National Aeronautics and Space Administration

SYSTEM FAILURE CASE STUDIES

JUNE 2009 VOLUME 3 ISSUE 04

Triple Threat

In the summer of 2003, a Honeywell International Inc. Baton Rouge, Louisiana chemical plant experienced three safety incidents in one month. First, a chlorine leak caused an emergency shutdown of the entire plant. Second, a worker opened a mislabeled cylinder of a highly toxic chemical, fatally exposing himself to its vapors. Third, while resuming operations after the emergency shutdown, an equipment operator was sprayed with hydrogen fluoride.

BACKGROUND

Honeywell International, Inc. manufactures refrigerants at its Baton Rouge plant. During the summer of 2003, personnel were exposed to three hazardous chemicals used to produce refrigerant: chlorine, antimony pentachloride, and hydrogen fluoride.

CHLORINE

At room temperature, chlorine is a greenish-yellow gas with an odor familiar from swimming pools; people can smell chlorine at concentrations as low as 0.2 parts per million. Chlorine is immediately dangerous to life and health at 10 parts per million, according to the National Institute for Occupational Safety and Health (NIOSH).

ANTIMONY PENTACHLORIDE

The second chemical, antimony pentachloride, is a yellowish, oily liquid that is corrosive to skin and eyes. Inhalation can result in severe respiratory problems and may fatally damage the liver, kidneys, or nervous system.

Figure 1: The Chlorine Cooler

HYDROGEN FLUORIDE

Hydrogen fluoride, the third chemical released at the Baton Rouge plant during the summer of 2003, was also used to manufacture refrigerants. It is a colorless substance that boils at 67 degrees Fahrenheit. Hydrogen fluoride exposure causes painful burns that are often slow to heal. Further side effects include pulmonary edema, which floods the lungs with fluid and can be fatal. NIOSH considers hydrogen fluoride exposure immediately dangerous to life and health at only 30 parts per million.

WHAT HAPPENED?

JULY 20 CHLORINE RELEASE

Because chlorine boils at -29 degrees Fahrenheit, the transfer system cooled the chemical along its journey from the railcar to the chemical reactor where the refrigerant is produced. The cooler – an 8 foot carbon steel shell – contains tubes of chlorine surrounded by liquid coolant (Figure 1).

At 3:10 am, operators inside the coolant system control room noticed a chlorine smell. Chlorine had infiltrated the coolant lines via holes in the cooler tubes and traveled to the coolant pump, which was not designed to withstand chlorine's corrosivity. The pump seals failed and released the chlorine into the atmosphere (Figure 2). Chlorine gas spread rapidly throughout the plant, entering the control room through unplugged holes and joint gaps in the heating, ventilating, and air conditioning (HVAC) system. The operators were overwhelmed by the odor and, struggling to breathe, evacuated the control room with the cooling process still running. Over the next fifteen minutes, all plant personnel evacuated. Water deluge towers suppressed the chemical vapors while plant personnel notified authorities that the leak

Summer 2003: three incidents released hazardous chemicals, injuring 8, killing 1, and exposing the surrounding community.

Proximate Cause:

- Holes in the chlorine cooler leaked chlorine into the coolant system
- A worker opened a mislabeled cylinder of contaminated antimony pentachloride
- An unofficial process for eliminating liquids sprayed hydrogen fluoride into the atmosphere

Underlying Issues:

- Inadequate hazard analyses
- Overly general instructions for non-routine situations
- Insufficient and overlooked written operating procedures

might affect areas outside the plant. During this time, the flow of liquid chlorine through the cooling system to the failed pump continued, because chlorine had corroded the control system that would have shut the process down. Fortunately, the wind was not strong that day (3-5 mph), so the chlorine gas did not spread quickly through the surrounding communities. At 6:46 am, over three and a half hours after the leak began, plant emergency response personnel manually closed the isolation valve between the chlorine railcar and the chlorine cooler to stop the leak. Eight employees were medically treated, and ten members of the general public also sought treatment.

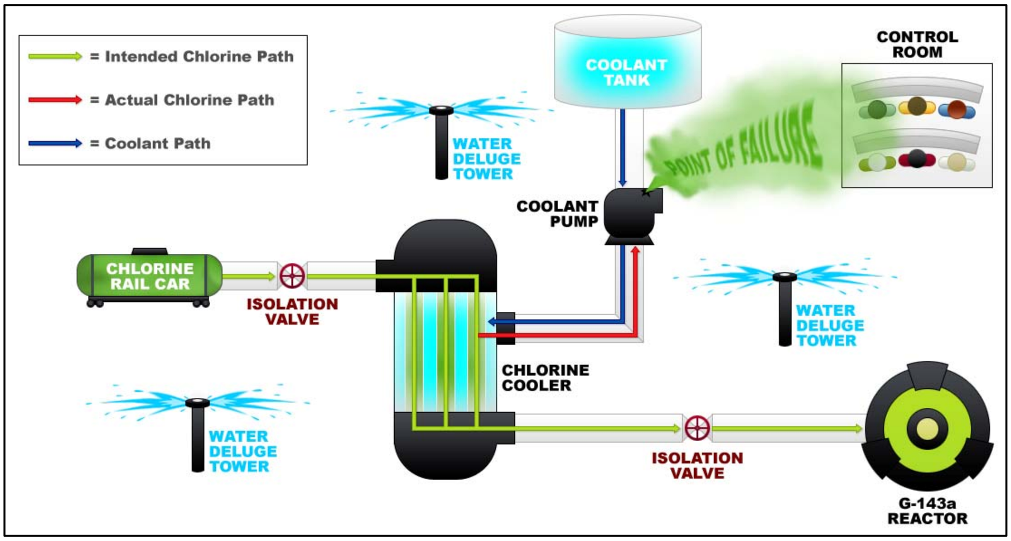

Figure 2: The Chlorine Cooling System

July 29 Antimony Pentachloride

At approximately 1:30 pm on July 29th, employees in the refrigerant cylinder recycling area of the plant noticed a cloud of contaminated antimony pentachloride (CAP) [1] and sounded the plant alarm. The cloud was visible offsite, and nearby residents reported a chemical smell. A worker had been trying to vent a one-ton cylinder labeled as refrigerant that actually contained CAP. The cylinder's valve was corroded and would not open. The worker then removed a plug from the end of a 1-ton cylinder he probably believed to be empty. The cylinder was actually full, and its contents were released. The CAP reacted with the moisture in the air and released a large cloud, engulfing the worker in its vapors. Employees saw the cloud and sounded the plant alarm. When the worker emerged from the cloud, they assisted him to an emergency shower for decontamination and summoned transport to the local hospital, where he died the next day.

The deadly CAP cylinder originated at another Honeywell facility in El Segundo, California. This facility stopped using antimony pentachloride in the early 90s. In 1998, it sent its last cylinders of CAP to a vendor for cleaning before transporting them to Baton Rouge. The vendor rejected this particular cylinder, mislabeling it as R-22, a kind of refrigerant. Four cylinders of this refrigerant had been sent mistakenly to the vendor in the previous two years. Records show the vendor identified the contents as "a tar-like solid with only a small amount of liquid" and sent it to Baton Rouge where it was sorted to the venting area.

The worker treated the CAP cylinder like a typical empty refrigerant cylinder. Since his training did not cover the key differences between refrigerant cylinders and other types of cylinders, he likely failed to notice that the weight recorded on the shipping papers exceeded the weight of a full refrigerant cylinder and that the cylinder had fusible plugs instead of the pressure release valve typical of refrigerant. The worker followed common practice at the plant by venting a cylinder labeled as R-22, despite written procedures not to vent R-22 like other refrigerants.

August 13 Hydrogen Fluoride Release

The July 20 chlorine release shut down the entire refrigerant manufacturing process for several weeks. This included a hydrogen fluoride vaporization process, which was shut down with liquid still in the vaporizer. During normal operations, only gas would have been left in the vaporizer.

On August 12th, the operations department began emptying the vaporizer to prepare the plant to resume operations. The procedure used a venturi stick, a suction device using a water flow past an orifice to create a vacuum. Operators secured the venturi stick with a rope and, with the help of pressure from a flow of nitrogen, sucked the liquid hydrogen fluoride out of the vaporizer and into a drainage sewer (Figure 3). While setting up the venturi stick, operators wore the plant-required personal protective equipment, but they later removed their acid suits and respiratory protection.

At approximately 9 am the next morning, the operator noticed a block in the system and opened and closed some valves in order to clear it. This created a pressure surge that lifted the venturi stick out of the sewer and sprayed its contents into the area. The operator closed a valve to stop the flow of hydrogen fluoride. Once the system was shut down, the operator noticed a red mark on his arm and went immediately to the emergency shower. A supervisor came to help him but soon experienced difficulty breathing. Both workers went to the hospital and were released the next day with no major complications.

[1] Antimony pentachloride is a catalyst for the reaction that creates refrigerant. The reaction contaminates the antimony pentachloride, which Honeywell sends offsite for cleaning before it can be reused. CAP contains unidentified materials which vaporize at room temperature.

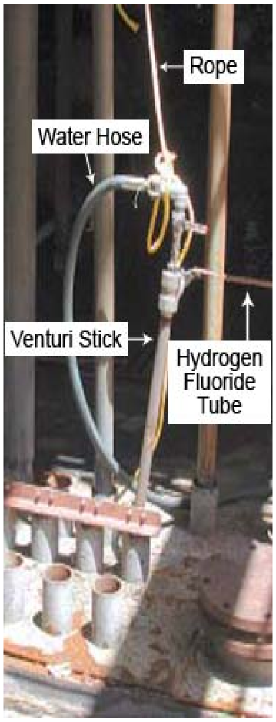

**Figure 3:
The Venturi Stick**

Proximate Causes

First event: On July 20, chlorine escaped through holes in the cooler tubes, disabled the coolant pump and sprayed into the atmosphere. This triggered an emergency plant shutdown.

Second event: On July 29, an operator opened a mislabeled cylinder of contaminated antimony pentachloride. The operator died from exposure to the chemical.

Third event: On August 13, as the plant prepared to resume operations, off-nominal shutdown conditions required workers to evacuate liquid hydrogen fluoride from a vaporizer. A pressure surge exposed two workers to hydrogen fluoride.

Underlying Issues

Following the chlorine release on July 20th, the U.S. Chemical Safety and Hazard Investigation Board (CSB) traveled to Baton Rouge to investigate. Since the CSB was still on-site when the second and third safety incidents occurred, the Board decided to expand its investigation to include all three safety incidents. The Board found that weaknesses in hazard analyses, insufficient plans for non-routine situations and ineffective written operating procedures were factors in all three incidents.

Hazard Analysis

The Baton Rouge plant did not apply the Occupational Safety and Health Administration (OSHA) Process Safety Management (PSM) Standard to its cooling system and control room even though the standard explicitly includes utilities like the cooling system. If the PSM standard had been applied, personnel might have investigated odors in the control room, conducted more routine maintenance of the HVAC system, and better protected operators. The hazard analyses that were conducted considered the coolant process as a whole, but not the coolant pump individually. The plant was not prepared for the possibility that chlorine might enter the coolant system.

Within the refrigerant cylinder recycling area, engineers had not conducted a hazard analysis despite OSHA requirements that potential hazards be identified and communicated to employees. Such an analysis would almost certainly have identified the possibility that non-refrigerant cylinders might enter the area, and employees would probably have been trained to identify abnormal cylinders.

Non-Routine Situations

The plant equipment and personnel were not given adequate instruction to recognize non-routine situations. Operators had smelled chlorine in the control room before July 20th, but did not recognize this situation as non-routine. Personnel took actions to eliminate the odor, but they did not conduct a formal investigation to identify how chlorine penetrated the control room. A formal investigation would have revealed the weaknesses in the HVAC system, which could have minimized the severity of the chlorine release incident.

Within the refrigerant cylinder recycling area, advice for dealing with non-routine situations was so general that employees could not discern between routine and non-routine situations. Despite receiving over 200 hours of classroom training, the operator had not learned to look for abnormal cylinders, nor how to handle an inoperable valve, because there were no specific guidelines for identifying and handling non-routine situations.

Similarly, employees did not think the use of the venturi stick with hydrogen fluoride was non-routine, because it was a documented process used in other parts of the plant. However, the venturi stick process the plant had developed was not appropriate for removing liquid hydrogen fluoride. A permanent system for this operation had been installed but did not function properly, so this alternate method was used.

Written Operating Procedures

Personnel overlooked written operating procedures. A detailed matrix specified what protective equipment and clothing should be worn when working with hazardous chemicals, but personnel commonly lowered protection levels once a process was set up. If the worker using the venturi stick had worn the level of personal protective clothing and equipment listed on the matrix, he most likely would not have been exposed to hydrogen fluoride.

In the refrigerant cylinder recycling area, written procedures specified that all refrigerant should be vented except one specific refrigerant, R-22. Common practice regularly deviated from this instruction, and no process was in place to segregate R-22 cylinders from other cylinders of refrigerant. Had more attention been paid to written procedures at the plant, the staging worker might not have attempted to vent the CAP cylinder labeled as R-22.

Aftermath

In response to the incidents, Honeywell made a number of system improvements. They enhanced accountability measures, implemented a comprehensive Health, Safety, and Environment (HSE) management system and structured safety process, revised procedures and enhanced training. They also installed new emergency shutdown equipment in response to the CSB's recommendations.

In 2005, the CSB held a news conference in Baton Rouge to discuss the final report on the summer 2003 incidents. Approximately 24 hours after the Board's presentation, the Baton Rouge plant had another chlorine release when a transfer hose burst. This time, the new emergency shutdown equipment allowed operators in the control room to push an

Questions for Discussion

- Have you systematically identified hazards to processes and outcomes, or merely identified risks that describe "known-unknowns"?
- Does your training emphasize the importance of looking for hazards and provide the skill to spot them?
- Have you thoroughly investigated all anomalies experienced in testing?
- How often do you review written operating procedures to ensure that actual practice conforms to recommendations?
- If employees are working around procedures instead of following them, have you found out why?

emergency shutoff button which closed valves on the rail car and plant sides of the failed hose, stopping the chlorine release in 45 seconds. No one was injured and the incident did not affect the community. CSB Chairman Carolyn Merritt praised Honeywell for acting on preliminary CSB findings while final recommendations were being drafted.

Applicability to NASA

Hazard Analysis

When working with hazardous chemicals, thorough and rigorous hazard analyses are instrumental to safety. Establish multiple layers of defense to protect personnel and equipment in the event of a system failure. At Baton Rouge, more systematic hazard analyses might have foreseen a) the need to protect the control room from a chlorine leak; b) how employees could recognize or contain mislabeled, hazardous material; or c) the effect an emergency plant shut down might have on the hydrogen fluoride vaporizer. Hazard assessments at NASA identify acceptable operational risks and monitor risks that are internal to the system and risks that are imposed by the environment. [2]

Non-Routine Situations

A NASA Center or Project often deals with unique processes and moving targets; hazard identification takes both skill and vigilance. At Baton Rouge, early chlorine leaks warned of problems in the system, but personnel did not dig to discover the root cause of odors in the control room because they did not recognize these odors as non-routine. If the operators had urged more prudent maintenance of the HVAC system, the corrosion of the control system could have been prevented and the duration of the July 20 chlorine release could have been reduced.

[2] NASA Pressure System Managers and owners employ NPD 8710.5 and NASA STD 8719.17 (which stem from the OSHA standards 29 CFR1910.119 and the National Consensus Codes & Standards for pressure systems) to bring rigor to the hazard assessment process. Pressure System Safety Standards at NASA for mechanical integrity evaluation include: periodic non-destructive testing, in-service inspections, remaining life calculations, code compliancy of repairs & modifications, and operational risk assessments to prevent safety incidents.

Written Operating Procedures

If the Baton Rouge plant had placed greater emphasis on following procedure, a) the worker in the refrigerant cylinder recycling area might not have attempted to vent a cylinder marked R-22 and b) the worker exposed to hydrogen fluoride might have been wearing the appropriate protective clothing and equipment. Effective implementation of well-designed procedures at NASA depends on a management culture that values excellence and communicates that value to its employees. Regularly review and validate routines and emergency procedures. Ask workers for input about the suitability of written procedures to their circumstances and ensure that they receive the resources and direction they need to consistently comply with those procedures.

References

CSB Investigators Return to Honeywell Baton Rouge Facility to Examine Chlorine Release Day After Agency Issued Report on Previous Chlorine Release and Other Incidents. U.S. Chemical Safety and Hazard Investigation Board. 11 August 2005. Accessed April 20, 2009. http://www.csb.gov/index.cfm?folder=news_releases&page=news&NEWS_ID=235

Final Investigation Report: Honeywell International, Inc., U.S. Chemical Safety and Hazard Investigation Board, August 2005.

NIOSH Pocket Guide to Chemical Hazards: Chlorine. The National Institute for Occupational Safety and Health. September 2005. Accessed April 27, 2009. http://www.cdc.gov/niosh/npg/npgd0115.html

NIOSH Pocket Guide to Chemical Hazards: Hydrogen Fluoride. The National Institute for Occupational Safety and Health. September 2005. Accessed April 20, 2009. http://www.cdc.gov/NIOSH/NPG/npgd0334.html

Ruptured Transfer Hose Caused August 11 Chlorine Release at Honeywell Plant in Baton Rouge; Rapid Shutoff Attributed to Upgraded Safety Systems. U.S. Chemical Safety and Hazard Investigation Board. 12 August 2005. Accessed April 20, 2009. http://www.csb.gov/index.cfm?folder=news_releases&page=news&NEWS_ID=236

Safety Data for Antimony Pentachloride. The Physical and Theoretical Chemistry Laboratory at Oxford University. Accessed April 20, 2009. http://msds.chem.ox.ac.uk/AN/antimony_pentachloride.html

Acknowledgements:

Special thanks to Vincent G. Verhoff PE for his insightful peer review.

SYSTEM FAILURE CASE STUDIES

NASA SAFETY CENTER

Executive Editor: Steve Lilley steve.k.lilley@nasa.gov
Developed by ARES Corporation

Visit http://pbma.nasa.gov to read this and other case studies online or to subscribe to the *Monthly Safety e-Message*.