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Project Summary

Prevention Reference Manual: Chemical Specific, Volume 8: Control of Accidental Releases of Hydrogen Fluoride

D. S. Davis, G. B. DeWolf, and J. D. Quass

The accidental release of a toxic chemical at Bhopal, India, in 1984 was a milestone in creating an increased public awareness of toxic release problems. As a result of other (perhaps less dramatic) incidents in the past, portions of the chemical industry were aware of this problem long before this event. These same portions of the industry have made advances in this area. 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 the preparation of technical manuals addressing accidental releases of toxic chemicals. This chemical specific manual is for hydrogen fluoride. The manual summarizes information to aid regulators and industry personnel in identifying and controlling release hazards associated with hydrogen fluoride.

Reducing the risk associated with an accidental release of hydrogen fluoride involves identifying some of the potential causes of accidental releases that apply to the process facilities that handle and store hydrogen fluoride. In this manual, examples of potential causes are identified as are specific measures that may be taken to reduce the accidental release risk. Such measures include recommendations on plant design practices; prevention, protection, and mitigation technologies; and operation and maintenance practices. Conceptual cost estimates of example prevention, protection, and mitigation measures 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

The accidental release of a toxic chemical, methyl isocyanate, in Bhopal, India, in 1984 was a milestone in creating an increased public awareness of toxic release problems. There have been other less dramatic incidents of toxic chemical releases in the past, and the chemical industry was aware of this problem long before this event. Safety and loss prevention have long been standard parts of industrial activity and, over the years, industry has made many advances in this area. There is renewed interest, however, in reviewing technology and procedures for preventing, protecting against, and mitigating accidental releases.

As an aid to regulators and industry personnel charged with reducing the probability and consequences of accidental toxic chemical releases, technical manuals have been prepared that address prevention, protection, and mitigation measures for releases. This chemical specific manual on hydrogen fluoride is part of that series.

Hydrogen fluoride is a major commodity chemical in industry. The major industrial uses of hydrogen fluoride are: petroleum refinery alkylation (as a catalyst), chlorofluorocarbon manufacturing, sodium

aluminum fluoride manufacturing, uranium processing, glass etching and polishing, and repackaging for resale.

Potential Causes of Releases

Both anhydrous hydrogen fluoride and hydrofluoric acid can be used safely in the appropriate processing and storage equipment; however, when exposed to the atmosphere, hydrogen fluoride vaporizes readily and combines with moisture in air to form hydrofluoric acid.

Liquid hydrogen fluoride can spill when anhydrous hydrogen fluoride is released at or below its boiling point of 19.5°C (67°F) or when a sudden release of hydrogen fluoride above this temperature results in vapor flashing, which cools the remainder of the chemical to 19.5°C (67°F). Direct releases of gaseous hydrogen fluoride can also occur.

Hydrogen fluoride releases can originate from many sources, including leaks or ruptures in vessels, piping, valves, instrumentation connections, and process machinery such as pumps and compressors. The sources of accidental releases may be broadly classified as failures in or problems with: the process or system of chemical production, the equipment, and operation or maintenance procedures, including human error.

Process causes of hydrogen fluoride releases include: (1) excess olefin feed to an alkylation reactor leading to an exothermic reaction, combined with failure of the cooling system; (2) backflow of alkylation process reactants to a hydrogen fluoride feed tank; (3) inadequate water and sulfur removal from hydrocarbon feeds to the alkylation process leading to progressive corrosion in downstream processing equipment; (4) excess feeds to any part of a system handling hydrogen fluoride leading to overfilling or overpressuring equipment; (5) loss of condenser cooling in distillation units; (6) loss of temperature control in heating and cooling units; and (7) overpressure in hydrogen fluoride storage vessels due to overheating or overfilling, perhaps caused by exposure to fire, unrelieved overfilling, or exothermic reactions from contamination.

Equipment causes of releases result from hardware failure, including: (1) excessive stress caused by improper construction or installation; (2) failure of vessels at normal operating conditions caused by excessive stress, external loadings, corrosion, or overheating; (3) mechanical fatigue and shock resulting from age, vibration, stress cycling, or collisions with moving equipment (e.g., cranes); (4) thermal fatigue or shock in alkylation reactors, heat exchangers, and distillation columns; (5) brittle fracture, especially in carbon steel equipment subjected to extensive corrosion; (6) creep failure in equipment subject to extreme operational upsets, especially excess temperatures; and (7) all forms of corrosion.

Incorrect operating and maintenance procedures include: (1) overfilled storage vessels; (2) improper process system operation; (3) errors in loading and unloading procedures; (4) inadequate maintenance, especially on water-removal unit operations and pressure relief systems; and (5) lack of inspection and nondestructive testing of vessels and piping to detect weakening by corrosion.

Hazard Prevention and Control

Prevention of accidental releases requires careful consideration of the design, construction, operation, and protective systems of facilities where hydrogen fluoride is stored and used.

Deviations from expected process design or operation can initiate a series of events that result in an accidental release. Process variables such as flow, pressure, temperature, composition, and quantity must be monitored and controlled. Most importantly, the overheating and overpressuring of systems containing hydrogen fluoride must be prevented. Equipment can fail in the absence of overpressure if corrosion has weakened process equipment. Temperature monitoring is also important because hydrogen fluoride's corrosiveness increases with temperature.

The proper selection of construction materials for hydrogen fluoride service is dictated by conditions that directly and indirectly affect corrosion (temperature, pressure, moisture content, flow velocity, aeration, and the presence of impurities such as sulfur). Vessels, piping and valves, process machinery, and instrumentation must resist corrosion. For example, for anhydrous hydrogen fluoride or concentrated hydrofluoric acid solutions, carbon steel pipe is commonly used. However, carbon steel is not appropriate for wet hydrogen fluoride or dilute hydrofluoric acid solutions.

The location of systems and equipment must also be considered with reference to the proximity of population centers, prevailing winds, local terrain, and potential natural occurrences such as flooding or earthquakes. Anhydrous hydrogen fluoride and aqueous hydrofluoric acid storage and handling equipment should be located away from other potentially hazardous storage and handling facilities.

Two types of protective systems for hydrogen fluoride facilities are enclosures and scrubbers. Enclosures are structures which would capture and contain any hydrogen fluoride spilled or vented from storage or process equipment, thus preventing immediate discharge of the chemical to the environment.

Scrubbers absorb toxic gases from process streams. These devices can be used to control hydrogen fluoride releases from vents and pressure relief discharges, from process equipment, or from secondary containment structures. Types of scrubbers include spray towers, packed bed scrubbers, and venturis.

Mitigation measures for minimizing the effects of a large release of hydrogen fluoride should be part of a facility's emergency preparedness. Mitigation measures include physical barriers, water sprays and fogs, and foams. Secondary containment systems for hydrogen fluoride storage facilities commonly consist of an adequate drainage system that leads to a lime-containing neutralization basin, or a diked area. Water sprays may not always be suitable for hydrogen fluoride spills, but soda ash or a strong soda ash solution can be used to neutralize the chemical and prevent the release of toxic vapors. Although foams have been used successfully in vapor hazard control for many volatile chemicals, no foam systems appear to be currently available for hydrogen fluoride.

D. S. Davis, G. B. DeWolf, and J. D. Quass are with Radian Corporation, Austin, TX 78766.
***T. Kelly Janes** is the EPA Project Officer (see below).*
The complete report, entitled "Prevention Reference Manual: Chemical Specific, Volume 8: Control of Accidental Releases of Hydrogen Fluoride," (Order No. PB 87-234 530/AS; Cost: $18.95, subject to change) will be available only from:
National Technical Information Service
5285 Port Royal Road
Springfield, VA 22161
Telephone: 703-487-4650
The EPA Project Officer can be contacted at:
Air and Energy Engineering Research Laboratory
U.S. Environmental Protection Agency
Research Triangle Park, NC 27711

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