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THE CHANGING NATURE OF ACUTE CHEMICAL HAZARDS: A HISTORICAL PERSPECTIVE

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ABSTRACT

Emergency situations may develop from a variety of circumstances when chemicals or chemically-related substances or materials are improperly used or inadequately controlled. The various processes or circumstances, which may result in an emergency endangering significant numbers of people and requiring response by emergency control personnel or systems, are placed in a historical perspective. Acute chemical emergencies may and do occur in several modes: fire, explosions, uncontrolled release of materials, uncontrolled reactions, and time-bombs of toxic or explosive materials from improper disposal. These modes are used to illustrate the difficulty of generalizing about the control of chemicals and to encourage wider appreciation of the changing nature of chemical emergencies. In all cases, it is the lack of adequate control which precipitated a crisis, not the chemical itself.

INTRODUCTION

The chemical and allied industries have excellent safety records, compared to all industry. According to the National Safety Council 1978 report, the chemical industry is one of the safest industries for workers, using the Occupational Safety and Health Administration (OSHA) formula based on 100 full-time equivalent workers (1). The chemical industry has historically been a leader in the safe and proper manufacture, use, and disposal of chemicals.

Each chemical substance, of which more than 4.5 million are recognized by Chemical Abstracts, may be considered units of energy, each possessing unique properties which make it a useful, profitable, and, hence, desirable member of our society. Properly made, used, and disposed of, chemicals are essential building blocks to the high standard of our life.

Improper handling and disposal may be unforgiving, and most chronic as well as acute chemical emergencies occur beyond the plant gate. In discussing emergencies arising from misuse or improper handling of chemicals, a historical perspective will put into focus the need for more complete understanding of control of chemical materials, both on the plant site and in the consumer domain.

FIRE

Perhaps the first acute chemical emergency resulted from an uncontrolled fire at the hands of ancient beings. Fire, chemical oxidation, is both a servant and a foe of humans. Simple fires first used for food preparation were supplemented by controlled fires for heating, for smelting, and working of metals (such as iron, copper, and lead), for clearing land, and for other constructive purposes.

Open fire sources have caused many emergency situations. In 1653, for example, a conflagration occurred in Boston, resulting in deaths and devastation of much of the new city and was caused by the ignition of a straw roof from chimney embers (2). Wooden roofing material is still a major factor for fire spreading, especially in the West.

Candles and lamps fueled by whale-oil and later, kerosene, were a prime source of illumination until 1882 when Edison first developed electric illumination and power in New York. Electricity, which replaced many fire sources, is a source of ignition itself unless it is properly controlled. The June 23, 1980 fire on the 20th floor of a building in Manhattan, which apparently originated in computer-related equipment, burned for 3½ hours and sent 100 firemen to emergency rooms, in spite of the availability of self-contained breathing apparatus for protection against smoke inhalation (3,4).

Somewhat similar situations have been reported in the numerous night club fires of the past, and, more recently, in the fire on the 10th floor of a major clinical center, May 23, 1979 in which furniture, carpets, drapes, wall coverings and other accessories ignited and fire spread rapidly. Most commonly used polymeric materials burn or decompose under fire conditions, and produce decomposition products which may include carbon monoxide, carbon dioxide, hydrogen chloride, and other gases with significant smoke. The comprehensive study of this subject by the National Research Council National Materials Advisory Board deserves careful reading in engineering, scientific, and emergency control circles (5).

BLEVE (boiling liquid expanding vapor explosion) may result from a fire situation if the boiling liquid has insufficient pressure relief. The inadequate attention which has been given to pressure relief over the years has resulted in many poorly engineered systems with inadequate relief systems. Pressure relief was studied in-depth by a National Research Council (NRC) committee which analyzed over 50 different formulae proposed or used. Although the NRC study was funded by the Coast Guard, the principles of calculation apply to all large tanks and containers, either fixed or mobile, which may become overpressured, as in fire situations, or from chemical reactions within the vessel (6).

BLEVEs have occurred sufficiently often that they must be recognized, especially as pressures and temperatures are increased to achieve higher production efficiency. In 20 years prior to 1970, for example, 18 BLEVEs occurred when liquified petroleum gas (LPG) or propane tanks were exposed to fire; between 1970 and 1975, 12 BLEVEs were reported. Substances which are reported to have been involved in BLEVEs include vinyl chloride, butane, butadiene, and propylene (7). Propylene, in the incident in Spain in 1978, was released from a tank truck near a camping area and resulted in over 200 deaths and many injuries. In 1962, a propane tank truck, out of control on a narrow road, overturned and released cargo in Berlin, New York, with significant damage and loss of life. The accident involved the release of 12,500 kilograms of LPG, which formed a cloud 122-183 meters in diameter and 24 meters high, that exploded (8). These experiences, and others, suggest that fire and other emergency personnel should use extreme care in approaching flammable gas or flammable liquid fires, or even fires in liquids of higher-flash points since a ruptured tank or vessel may fragment and travel hundreds of feet horizontally and many feet vertically, even from stationary, as well as from mobile tanks on trucks, rail, or barges.

EXPLOSION

Explosion may be crudely defined as release of energy in a rapid and uncontrolled manner. The potential for explosion, deflagration, or detonation is far greater than usually appreciated. For thousands of years, mankind has been making and using explosive materials; the Chinese are credited with invention of black powder. Even today, it may be encountered in fireworks and other pyrotechnic devices. The potential for creation of a sudden force by chemical means has long been recognized and used as a constructive force in construction, mining, and earth-moving. The first powder plant in America was on the Brandywine River and began operations in 1802. Later, Nobel invented nitroglycerine, and added dynamite, which is nitroglycerine absorbed on an inert base, to the workhorses of industry. Unfortunately, black powder and nitroglycerine are shock and heat sensitive, and numerous accidental explosions have been recorded in their manufacture, handling, and storage. A detailed study of the effects of these explosions, both in the United States and abroad, resulted in the development of an American Table of Distances, widely recognized as the basic reference for safe storage of various quantities of explosive materials with respect to railroads, highways, and inhabited dwellings (9). In recent times, the use of water-base gelled slurries has largely replaced the previously-used blasting agents.

While similar in its effects to the BLEVE discussed earlier, UVCEs (unconfined vapor cloud explosions) are another combustion process creating major emergency problems but only recently recognized as a threat of total devastation to process plants and surroundings. The delayed ignition of a large vapor cloud in air can create pressure effects which may be highly damaging long distances from the incident. In a recently published book, Gugan discusses the UVCE process in detail, noting that even today much is not understood or agreed upon (10). A compilation of 100 incidents prior to February 1977, for which technical data is available, is included. The Ludwigshaven, Germany UVCE on July 28, 1948 which the author mentions, is of particular interest. In this incident, which is poorly documented in American literature, over 200 were killed and 3,800 injured when 33 metric tons of dimethyl ether was released from a tank car, probably due to hydrostatic overfilling and thermal expansion on a very warm day. Chemicals as diverse as hydrogen, ethylene, butane, LPG, cyclohexane, ethylene oxide, ethyl chloride, isopropyl alcohol, acrolein, and vinyl chloride, as well as crude oil, have caused serious UVCEs. It is hoped that more attention will be given to this process so more complete understanding and effective protective measures may be developed.

UNCONTROLLED RELEASE OF MATERIALS

When a container or containment system fails, the resulting spill or release may have effects which may be noticeable or undetected. Chemical materials have a wide range of properties, producing effects of diverse nature. It is difficult to separate "chronic" from "acute" emergencies in this context since at some point the "chronic" low level release may reach a point or concentration that at least for some persons at high risk is very "acute".

Containment failures may take many forms. On January 15, 1919, a large tank of molasses in Boston ruptured, producing a flood of perhaps two million gallons of viscous material which killed 19 persons and caused heavy property loss. One interesting factor in this release is that the tank was constructed of steel plate sufficiently strong for water containment (62½ pounds per cubic feet) but not for the molasses (90 pounds per cubic feet) (11). Even well designed and constructed vessels can break with amazing speed, as was witnessed in the release of anhydrous ammonia from a tank car on a siding in Crete, Nebraska, February 18, 1969. Half of the tank car was intact; the other half was broken into several fragments of various sizes as though the heavy steel were an egg shell. The car had been struck by another train (12).

Water-reactive chemicals deserve special attention, since the release almost always results in water contact with the material. In the Somerville, Massachusetts tank car rupture, April 3, 1980, phosphorous trichloride leaked from the car into a ditch. One observer reported that the responding fire company deliberately applied water to hasten the hydrolysis and, hence, increased the acidity and opacity of the cloud. In any event, 10,000 persons were reported evacuated, 120 persons reported to the area hospitals for treatment, and corrosion damage alone from the acid gases formed was estimated at $500,000 (13).

Information on hazardous material spills has not been readily available until the reporting requirements of the Federal Water Pollution Control Act Amendments of 1972 and the operation of the National Spill Contingency Plan by the U.S. Environmental Protection Agency and the U.S. Coast Guard. One estimate places the annual number of hazardous material spills at approximately 3,000. Reported spills range in size from a few pints to hundreds of gallons. In most cases, such spills hardly constitute an acute chemical emergency, but when the substance enters the water supply of an individual, a community, or a city, serious "acute" problems can develop. Since 89 of the 100 largest cities in the U.S. derive most, if not all, of their domestic water from navigable waterways or tributaries, the potential is serious. Substances which were not previously recognized as hazardous, but now known to be, may have been discharged or leached into waterways for years. As an example, polychlorinated biphenyls (PCBs) have been widely used as a dielectric fluid in electrical capacitors and transformers, and the release of even gram quantities is now seen as a cause for great concern. Our level of knowledge and understanding is often a factor in chemical emergencies (14).

On the basis of a study of over 15,000 spill reports, Buckley and Wiener rated primary causes and their high hazard potential probability as follows: tank rupture or puncture - .23; tank overflow and other leakage - .19; hose, transfer system failure - .08; and non-tank container rupture or puncture - .03. The five materials most frequently reported spilled were sulfuric acid, ammonium nitrate fertilizer, sodium hydroxide, hydrochloric acid, and ethyl parathion (15).

One major factor in any spill or emergency is the prompt procurement of technical data and information useful to personnel at the scene, no matter how remote. In 1969, the National Academy of Sciences Committee on Hazardous Materials reviewed the status of information resources and recommended that systems be developed for immediate guidance of on-scene personnel. From this recommendation has come three systems presently available: CHEMTREC, which is a telephone 24-hour response service of the Chemical Manufacturers Association; CHRIS, which is a response information system primarily available through the Coast Guard; and EPA-OHM-TADS, or technical assistance data, available from regional Environmental Protection Agency (EPA) offices. All three of these systems have performed well in emergencies. CHEMTREC has responded to over 33,000 calls since its activation in September 1971. Unfortunately, not all the information in all three is correct or documented, and the total number of chemicals covered by the three systems (eliminating duplication of names) is perhaps less than desired. However, the existence of these systems is a major step forward in control of chemical and related emergencies. Hopefully, the requirement of the United Nations identification number will not set back the information systems (16).

In regard to hazardous material (HM) releases in the past two years, some progress has been reported by the Federal Railroad Administration. In 1978, 1,205 cars were damaged; 338 cars released hazardous materials; 25,981 people were evacuated; 24 were killed; and 221 were injured. However, in 1979, 1,057 cars were damaged; 165 cars released hazardous materials; 16,093 people were evacuated; no one was killed; and only 15 people were injured (17).

UNCONTROLLED CHEMICAL REACTIONS

In 1940, the late George Jones, a chemist in the Bureau of Mines, began to compile a list of hazardous chemical reactions which had not been previously recognized. In 1950, a committee on hazardous chemical reactions, now known as NFPA 491, was formed to review and expand that listing. Several editions of the work on hazardous chemical reactions have since been published, and new items are being added regularly. Meanwhile, Leslie Bretherick, a research chemist with British Petroleum in England, became interested and has produced a book, now in its second edition, with 7,000 entries (18). It should not be necessary to re-discover hazardous reactions by an emergency, and emergency personnel would be well advised to become familiar with these and related publications.

TIME-BOMBS OF TOXIC OR EXPLOSIVE MATERIALS FROM IMPROPER DISPOSAL

Hazardous waste management is not a new problem, but one whose effects, while still largely unappreciated, are rapidly becoming "acute" emergencies. Movements in the early 1970s to deal with air and water pollution, as evidenced by the Clean Waters and Clean Air Acts, forced the closing of many incinerators and other disposal facilities, with the result that land disposal of hazardous wastes today represent a major problem. Pollutants previously discharged into waterways and the atmosphere often accumulate, even when diluted, and become part of the biological chain. The fact is that over 3,000 hazardous waste disposal sites have been identified, including perhaps 500 to 1,000 potential time-bombs of the Love Canal magnitude (19).

Hazardous wastes may contain toxic chemicals, pesticides, acids, or caustics as well as infectious, radioactive, carcinogenic, flammable or explosive materials.

According to the EPA, ten states, namely, Texas, Ohio, Pennsylvania, Louisiana, Michigan, Indiana, Illinois, Tennessee, West Virginia, and California generate 65% of all hazardous waste . To these must be added Massachusetts, New Jersey, New York, North and South Carolina, Kentucky, Alabama, Arizona, Washington and Oregon, for the second ten, or about 25%. Only 10 to 15% of wastes are believed "hazardous", but the sheer quantity is such that 57 million metric tons may be classified as hazardous.

The scope of this paper does not include a detailed discussion of hazardous wastes. However, the potential "time-bomb" aspect must be recognized. As this is written, the much-discussed "superfund" legislation, to provide significant funds for clean-up of known sites injurious to health and property, is still in Congress. Acute chemical emergencies may occur at any time in the hundreds of hazardous waste sites which have been identified, and perhaps many more (20, 21, 22, 23, 24)

In summary, the acute chemical emergency has changed from the obvious situations when fires and explosions, regardless of their origin, were tangible and of relatively short duration to less obvious "chronic" potential problems which manifest themselves as "acute" with little or no warning.

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