physical and Chemical Properties
Formula: $CH_2=CHCH_2OH$
Molecular weight: 58
Flash point: 70°F
Lower Explosive Limit: 2.5%
Upper Explosive Limit: 18%
Auto Ignition Temp.: 713°F
Boiling point: 205°F
Melting point: -200°F
Rel Vapor density @68°F: 2 (Heavier than air)
Vapor pressure @68°F: 0.02 atm
Liquid Specific gravity: 0.85 (Lighter than water)
Ionization Energy: 9.67 eV
RAE Systems PID correction factor for 10.6 eV: 2.4
RAE Systems PID correction factor for 11.7 eV: 1.7
Yield Factor: 0.03

Toxic Levels of Concern
IDLH: 20 ppm
TWA: 2 ppm
STEL: 4 ppm
TEEL-1: 4 ppm

Allyl alcohol

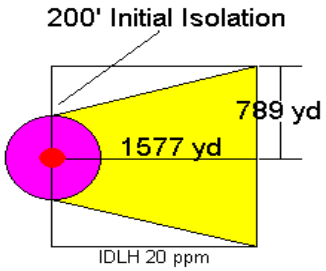
CAS 107-18-6
UN 1098
GUIDE 131 - Flammable liquids - toxic

Location and Time
Dalton, GA
Latitude 34° 45' N Longitude 84° 58' W
4/12/2004 21:48

Meteorology
Temperature: 60 °F
Wind Speed: 2 mph
Cloud Cover: 60 %
Terrain: Urban/Forest

Source
Spill Type: Instantaneous
Mass: 500.0 lb

Results
Level of Concern: 20 ppm
Initial Isolation Distance: 200 ft
Protective Action Distance: 1577 yd



The information contained in the 2004 Emergency Response Guidebook (ERG) is also in the PEAC tool. The ERG is intended for use in transportation accidents and not runaway chemical reactions which might occur during synthesis. Nevertheless, there is still some useful information in the ERG. The information under Guide 131 is displayed below.

GUIDE 131 Flammable LIQUIDS - TOXIC

Initial Isolation and Protective Action Distance

Small Spills			Large Spills		
Initial Isolation	Day	Night	Initial Isolation	Day	Night
100 ft	0.1 mi	0.1 mi	200 ft	0.2 mi	0.4 mi

POTENTIAL HAZARDS

HEALTH

* **TOXIC; may be fatal if inhaled, ingested or absorbed through skin.**
* Inhalation or contact with some of these materials will irritate or burn skin and eyes.
* Fire will produce irritating, Corrosive and/or toxic gases.
* Vapors may cause dizziness or suffocation.
* Runoff from fire control or dilution water may cause pollution.

FIRE OR Explosion

* **Highly flammable: Will be easily ignited by heat, sparks or flames.**
* Vapors may form Explosive mixtures with air.
* Vapors may travel to source of ignition and flash back.
* Most vapors are heavier than air. They will spread along ground and collect in low or confined areas (sewers, basements, tanks).
* Vapor Explosion and poison hazard indoors, outdoors or in sewers.
* Those substances designated with a **"P"** may polymerize explosively when heated or involved in a fire.
* Runoff to sewer may create fire or Explosion hazard.
* Containers may explode when heated.
* Many liquids are lighter than water.

PUBLIC SAFETY

* **CALL Emergency Response Telephone Number on Shipping Paper first. If Shipping Paper not available or no answer, refer to appropriate telephone number listed on the inside back cover.**
* As an immediate precautionary measure, isolate spill or leak area for at least 50 meters (150 feet) in all directions.
* Keep unauthorized personnel away.
* Stay upwind.
* Keep out of low areas.
* Ventilate closed spaces before entering.

PROTECTIVE CLOTHING

* Wear positive pressure self-contained breathing apparatus (SCBA).
* Wear chemical protective clothing that is specifically recommended by the manufacturer. It may provide little or no thermal protection.
* Structural firefighters' protective clothing provides limited protection in fire situations ONLY; it is not effective in spill situations where direct contact with the substance is possible.

EVACUATION

Spill

* See the Table of Initial Isolation and Protective Action Distances for highlighted substances. For non-highlighted substances, increase, in the downwind direction, as necessary, the isolation distance shown under "PUBLIC SAFETY".

Fire

* If tank, rail car or tank truck is involved in a fire, ISOLATE for 800 meters (1/2 mile) in all directions; also, consider initial evacuation for 800 meters (1/2 mile) in all directions.

EMERGENCY RESPONSE

FIRE

CAUTION: All these products have a very low Flash point: Use of water spray when fighting fire may be inefficient.

Small Fires

* Dry chemical, CO_2, water spray or alcohol-resistant foam.

Large Fires

* Water spray, fog or alcohol-resistant foam.
* Move containers from fire area if you can do it without risk.
* Dike fire-control water for later disposal; do not scatter the material.
* Use water spray or fog; do not use straight streams.

Fire involving Tanks or Car/Trailer Loads

* Fight fire from maximum distance or use unmanned hose holders or monitor nozzles.
* Cool containers with flooding quantities of water until well after fire is out.
* Withdraw immediately in case of rising sound from venting safety devices or discoloration of tank.
* ALWAYS stay away from tanks engulfed in fire.

(information partially displayed for sake of briefness; words in color can be selected to get definitions or additional information)

One thing jumps out. The NFPA Hazmat diamond gives allyl alcohol a "4" rating for a health hazard… **deadly**. Some reference sources might give allyl alcohol a "3" rating instead of a "4" rating. Toxic effects of allyl alcohol include severe eye and respiratory irritation. There may be lung, liver, and kidney complications for prolonged exposure. The toxic effects of allyl alcohol are in the public domain at the government Toxicology Data Network (Hazardous Substance Data Base) , available on the Internet at http://toxnet.nlm.nih.gov/cgi-bin/sis/htmlgen?HSDB.

The Immediately Dangerous to Life and Health (IDLH) concentration in air is 20 parts per million (ppm). This is the Level of Concern used in the PEAC tool example displayed, but the user can use other levels of concern. Allyl alcohol has an irritating odor somewhat like mustard. The map drawn by CSB was based on resident complaints and interviews of residents after the event. The limits of odor detection varies between individuals, but the Hazardous Substance Data Base list the limit of odor detection as 0.78 ppm. The boundaries drawn in the CSB diagram for the toxic cloud probably are closer to 10 or 20 ppm (based on the complaints) rather than the limit of odor detection.

The normal boiling point of allyl alcohol is 208°F. The rupture disk failed at 75 psig. This means that the temperature inside the reactor at the time of rupture must have been considerably greater than the normal boiling point. When the pressure is released, the allyl alcohol would escape to the air as vapor and form a vapor cloud. There would be an instantaneous release of vapor followed by a continuous and declining release of more vapor. The vapor density is 2, which suggests that the vapor cloud should tend to hug the ground at least away from the reactor after it cools.

The other components used in the reactor can be pulled up in the PEAC tool and can be seen to have much higher boiling points (except hydrogen chloride). CSB concluded that the other chemicals were not released in any significant quantity based on the higher boiling points.

Vapor clouds from transportation accidents do not consider fixed chemical reactors. In the case of allyl alcohol, the assumption is made that a storage tank or drum is spilled, forms a liquid pool of chemical, and this evaporates forming a toxic cloud. Therefore the protective action distance (PAD) for a given amount of chemical would be less than if it were released all as once as a vapor.

Fortunately, in the case of this accident there was no vapor cloud explosion or fire. The lower explosive limit for allyl chloride is 2.5% (25000 ppm).

The best way of modeling the reactor release is to assume a reasonable mass and treat as if it were released instantaneously. This requires information that an emergency responder would not know but is better answered by the industry operating the reactor, with various scenarios worked out in advance.

Example: Phenol-Formaldehyde Runaway Reactions

Information from "How to Prevent Runaway Reactions. Case Study: Phenol-Formaldehyde Reaction Hazards". EPA document 550-F99-004. August 1999. available from http://ncsp.tamu.edu/reports/epa/govcasstd.pdf .

The U.S. Environmental Protection Agency (EPA) examined seven phenol-formaldehyde runaway reaction incidents resulting in explosions or chemical releases at different industrial facilities between 1989 and 1997. An example is an 8000-gallon reactor explosion at the Georgia-Pacific Resins, Inc. facility in Columbus, Ohio, at 10:42 AM on 10 September 1997. The accident was investigated jointly by EPA and the Occupational Safety and Health Administration (OSHA) under a 1997 Memorandum of Understanding [CSB did not become operational until 1998].

The phenol and formaldehyde chemicals are mixed in a reactor in the presence of a catalyst to form a phenolic resin product. Phenolic resins are used in adhesives, coatings, and molding products. There may be variations in the starting chemicals and catalyst used by industry to make these resin products; for example a substituted phenol or a different aldehyde than formaldehyde might be used to get a different resin, or methanol might be used. All of these reactions are exothermic, that is, they give off heat. Not only do they give off heat, but the heat increases the rate of reaction which in turn generates more heat. If there is no intervention, a very large amount of heat will be generated within a short time. The heat generated evaporates the liquid causing pressure to build up in the reactor. The excess heat is normally removed by a combination of a reactor cooling jacket and by removing the vapor/gases produced, condensing them in an external condenser, and returning the liquid to the reactor (reflux cooling). Typically, the reactor also contains rupture disc(s) for emergency relief. If the procedure is not carried out properly, too much heat will be generated in a short time resulting in a sudden build up of pressure. The result may be either a reactor tank explosion or a release of toxic chemicals from the reactor, and possible vapor cloud explosion and fire.

The reactor explosion at the Georgia-Pacific Resin facility on 10 September 1997 in Columbus, Ohio, killed one worker and injured four others. The blast was reported in the local paper (*Dispatch*, Sept. 11, 1997) to be felt at least 2 miles away and heard possibly 7 miles away. The explosion extensively damaged the plant. The reactor rupture also resulted in the release of a large quantity of liquid resin, phenol, and formaldehyde requiring the evacuation from homes, businesses, and a vocational school within a ¾ mile radius. Three fire fighters were injured and treated for first-degree chemical burns.

The EPA-OSHA investigation revealed that contrary to Standard Operating Procedure (SOP) the operator charged the raw chemicals to the reactor at once and turned on the steam to initiate the reaction. A high temperature alarm sounded and the operator turned off the steam. Shortly after, the top of the reactor blew and the sides of the reactor split killing the operator and injuring four other workers. The top landed 400 feet away. The reactor had heated up too fast resulting in a sudden increase in pressure overwhelming the safety release devices and the reflux cooling system.

The EPA publication did not publish the SOP used at Georgia-Pacific Resins, Inc., but stated that the information is in the public domain [see Kirt-Othmer Encyclopedia of Chemical Technology, Phenolic Resins, (1966), page 614]. Molten phenol is first placed into the reactor followed by a precise amount of acid catalyst. The formaldehyde is added slowly either continuously or as small incremental steps. It is not added all at once as what was apparently done on September 10.

The EPA report emphasized the need to have clear, easy to understand SOP and employee safety training. The EPA report also discussed reactor safety features including implementation of interlocks to eliminate opportunities of human error in critical manual operations. Also discussed was the design of emergency relief systems to handle an appropriate worst case scenario. Also recommended was an evaluation of measures such as a rapid water or chemical quench for inhibiting a runaway reaction.

What Can the PEAC Tool Do?

Again, the PEAC tool is designed for emergency responders. The PEAC tool does not contain information on run-away chemical reactions which might potentially happen during synthesis. It does not contain SOPs for chemical synthesis. It is still the job of industry to instruct workers on safety and inform emergency responders what chemicals are stored or used on the facilities and provide an off-site consequence analysis of accidents which may potentially happen, and do this ahead of time.

The PEAC tool does provide information on chemicals. The PEAC tool can help industry provide a consequence analysis in case of a hazardous release of chemicals [in this case, formaldehyde] to the air. It can also predict consequences in case of a vapor cloud explosion and fireball. The PEAC tool is set up to run through different scenarios rapidly. The PEAC tool can be a valuable instrument in employee safety training in examining the consequence of accident scenarios involving chemicals including flammables.

Industrial Accident Investigations and Reports

Investigative Reports on industrial chemical accidents by the U.S. Chemical Safety and Hazard Investigation Board can be obtained through the website,
http://www.csb.gov/

Investigative reports from other agencies including that conducted by foreign governments and by industry can be obtained through the website,
http://ncsp.tamu.edu/reports/default.htm

These reports are in the public domain. The root causes of accidents are varied. They may include running a fork lift into a chemical storage tank, overfilling of tanks or process equipment, an unstable explosive byproduct produced, as well as runaway reactions in reactors, or a fire caused by an unrelated incident. Each report is interesting and provides valuable information for prevention and response to accidents.

Industry is required by law to prevent and mitigate accidental releases of hazardous substances and provide worker training.

- Clean Air Act Amendments of 1990, Section 112 (r): Facilities have a general duty to prevent and mitigate accidental releases of extremely hazardous substances.
- Risk Management Program, 40 CFR 68, EPA requirement: Facilities with listed substances in quantities greater than the threshold planning quantity must develop a hazard assessment, a prevention program, and an emergency response program.
- Process Safety Management Standard 29 CFR part 1910.119, OSHA requirement: Facilities with listed substances at or above the threshold planning quantity are subject to a number of requirements for management of hazards, including performing a process hazards analysis and maintaining mechanical integrity of equipment.

The PEAC tool provides (1) information on many chemicals, (2) aids industry in doing a consequence analysis rapidly for many accidents which may potentially occur, (3) provide information on personal protective equipment in case of a chemical release, and (4) cleanup of spills. There is also capacity in the PEAC tool to add specific information relative to the chemicals used at a particular facility.