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Project Summary

Prevention Reference Manual: Chemical Specific, Volume 15: Control of Accidental Releases of Sulfur Trioxide

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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 a series of technical manuals addressing accidental releases of toxic chemicals. This project summary is for a chemical specific manual for sulfur trioxide (SO_3). The manual summarizes information to aid regulators and industry personnel in identifying and controlling release hazards associated with SO_3.

Reducing the risk associated with an accidental release of SO_3 involves identifying some of the potential causes of accidental releases that apply to the process facilities that handle and store the chemical. In this manual, examples of potential causes are identified as are measures that may be taken to reduce the accidental release risk. Such measures include recommendations on plant design 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 release in the past, and the chemical industry was aware of this problem long before this event. Safety and loss prevention has long been a standard part of industry 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 mitigation of accidental releases.

As an aid to regulators and industry personnel charged with reducing the probability and consequences of accidental toxic chemical releases, a series of technical manuals were prepared that address prevention, protection, and mitigation measures for releases. This chemical specific manual on sulfur trioxide (SO_3) is part of that series.

SO_3 is a commodity chemical, produced by the catalytic oxidation of sulfur dioxide (SO_2). Data on the production of SO_3 are not available but, based on the relative production of surfactants, a use of 300 million lb (136 million kg) per year of SO_3 is estimated for recent years. The primary use of SO_3 is as a sulfonating/sulfating agent to produce anionic surfactants, including linear alkylbenzene sulfonates, alcohol sulfates, and alcohol ether sulfates.

Storage systems for liquid SO_3 include 55-gal. ($0.21 m^3$) drums and bulk storage tanks.

In addition to anhydrous SO_3, oleum (fuming sulfuric acid composed of sulfuric acid and SO_3) is also used. This manual focuses primarily on anhydrous SO_3, but some considerations also apply to oleum.

Potential Causes of Releases

Anhydrous SO_3 is a clear, colorless, oily liquid with a strong, acrid odor. Liquid SO_3 begins to freeze at around 90°F (32°C). SO_3 is hygroscopic and fumes upon exposure to moist air. Traces of water or sulfuric acid can catalyze the polymerization of liquid SO_3 to solid forms that are difficult to remelt.

Because liquid anhydrous SO_3 has a large coefficient of thermal expansion, an overpressurization hazard exists if storage vessels have insufficient expansion space or if pipelines full of liquid SO_3 are sealed at both ends. In these situations, thermal expansion of the liquid can result in containment failure from the hydrostatic pressure exerted by the liquid.

Failures leading to accidental releases may be broadly classified as due to process, equipment, or operational causes. Causes discussed below are intended to be illustrative, not exhaustive.

- Excess organic feed to a sulfonation/sulfation reactor leading to excessive exothermic reaction, combined with failure of the cooling system;
- Backflow of process reactants to a SO_3 feed tank;
- Inadequate water removal from organic feeds to the sulfonation/sulfation process over a long period of time, leading to progressive corrosion;
- Excess feeds in any part of the system, leading to overfilling or overpressuring equipment;
- Loss of temperature control in cooling units (reactor) or heating vents (vaporizer); and
- Overpressure in SO_3 storage vessels due to overheating or overfilling. These situations may be caused by exothermic reactions from contamination, fire exposure, or unrelieved overfilling.

Equipment causes of accidental releases result from hardware failures. Some possible causes include:

- Excessive stress due to improper fabrication, construction, or installation;
- Failure of vessels at normal operating conditions due to weakening of equipment from excessive stress, external loadings, or corrosion. Overheating is also a possibility, especially for sulfonation reactors or SO_3 vaporizers;
- Mechanical fatigue and shock in any equipment. Mechanical fatigue could result from age, vibration, or stress cycling, caused by pressure cycling, for example. Shock could occur from collisions with moving equipment such as cranes, or other equipment in process or storage areas;
- Thermal fatigue and shock in sulfonation reactors or heat exchangers;
- Brittle fracture in any equipment, but especially in carbon steel equipment subjected to extensive corrosion where hydrogen embrittlement from hydrogen release by sulfuric acid attack may have occurred. Equipment constructed of high alloys, especially high strength alloys selected to reduce the weight of major process equipment, might be especially sensitive where some corrosion has occurred, or severe operating conditions are encountered;
- Creep failure in equipment subjected to extreme operational upsets, especially excess temperatures. This can occur in equipment subjected to a fire that may have caused damage before being brought under control; and
- All forms of corrosion. External corrosion from fugitive emissions of sulfuric acid mist could lead to equipment weakening.

Operational causes of accidental releases are a result of incorrect operating and maintenance procedures of human errors, including:

- Overfilled storage vessels;
- Improper process system operation;
- Errors in loading and unloading procedures;
- Inadequate maintenance in general, but especially on water removal unit operations, pressure relief systems, and other preventive and protective systems;
- Lack of inspection and nondestructive testing of vessels and piping to detect corrosion weakening; and
- Incomplete knowledge of the proper ties of a specific chemical, of the pro cess, or of the chemical system.

Hazard Prevention and Control

Prevention of accidental releases relie on the proper design, construction, an operation of facilities where SO_3 is store and used and on the protective system that guard against an accidental release.

Process design involves the basi chemistry of a process and how thi chemistry is affected by the variables c flow, pressure, temperature, compositior and quantity. Any aspect of a proces may be modified to enhance the integrit of the system. Such changes could ir volve the quantities of materials, proces pressure and temperature conditions, th sequence of operations, process contr strategies, and the instrumentation used.

Physical plant design covers equip ment, siting and layout, and trans fer/transport facilities. Mild steel is ger erally satisfactory for storage and har dling of SO_3. Where moisture may b present, or for pumps, valves, and oth areas of high turbulence, Alloy 20, 3C SS, or 316 SS is recommended. Gaske or packing should be made of a fluor carbon material.

The siting and layout of any facili handling SO_3 and of individual equipme items should be designed to reduce pe sonnel exposure during a release. Sitir should allow ready ingress and egre and take advantage of barriers that r duce release exposures. Considerab distance between large inventories ar sensitive receptors is desirable. Tr ground under process equipment ar storage vessels should be sloped so th fire water and liquid spillage flow aw from equipment into drains. Storage fac ities should be located in cool, dry, we ventilated areas.

Because heat causes significa thermal expansion of SO_3 and can lead thermal decomposition, piping, stora vessels, and other equipment should r be located adjacent to piping contain flammable materials, hot process pipir equipment, or other sources of direct radiant heat. Special consideration shou be given to the location of furnaces a other permanent sources of ignition in t plant.

Protection technologies for containm and neutralization include enclosures a scrubbers. Enclosures would capture a SO_3 spilled or vented from storage process equipment, containing the spil liquid until it could be transferred to ot containment and discharged at a ɔntrolled rate or to scrubbers for abɔrption.

Scrubbers can also be used for controlling SO_3 releases. SO_3, which is soluble in sulfuric acid, can be absorbed into sulfuric acid in scrubbing devices such as spray towers, packed bed scrubbers, and venturis.

If an accidental release occurs, mitigation technologies can reduce the consequences. Such measures include physical barriers, water sprays and fogs, and foams that will divert, limit, or disperse the released chemical to the atmosphere. Since SO_3 reacts exothermically with water, water sprays or water-based foams should be used with caution when controlling vapors from a spill. Spills may also be absorbed onto expanded clay or diatomaceous earth.

Since accidental releases of toxic materials result not only from deficiencies of design but also from deficiencies of operation, safe operation of plants using SO_3 requires competent, experienced managers and staff trained in the proper way to handle and store SO_3.

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The complete report, entitled "Prevention Reference Manual: Chemical Specific, Volume 15: Control of Accidental Releases of Sulfur Trioxide," (Order No. PB 89-155 055AS; Cost: $21.95, subject to change) will be available only from:
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