Overview

In the late 1980’s, trace levels of dioxin (2,3,7,8-TCDD) were identified as a byproduct of the prevailing chlorine-based chemical pulp bleaching process. As a result, the paper companies took action to reduce the release of dioxin. A key component of their strategy to eliminate dioxin from mill waste water involved substituting chlorine dioxide for chlorine in the first stage of chemical pulp bleaching. As a result of this substitution process, dioxin discharges from one major North American paper mill into adjacent waterways have decreased by 90% from 1988-1994. In turn, sports fishermen consumption advisories have been and continue to be lifted as dioxin levels in fish downstream of the pulp mills declines.

Today, the most significant use of chlorine dioxide worldwide can be attributed to bleaching paper pulp and cellulose. The release of chlorine dioxide to the environment is almost exclusively to the air. The U.S. Toxic Release Inventory reports total releases of chlorine dioxide in 1996 at approximately 550 tonnes to the atmosphere, of which more than 98% was via stacks and the remainder as fugitive air releases. The majority of reported releases were from chlorine dioxide in pulp bleaching with the remainder in food processing.

Due to restrictions in the transportation of chlorine dioxide as a hazardous chemical, this bleaching agent is typically produced at the paper mill site. While the increased use of chlorine dioxide has reduced dioxin, the potential spills of chlorine dioxide can pose a serious threat not only to mill employees but also to the local population near paper mill facilities.
Characteristics of Chlorine Dioxide (ClO₂)

Chlorine dioxide free radical exists as a greenish-yellow to orange gas at room temperature with a characteristic pungent chlorine-like odor. Chlorine dioxide gas is strongly oxidizing; it is explosive in concentrations in excess of 10% v/v at atmospheric pressure and will easily be detonated by sunlight or heat.

The chemical structure of chlorine dioxide is... • O = Cl = O •

Its melting point is -59°C, its boiling point is 11°C (at 101.3 kPa), and its vapor density is 2.34 (Air = 1). Chlorine dioxide has a water solubility of 3.01 g/liter at 25°C at 34.5 mm Hg, with slight hydrolysis to chlorous and chloric acid. ClO₂ is also soluble in alkaline and sulfuric acid solutions.

The American Conference of Governmental Industrial Hygienists has set work place standards for chlorine dioxide. The Threshold Limit Value (TLV) for ClO₂ is 0.1 ppm. The TLV is an exposure that is typically weighted to a normal work day. A second value, the Short-Term Exposure Limit (STEL) for chlorine dioxide is set at 0.3 ppm. The STEL is a maximum exposure during the workday that should not be exceeded, typically 15 minutes. Finally, and most significantly, exposures above 10 ppm of ClO₂ are considered Immediately Dangerous to Life and Health (IDLH).

Adding to Existing Safeguards

This case study highlights a large North American paper company. It is common practice for this mill, when using ClO₂, to employ continuous gas detection systems with remote monitoring to detect for leaks and spills. Workers in the hazard area are trained in emergency response tactics and carry escape respirators.

Recently, workplace safety was further enhanced by providing TARGET-7® Medium-Expansion Foam as a means of suppressing vapors and, where needed, to neutralize spilled materials.

Applying the New Technology

Ansul foam systems protect various types of hazards, from flammable liquid storage to fuming compounds like oleum, chlorine dioxide, and chlorosulfuric acid. This particular case study will focus on the protection of a 812 sq ft (75 m²) storage and containment room holding 176,000 gal (666,230 L) of ClO₂. TARGET-7 agent is applied through medium-expansion nozzles, and in the event of a chemical release, will work to suppress ClO₂ vapors and limit exposure.

Design Criteria

The TARGET-7 system is designed to produce a 2-ft (0.6 m) minimum depth of foam within the 812 sq ft (75 m²) area during a one-minute discharge period. The capacity of the foam concentrate tank is sized as per NFPA 11 (Local Application for Medium Expansion Foam) to provide an initial application of 12 minutes plus a minimum of 10 additional one-minute discharges (based on a one-minute application every 30 minutes) over a subsequent five-hour time period.

Calculations

Using the Ansul KRM-4F fixed medium-expansion nozzle at a minimum inlet water pressure of 50 psi (3.4 bar), it is determined that the flow rate of foam solution per nozzle would be 85 gpm (322 Lpm). This nozzle produces a minimum expansion ratio of 30:1, corresponding to 341 cm³ (9.66 L/m³) of expanded foam per nozzle.

The NFPA 11 design criteria called for five nozzles requiring 645 gal (2,442 L) of TARGET-7 foam concentrate.

(812 ft² x 2-ft depth) / 1 minute / 341 cm³ per nozzle = 4.76 nozzles required

5 nozzles x 85 gpm x 22 minutes x 1.15 overage x 0.06 (6%) = 645 gal foam

Basic System Components

Based on the above design criteria the basic components of the foam system were as follows:

1 - Horizontal Bladder Tank – 700-gal (2,650 L) capacity
1 - 4-in Between-The-Flange 6% Proportioner
5 - Medium-Expansion KRM-4F Fixed Nozzles
645 gal (2,441 L) of TARGET-7 6% Foam Concentrate

System Discharge Test

The system was discharged for 30 seconds during start up and commissioning. At the end of the discharge, a 5-ft (1.52 m) deep blanket of TARGET-7 foam was measured on the floor of the containment room.

Conclusion

The end-user considered the system installation and testing high successful including the system layout, start up, and the performance of the new TARGET-7 Vapor Mitigation and Neutralizing Agent.

This technology significantly adds to existing safeguards at chlorine dioxide bleach plants due to its ability to immediately smother toxic vapors caused by a process leak or tank failure. The stability and long duration of the foam blanket also allows emergency response teams to quickly control the event by neutralizing any ClO₂ leaks.

TARGET-7 can be used for suppressing vapors from other higher vapor pressure compounds.

If you have any questions concerning a stored chemical at your facility or the design of a foam system, please call Ansul Technical Services at 800-862-6785 or 715-735-7415. See our Web Site at www.ansul.com.