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Project Summary

Prevention Reference Manual: Chemical Specific, Volume 10: Control of Accidental Releases of Hydrogen Cyanide

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Interest in reducing the probability and consequences of accidental toxic chemical releases that might harm workers within a process facility and people in the surrounding community prompted preparation of a series of reference manuals on loss prevention in process industries. The manual on hydrogen cyanide (HCN) is one of a series of chemical-specific manuals that addresses accidental release issues. HCN has an IDLH (Immediately Dangerous to Life and Health) concentration of 50 ppm, making it an acute toxic hazard.

To reduce the risk associated with an accidental release of HCN, the potential causes of such releases in facilities using HCN must be identified. Examples of such causes are discussed and measures that can reduce the accidental release risk are identified. Such measures include possible changes to plant design; release prevention, protection, and mitigation technologies; and more responsible operation and maintenance practices. Conceptual cost estimates of example prevention, protection, and mitigation technologies are provided.

This Project Summary was developed by EPA's Air and Energy Engineering Research Laboratory, Research Triangle Park, NC, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

Increasing concern about the potentially disastrous consequences of accidental releases of toxic chemicals has prompted the preparation of a series of reference manuals on chemical loss prevention and control. This manual compiles technical information on HCN, specifically on preventing, protecting against, and mitigating accidental releases of HCN.

Two processes for manufacturing HCN account for most of the chemical produced in the U.S. The most widely used process produces HCN by reacting natural gas (methane), ammonia, and air. A second process, called the BMA process, produces HCN by reacting methane with ammonia. HCN is also produced as a by-product of acrylonitrile manufacture. As of 1983, the major use of HCN in the U.S. was in the production of nylon-6.6. HCN is also used in the production of polymethyl methacrylate, or Plexiglas ®, and in the manufacture of various pesticides, chelating agents, and sodium cyanide. In the U.S., HCN is stored in small cylinders (approximately 150 lb or 68 kg), railroad tank cars, and bulk storage tanks.

Process Hazards

Anhydrous HCN is a colorless or pale yellow liquid with a mild odor of bitter almonds. The liquid boils at 78.3°F (25.7°C) at 1 atm (1 kPa) and forms a colorless, flammable, toxic gas. Three chemical properties of HCN contribute to its accidental release potential: 1) it is flammable in air at concentrations of 6 to 41%; 2) the addition of alkaline chemicals, water, and/or heat may promote exothermic self-polymerization and decomposition of the HCN; and 3) the addition of large quantities of acid can cause the rapid exothermic decomposition of the HCN.

Potential HCN releases may be in the form of either liquid or vapor. Liquid spills can occur when HCN is released at or below its boiling point of 78.3°F, or when a sudden release of the chemical above its boiling point results in vapor flashing.

Failures leading to accidental releases may be due to process, equipment, or operational problems. Process causes are related to the fundamentals of process chemistry. Examples of possible process causes of a HCN release include:

- Overheating of cyanide manufacturing reactor, resulting in rapid thermal decomposition;
- Loss of flow or composition control when acid stabilizer is added to a HCN stream, resulting in excess acid (high acid levels can lead to rapid decomposition and overpressure);
- Loss of flow or composition control, as above, but resulting in low acid levels that can lead to polymerization-decomposition;
- Loss of pH control where acetone cyanohydrin is present, resulting in the decomposition to acetone and HCN, which could lead to overpressure;
- Excess HCN feed leading to overfilling or overpressuring equipment; and
- Catalyst decay in HCN production reaction, resulting in overheating of the reactor.

Equipment causes of accidental releases that result from hardware failure include: excessive stress caused by improper fabrication, construction, or installation; mechanical fatigue and shock from age, vibration, stress cycling, or collisions; creep failure in equipment subjected to extreme operational upsets, especially excess temperature; and corrosion.

Operational causes of accidental releases result from incorrect procedures or human errors, including: overfilled storage vessels; errors in loading and unloading; inadequate maintenance, especially of pressure relief systems and other protection and prevention systems: and lack of inspection and nondestructive testing of vessels and piping to detect weakening from corrosion.

Hazard Prevention and Control

To prevent, protect against, or mitigate an accidental toxic chemical release, the following areas must be considered: process design, physical plant design, operating and maintenance practices, and protective systems.

Most large manufacturers of HCN assist their customers in understanding proper storage and handling procedures. Equipment and procedures must accord with applicable codes, standards, and regulations. One company requires all customers to comply with their safety practices and routinely inspects customers' facilities for compliance.

Process design and chemistry must be evaluated to see how deviations from expected conditions could initiate a series of events that would lead to an accidental release. The primary focus is on how the process is controlled: by the basic process chemistry; by the variables of flow, temperature, pressure, composition, and quantity; and by control instrumentation and fire protection. Process design can be modified to enhance the overall integrity of the system or that of specific units within the system.

Physical plant design concerns equipment (vessels, piping, valves, instrumentation), siting and layout, and transfer/transport facilities. Anhydrous HCN is not generally corrosive; therefore, carbon steel is an acceptable construction material appropriate for ambient storage of the chemical. Elevated temperatures, acid stabilizers, and water will affect the corrosiveness of HCN solution, possibly resulting in the stress corrosion cracking of stainless steels and nickel-chromium and nickel-copper alloys. Water solutions of HCN containing sulfuric acid as a stabilizer severely corrode carbon steel (about 100°F or 38°C) and stainless steels (above 175°F or 79°C).

Most HCN is stored in refrigerated atmospheric storage vessels. Safety features that address the ability of HCN to undergo polymerization-decomposition should be incorporated into the design of any storage tank. All vessels that handle HCN must be equipped with adequate overpressure protection. The contents of HCN vessels should be kept under an inert atmosphere because of its flammability. Because HCN is so toxic, even small leaks in a piping system could be dangerous to operating personnel. Piping should be constructed with welded connections that are fully radiographed. Threaded fittings should never be used. Piping, valves, and fittings should all be constructed of 316 stainless steel.

Facilities and equipment should be laid out to reduce personnel exposure in the event of a release. HCN piping should not be adjacent to other piping, and inventories of the chemical should be kept away from sources of possible fire or explosion. Storage should be situated away from control rooms, offices, utilities, other storage areas, and laboratory areas. Multiple means of emergency access to the facility should be provided.

Transfer and transport facilities should be equipped with grounding connections for rail cars and rails, drainage control systems, rail car temperature monitor and alarms, warning signs and lights, and a deluge system or sufficient fire hoses or monitors.

Protection technologies, used to contain, treat, and neutralize a released chemical, include: enclosures, flares, and scrubbers.

If, in spite of all precautions, a large amount of HCN is released, workers in the immediate vicinity must be rescued, and persons downwind must be evacuated. The source of the release should be determined and the leak should be stopped, if possible. To reduce the effects of the released chemical, mitigation measures (e.g., physical barriers, water sprays and fogs, and foams) may be employed. Physical barriers include dikes, high impounding walls, and excavated and natural basins. A spill of HCN can be diluted with water, which will also reduce the vapor generation rate. Water sprays and fogs are also useful for dispersing and/or removing HCN vapor from the air. Large fans or blowers can direct the vapor away from populated or other sensitive areas, if the weather is calm.

Although quality hardware, contained mechanical equipment, and protective devices all increase plant safety, they must be supported by the safety policies of management and by appropriate training, operation, and maintenance procedures that relate to the prevention of accidental releases of HCN. Management is responsible for such things as: ensuring worker competency; developing and enforcing standard operating procedures; adequately documenting policy and procedures; communicating and promoting feedback on safety issues; identifying, assessing, and controlling hazards; and conducting regular plant audits.

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The complete report, entitled "Prevention Reference Manual: Chemical Specific, Volume 10: Control of Accidental Releases of Hydrogen Cyanide," (Order No. PB 88-107 032/AS; Cost: $18.95, subject to change) will be available only from:

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