

Accidental Release Prevention:Recent EPA

Actions

Facilities must contemplate potential releases that travel beyond their fencelines.

by Zoltan C. Mester

Industry should expect a resurgence in EPA accidental release prevention mandates. Among recent federal rulemakings, a list of substances and their thresholds for accidental releases were addressed in a final rule March 1994 (40 CFR 9 and 68; 59 FR, January 31, 1994, p. 4478). Risk management of accidental releases was addressed in a related, proposed rule (40 CFR 68; FR October 20, 1993, p. 54190). The rules will affect an estimated 118,000 facilities nationwide.

The Clean Air Act Amendments (CAAA) of 1990 are the driving force. CAAA Title III Section 112 (r) requires EPA to formulate and implement requirements for accidental release prevention. Section 112 (r) provisions can be viewed as the culmination of federal legislative efforts to prevent accidental releases and protect the public. Federal interest was fanned by a number of serious accidents in the United States and worldwide in the past 20 years.

Substances and listing criteria

The CAAA mandated 16 substances for listing, based on their accident histories and propensities for causing serious damage in accidental releases. This core group included chlorine, ammonia/anhydrous ammonia, methyl chloride, ethylene oxide, vinyl chloride, methyl isocyanate, hydrogen cyanide, hydrogen sulfide, toluene diisocyanate isomers, phosgene, bromine, anhydrous hydrogen chloride, hydrogen fluoride, anhydrous sulfur dioxide and sulfur trioxide.

Section 112 (r) (3) mandated that at least 100 substances be identified and listed within 24 months of the enactment of the CAAA. Substances can fall under the rule either by specific listing (regulated

substances) or applying the general duty provision. This latter provision allows EPA to include any extremely hazardous substance not specifically listed.

EPA chose toxicity, flammability and explosivity as primary characteristics for listing. Radioactivity and reactivity were dropped in the final rule due to insufficient technical data and potential regulatory conflict.

Toxicity based listing

Accidental releases typically involve short-term and high-exposure scenarios; therefore, materials with acute toxicity have been given primary consideration for listing. For this purpose, the most relevant chemicals were on the EPCRA Section 302 (SARA Title III) list of extremely hazardous substances (EHS) having acute toxicity. This choice also conformed to the CAAA.

Criteria for acute toxicity were:

Inhalation: LC50 > 0.5 mg/l of air for over 8 hours of exposure.

Dermal: LD50 > 50 mg/kg of body weight.

Oral: LD50 > 25 mg/kg of body weight.

LC50 and LD50 are the median lethal concentration and lethal dose at which 50 percent of the test animals died.

Because ease of plume formation is important in a material's "beyond-the-fenceline" impact, volatility and acute toxicity have been considered jointly. A cut-off vapor pressure of 10 mmHg was applied to acutely toxic EHSs on the EPCRA list. This narrowed consideration to toxic materials with appreciable volatilities. Additional listing attributes included accident history and production volume.

A total of 77 toxic substances were identified in the final rule. The list encompasses organic, inorganic and organometallic compounds. Organics include chloroform, ethylene oxide, furan, allyl alcohol and methyl isocyanate. Inorganics include ammonia, phosphine and sulfur trioxide. The organometallics are chloro-methyl-silanes and tetramethyl lead.

After lengthy deliberations, EPA did not list sulfuric acid but included oleum. Of acids produced in large volumes, hydrochloric acid (greater than or equal to 30 percent), hydrofluoric acid (greater than or equal

to 50 percent) and nitric acid (greater than or equal to 80 percent) have been listed.

The determination of threshold quantities involved the total amount of a regulated substance in a single unit, in several interconnected units, or in units not physically connected but having the potential of being jointly released in an accident.

The last scenario would allow storage of larger-than-threshold quantities of a regulated substance, provided the sum of the individual quantities was not expected to be involved in a single accidental release. The burden of proof would be on the facility claiming an exemption in this situation.

EPA developed a ranking system for toxics threshold quantities that combined toxicological and physical/ chemical properties. The toxicological indices were obtained from OSHA's Immediately Dangerous to Life and Health (IDLH) values. The physical/chemical indices (V) included the phase of the material and its potential to volatilize. The ranking factor was defined as the ratio (IDLH/V) of these quantities.

The following threshold categories were assigned (the number of toxics per category are in parentheses): 500 lbs (2); 1000 lbs (6); 2500 lbs (6); 5000 lbs (13); 10,000 lbs (25); 15,000 lbs (15) and 20,000 lbs (10). The lowest threshold corresponds to a quantity stored in a drum, while the highest is representative of a bulk operation.

When toxic substances also qualify for listing based on flammability, the rule requires the application of the lower of the two thresholds. For mixtures, two alternatives exist. If the concentration of the toxic component is below one weight percent (de minimis concentration) in the mixture, the amount of that substance is not to be considered in determining threshold quantities. If the concentration is equal to or greater than one weight percent, the facility must demonstrate the partial pressure of the toxic component will not exceed 10 mmHg. This potential exemption, however, is not applicable to mixtures containing oleum and isomers of toluene diisocyanate.

Flammability based listing

An accidental release of a flammable material can cause a blast wave, fire ball and heat damage caused by a vapor cloud explosion or boiling liquid-expanding vapor explosion (BLEVE). Studies indicate gases and flammable liquids in a vapor cloud explosion pose the

greatest danger to off-site populations. The rule addressed flammable gases as well as liquids, the latter having a flash point of less than 73°F (23°C) and a boiling point below 100°F (38°C).

The final rule listed 63 flammable substances. Organics include acetylene, methane, vinyl chloride and ethyl ether. Examples for inorganics are hydrogen, carbonyl sulfide and silane. Tetramethyl silane in the list can be classified as an organometallic compound. By physical state, 44 on the list are gases and 19 are liquids.

Lacking adequate information to determine individual thresholds, EPA set a uniform 10,000-lb threshold for all regulated flammables. This value was based on experience that vapor clouds containing less than 10,000 lbs of flammable material are unlikely to explode. Considering the 10,000-lb threshold refers to the stored (unevaporated) quantity of the regulated substance, and assuming the entire amount is not likely to vaporize, the threshold appears to be on the conservative side.

For mixtures, no threshold criteria applies if the flammable component is present at equal to or less than one weight percent concentration. To exempt concentrations of greater than one weight percent, a facility must demonstrate the flammability criteria are not applicable for the entire mixture.

Explosivity based listing

EPA selected explosives listed by DOT in the Hazardous Materials Table (49 CFR 172.101). These high explosives have the tendency to detonate, meaning the entire mass disintegrates instantaneously, releasing much energy and gases. Detonations are caused by chemical reactions proceeding at supersonic rates.

Some low explosives also can detonate under certain conditions. The rule did not refer to this scenario because of a lack of technical information.

The uniform threshold quantity for explosives was set at 5000 lbs. This amount of high explosive generates approximately 3 lbs overpressure at 100 m distance. A blast wave of this magnitude at 100 m can injure eardrums, and represents the lower limit of serious structural damage. Flying objects also are a hazard. Threshold exemptions could be claimed for controlled, intentional explosions.

Elements of the proposed rule

As mandated by the CAAA, the risk management plan (RMP) must encompass hazard assessment, prevention and emergency response. EPA is expected to issue the final rule in March 1996.

A range of potential releases must be evaluated, with the focus on "worst-case" and "more-likely significant" release scenarios.

The worst case scenario is characterized by the instantaneous loss of all of a regulated substance, with the failure of both active and passive safety devices.

If several regulated substances are present, the risk assessment must consider each of these substances individually to determine the worst-case scenario.

In the more-likely significant release scenario, passive control systems, such as secondary containment, are assumed to function properly but active safety systems (relief valves, scrubbers, sprinklers) are supposed to fail.

Unlike OSHA requirements, the EPA risk assessment evaluates consequences beyond the facility fence line. These include toxic plume formation and dispersion, damage caused by explosion shock wave, flying debris and flames.

While the worst case scenario lends itself to a fairly straightforward, generic hazard assessment, this methodology cannot yield realistic results for the more-likely significant release scenarios. The proposed rule also will require facilities to report a five-year history of accidental releases, including "near misses" with potential off-site consequences.

Facilities will be required to register their RMP with EPA within three years of the publication of the final rule. EPA will track facilities that use Section 112 (r) regulated substances over the threshold.

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Analyzing Process Hazards and Safety

The CAAA Section 112 (r) prevention program addresses several areas of compliance, including process hazard and safety analyses.

Elements of process hazard analysis include hazard identification and the evaluation of release probabilities, consequences and safety

system operabilities. A "what-if" checklist, fault-tree analysis, hazard and operability (HAZOP) study and failure-mode analysis must be developed.

Process safety analysis must address all equipment associated with regulated substances above the threshold level. Information must be collected on mass and energy balances, equipment design and operating parameters, and the chemical/physical properties of regulated substances. Facilities must prepare standard operating procedures (SOP) and provide worker training on SOP.

The pre-startup review must ensure SOP have been instituted and all safety equipment associated with regulated substances functions properly. The maintenance program is important because many accidents have been linked to preventable equipment failures.

Under the proposed rule, a facility must evaluate and document process changes involving regulated substances, then implement safety training reflecting the changed conditions. Provisions on safety audits, emergency responses and accident investigations complete the requirements of the Section 112 (r) prevention program.

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