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OAK RIDGE NATIONAL LABORATORY

# **Countermeasures to Hazardous Chemicals**

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# MARTIN MARIETTA

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Interagency Agreement FEMA EMW-84-E-1737, DOE 1457-1457-A1 formerly 40-1457-84 Work Unit No. 2411K

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# COUNTERMEASURES TO HAZARDOUS CHEMICALS

by

J. M. Holmes C. H. Byers

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# **EXECUTIVE SUMMARY**

# **I. INTRODUCTION**

Recent major incidents involving the release of hazardous chemicals have heightened the awareness of both the public and the private sectors that effective strategies must be developed to prevent and to deal with emergencies. A number of federal, state, and local government agencies share portions of the responsibility for various aspects of the problem. With the very considerable overlap, as well as holes in the coverage, a study of this picture has been performed to review the entire collage of activities and to recommend appropriate roles for FEMA and other agencies.

While the entire area of hazardous materials may require such a treatment, the most chronic needs for a strong direction are cases where an airborne hazard is involved. The materials might be in any form, but the means by which the threat overtakes people is such that little warning is possible and immediate means of protection are very limited. There are, in fact, many parallels to be drawn between airborne spread of hazardous chemicals and the airborne dispersion from a nuclear incident. Since these parallels exist and since the Federal Emergency Management Administration (FEMA) has taken a leading role in preparedness for nuclear problems, it is natural that the experience and planning for hazardous materials, particularly airborne ones, should fall in that agency. However, the nature of the disasters which are possible and the short periods during which they occur make it absolutely mandatory that the responsibility for dealing with the problems in local entities must lie with the local authorities.

The comprehensive study of FEMA and the various other entities required that the project be divided into a number of tasks. These included:

- 1. Task 1 The nature of the threat from incidents involving airborne hazardous chemicals is described.
- 2. Task 2 Existing responsibilities of federal, state, and local agencies, as well as the part played by the private sector, have been examined. Institutional options to new and existing approaches for reducing risk are reviewed, and recommendations are made for these approaches.

3. Task 3 - Technical options are discussed in light of the most hazardous situations, and recommendations are made for action or research where needed.

# 2. THE NATURE OF THE THREAT - TASK I

Several airborne hazardous-chemicals incidents that have occurred during the last several years have focused the attention of the public on preparedness for such emergencies. Perhaps the greatest attention has been paid to the disaster at the Union Carbide plant in Bhopal, India, in December 1984. This and other selected incidents are reviewed, with the objective to show the extremes in the types of incidents that can happen. The Bhopal disaster illustrates an incident where toxicity was the causative mechanism. On the other hand, the Pemex explosion in Mexico City during November 1984 illustrates a chemical incident where fire and explosion were operative. The Institute, West Virginia, release at a Union Carbide plant in August 1985 clearly illustrates that there is cause for concern in the United States as well as abroad. The commonality here is the sudden victimization of a population from a lethal situation against which they cannot gain protection. The extent of the problem in the United States has been studied for the Environmental Protection Agency (EPA) and reported in the "Acute Hazardous Events Data Base" (AHE). We have drawn recommendations from these experiences on different approaches to promoting better planning, accident avoidance, and loss control. The AHE statistically reviewed 6928 separate events that were reported between 1980 and 1985. Of these events, 468 led to a total of 138 deaths and 4717 injuries. It was concluded by EPA that neither high toxicity nor large quantities alone create conditions for human casualties. In the events reported, most injuries were the result of toxic chemical incidents, while most deaths were caused by the fire and explosion. Transportation releases were involved in one-quarter of the incidents, while fixed facilities and storage areas accounted for the remainder. Because of the quantities of hazardous materials kept in storage, these are generally responsible for the largest releases.

There appears to be a relationship between the annual production rates of certain hazardous chemicals and the frequency of their inadvertent release. The relationship indicates a definite trend toward increased releases for heavy tonnage chemicals. It also shows a significant number of releases at lower annual production rates for chemicals such as  $H_2S$ , tetrachloroethylene,  $SO_2$ , and methyl chloride.

It is evident from the diversity of industry and transportation in the United States that there is indeed a very large potential for disasters of the Bhopal or Pemex types. The number of incidents clearly point the need for greater vigilance. Given the enormous potential for transportation incidents, no community of any size can ignore this potential source of disaster. Communities with chemical plants have an added danger, but this danger is compensated for by the existence of expertise in the community.

# 3. EXISTING RESPONSIBILITIES AND INSTITUTIONAL OPTIONS - TASK II

In Task II, an overview is provided of the existing responsibilities of federal, state, and local agencies, along with a review of the activities in the private sector. Overlaps and gaps in the responsibilities of the various agencies are identified, and their relationship to current government activities is described. To provide a framework for the wide range of responsibilities, we divided them into the following categories: planning, prevention, response systems, and training. Gaps and overlaps in the responsibilities are delineated according to these categories. Institutional options for new and existing approaches are also reviewed. The major federal statutes that impact hazardous materials response are as follows:

- 1. Clean Water Act (CWA);
- 2. Hazardous Materials Transportation Act (HMAT);

3. Clean Air Act;

4. Toxic Substance Control Act (TSCA);

5. Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA);

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- 6. Resource Compensation and Recovery Act (RCRA);
- 7. Superfund Reauthorization (SARA); and
- 8. Occupational Safety and Health Act.

These statutes are described briefly, along with several recent state statutes concerned with prevention of and response to hazardous-materials incidents.

# **3.1 FEDERAL RESPONSIBILITIES**

A review of the responsibilities of the major federal agencies concerned with response at the federal level is presented. Included is the role of the National Response Team (NRT) and the Regional Teams (RRTs), who have the primary coordinating responsibility for hazardous material (hazmat) emergency response at the federal level. In addition to the federal emergency response programs, an overview of the involvement of federal agencies in extensive planning, training, and prevention activities is presented. Responsibilities delegated to the federal agencies by the Superfund Amendments and Reauthorization Act of 1986 (SARA) are emphasized.

# 3.2 STATE AND LOCAL RESPONSIBILITIES

The Tennessee Emergency Management Agency (TEMA) is selected as an example of one of the foremost state emergency agencies in the country. TEMA's structure and facilities are described along with Tennessee's implementation of the SARA provisions applicable in establishment of state emergency response commissions. Local/regional emergency activities for emergency response are included using the Memphis/Shelby County, Tennessee Hazardous Materials Advisory Council (HMAC) as an example.

# 3.3 PRIVATE SECTOR ACTIVITIES

An impressive effort with respect to emergency response planning, training, and coordination has been implemented by industry and private organizations, including technical societies. Probably one of the most extensive efforts involves the programs initiated by the Chemical Manufacturers Association. The programs of other organizations are also included.

# 3.4 OVERLAPS AND GAPS IN RESPONSIBILITIES AND PROGRAMS

As noted, overlaps and gaps identified during this study have been categorized under planning, prevention, response systems, and training.

For planning, the federal statues do not clearly define the roles and responsibilities of the various agencies. Although interagency coordination is accomplished through the NRT as mandated by SARA Title III, it is the responsibility of the state emergency response commissions to develop regional and local community emergency plans. However, the statute specifies only that the RRTs may review these plans when requested but does not provide federal oversight of the state, regional, and local planning programs. In our judgement, it is quite optimistic to assume that individual communities will have the resources and expertise to develop comprehensive plans without extensive support from governments, industry, and concerned private citizens. A list of the types of support required for this planning is delineated, and recommendations are made concerning their implementation. Of particular importance is a recommendation for development of a computerized "National Hazardous Materials Data Bank," which would enable a planner to identify the hazardous chemicals of local concern listed in the order of their relative risk to the local community. This ranking would be established for both fixed facilities and transportation in the vicinity. Such a system would enable a local community to a prepare preliminary risk assessment as a first step in the planning process. Sources of the data could be the information currently required by provisions in the SARA Title III statute. Additional data such as historical incident information on the selected hazmats, toxic properties, average local weather conditions, and potential countermeasures for these hazmats should also be included. Federal development of guidelines for the selection of competent consultants for technical assistance to community planning teams is also recommended.

#### 3.5 PREVENTION

Control of the release of hazmats throughout their entire life-cycle is a prime requisite for the prevention of emergency releases. Here, responsibility falls under the jurisdiction of many agencies and statutes. Coordination of the federal prevention programs under an agency or council

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comparable to the role played by the National Response Team for emergency response activities is recommended. Responsibilities of this organization could include: information systems coordination, federal research, and development program coordination and oversight review of facility safety and siting standards, coordination of operator training and certification, etc.

Probably one of the major activities concerning prevention is centered in the recently passed state statutes that require manufacturers of hazmats to develop risk analyses and emergency procedures for their facilities. New Jersey's "Toxic Prevention Catastrophe Act" is an example of such a statute. Another excellent model for future prevention programs is the OSHA Pilot Program (CHEMSEP). We recommend that consideration be given to establishing a comparable OSHA program that would enforce a federal range of rules developed for the prevention of industrial hazmat releases. Extension of the current OSHA standards for hazardous waste operators and emergency response personnel to all workers handling hazardous chemicals is strongly recommended. 3.6 RESPONSE SYSTEMS

One of the most critical aspects of emergency response to hazmat releases is the immediate notification of local, state, and federal authorities when an incident occurs. The fact that delays in notification have occurred or, at times, releases were not reported at all is well documented in the literature. In our judgment, more stringent regulations are needed requiring immediate notification (within 15 min. as required by nuclear regulations) of significant releases from any storage vessel or other item of equipment or any transportation vehicle.

Current statutes do not address the issue of emergency classification which refers to the gradation of emergency conditions from small incidents to catastrophic ones. The statutes also neglect the situation in which there is imminent danger of a hazmat release but the event has not yet occurred. In each case, the public's welfare would be better served if the incident seriousness were classified so that response organizations could be alerted to an appropriate emergency action level.

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Many very hazardous materials such as gasoline, petroleum solvents, liquefied petroleum gas (LPG), and carbon monoxide are not included as CERCLA reportable quantities, although they are extremely reactive and/or toxic materials. LPG was the hazmat responsible for the deaths of 500 people and injuries to 2500 people reported in the Pemex disaster that occurred in Mexico City in 1984. It is apparent that continuous evaluation and updating of the CERCLA "reportable quantity" list are needed in order to include hazmats not currently listed and to develop more stringent requirements for listed hazmats where n-ore recent data on hazmat releases indicate that additional protection is needed.

# 3.7 TRAINING

It might appear from the number of available training programs offered by various governmental and private organizations, in addition to the requirements for training specified by SARA Title III, that the needs for support for this aspect are being adequately addressed. However, various sources indicate that the effectiveness and extent of coverage of current training programs are not equitable for the following reasons:

- 1. **Consensus standards for training** Consensus standards are needed for the competency levels required for each level of response personnel.
- 2. Course evaluation The content and quality of existing courses are very diverse. Evaluation of these programs is needed to ensure consistency and to provide for adequate training at all levels of response personnel.
- 3. Coordination of training courses Numerous separate organizations offer courses but there is little coordination so that programs are not evaluated and trainees have difficulty finding useful courses.
- 4. Extent of coverage by training programs Only a fraction of the widerange of response personnel needing training are actually receiving it. One reason for this is the lack of adequate support for training expenses.

Several recommendations to meet these training needs are included in this study.

# 4. TECHNICAL OPTIONS FOR COUNTERMEASURES - TASK III

Task III provides a characterization of emergency releases of hazmats, the technical basis for needed countermeasures, and an evaluation of our available resources. New technical approaches for reducing the risk of hazmat releases are discussed. A methodology is proposed for measuring the relative threat from various hazardous chemicals, and the system that was developed was tested on 120 selected hazardous chemicals.

# 4.1 CHARACTERIZATION OF EMERGENCY RELEASES

A review of the principal methods currently used to characterize the nature of emergencies produced a wide range of proposed definitions. The response levels as defined by the NRT Planning Guide, which provides guidelines to the public for determining the extent of the emergency, are (1) a potential emergency, (2) a limited emergency, or (3) a full emergency condition. Response recommendations in terms of the emergency contacts to be made are also included. A comparison of the NRT Response Levels with the Nuclear Emergency Classifications indicates that the latter contains four levels of classification, including an "unusual event" category. This alerts responders of potential degradation in the system but no release of radioactivity. Consideration of the addition of this level to hazardous-materials emergencies is proposed in order to provide notification where a potential emergency exists or where the first responder is unable to specify the level of response when an actual release has occurred. The types and extent of response required are also included in the NRT Response Level Definitions.

# 4.2 TECHNICAL BASIS FOR NEEDED COUNTERMEASURES

The technical issues are categorized, and their technical basis is defined for the following areas:

- Prevention
- Planning
- Response
- Training.

The technical bases cover a broad range of technical activities that will involve experts from a wide variety of disciplines such as engineering, mathematics, physics and chemistry, education, social science, and medicine.

# 4.3 EVALUATION OF AVAILABLE RESOURCES

Technical countermeasures for mitigation of hazardous-materials releases include a wide variety of considerations, including emergency equipment, mathematical models, probabilistic risk assessments, training programs, etc. An overview of the resources currently available to local response organizations and chemical facilities that produce, store, or transport hazardous materials is developed along with a partial identification of commercial sources.

#### 4.3.1 Vapor Hazard Control

The control of vapors from a toxic release is the initial line of defense against the spread and eventual damage to the public health that would occur. The control of fires and explosions has equal priority because of possible dispersion of toxic chemicals and the general safety of the surrounding community. Countermeasures evaluated include the following:

- Mechanical covers
- Vapor curtains
- Induced air movement
- Gelling equipment
- Foam systems.

Three basic mechanical cover techniques are considered: (1) total cover of the spill area by cloth or other continuous material, (2) spray of a continuous cover such as urethane, and (3) buoyant particles that can be floated on the surface to reduce vaporization. Floating cover assemblies as well as particulate covers are available commercially, but cost may be a deterrent to the latter technique.

Water spray barriers can achieve worthwhile enhancement of the rate of dispersion and dilution of heavy gas spills but, practical problems exist. Wind direction changes necessitate the use of barriers wider than the actual vapor cloud and may require frequent redeployment of the equipment. Sprays have been shown to be effective in reducing the flammable plume size downwind of LNG spills.

Simple dilution provides a direct approach toward toxic and flammable vapor concentration reduction. This involves the transport and mixing of uncontaminated air with the released vapors. Large blower equipment, such as surplus jet engines, is available commercially and is currently being used by railroads to remove snow and by airports to disperse fog.

Foams have the ability to suppress vaporization when applied over the surface of a volatile chemical. The foam forms a barrier with a high resistance to both convective and molecular diffusion; in addition, it has the ability to absorb the vapors to a certain extent. The efficiency of vapor suppression depends on the vapor pressures and the aqueous solubilities of the vaporizing chemical. Foams also reduce vaporization by insulating the chemical from solar radiation and the ambient air. However, foams lose their effectiveness for vapor suppression due to aging and the effects of wind, temperature, humidity, or intensity of sunlight. Additional layers of foam must be applied when this occurs. Results of vaporization reduction tests (vaporization reduction is the ratio of actual concentration in the ambient air using foam to the monitored concentrations for free vaporization) indicate reductions that vary between 40 and 90% over duration periods up to 120 min. The results for ammonia showed reduction of about 50% for up to 120 min. Results for the flammability suppression by foams were measured in terms of the secure time before ambient air concentrations reached the lower explosive limit for particular flammable chemicals. Secure times of 60 min, were achieved using foam depths of up to 10 in. In general, the data indicate that substantial improvements in vapor suppression of many toxic chemicals must be achieved before this method can be considered as a viable countermeasure. However, foams do appear to be quite effective in preventing fires during the release of certain flammable chemicals.

4.3.2 Emergency Equipment

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A wide variety of equipment is available for prevention of toxic-material spills and response to emergencies involving these materials. Many of these items are included in the equipment and supplies carried by emergency response teams responsible for mitigating the effects of chemical spills. Items described include the following:

- Chlorine emergency kits
- Off-loading pumping systems
- Patching and plugging equipment
- Response and communications equipment
- Equipment for fires
- Personal safety equipment
- Labels and placards.

In addition to the above items, inert-gas systems used for the prevention of fires and explosions in vessels and storage tanks are also included.

#### 4.3.3 Emergency Warning and Evacuation Systems

Emergency warning and evacuation systems are of utmost importance in the prevention of injuries and fatalities from releases of toxic chemicals. For fires and explosions, warnings and evacuations may be less effective due to the short lead times and the possible wide area effects. More statutory emphasis should be placed on requiring immediate notification and evacuation in cases where there is imminent danger of a fire or explosion even when no release of hazardous materials has occurred. For toxic chemical releases, the effectiveness of large-scale evacuations has been shown to be a function of the area to be evacuated, the population density, and the warning time. Warning time is a particularly important factor. Other issues that impact the effectiveness of evacuations include uncertainties in the physical hazards, uncertainties in the warnings, social factors, organizational factors, and certain behavioral factors. In general, the public is more likely to evacuate their homes when they perceive the situation to be personally threatening. However,

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most local communities are not well prepared for evacuations, and disaster preparedness for chemical emergencies is not currently accorded high community priority and, therefore, is not systematically addressed

Public warning systems for the types of events considered must not only warn the community but also essentially provide specific directions for evacuation and/or sheltering. Systems available include alerting components such as sirens, bells, whistles, and horns plus communication components such as public address, telephone, radio, and TV broadcasts. Combined alert and notification systems are available and are used at certain chemical plants.

The determination of the zone to be evacuated during an emergency involves complex procedures that are dependent on many factors. Probably the most effective systems for this determination are the computerized atmospheric dispersion-emergency response programs available commercially. This judgment assumes that the release is of sufficient duration to allow operation of the computer system. Further, operation of the computer in a real-time mode enables periodic updating of the vapor cloud location, composition, and predicted direction of transport.

In the absence of available computerized systems or in cases where time will not permit their application, quick estimates of the emergency response zone can be developed by using a variety of published methods. These include evacuation tables, tables of maximum distances over which hazardous gases may be harmful, simple mathematical formulas for estimating an evacuation zone, and charts based on Gaussian dispersion equation calculations. Development of a simple low-cost hand calculator that could be used by emergency response personnel to determine emergency response zones is recommended.

As an alternative to evacuation, in-place sheltering may be a viable means of self-protection at large distances downwind from the release point where the concentration of hazardous material is well below the flammable limits but may still be toxic. Calculations indicate that for short-time puffs of toxic gases, the dose to inhabitants of typical dwellings would be one or two orders or magnitude less than if they were exposed to the vapor cloud outside. Although the dose to the

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inhabitants short-term is low, over a long period of time (hours) the dose would be the same as that outside if the dwelling were not opened and flushed clean as soon as possible after the cloud has passed. If this is not possible, evacuation from the contaminated area may be necessary.

4.3.4 Hazmat Monitoring and Ambient Air Dispersion Modeling

Response to a recent survey of monitoring activities by various chemical plants indicated that over 45% of the respondents routinely monitor emission of chemicals from their plants. The following methods

are used:

1. detection of odors by operating personnel,

- 2. industrial hygiene monitoring,
- 3. portable gas detectors,
- 4. detector tubes,
- 5. grab samples,
- 6. fixed-point continuous monitors, and
- 7. personal dosimeters.

Although advances in technology are in progress, the capability is not currently available for measuring all hazardous substances in the ambient air using a single system. Various instruments are designed for different chemicals; for the most part, however, the chemical species and its expected concentration range must be specified before a reliable system can be installed for emergency detection and monitoring. The survey also revealed that most of the monitoring done by chemical facilities is performed within the process unit areas; little monitoring is done at the plant boundaries or beyond.

The two main categories of monitors are point sensors, which analyze the air at one or more locations in or around a facility, and remote sensors, which are capable of continuously monitoring an entire plant area. The point sensors that were reviewed include the following:

1. ion mobility spectrometers,

2. amperometric and voltammetric analyzers,

3. colorimetric analyzers,

4. flame photometry analyzers,

5. nondispersive absorption spectrometers,

6. dispersive absorption spectrometers,

7. fourier transform infrared spectrometers, and

8. mass spectrometers.

Two remote scanning monitors were considered: (1) differential absorption light detection and ranging (DIAL), (2) lidar systems.

Portable instruments for the detection of toxic or flammable chemical leaks that were also identified include:

- 1. gas detector tubes,
- 2. combustible gas detectors, and
- 3. portable gas chromatographs.

Many computer-based dispersion models for predicting the spatial and temporal dispersion of toxic and flammable vapor clouds have been developed and are now commercially available. In addition to their dispersion capabilities, certain models include features such as inclusions of local emergency action plans, graphical displays of emergency action zones, information tailored to special population (hospitals, etc.) needs, facility on-site features to indicate process features at the location of the leak, and emergency plan checklists to monitor the progress of an emergency response.

A recent review of a group of 80 emergency response models identified 10 commercial emergency response systems. Four of these ten models were then subjected to detailed evaluations, which included simulations of actual dispersion tests. Results of the comparisons showed reasonable agreement for several models and identified potential problem areas in others. A major deficiency in all the models was the exclusion of simulations for chemical reactions, fires, and explosions. Seven commercially available emergency systems are identified, and their features and approximate costs are compared.

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# 4.3.5 Hazards Evaluations of Processing Facilities

Predictive Hazards Evaluations (PHE) is the title given to a group of procedures used for detailed qualitative and quantitative safety studies performed on chemical processing facilities. They are used to identify and evaluate process hazards throughout all phases of the life of a facility: design, construction, startup and shutdown, normal operations, and plant modifications. PHE has been developed and used extensively over the past ten years by chemical, petrochemical, and petroleum refineries throughout the world.

The procedures that are developed may be divided into two categories: (1) those which provide identification of the specific hazards in a process plant and (2) a group of quantitative mathematical models capable of estimating the risks associated with both normal and abnormal plant operations.

Predictive Hazards Analyses (PHA) range from simple relatively inexpensive identification studies to very detailed, complex, and expensive systems. Decisions as to which systems are to be employed by a particular plant depend primarily on the levels of risk existing at the plant, the complexity of the process, the potential for serious consequences from an accident to the plant personnel and the local community, and the technical and financial resources available to the plant management.

Acceptance by the chemical industry of PHA systems varies considerably among the various methods. Widespread acceptance has occurred for Preliminary Hazard Analysis; Failure, Model, Effects, and Criticality. Analysis; and the HAZOP procedure. These are primarily procedures that force the plant designer operators to review the process in intensive detail and identify those areas where significant risks exist and provide information to management concerning the corrective actions required. A partial list of contractors who offer PHA analysis services to the chemical industry is included.

4.3.6 Emergency Response Information and Data Base

Information requirements for the development of local community emergency response plans is very extensive, and obtaining it can consume significant amounts of time and resources. The types

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of information bases to be developed include:

- 1. hazardous materials properties (toxicity, flammability, reactivity, physical properties, etc.)
- 2. historical data on hazmat accidents; and
- 3. inventories and materials flow for hazmats.

Several excellent data bases are available for the properties of hazardous materials, including the EPA List of "Extremely Hazardous Substances," the Material Safety Data Sheets (MSDS), the MEDLARS Data Base, the CHRIS Hazardous Chemical Data Base, the Association of American Railroads Data Base, DOT's Guidebook for Hazardous Materials Incidents, and NFPA's Fire Prevention Guide on Hazardous Materials.

The most complete resource information for historical data on hazmat incidents is the EPA Acute Hazardous Events Data Base. Transportation events are recorded under the DOT Hazardous Materials Information Systems; and, by law, all significant hazmat events are to be reported to and recorded in the National Response Center Data Base. This data base will probably improve significantly under the reporting provisions of the new SARA Title III statute.

The only federal materials flow data base for transportation of hazmats is the Commodity Transportation Survey. However, these data are usually aggregated and not useful for specific materials flows. Data concerning hazmat transportation by rail or by water are available, but truck data are far less plentiful. Local surveys are usually required to determine the flows of hazmats through local communities for emergency planning purposes.

# 4.3.7 Community and Facility Planning for Toxic Chemical Emergencies

Guides, planning procedure handbooks, and reports of successful planning projects have been developed under sponsorship of the federal government, industry, trade organizations, and private engineering organizations. Descriptions of the various documents available for planning operations are included, along with a partial list of organizations available for consulting in this area.

# 4.4 NEW TECHNICAL APPROACHES

# 4.4.1 Prevention of Chemical Accidents

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Increased emphasis has been placed recently on the technical countermeasures involved in the prevention of chemical accidents and the interaction between the prevention and the emergency response aspects. Technical approaches reviewed in the area of prevention include the following:

1. human factors in accident prevention,

- 2. prevention at chemical production and storage facilities,
- 3. prevention through education and certification, and
- 4. community awareness programs.

Prevention countermeasures that appear promising for existing plants include:

- 1. plant risk analysis (HAZOP, Failure Mode and Effects, etc.);
- 2. equipment depressurizing during emergencies;
- 3. secondary containment systems;
- 4. reduction of toxic material inventories;
- 5. substitutes for hazardous materials;
- 6. explosion suppression systems;
- 7. machinery vibration programs; and
- 8. improvements to storage systems;

Many of these countermeasures have already been implemented in various chemical plants. Their adoption by the entire sector would almost certainly improve the overall safety and reliability of the process industry and significantly reduce the frequency of chemical releases.

4.4.2 Detection and Warning Systems

Probably the most critical need with respect to detection systems concerns the requirement for a remote sensing instrument that will detect releases of a wide range of chemicals over the entire area or boundary of a plant site. Instruments are currently available to perform this task for one or perhaps several chemicals but not for a broad range of materials. Also, they are not currently capable of detecting a mixture of hazardous materials in the ambient air. Costs for the available instruments for remote sensing are very high - probably beyond the range of most communities concerned with monitoring local highways, truck stops, rail yards, etc. The only realistic detection systems for local monitoring appear to be low-cost point sensors for particular chemicals such as ammonia, chlorine, and hydrogen sulfide. Selection of the hazards to be monitored can be accomplished by hazard evaluations for a particular community and by identifying those chemicals that are most likely to present a risk to the community.

#### 4.4.3 Minimizing Transportation Risks

Improved data and information systems concerning highway and rail transportation of hazardous materials are probably the most critical countermeasures needed by local planning committees. Data are not currently available for the flow of these materials through the nation, and the only feasible approach for their development is through local surveys. While some communities have already made such surveys, the costs are probably too high for the resources of most local areas. It may be feasible to utilize the data required by the new SARA Title III statute to develop a materials flow data base; thus, studies of this potential resource are recommended.

The installation of adequate monitoring and warning equipment at transportation vehicle concentration points such as rail yards and truck stops appears to be a critical need. Recent experience has demonstrated that these points are potential locations of toxic releases, and they represent significant risks to the nearby populations.

Another proposed countermeasure concerns the use of radio warning systems installed in vehicles carrying hazmats. These systems would be activated during an accident and would provide first responders a description of the cargo and recommended response procedures from a remote position. It is suggested that this practice, if adopted, would permit identification of the cargo much more rapidly and remove doubt as to the proper procedures to be used in response to chemical transportation accidents.

Development of remotely operated emergency response equipment, advanced computer programs that utilize artificial intelligence for emergency response situations, and investigation of the feasibility

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of controlled burning during hazardous chemical releases are also recommended.

# 4.5 METHODOLOGY FOR RANKING OF CHEMICAL HAZARDS

A system for developing a uniform approach to the measurement of the relative threat from various chemicals has been developed. This approach, which is needed because of the wide diversity in these materials, assigns ratings for toxicity, fire, reactivity, mobility, domestic production, and domestic shipments to each material. Each rating is then multiplied by an importance factor, and the results are combined mathematically to obtain an overall ranking which can be used to compare the relative risks for each material.

The rating system was tested on 120 hazardous materials selected from the EPA list of "Extremely Hazardous Substances" and other sources. A broad range of variables was used as the criteria for selection of these materials, including the following:

1. very acute to low toxicity,

- 2. bulk industrial chemicals to low annual production rate chemicals,
- 3. highly flammable/explosive to nonflammable/nonreactive materials,
- 4. chemicals that have caused zero to many injuries or deaths during 1980-1985, and
- 5. very volatile (mobile) to slightly volatile chemicals.

Results of this rating system are tabulated in four categories representing materials of descending levels of relative risk:

- 1. very high risk,
- 2. high risk,
- 3. moderate risk,
- 4. lesser risk.

No attempt was made toward ranking the individual materials within their individual categories. The 120 chemicals selected were spread roughly equally among the four categories.

In our judgment, this ranking system should be of value to planners responsible for selecting those materials which represent the maximum danger to their local communities and also for

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determining the hazard ranking of new chemicals entering the market. Extension of this procedure to the entire list of "Extremely Hazardous Materials" is recommended.

# ABSTRACT

Recent major incidents involving the airborne release of hazardous chemicals have led to this study of effective strategies must be developed to prevent and to deal with emergencies. The comprehensive study of FEMA and the various other entities required that the project be divided into three tasks. These included:

Task 1 - The nature of the threat from incidents involving airborne hazardous chemicals is described. Based on available databases, a new methodology for ranking chemical hazards is proposed and tested.

Task 2 - Existing responsibilities of federal, state, and local agencies, as well as the part played by the private sector, have been surveyed. Legislation at all levels of government are reviewed and in light of this analysis, the role of FEMA is examined. Institutional options to new and existing approaches for reducing risk are reevaluated, and recommendations are made for these approaches. Task 3 - Technical options are discussed in light of the most hazardous situations, and recommendations are made for action or research where needed. Emphasis is laid on new and emerging technologies in the area. Finally recommendations are offered regarding actions which would improve preparation, training, mitigation, and response on the part of FEMA to the release of hazardous chemicals.

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# **1** INTRODUCTION

Recent major incidents involving the release of hazardous chemicals have heightened the awareness of both the public and private sectors that effective strategies must be developed to prevent and to deal with emergencies. A number of federal, state, and local government agencies share portions of the responsibility for various aspects of the problem. With the very considerable overlap, as well as holes in the coverage, it is desirable to perform a study of this picture and to review the entire collage of activities and to recommend appropriate roles for FEMA and other agencies. FEMA's role in the hazardous materials area, as in other emergency management problems, is one of coordination. FEMA is not a resource agency with extensive substantive expertise or operational responsibility. The implication of coordination is that multiple organizations which usually function separately are to work together, similar in a general sense to what is understood by physical or mechanical coordination: the pieces connect where they are supposed to and work together to move ahead in a common direction. In his coordination role, the Director of FEMA is responsible for assuring that legally mandated elements of emergency management do in fact exist, that when they should they can and are likely to work together rather than independently, or, worse at cross purposes, and that the approaches used to manage the various aspects of the problem are reasonable and likely to meet the requirements to the extent that current knowledge, technology and management allow.

While the whole area of hazardous materials may require such a treatment, the most chronic need for a strong direction is cases where an airborne hazard is involved. The materials might be in any form but the means by which the threat overtakes people is such that little warning is possible and immediate means of protection are very limited. There are, in fact, many parallels to be drawn between airborne spread of hazardous chemicals and the airborne dispersion from a nuclear incident.

Since these parallels exist and since FEMA has taken a leading role in preparedness for nuclear problems, it is a relatively small step for FEMA in its coordination role and through its emergency management assistance program to support state and local governments, to deal with planning for hazardous materials, particularly airborne ones, in conjunction with other agencies. However, the nature of the disasters which are possible make it absolutely mandatory that the responsibility for dealing with the problems in local entities must lie with the local authorities. While accidents are a large portion of the hazard, obviously one must also have a concern for bostile acts. Again, the airborne segment of the hazards in such events is the primary focus of this investigation.

The comprehensive study of the role of FEMA and the various other entities in preventive measures and planning requires that the project be divided into a number of tasks. Quoting from the work statement for this project (see Appendix A), these include:

1. <u>Task 1 - The Threat</u>. There appears to be no consensus on how to define the threat. Several measures of toxicity and exposure are available and are used for various purposes, but toxicity of the chemical agent is only one aspect of the threat, however central. Approaches will be summarized and evaluated, and recommendations will be developed for a systematic approach. The emphasis will be on acute, emergency conditions, as opposed to chronic, long-term situations.

The interest is in chemicals that have the potential for endangering people over significant areas. Emphasis will be placed on chemicals that can become airborne (gases, vapors, and aerosols), and to a lesser extent, waterborne.

The mechanism of dispersal can be chemical plant accidents, transportation accidents, or malevolent dispersal, including nuclear attack. Relative hazards may be proportioned to the product of the acute toxicity (reciprocal of  $LD_{50}$ ) and quantities normally present or easily obtainable.

2. <u>Task 2 - Current Responsibilities</u>. The statutory and regulatory responsibilities of federal agencies, including overlap and or gaps, will be identified. Significant activities at the state and local levels will be summarized. Strategies being developed by many private organizations and trade groups to handle emergencies and reduce risk will be described. More effective

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methods are to be identified of dealing with problems that still pose substantial risk for which truly effective countermeasures have not yet been developed. Organizations and institutions with the capability of solving the problems will be identified, and possible arrangements to ensure resolution will be explored.

3. <u>Task 3 - Technical Options</u>. Principal methods to characterize the nature of emergencies and to identify the technical basis for needed countermeasures will be reviewed. The effectiveness of these actions will be evaluated, and needs for improved response actions will be identified. Resources will be evaluated in the context of current or potential availability to local emergency teams and capabilities of FEMA to coordinate access to resources. Existing and potential new approaches to reducing risks and consequences will be considered. Approaches will include warning systems (technologies), data bases (such as CHEMTREC), training and safety programs, emergency plans, and so forth. In particular, needs for new approaches and opportunities for FEMA will be highlighted.

Task I (Sects. 1 through 3) is divided into sections describing the nature of some of the major airborne disasters that have occurred recently and have served as a catalyst for the current study. Accident frequency and severity statistics are divided into transportation and processing sectors. The former is further subdivided into the various transportation modes such as rail, truck, air, and ship. The processing category includes actual processing and storage. Task II (Sects. 4 through 9) provides an overview of the existing statutory and regulatory responsibilities of federal, state, and local agencies with respect to emergency response to hazardous chemical releases. Overlaps and gaps of the responsibilities of the various agencies are summarized. Also, the activities of private organizations and trade groups are identified, and their relationship to current governmental activities is described. The intent of Task II is to provide FEMA with a current overview of these responsibilities and activities, which will assist in the determination of appropriate roles for FEMA and other federal agencies in this area. To provide a framework for the wide range of emergency response responsibilities, we have divided them into the following categories: prevention, planning,

response, and training.

Task III (Sects. 10 through 18) reviews the principal methods to characterize the nature of emergencies and defines a technical basis for the countermeasures that are currently available, under development, or projected as future approaches. An evaluation of these countermeasures is developed, and requirements for improved response actions are summarized. Also, existing and potential new approaches to reducing the risks and prevention of hazardous chemical releases are included. In particular, the need for new technical approaches that present opportunities for FEMA programs is emphasized. Task II deals with the development of the methodology for ranking chemical hazards (Sect. 16). The principal factors include type and intensity of hazard (toxicity, fire, and explosion) and the extensive factor (production, location shipments). In Sect. 17, the proposed methodology is tested on a number of chemicals which were selected to exhibit a wide range of risks.

The many acronyms used in this document are identified in the Glossary of Acronyms in Sect. 20. In addition, when an acronym is used for the first time, the full term is also given in order to assist the reader.

# **2 OVERVIEW OF RECENT CHEMICAL EMERGENCIES**

Several airborne hazardous-chemicals incidents that have occurred during the past several years have focussed the attention of the public on preparedness for such emergencies. Perhaps the greatest attention has been paid to the disaster at the Union Carbide plant in Bhopal, India. This disaster and other selected incidents are reviewed here. Our objective is to show the extremes in the types of incidents that can happen. The Bhopal disaster illustrates an incident where toxicity was the causative mechanism. On the other hand, the Pemex explosion illustrates a chemical incident where fire and explosion were operative. The release at Institute, West Virginia clearly illustrates that there is cause for concern in the United States as well as abroad. The commonality here is the sudden victimization of a population from a lethal situation against which they cannot gain protection. The extent of the problem in the United States has been studied for the U.S. Environmental Protection Agency (EPA), the results of which are summarized in Sect. 3. We have drawn recommendations from these experiences on different approaches to promoting better planning, accident avoidance, and loss control.

#### 2.1 BHOPAL DISASTER

Millions of words have been written and spoken in the news media about this accident. In its barest outline, the following events occurred. Sometime during the late evening of Sunday, December 2, 1984, the contents of a methyl isocyanate (MIC) storage tank at the Union Carbide India, Limited, pesticide plant in the center of Bhopal, India, became dangerously hot because the tank's refrigeration unit was not operational. Pressure in the tank rose to an untenable level at about the time of a shift change. Shortly after midnight, the rupture disk on the tank released and remained open for 2 h, allowing 40 tons of MIC to be released into the atmosphere. The safety backup systems, which included caustie scrubbers and a flare, were not functional at the time. The vapor release covered a heavily populated slum area of the city, killing 2000 to 3000 people and seriously injuring 20,000 others. Approximately 200,000 of the city's 800,000 inhabitants were

affected by the release.

Investigation into the incident has been widespread and has included Indian federal and state government studies, a company investigation, and a number of independent inquiries. Since the accident is still in litigation, the plant personnel closest to the scene are prohibited from discussing the details; however, the hypotheses that have been presented to date paint a picture of plant operation which, at best, could be described as lax.

If any one of the following five safety devices had been functional, the disaster would have been averted:

- There appeared to be a great deal of water in the storage tank. Its source is unknown, but it
  is a major goal of the process to keep the MIC anhydrous. Without water, the reaction would
  not have been initiated and the disaster would not have occurred.
- 2. The refrigeration unit that is used to keep the MIC in the storage tank below a temperature where it is reactive was not functional and had not been for months. With refrigeration, the reaction would have been too slow to cause any problem, even with water present in the system.
- 3. Alarms that would have alerted operators to the problem either did not function or were ignored. Temperatures in the tank were observed, but the critical time in the temperature rise occurred at a shift change so it was not sufficiently well followed.
- 4. The caustic scrubber, which is an emergency device used to absorb released MIC, could not be made to function from the control room. The caustic feed pump required on-site activation, which was not done. An operational scrubber would have eliminated the release.
- 5. The release was vented through a vent pipe which is equipped with a flare. The flare was undergoing maintenance at the time of the disaster; if it had been functional, no disaster would have occurred.

If the above-mentioned items are indeed facts, one can only conclude that the management personnel were either derelict in their duty or very ill-trained for their jobs.

The lessons to be learned from this incident are very fundamental. First, maintenance of safety equipment is an absolute necessity. Second, training of the personnel in the handling of emergencies is a necessary part of the job. Evening and night shifts require engineering staff in plants where airborne disasters are a possibility.

# 2.2 PEMEX DISASTER

On November 19, 1984, a natural gas explosion occurred at San Juan Ixhuatepec, a suburb of Mexico City, which caused the deaths of 500 people and injured 2500 others. Approximately 200,000 persons were left homeless. The plant in question was a liquefied petroleum gas plant and distribution center. A leaking truck at the distribution center was apparently ignited either by the flare or a welder's torch. The fire heated the nearby storage vessels, of which 12 subsequently burst, adding enormously to the conflagration in a plant which was not laid out with a view to preventing the spread of such disasters. As in Bhopal, a "shanty town" had grown up next to the plant, a situation that added greatly to the casualties. As has been the case in a number of instances, a population has exposed itself to a hazardous situation subsequent to the locating of a plant in a remote area.

In this case the airborne release itself was not lethal; it was the potential (or, actually, the realization of the potential) an explosion which caused the disaster. This sort of threat is readily distinguishable from the case of a poisonous gas release. It is important to note that a gas explosion is an even more rapidly developing situation than the exposure to a lethal gas. Hence, the precautions that are necessary in such cases fall entirely upon the operators of the production or storage facility. Because of the quantities of materials involved and the diversity of locations in which explosive materials (such as liquefied natural gas) are stored, this is a very significant concern.

#### 2.3 ISCIDENT AT INSTITUTE, WEST VIRGINIA

On August 11, 1985, Union Carbide suffered another gas leak, this time at its plant located in Institute, West Virginia. Again, a pesticide precursor facility was involved. This time, a 5000-gal vessel containing 500 gal of aldecarb oxime, dissolved in methylene chloride, was the source of the release. Steam was piped to the jacket surrounding the vessel. The pressure increase caused by the highly volatile methylene chloride initiated a series of releases, which included the safety valve to the scrubber and flare systems and three gaskets on the ports to the tank. The failure of a rupture disk on the scrubber and flare system caused much of the gas to be released to the atmosphere. The cloud drifted over the plant boundary into a residential neighborhood. Overall, 135 people were exposed and were treated for eye, throat, and lung irritation. The tank was part of a temporary aldecarb system originally built for other purposes and was being phased out at the time of the accident. It was replaced by a new, larger system which was in startup at the time of the accident. With this accident as with Bhopal, multiple safety nets failed or were in ill repair. The following are the concerns:

- 1. Why did the safety valve on the flare system fail after the port gaskets?
- 2. Why did the rupture disk burst on the flare-scrubber system?
- 3. Why was the water spray system around the tank insufficient to contain the leak?
- 4. Why did Carbide personnel wait 20 min before alerting the community?

The response to the last question is the Carbide personnel relied on the Safer computerized dispersion-modeling system to predict whether the release would affect the community. A faulty prediction that the cloud would not be dangerous beyond the plant gates led to the delay of notification. It was subsequently revealed that (1) no constants for aldecarb oxime were included in the program's data base and (2) insufficient data were available on the effects of exposure to aldecarb oxime.

In this case, more safety and health information, as well as greater attention to details of maintenance and operation, would have completely averted this disaster. Union Carbide was subsequently cited by the Department of Labor for "willful violations" of health and safety standards.

Thousands of other chemical incidents have occurred over the years. Most have not been as dramatic nor have most caused any injury, but the potential for major disasters is always present. Therefore, we must plan for minimization of the effects of the unavoidable few that occur.

# 2.4 ACUTE HAZARDOUS EVENTS DATA BASE

As a response to concerns about the safety of the domestic chemical industry raised by the Bhopal disaster, the Office of Toxic Sub. tances of the U.S. EPA commissioned a study of the nature and extent of incidents of accidental chemical releases in the United States. The resulting report, "Acute Hazardous Events Data Base" (EPA 560-5-85-029) statistically reviews 6928 separate events that were reported between 1980 and 1985. The objective was to characterize the types of events releasing acutely toxic substances, the substances involved, and the factors leading to the airborne releases.

The events recorded come from reports made to two federal offices, five offices within four state governments, one engineering firm's collection of event reports, and five electronic or print media sources. Most of the sources did not cover the entire 1980-85 period and did not include 69% of the records from the 1983-84 period. The AHE Data Base is best characterized as a partial listing of accidental chemical releases, based on an informal sampling of public, readily available data sources.

About 418.7 x  $10^8$  lb of various chemicals were among the events in the study released. About 25% of the records failed to indicate  $\gamma$  quantity released. In all, 200 substances were involved with events in which there were reported casualties, with 25% of these being attributable to high-volume inorganic chemicals (chlorine, ammonia, hydrochloric acid, and sulfuric acid). Another 30% of the events with reported casualties were associated with the release of industrial organic chemicals.

It was concluded that neither high toxicity nor large quantities alone can create conditions for human casualties. In the events reported, most injuries were the result of toxicity, while most deaths were caused by fire and explosion. However, it is obvious that a single Bhopal disaster would skew

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this in the other direction.

Transportation releases account for 25% of the incidents in the AHE and 33% of the casualties. The leading causes of transportation releases are leaks (38%) and collisions (20%). As expected, trucking incidents account for more than half of the recorded events, while rail cars contribute 38%. Expelines report few events, but the quantities involved in each case are very much larger than other transportation incidents.

In fixed facilities, spills (70%), and vapor releases (25%) occur more frequently than fires and explosions (5% or less). Equipment failure and operator error are the most frequently reported causes. Processing vessels, storage facilities, and the piping systems of plants contribute roughly equally in terms of frequency of incidents. Because of the quantities of materials kept in storage areas, these are generally responsible for the largest releases.

It is evident from the diversity of industry and transportation in the United States that there is a very large potential for disasters of the Bhopal or Pemex types. It should be added that these incidents, for the most part, clearly point to the need for greater vigilance. Given the enormous potential for transportation incidents, no community of any size can ignore this potential source of disaster. Although communities with chemical plants have an added danger, this danger is compensated for by the existence of expertise in the community. The AHE data base provides an excellent source of information on which to base tests of our criterion.

# 3 RELATIVE ACCIDENT FREQUENCIES AND SEVERITY

There is reasonable agreement that the development of a preliminary hazards analysis is mandatory as a prerequisite to community planning for hazardous chemicals emergencies. However, such a task requires that the principal hazards be identified and assessed with respect to the chemical properties, source, and potential quantities of materials released, demographic factors such as nearby population, average weather conditions, and probabilities of release from various sources based on historical data. This section presents an overview of recent information concerned with the relative frequencies and severity of hazardous chemical accidents.

# 3.1 RELATIVE ACCIDENT FREQUENCY BY SECTOR

Zaccor<sup>2</sup> analyzed release frequencies for the various sectors shown in Table 1, which were based on EPA data collected between 1967 and June 1973.<sup>3</sup> More recent information for the period 1980-1985 as was developed for EPA, the Acute Hazardous Events (AHE) Data Base, is also tabulated by sector in Table 1.<sup>3</sup> This information may indicate a shift in frequency from transportation events to in-plant events, but the two data sets used had different underlying sample frames and selection criteria so that a direct comparison of the results is unwarranted.<sup>20</sup> Zaccor also tabulated the transportation data by transport mode as shown in Table 2. Highway events dominate the total number of events, but published frequency data per mile per vehicle indicate only a slightly higher highway rate.<sup>4</sup> This is probably due to a lower number of railway miles traveled per shipment as compared with highway shipments.

Caution should be used in utilizing these data for other than qualitative purposes since the requirements for reporting events in the transportation sector are very stringent; therefore, the data may not reflect numerous incidents that occurred in industrial plants. The decrease in transportation percentages for the 1980-1985 EPA data shown in Table 1 may be an indication of this bias since reporting requirements have been tightened recently by the Comprehensive Environmental Response, Compensation and Liability Act (CERCLA) of 1980. Also, not all the

Sector	Percent of total events (1967-1973)	Percent of total events (1980-1985)	
Transportation	57	25	
Loading/unloading	25		
In-plant processing	10	75	
In-plant storage	8		
Total events	1441	6928	

Table 1. Frequency of release of hazardous materials by sector

Table 2. Release of hazardous materials release by transport mode

Transport sector	Percent of total events (1967-1973)	Accident frequency (per_mile_per_vehiclea
Highway	90	2.5 X 10-6
Rail	9	1.5 X 10-6
Air	0.8	1.0 X 10-8
Water	0.2	
Pipeline	low	

reported events during the indicated periods were included in either set of data; thus, the results do not represent a complete picture of chemical accidents during the indicated time frames. Further, the two studies used different groups of data sources, so there may be systematic bases toward events from fixed facilities or from transportation accidents.

## 3.2 RELATIVE ACCIDENT SEVERITY BY SECTOR

An analysis of event severity from the EPA data indicates that the transportation sector does not dominate the severity data. Table 3 indicates the relative severity (as described in the table) as a function of the sector. Ranking of the "hazard potential" for the data in the 1967-1973 EPA data<sup>3</sup> indicated that the sector order for decreasing risk was reversed (storage, processing, transportation) when compared with the frequency rating in Table 1. The later EPA data (1930-1985)<sup>1</sup> confirm this trend, as shown in Table 4. The average release from storage vessels is far greater than that from process - or in-transit-related events (except pipeline events that were not specifically listed in the 1967-1973 data). Reasons for the excess storage vessel hazard probablyinclude the larger quantities of hazardous materials stored and lower levels of operator attention to the stored materials as compared with the surveillance during normal processing and truck/train transport. These were significant factors in the release of methyl-isocyanate during the Bhopal disaster in 1985 (see Sect. 2).

## 3.3 RELATIVE ACCIDENT FREQUENCIES AND SEVERITY BY HAZARDOUS CHEMICAL

Table 5 indicates the frequency data and quantities released for the most important 18 chemicals arranged in terms of decreasing number of events for the period 1980-1985; also included are frequency data for 15 other selected hazardous chemicals. Although PCBs head the list, they were not responsible for the greatest number of events where injuries were reported (and none of the PCB records had a reported fatality). Chlorine is the major hazard in this area, followed by anhydrous ammonia, hydrochloric acid, and sulfuric acid. Surprisingly, the average quantities of chlorine released per event are low (300 to 400 lb per event). Note that the data in Table 5 should

Sector	Mean hazard potential <sup>a</sup>
In-plant storage	4.58
In-plant process	4.18
In transit	2.88
Loading/unloading	2.31

Table 3. Ranking of operational areas by severity-hazard potential (1967-1973 data)

<sup>3</sup>Hazard potential is a function of the quantity of the material spilled and the relative hazard level (RHL) of the substance as determined by its toxicity.

Events	Estimated number of events	Estimated amount Released (x 10° lb)	Estimated Mean amount (lb/event)	Estimatec median amount (lb.week)
		In-Plant Locatio	<u>on</u>	
Process vessels	529	11.7	22,100	420
Storage vessels	794	320.0	403,000	2,000
Valves pipes	884	9.0	10,200	1,200
Other locations	1236	27.5	22,200	55
Total	4114	370.3	90,000	14()
		In-Transit Mod	<u>le</u>	
Trucks	748	7.6	10,200	710
Railroads	258	7.0	27,100	410
Pipelines	32	25.7	803,100	6,800
Barge	29	3.3	113,800	230
Other modes	26	0.03	1,200	100
Total	1093	43.63	39,900	460
Total (all sectors)	5207	413.93	79,500	32()

Table 4.	Frequency and re-	elease of	hazardous	chemicals by	sector
	(1	980-1985	data)		

'Events where release quantities were reported.

be interpreted with caution. Namely, the events summarized are from a partial, informal sampling of events from the 1980-85 period. The quantities released are often approximations in the AHE, and  $z_1 u_2 M_2$  2507 of all the records do not include esclusives of the quantities released.<sup>5</sup>

The relationship between the annual product on rates of the chemicals listed in Table 5 and the number of releases is of interest in the development of a hazards analysis. Figure 1 indicates the frequency of release as a function of annual production for 28 of these chemicals. The data do not show a good correlation (correlation coefficient = 0.83), but they do indicate a trend toward increased releases for the heavy tonnage chemical production. They also show a significant number of releases at production rates of less than 1 billion lb per year for H<sub>2</sub>S, tetrachloroethylene, SO<sub>2</sub>, and methyl chloride.

Figure 2 indicates the quantities of the top 17 chemicals (based on events) released as a function of their annual production rates in 1984. Again, the data indicate a trend toward greater quantities released at higher production rates, but the correlation is not significant (correlation coefficient = 0.43). A ratio which assumes that the release quantities reported in Table 5 approximate the total releases experienced during the 1980-1985 period indicates that between 3 and 730 tons of these chemicals were manufactured per pound of chemical released during the period.

#### 3.4 EVENTS INVOLVING DEATH OR INJURY

The data from the 1980-1985 EPA data base indicate that death or injury was reported for 6.8% of all the events and in 0.9% of all the events one or more fatalities were reported. The total number of reported injuries was 4717, with an average per injury/death event of 10. The total number of deaths reported was 138, and the average death per event was 2 (range = 1 to 11). The earlier (1968-1973) data indicate an average injury per injury/death event of 3.3 and an average death/death event of 1.3. This may be an indication of increasing severity of events, underreporting of hazardous incidents, or the different sampling frames for the data sets. Fires and explosions

Hazardous chemical	Data point <sup>a</sup>	1984 U.S. Production (10 <sup>3</sup> 1b/year)	Number of releases	Quantity released (lb)
PUB			1590	1,204,448
Sulfuric acid	1	83.6	453	3,987,566
Ammonia	2	33.4	258	2,756,031
hlorine	3	21.4	245	80,897
tydrochloric acid	4	5.5	213	3,046,381
Sodium hydroxide	5	21.8	181	12,058,177
fethanol	6	8.2	115	2,883,823
litric acid	7	15.5	115	3,939,974
fethyl chloride	8	0.4	98	70,214
Tolitené	9	5.3	95	4,820,857
/invl_chloride	10	6.1	79	200,812
hosphoric acid	11	22.7	72	530,680
Senzene	12	9.7	65	677,450
Ethylene dichloride	13	10.7	63	676,345
stvrene	14	7.7	62	251,130
lydrogen sulfide	15	1	58	128,488
Tetrachloroethvlene	16	0,6	50	770,858
Sulfur dioxide	17	0.4	46	898,668
Ethylene oxide	18	5.2	27	b
'invl acetate	19	2.0	21	b
Phosgene	20	1.5	14	b
lvdrogen cyanide	21	0.7	12	b
fethvl mercaptan	2.2	0.005	8	b
Chlordane	23	0.006	6	b
11BK solvent	24	0.2	4	ь
Acrolein	25	0.07	2	b
Epichlorohydrin	26	0.36	2	b
lethvl isocyanate	27	0.04	1	b
Fluorine	28	0.01	1	b

Table 5. Hazardous chemical releases during 1980-1985 (1984 production quantities)

<sup>a</sup>Please see Figs. 1 and 2. <sup>b</sup>Indicates release quantities not tabulated in ref. 3.

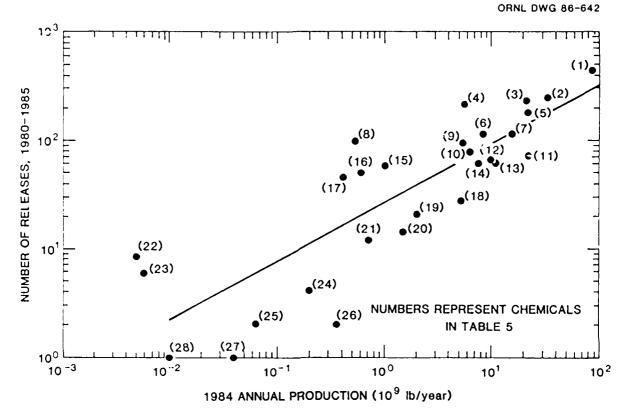


Fig. 1. Frequency of chemical releases 1980-1985.

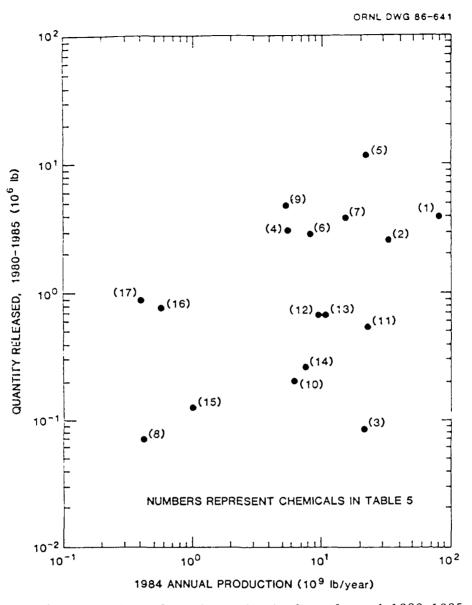


Fig. 2. Quantity of various chemicals released 1980-1985.

predominate as the cause of death, while toxic exposure by spill or vapor release was nearly always associated with injuries. Representative chemicals where toxicity caused injuries included ammonia, chlorine, hydrochloric acid, phosgene, and nitric acid. For deaths in which fire and explosion were apparently the main cause, representative chemicals were chlorine, gasoline, oil and propane. No attempt was made in the EPA data base to develop a fatal accident frequency rate but Ozog<sup>6</sup> reports a value of 4 for the chemical processing industry and a recommended value of 0.4 for new chemical facilities. This rate represents the number of fatal accidents in a group of 1000 persons over an aggregate working lifetime of 10<sup>8</sup> h.

## **4** CURRENT RESPONSIBILITIES

The results from Task 2 in the work statement (Sect. 1.0), which covers current responsibilities, are numbered in sects. 4 to 10. They provide an overview of the existing statutory and regulatory responsibilities of federal, state, and local agencies with respect to countermeasures to hazardous chemical releases. Overlaps and gaps of the responsibilities of the various agencies are summarized in Sect. 10. Also, the activities of private organizations and trade groups are identified and their relationship to current governmental activities are described in Sect. 8.

To provide a framework for the wide range of emergency response responsibilities, we have divided them into the following categories: prevention, planning, response, and training.

## 4.1 PREVENTION

Prevention of hazardous materials (hazmat) releases is primarily the responsibility of the management of fixed production, storage, or conversion facilities or the owner/operators of vehicles that transport these materials.

Statutes for the regulation of the fixed facilities with respect to release prevention have only recently been promulgated by several states. However, a comprehensive set of federal and state regulations are in force for the transport of hazmats. Federal and state statutes are discussed in Sect. 5.

#### 4.2 PLANNING

Probably one of the most important aspects of emergency response mitigation is concerned with the planning for possible events at all levels of government (federal/state and local). Past experiences have demonstrated that poor or inadequate planning for hazmat emergencies has led to disastrous consequences in terms of lives lost, injuries sustained, and property damage. The disaster in Waverly, Tennessee, in 1978, where an ineffective evacuation was attempted, is a good example of this.<sup>7</sup> After the Bhopal disaster, it became very apparent that adequate planning is essential; as a result, several federal and private organizations have developed guidance documents

for community planning. Recently, new federal and state statutes have been enacted which require planning for hazmat emergencies at all levels of government. Descriptions of these activities and statutes are included in Sects. 5.7 and 5.9.

## 4.3 RESPONSE

Responsibility for emergency response to hazmat air releases almost always resides at the local level. For events such as the Bhopal disaster, the duration is usually only a few hours and sufficient time to activate state or federal agency support teams is not available. Therefore, the roles of the state and federal governments are primarily in the areas of preparedness/planning, training, technical assistance, information exchange, and provision of proper support such that communities are prepared for these emergencies. A summary of the operational support available at all levels of government, as well as from industrial and private organizations, is included.

#### 4.4 TRAINING

Training for personnel to respond to hazmat emergencies is available through federal, state and local government agencies, and private training vendors. These activities are directed toward all response levels from "first responder" through management of emergency organizations. An overview of training activities is included with this study, and problems with the current system are identified (see Sect. 10.4)

# 5 FEDERAL AND STATE STATUTES FOR HAZARDOUS MATERIALS

The major federal statutes that impact hazardous materials response are the: 1. Clean Water Act (CWA),

2. Hazardous Materials Transportation Act (HMTA),

3. Clean Air Act,

4. Toxic Substance Control Act (TSCA),

5. Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA).

6. Resource Compensation and Recovery Act (RCRA),

7. Superfund Reauthorization (SARA), and

8. Occupational Safety and Health Act.

These statutes, along with several recent state statutes, are described briefly in the following sections.

# 5.1 CLEAN WATER ACT (CWA) OF 1977

The Clean Water Act (CWA) of 1977 was passed by Congress in response to the deficiencies in the amendments (PL 92-500) to the 1972 Water Pollution Control Act (FWPCA). The act amends the FWPCA with respect to discharges of hazardous substances and a listing of those substances (40 CFR 116). In regulation 40 CFR 117, the reportable quantities for each hazardous substance listed are tabulated. This regulation applies to quantities equal to, or in excess of, the reportable quantities discharged to navigable waters in the United States or its adjoining shoreline. Each hazardous substance is categorized by a letter code (X, A, B, C, or D) associated with reportable quantities of 1, 10, 100, 1000, and 5000 lb, respectively. The act provides that discharges from a vessel, onshore or offshore facilities equal to or in excess of the reportable quantities during a 24-h period, should be reported immediately to the appropriate agency of the federal government. It also specifies fines for failure to report hazardous substance spills. Additional provisions of the CWA of interest include the following:

- 1. states were specifically mandated prime responsibility for water quality and water use;
- construction grants and training assistance for water treatment were made available to municipalities;
- 3. effective enforcement and incentive guidelines directed toward achievement of fishable and swimmable waters were included; and

4. extensions to industry of compliance deadlines under effluent discharge limitations were defined.

# 5.2 HAZARDOUS MATERIALS TRANSPORTATION ACT (HMTA)

The Hazardous Materials Transportation Act of 1975 (PL 93-633, as amended PL 95-363), which was signed by the President in January 1975, centralized the authority for all modes of transportation of hazardous materials with the Secretary of Transportation. The regulation governs safety aspects for hazmat transport (i.e., packing, repacking handling, labeling, marking, placarding, and routing). Container regulations covering all aspects from manufacture to reconditioning and testing are also included. The law also establishes criteria for hazmat handling, such as:

1. minimum qualifications and training of personnel;

2. inspection requirements;

3. hazmat detection equipment specification; and

4. safety assurance monitoring procedures.

It also permits the DOT Secretary to require registration of transporters who ship hazmats or who manufacture containers for their shipment. Strict penalties, which includes civil penalties (fines) and criminal penalties (fines and imprisonment), were established by HMTA.

A new Materials Transportation Board (MTB) was established by the DOT Secretary to coordinate DOT's responsibilities for hazmats. Included in this Board are the Office of Hazardous Materials Regulation and the Office of Pipeline Safety Operations. Enforcement of the hazmat

regulations resides with the (1) Federal Aviation Administration, (2) Federal Highway Administration, (3) Federal Railroad Administration, and (4) Commandant of the Coast Guard.

Materials undergoing transportation that are hazardous transportation were defined for the first time by HMTA as follows:

"A substance or material in a quantity or form which may pose an unreasonable risk to health and safety or property when transported in commerce."

The Secretary of DOT may designate what constitutes a hazardous material, and Title 49 CFR defines the following materials considered hazardous during transportation:

1. explosives,

2. compressed gases,

3. flammable liquids and labels,

4. combustible liquids and labels,

5. organic peroxides,

6. oxidizing materials,

7. poisons,

8. corrosive materials,

9. etiologic agents (disease-causing microorganisms),

10. radioactive materials, and

11. other regulated materials.

State and local regulations that are inconsistent with federal regulations for transporting hazmats are preempted.

## 5.3 CLEAN AIR ACT OF 1970 AND CLEAN AIR ACT AMENDMENTS OF 1977

In the Clean Air Act of 1970, Congress authorized the Environmental Protection Agency (EPA) to establish the minimum air quality and regulatory goals the state and local governments were to achieve. The EPA was directed to set emission standards for pollutants from new motor vehicles. Fuels or fuel additives that would endanger public health were to be controlled. The EPA was also

required to publish primary and secondary air quality standards for all designated air pollutants.

In the Clean Air Amendments of 1977, new provisions were added to prevent significant deterioration of air quality (PL 95-95). This amendment imposes strict requirements for areas that fail to meet national air quality standards and strengthened enforcement of the law, particularly with respect to the performance of new sources of pollution.

With respect to the control of hazardous substances, the most important provisions are covered in Sect. 112 of the Clean Air Act. This section establishes the National Emission Standards for Hazardous Air Pollutants (NESHAP), which are those that

"... may reasonably be anticipated to result in an increase in mortality, or an

increase in serious irreversible, or incapacitating irreversible illness."

Chemicals that have been listed in this category include:

I. asbestos,

- 2. beryllium,
- 3. mercury,
- 4. vinyl chloride,
- 5. benzene,
- 6. radionuclides, and
- 7. arsenic.

NESHAPS are supposed to be set at levels that will protect public health, and consideration of costs or available control technology is not included in the provision. However, there is a problem in implementing the NESHAP provisions since the only absolutely "safe" standard for some carcinogens would be zero emissions, which would probably shut down the producers of those substances. Thus, the problem becomes one of benefit/risk analysis, and a consensus solution has not yet been reached by EPA and Congress.

# 5.4 TOXIC SUBSTANCES CONTROL ACT (TSCA) OF 1976

The Toxic Substances Control Act was enacted in 1976 in order to close gaps in the federal government's authority to test and regulate hazardous chemicals (PL 94-469). Other statutes such as the Clean Air Act, the Federal Water Pollution Act, and other statutes controlled hazardous chemicals only when they entered the environment as wastes. In addition, there was no control over the testing and surveillance of new chemicals entering the marketplace. Although the Occupational Safety and Health Act and the Consumer Product Safety Act deal with various phases of chemical production and consumer-usage safety, these statutes do not contain authority to prevent environmental hazards from toxic substances. Thus, the TSCA was designed to regulate toxic substances in the environment and, consequently, limit exposure to them.

One of the important regulations in TSCA is the Premanufacture Notification requirement (PMN). Under this rule, a manufacturer must notify the EPA 90 d before producing a new chemical. A "new" chemical is defined as one that is not included on a special list of 44,000 chemical substances compiled by United States chemical companies by May 1979. However, notification may even be required for chemicals on the list if there is a significant increased usage that increases the risk to the public. Upon receiving notification of a new chemical, EPA must publish data concerning identification, description of its intended usage, and descriptive tests required to demonstrate that there will be no unreasonable risk to the public. If the EPA decides there is a possible risk, the agency can restrict or prohibit its production. If a chemical was not added to the list by August 1980 or subsequently added under the PMN process, then it must undergo premanufacture review and testing before being manufactured in the United States or imported.

TSCA also contains extensive reporting requirements for manufacturers or distributors of chemical substances. This includes health and safety studies performed by the manufacturer, or known by the manufacturer to exist. Also, for a list of toxic chemicals, manufacturers must report

production, release, and exposure data that will be used by the EPA to determine which chemicals are to be further tested.

# 5.5 COMPREHENSIVE ENVIRONMENTAL RESPONSE, COMPENSATION, AND LIABILITY ACT (CERCLA) OF 1980

The Resource Conservation and Recovery Act of 1976 (RCRA, see Sect. 5.6) was not complete in defining the responsibilities and liabilities concerning hazardous materials. For example, RCRA did not establish reporting requirements for spills of hazardous substances. In CERCLA (PL 96-510), releases or spills are broadly defined to cover almost all types of discharges of hazmats to the air, land, and water. It also requires that the National Response Center be notified when a release of a "reportable quantity" has occurred. These quantities have been specified for a comprehensive list of chemicals in terms of the number of pounds released, which must be reported and is dependent on the relative toxicity of each chemical. For example, the reportable quantity for methylisocyanate, which was the toxic chemical released at Bhopal, is currently set at 1 lb.

Probably the most important part of CERCLA with respect to hazmat response procedures is that concerned with the National Oil and Hazardous Substances Pollution Contingency Plan (40 CFR P 300). This is generally referred to as the National Contingency Plan (NCP), which is authorized by several statutes, including CERCLA (42 USC 9605 Sect. 105) and the CWA (33 USC 1321(C)(2) Sect. 311c). Executive Order 12316 (46 CR 42237) assigns to the EPA the responsibility for amendments to and coordination of changes to NCP. The plan covers in its scope the release or substantial threat of release of hazmats that may be a threat to the public health and welfare. It specifies the response action responsibilities among the federal, state, and local governments and designates appropriate roles for private organization. Requirements for federal regional and federal local contingency plans for federal response are established, and encouragement for preplanning for response by other levels of government is suggested. CERCLA specifies that the planning and coordination requirements are to be accomplished by the National Response Team (NRT), which consists of representatives of the 14 following agencies: USDA, DOC/NOAA, DOD, DOE, HHS,

FEMA, DOI, DOJ, DOL, DOT/RSPA, DOT/USCG, DOS, EPA, and the Nuclear Regulatory Commission (NRC). When not activated by a response action, the NRT serves as a standing committee to evaluate response systems and recommend changes to the plan. Regional response activities are the responsibility of the Regional Response Teams (RRT) located in each federal region except for Alaska, the Caribbean, and Oceania (Hawaiian and Pacific Islands) which have their own RRTs. The NRT is responsible for maintaining national readiness for response to hazmat releases that are beyond the RRT capabilities. The NRT is also responsible for reviewing RRT responses to releases, developing procedures to ensure federal, state, and local government coordination for response and monitoring response-related training and research and development activities.

The RRTs provide mechanisms for regional planning and for coordination during response actions. There are two principal components of each RRT: a standing team, which is made up of representatives from each federal, state and local participating agency; and incident-specific teams, which are concerned with the technical and geographical aspects of hazmat releases. The standing RRTs have a role in the communications, planning, coordination, training, and evaluation preparedness on a region-wide basis.

Responsibility for directing federal fund-financed response efforts at the scene of a hazmat release resides with the regional on-scene coordinators (OSCs), who are predesignated by the EPA or the U.S. Coast Guard (USCG), except in the case of releases from facilities where the OSCs will be designated by the DOD, or for nuclear releases according to an agreement between the DOD, DOE, and FEMA. Proposed amendments to the NCP will include DOE designation of an OSC in the event of a release from a DOE facility. The EPA furnishes the OSC for inland events, and the USCG provides the OSC for navigable water for hazmat events. Remedial actions required by hazmat releases are the responsibility of the Remedial Project Managers (RPMs) who are designated for the federal regions or USCG districts. During response actions, the members of the RRT will make the resources of their agencies available to the OSC as specified by predetermined federal,

regional, and local contingency plans. Duties of the OSC/RPM during a federal fund-financed response include:

- 1. the establishment of priorities for protecting the exposed public's health and welfare;
- 2. the collection of pertinent data concerning the release such as the source causes, nature of the materials released, probable direction, potential impact on exposed public; and
- 3. the identification of potentially responsible parties.

For federal fund-financed response efforts, the OSC/RPM will direct the response operations and coordinate these efforts with appropriate federal, state, local, and private response agencies. In a potentially major disaster situation, the OSC/RPM must advise FEMA of situations potentially requiring evacuation, temporary housing, and permanent relocation. Where possible public health emergencies arise, the OSC/RPM must notify HHS for assistance in protecting the public health and on worker health and satety problems.

Several special forces and teams are available to the RRTs during hazmat emergencies. These include:

1. USCG National Strike Force (NSF),

2. EPA Environmental Response Team (ERT),

3. Scientific Support Coordinators (SSC) provided by NOAA or EPA, and

4. public information teams supplied by EPA or the USCG.

Incident-specific RRTs may be activated upon request of the OSC/RPM or by any RRT representative. The NRT may be activated for major response actions that exceed the capabilities of the affected regions. Its actions recommended through the RRT may include providing federal, state, and local government resources and coordinating the supply of resources to the affected region from other regions or districts.

The National Response Center (NRC), located at the USCG (headquarters - Washington, D.C.), serves as the national communications center for activities related to response actions. All releases of hazmats equal to or greater than, the reportable quantities must be reported to the NRC,

who then relays the information to the regional OSC or the lead agency (HOCFR 300.36). The NRC also provides the facilities to the NRT for use in coordinating a national response when required.

In addition to their emergency responsibilities, the RRTs must work with the states in which they function to develop federal regional contingency plans for each standard federal region, Alaska, the Caribbean, and Oceania. Plans are to include information on facilities and resources in the region, and the RRTs should coordinate these regional plans with the state plans as well as federal local plans. Local contingency plans are to be developed by the OSCs in consultation with the RRTs for each region. These plans are to provide for:

"a well coordinated response that is integrated and compatible with the pollution response, fire emergency, and disaster plans of local, state, and other nonfederal entities. The plan should identify the probable locations of discharges or releases; the available resources to respond to multimedia incidents; where such resources can be obtained; waste disposal methods and facilities consistent with local and state plans developed under RCRA; and a local structure for responding to discharges and releases."

The local contingency planning effort will depend on the development of local capabilities to respond to discharges and releases. Thus, the development of federal local plans will depend very strongly on the existence or development of local multiagency response teams; and although CERCLA emphasizes that particular attention should be given to this aspect, the statute does not contain specific procedures for supporting and assisting local communities in developing these capabilities.

# 5.6 RESOURCE CONSERVATION AND RECOVERY ACT (RCRA)

The Resource Conservation and Recovery Act (RCRA), passed by Congress in 1976, focused on large-scale generators of hazardous wastes, which include industrial process wastes, chemical intermediates, and products that the manufacturer intends to discard (PL 94-580). The RCRA includes an "acutely hazardous list" and a "toxic list" of generic chemical names. These lists apply oaly to chemicals that are intended to be discarded, thus rendering them hazardous wastes. In addition to the listing of various hazardous chemical wastes, RCRA also specifies characteristics that, when applied to a particular waste, may classify it as a hazardous waste. These characteristics include: ignitability, corrosivity, reactivity, and extraction procedure (EP) toxicity. Thus, several of the characteristics of a hazardous waste under RCRA would also apply to the hazardous materials under consideration in this report. In addition, Sect. 7003 of the RCRA contains a provision known as the "Imminent Hazard Action" that specifies that "enforcement actions may be brought pursuant to Sect. 7003 of RCRA," even though compliance is acceptable under other provisions of the regulation. This section defines an imminent hazard as a situation where past or present management of hazardous waste presents an imminent hazard to human health.

Another section of RCRA that relates to facilities producing hazmats is the preparedness and prevention program required of hazardous waste generators and storers (40 CFR 265, Subpart C). The regulation specifies that accumulation areas for hazardous wastes be maintained and operated so as to minimize the possibility of fire, explosion, or unplanned sudden release of hazardous waste or waste constituents to the air, soil, or surface water. The preparedness provisions specify the appropriate type of emergency equipment, required arrangements with state and local authorities for emergency response coordination, and development of contingency plans and emergency procedures for possible emergencies involving hazardous wastes. Such contingency plans may not be restricted to hazardous wastes but could cover all incidents involving emergencies concerned with hazardous materials. Thus, although RCRA applies to generators and storers of hazardous waste, its provisions may serve as a precedent and be extended to all facilities producing, storing, or transporting hazardous materials. As outlined in Sect. 2.9, the state legislatures of New Jersey and Illinois have already passed similar provisions to improve the safety of manufacture of hazardous chemicals within their state boundaries.

In 1984, Congress passed a series of Amendments to RCRA known as the Hazardous and Solid Waste Disposal Amendments (HSWDA). These amendments were intended to close gaps in the original 1976 Act and its later amendments and regulations. (PL 98-616) Included in the amendments are provisions that: (1) direct EPA to ban, in whole or in part, the land disposal of all RCRA listed hazardous wastes and sets a timetable for EPA to supplement the plan; (2) provides regulations for small quantity generators (generators, transporters, and disposers of between 100 and 1000 K of waste per month); (3) prohibits noncontainerized or bulk liquid hazardous waste disposal in landfills; (4) provides minimum technical requirements for new landfills and surface impoundments; (5) regulates fumes and blenders of fuels derived from hazardous waste or used oil; (6) regulates interim status waste facilities; and (8) authorizes citizen suits where hazardous waste management presents an "imminent hazard." The act also includes periodic inspection requirements, establishes a national water commission, and requires companies seeking hazardous waste facilities.

The provision in the HSWDA relating to underground tanks also covers the storage of hazmat products as well as hazardous wastes. This is included under Subtitle I, which establishes the control of underground tanks containing "regulated substances" (petroleum and CERCLA hazardous chemical products). An underground tank is defined as a tank with more than 10% of its volume underground. The law requires the EPA to issue regulations to protect human health by requiring the following safeguards and documentation be observed with regard to existing tanks:

- 1. leak detection or inventory control systems and tank testing;
- 2. record keeping and reporting of tanks to state agencies;
- 3. corrective action for leaking tanks;
- 4. financial responsibility; and
- 5. tank closures for petroleum and other hazardous substances.

For new tanks the EPA must issue regulations for design, construction, installation, release detection, and corrosion resistance. Thus, RCRA currently includes provisions that will ultimately regulate the storage of hazardous materials in underground tanks, and these provisions will impact the prevention issue in one area of process equipment (underground tanks).

The 1984 amendments also direct the EPA to evaluate additional types of waste, including inorganic chemical wastes, refining wastes, chlorinated aromatics, chlorinated aliphatics, dioxin, and solvents. The EPA also must develop new tests, which probably could be used eventually to determine whether a waste is hazardous.

## 5.7 SUPERFUND AMENDMENTS AND REAUTHORIZATION ACT (SARA) OF 1986

On October 17, 1986, President Reagan signed into law the 5-year reauthorization (PL 97-499) of the Superfund Program. The new SARA bill specifies funding of S9 billion (S8.5 billion for superfund and S500 million for an underground storage tank cleanup program). Support for SARA will come from the following sources:

1. environmental surtax on businesses with annual incomes greater than \$2 million,

2. petroleum tax,

3. chemical feedstocks tax,

4. general revenues,

5. interest on Superfund Trust Fund, and

6. recovery costs from parties responsible for the hazardous wastes stored at waste sites.

#### 5.7.1 SARA Title III

SARA provides revisions to Superfund, which include new cleanup standards that require use of permanent remedies; sets a minimum number of superfund site cleanups over the next 5 years; and specifies liability and penalties for parties responsible for improper hazardous waste disposal. Of particular significance to the control of hazardous chemicals is Title III, which concerns

- 1. emergency planning,
- 2. emergency notification,
- 3. community right-to-know reporting on chemicals, and
- 4. emissions inventories.

These provisions are intended to close some of the gaps in federal responsibilities previously identified in this report. Sect. 5 includes issues that are impacted by Title III provisions.

## 5.7.1.1 Emergency Planning

Each state is required to establish a state commission and emergency planning districts and to implement the formation of local emergency planing committees. The purpose is to prepare state/local responses to hazmat releases and facilitate the participation of local chemical manufacturers in the planning efforts. The EPA will establish threshold limits for their list of "extremely hazardous chemicals" in EPA's CEPP; and if facilities have these substances in excess of the threshold limits, they must report this situation to their state commission. The NRT will provide guidance for the state/local plans, and the RRTs will review them upon request.

## 5.7.1.2 Emergency Notification

This provision requires that owners/operators of hazmat facilities notify the state commissions and local committees of hazmat releases in excess of the reportable quantities (see Sect. 2.6) or threshold releases (to be set by EPA) of any of the chemicals from the CEPP list. Interim threshold release levels are set at 1 lb until EPA sets the release levels.

## 5.7.1.3 Community Right-to-Know Reporting

Owners/operators of facilities are required to provide information on the production, use, and storage of hazmats in their plants. The state commissions, local committees, and local fire departments, as well as the general public, must be informed. The information is to be submitted as Material Safety Data Sheets (MSDS) and as an Emergency and Hazardous Chemical Inventory Form, which will state the amounts and location of MSDS chemicals.

#### 5.7.1.4 Toxic Chemical Releases

The EPA is required to establish an emissions inventory based on toxic chemical release data submitted by hazmat facilities. These data are required if the facilities produce, use, or process hazmats in excess of the threshold limits to be compiled by the EPA.

## 5.7.1.5 Miscellaneous Provisions

Several additional provisions impact on emergency response training and planning. The EPA and other agencies having existing training programs are authorized to place special emphasis on hazardous chemicals response. FEMA will make grants to state and local governments and universities to improve emergency response preparedness. The EPA is also required to review monitoring and detection devices at hazmat facilities and to study the current technical statue of these instruments. Penalties for failure to comply with Title III provisions are also included.

#### 5.7.2 Research, Development, Demonstration, and Training Provisions (RDDT)

Amendments in this section set up a comprehensive federal program to establish a variety of RDD&T programs. They include the following:

- 1. Research and Training. The National Institute of Environmental Health Sciences will support studies and training on human health effects from hazmats.
- 2. Alternative Technology Research and Demonstration Program. The EPA program authorizes alternative treatment technologies (authorization for demonstration programs at waste sites and ten field demonstration projects at CERCLA sites).
- 3. University Hazardous Substances Research Centers. The EPA will establish at least five hazardous substances research centers at universities.
- 4. Other Research Centers. Specific instructions are given for EPA to establish research centers in specified areas.

The magnitude of the implications of this act upon the area studied in this report is very great.

As this report was being prepared, the ramifications of SARA were unfolding, changing the complexion of the entire area.

#### 5.7.3 Worker Protection Standards

SARA Title I, Sect. 126. requires promulgation of standards for the protection of workers engaged in hazardous work operations. The Secretary of Labor must issue proposed regulations on the following:

- 1. site analysis;
- 2. training;
- 3. medical surveillance;
- 4. protective equipment;
- 5. engineering controls;
- 6. maximum exposure limits;
- 7. an informational program for workers;
- 8. handling, transporting, labeling, and disposing of hazardous wastes;
- 9. a new technology program;
- 10. decontamination procedures; and
- 11. emergency response procedures.

Although Sect. 126 applies to workers engaged in hazardous waste operations, Sect. 126 (d)(H) concerned with training of emergency response personnel specifically states that the "training standards shall set forth requirements for the training of workers who are responsible for responding to hazardous emergency situations who may be exposed to toxic substances in carrying out their responsibilities." This provision was the result of a clarification of the original House amendment in order to make the training standards applicable to all employees whose jobs cause them to work directly with hazardous substances.<sup>39</sup> The training requirements specify that workers must have at least 40 h of instruction and a minimum of 3 d of actual field experience under the direct supervision of a trained supervisor.

The Occupational Safety and Health Administration (OSHA) issued a proposal to amend the OSHA standards on Aug. 10, 1987, in compliance with the SARA Section 126 provision.<sup>9</sup> The proposed rule would not only apply to hazardous waste operations but also to employees involved in any emergency responses involving hazardous substances. Thus, the proposed rule will regulate employee safety and health at hazardous waste operations and "emergency response operations for releases or substantial threats of releases of hazardous substances, and past emergency response operations to such releases at all workplaces." This indicates that employers whose employees have a reasonable possibility of engaging in emergency response to a spill at a facility, on a highway, or from a railway tank car, are covered.

The general requirements of the proposed OSHA standards include the provisions listed above specified by SARA, Section 126 with the following additions:

1. illumination,

2. sanitation,

3. site excavation, and

4. contractor and subcontractor provisions.

Final regulations promulgated by the proposed standards are to take effect 1 year after the date they are promulgated.

# 5.8 OCCUPATIONAL SAFETY AND HEALTH ACT

The Occupational Safety and Health Act (OSH ACT) of 1970 was established to ensure that employees working in areas having recognized hazards to their safety and health would be protected from these dangers. The goal of the act is to ensure that "no employee will suffer material impairment of health or functional capacity" from a lifetime of exposure. The act also stipulates that the provisions must be met "to the extent feasible" which was included to replace previous flexible state standards in force prior to the act (PL 91-596). The U.S. Occupational Safety and Health Administration (OSHA), which is a Division of the Department of Labor, has prime responsibility not only for setting health and safety standards but also for enforcing them through federal and state inspectors. In addition, OSHA has responsibility for public education and consultation on health and safety matters in the workplace. The National Institute for Occupational Safety and Health, which is in the Department of Health, and Human Services, was to conduct research on occupational safety and recommend standards to OSHA.

Within the OSHA organization, there are two distinct parts: one devoted to setting safety standards for accidental injury, such as burns, electrical shock, falls, loss of limbs, etc., and the other occupational hazards concerned with chemical hazards. The initial effort involved setting consensus standards for air concentrations of several hundred toxic chemicals in the workplace. Problems inherent in these consensus standards included the lack of requirements for warning labels, monitoring equipment, medical record keeping, and definitions as to the cumulative time of exposure for the workers. These standards were published in 1974 and were to be replaced by permanent standards within a set period of time. However, as of 1984, only ten final health standards were promulgated, which included:<sup>10</sup>

1. asbestos,

2. a list of 14 carcinogenic chemicals,

3. vinyl chloride,

4. lead,

5. ethylene oxide,

6. arsenic,

7. coke oven emissions,

8. cotton dust,

9. acrylonitrile, and

10. 1,2-dibromo-3-chloropropane.

In November 1983, OSHA published a "Hazard Communication Standard," which requires chemical manufacturers to provide information on chemical hazards to their employees. The standard requires manufacturers and importers to develop labels and material safety data sheets (MSDS) to inform their employees about the hazardous chemicals they handle. The standard also requires the facilities to provide training to ensure that their employees handle the chemicals safely. Extension of the Hazard Communication Standard to industries other than the chemical manufacturers and importers is also under consideration.<sup>10</sup>

# 5.9 STATE STATUTES FOR HAZARDOUS MATERIALS

Recently passed state statutes require manufacturers to notify communities of the hazardous chemicals that they process and to develop risk analyses and emergency procedures for their facilities. For example, New Jersey enacted a "Toxic Catastrophe Prevention Act" on January 8, 1986, <sup>11</sup> which contains the following provisions:

- 1. cstablishment of an extraordinary hazardous substance list;
- 2. requirement of risk management programs for manufacturers (including design safety review, standard operating procedures, and preventive maintenance programs, operating-training-accident investigation procedures, risk assessment of equipment, emergency response planning), and the establishment of auditing procedures to ensure execution of the required program;
- 3. registration of manufacturers of extraordinary hazardous substances; and
- reviews of risk management programs developed by the registrants. The state of Illinois enacted a "Chemical Safety Act" in 1985.<sup>12</sup>

Its purpose is:

To establish an orderly system to assure that responsible parties are adequately prepared to respond to the release of chemical substances into the environment and to improve the ability of state and local authorities to respond to such releases.

The act requires the following of each chemical producer:

- 1. identification, storage, and use of chemicals used at each site;
- 2. probable nature of chemical releases;
- 3. notification procedures;
- 4. emergency response plans;
- 5. notification of local agencies of the plans; and
- 6. employee emergency response training programs.

As examples of state community notification regulations, 23 states had community right-to-know statutes in 1985.<sup>12</sup> These laws generally require industry to provide information to state or local authorities and/or the public about hazmats that they use or produce. New Jersey's law, signed in August 1983, requires manufacturers producing any of approximately 1000 chemicals to provide this information to local communities. Louisiana's law was signed in July 1985 with the regulations scheduled to be effective in May 1986, while Michigan's legislation was signed into law in April 1986. A number of similar laws are pending in other states.

# 6 FEDERAL AGENCY RESPONSIBILITIES AND PROGRAMS

Although many federal agencies have various responsibilities for hazmat emergency response, prime responsibilities reside with the following:

- 1. National Response Team;
- 2. Regional Response Teams and On-Scene Coordinators;
- 3. Environmental Protection Agency;
- 4. Federal Emergency Management Agency;
- 5. Department of Transportation Research and Special Programs Administration;
- 6. U.S. Coast Guard; and
- 7. National Oceanic and Atmospheric Administration.

The major federal authorities that establish these responsibilities are reviewed in Sect. 5 of this study. An overview of the responsibilities delegated to each of these agencies follows.

# 6.1 FEDERAL EMERGENCY MANAGEMENT AGENCY

The primary responsibility of FEMA for national security emergency preparedness is defined by Executive Order 11490:

- 1. The Director of FEMA shall serve as an advisor on issues of emergency preparedness, mobilization preparedness, civil defense, continuity of government, material and technological disasters, and other issues as appropriate.
- 2. The Director of FEMA shall assist in the implementation of national security emergency preparedness policy through a coordinating role with other federal departments and agencies and with state and local governments; provide periodic reports to the National Security Council on implementation of national security emergency preparedness policy; and provide staff support as requested by the National Security Council.

The above does not apply to emergencies unless the situation constitutes a national security emergency, which is defined as "any occurrence, including natural, technological, or other emergency which seriously degrades or threatens the national security of the United States." A major technological hazmat release that threatened the health and safety of a large population segment would possibly be classified as a national security emergency. In the NRT Planning Guide,<sup>13</sup> the specific functions and assistance of FEMA during releases of hazardous substances is given as tollows: "FEMA provides assistance in coordinating civil emergency planning. In the event of a major disaster declaration by the President, FEMA coordinates all disaster or emergency actions with the OSC RPM (On-Scene Coordinator and the Remedial Project Manager)."

#### 6.1.1 National Emergency Management System (NEMS)

The National Emergency Management System fulfills one of FEMA's basic responsibilities by facilitating the rapid and orderly flow of emergency-related information between federal, state, and local governments, private industry, and volunteer organizations. Essentially, NEMS acquires, processes, and delivers information to assist in decision making and implementation during pre-, trans-, and post-emergency periods. It is designed to transmit the information base and provide the means of communication for emergency mitigation, preparedness, response, and recovery. The NEMS includes three basic types of components for coordinating emergency operations: physical facilities, telecommunications, and information systems. These are briefly described in Table 6.

The telecommunications system includes a number of systems related to warning systems by voice, radio teletype, teletype, or other means of communication. In addition, FEMA has telecommunication systems in other federal agencies available when needed.

With regard to information systems for hazmat events, FEMA has a Disaster Management Information System which can be used for disaster assistance reporting, planning, and program management and also the National Fire Incident Reporting System. There are also many other available data bases specific to various management information systems owned by FEMA or available from other agencies.

Facility	Location	Purpose
Emergency Information Coordination Center (EICC)	FEMA Headquarters, Washington, DC	Emergency coordination
National Emergency Coordination Center (NECC)	Virginia	Alternate to above
National Warning Center (NWC)	Located with NORAD	
Alternate National Warning Center (ANWC)	Co-located with NECC	Alternate warning center
Regional Emergency Information Coordination Centers (REICC)	FEMA Regional Centers	Regional information centers
Disaster Field Office (or other temporary location)		Operating/recovery set up near emergencies

Table 6. National Emergency Management System physical facilities (14)

# 6.1.2 Integrated Emergency Management Information System (IEMIS)

The Integrated Emergency Management Information System provides a national interagency data base to states and local governments for data sharing, joint planning, exercising, and coordinating response operations. Various data bases, including a standard national map, are combined with several dynamic analysis models. The models can analyze toxic plume movement, based on meteorological conditions, supporting decisions to select sheltering and evacuation options. The hazmat activities of particular interest are listed:

- National Map Data Base A digital cartographic data base designed from sectional maps from the National Atlas of the United States. The program is capable of graphically displaying boundaries, roads, railroads, streams, lakes, populated areas, and topological relationships.
- 2. Exercise, Evaluation and Simulation Facility (EESF) Developed for planning and training related to nuclear accidents but is being adapted for other emergency applications. Models in this program include an evacuation model for predicting the effectiveness of an evacuation as it proceeds, a meteorological model for predicting location and intensity of a radioactive plume released to the atmosphere, and a dose model to predict radiation doses to the population.

At the present time, IEMIS is operational at FEMA Headquarters, the ten FEMA regional centers, and the National Emergency Training Center. Use by states and local communities is planned. The extension of IEMIS to include hazardous materials modeling capabilities would be of value in terms of local community planning, training, and emergency response systems. The discussion in Sect. 10 includes a review of the potential benefits to be derived from a revision of FEMA data bases to include a ranking procedure for a selected list of hazardous chemicals.

#### 6.1.3 National Emergency Training Center (NETC)

FEMA provides training in emergency response procedures at their regional centers and at the National Emergency Training Center (NETC) at Emittsburg, Maryland. The NETC includes the

National Fire Academy (NFA) and the Emergency Management Institute (EMI). The NFA provides courses directed toward personnel engaged in fire prevention and control activities, but the course content is directed toward all types of hazardous materials, including toxic chemicals. A list of the courses associated with hazardous materials is included in FEMA's NETC Course Catalog.<sup>15</sup> These courses are primarily directed toward fire officers who may become involved in a hazardous materials incident, the inspection of a facility storing hazardous materials, the command of an incident involving hazmats, or the planning for incidents involving hazmats. In addition to regular residency courses, the NFA also offers weekend-residence educational activities and field training programs designed to support state and local fire training programs at various locations around the country. The NFA also conducts a "Train-the-Trainer" program, which teaches personnel how to conduct in-house training sessions for fire fighters at their local headquarters or in-state training programs.

The EMI offers a wide range of courses primarily directed toward managers concerned with emergencies involving hazardous materials. Many of the courses are directed toward radiological materials. Included in the EMI program are workshops, teleconferences, seminars, and a self-study program. Most of the training is conducted through state emergency agencies under cooperative agreement. EMI also provides instructional materials and student allocations in selected course offerings to nonprofit schools, agencies, and professional associations.

The training opportunities offered by FEMA through the NETC and FEMA sponsored training by states comprise only a fraction of the training activities sponsored by various governmental, institutional, and private sector organizations. The recent DOT-FEMA survey<sup>15</sup> received responses from 283 training organizations who provide a total of 412 emergency response courses. The federal government provides only 5% of these courses but is high on the list of total student hours because of its longer courses.

Section 305a of SARA Title III authorizes officials of the U.S. Government carrying out existing federal programs for emergency training to specifically provide training for the following:

- 1. hazard mitigation,
- 2. emergency preparedness,
- 3. fire prevention and control,
- 4. disaster response,
- 5. long-term disaster recovery,
- 6. technological and natural hazards, and
- 7. emergency processes.

Special emphasis is to be provided during this training on hazardous chemicals. FEMA is to be appropriated \$5 million per year during 1987-1990 for grants to support state and local governments and to support university-sponsored training programs in the areas of emergency planning, preparedness, mitigation, response, and recovery. Again, special emphasis is to be placed on emergencies associated with hazardous chemicals. FEMA is currently carrying out this mandate. The total current funding for the program through FEMA/State Comprehensive Cooperative Agreements (CCA) is approximately equal to FEMA's annual support for other training programs.

#### 6.1.4 FEMA Emergency Operations PLans (EOP)

Section 44 CFR 302 provides for federal financial contributions to the states and their political subdivisions for the support of up to one-half the state and local civil defense personnel and administrative expenses. This comes under the FEMA Emergency Management Assistance (EMA) Programs.<sup>17</sup> In addition to civil defense use, funds for this program may be used for emergency assistance in response to natural disasters, including man-made catastrophes, providing such aid contributes to and does not detract from FEMA's attack preparedness. Jurisdictions receiving EMA funds are required to prepare emergency operating plans that conform to the requirements for plan content contained in FEMA CPG 1-3, CPG 1-8, and CPG 1-8A. Thus, state and local governments must include items in their emergency planning such as available personnel, equipment, facilities, supplies, and other resources in their jurisdiction and develop the framework for the coordination between individuals and government services in the event of a hazmat release or other disaster. As

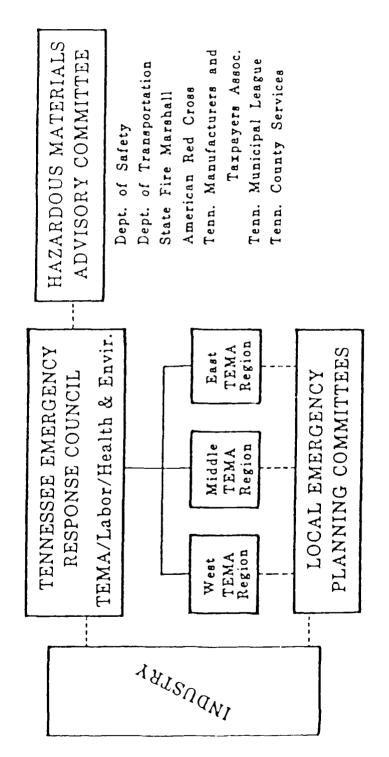
set forth in CPG 1-8,<sup>18</sup> an emergency operations plan includes (EOP) the components indicated in Fig. 3. The EOP also designates the Emergency Program Manager, "who is directly responsible on a day-to-day basis for the jurisdiction's effort to develop a capability for coordinated response to and recovery from the effects of large-scale disasters." However, the FEMA Director in a letter to the states has told them that civil defense funds cannot be used to support the specific hazmai planning requirements for SARA.<sup>18</sup>

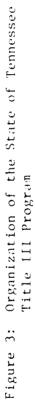
#### 6.2 NATIONAL RESPONSE CENTER (NRC)

Although the National Response Center (NRC) is not a FEMA program, it is part of the National Contingency Plan and serves as the communications center for activities related to response actions. The NRC is located at the USCG Headquarters in Washington, D.C., and its responsibilities include the receipt and relaying of notices of hazmat releases in amounts equal to, or greater than, the reportable quantities to the On-Scene-Coordinators (OSC) or lead agencies for the particular emergency. CERCLA (PL 96-510) specifies that the OSC must then notify the governor of the state affected by the release. The NRC also serves to disseminate OSC and RRT reports, as appropriate, and provides facilities for the NRT to use while coordinating a national response action when required. The NRC records were the most comprehensive and readily available data base used in the recent development of the Acute Hazardous Events Data Base developed by EPA.<sup>1</sup>

#### 6.3 NATIONAL AND REGIONAL RESPONSE TEAMS

The responsibilities and makeup of the National Response Team (NRT) and the Regional Response Teams (RRT) are described in detail in Sect. 6.3 under CERCLA. The NRT serves as the primary vehicle for coordinating federal agency response activities under the National Contingency Plan. The teams, which consist of representatives from 14 federal agencies, including FEMA, serve as the head of the federal emergency response network. In addition, each of the 10





federal regions (plus Alaska, the Caribbean area, and Oceania) has a regional response team which participates in response planning and preparedness prior to a response and coordinates activities when the federal government response program is activated within the region. Each RRT is made up of regional representatives of the NRT agencies, as well as state and local governments.

The primary responsibility for emergency response actions resides with the OSCs. During a response action, the RRT members provide the resources of their agencies to the OSC as specified by federal-regional and federal-local contingency plans. The EPA designates OSCs for inland zones and the USCG designates OSCs for navigable water zones in advance of an incident.

The National Contingency Plan also provides for assistance to state and local governments in planning and preparing for hazmat events. Federal assistance includes guidance, technical assistance, and training. SARA (see Sect. 5.7.1) also requires each state to establish a state commission and emergency planning districts and local emergency planning committees to develop emergency response plans with respect to facilities that produce or store hazmats. Federal support for these activities has not yet been structured. FEMA may provide the support through its various programs set up through the state governments to fund local governments for planning and training activities.

The state commissions required by SARA are appointed by the governor of each state and have the following responsibilities:

1. designation of emergency planning districts;

2. appointment of local emergency planning committees for each district;

3. supervision and coordination of activities of the planning committees;

4. review of emergency plans and chemical release notifications; and

5. establishment of procedures for receiving and processing requests from the public for information concerning emergency plans, data, and hazmats.

Representatives on the local emergency planning committees must include a representative from:

- 1. elected state and local officials;
- 2. law enforcement, health department, first aid, fire protection, transportation, civil defense personnel;
- 3. media members;
- 4. community group members; and
- 5. owners/operators of facilities manufacturing, processing, and storing hazmats that are under the SARA rules.

Facilities that come under SARA are also subject to emergency planning and notification requirements if the substances they handle appear on EPA's list of extremely hazardous substances and are presently in excess of the EPA threshold quantities for that substance.

The NRT's responsibility with respect to this local planning structure includes publishing guidance for the preparation and implementation of emergency plans. Its Hazardous Materials Emergency Planning Guide<sup>13</sup> was prepared in response to this requirement. The NRT Preparedness Committee also developed a set of criteria to be used by the RRTs to assess state and local emergency response preparedness programs. These criteria include the following six categories:<sup>16</sup>

- 1. hazards analysis for the area;
- 2. authority vested in emergency organizations for emergency response;
- 3. organizational structure;
- 4. communications;
- 5. resources personnel, equipment facilities, etc.; and
- 6. emergency plans.

Although few state or local governments will have a need and capability for all of these criteria, the assessment by the RRT should help identify those resources needed by the governmental units and encourage their acquisition. Thus, SARA has provided authorization for direct federal assistance in the development and review of state and local emergency planning through the NRT and RRTs.

However, current support in this area by the federal government is very limited.

Additional NRT, RRT, and OSC technical assistance to state and local response planning includes:

- 1. designation of priority areas within each region with a high potential for hazmat incidents;
- 2. dissemination of information concerning hazmat R&D, transportation, risk assessments, lessons learned, response data, etc.; and
- coordination of government.private industry interfaces for all aspects of hazmat emergency response.

The NRT and the RRT agencies will also be involved in the hazmat training programs with respect to improving coordination of federal, state, local, and private training and to developing a national interagency training strategy and regional training plans.<sup>11</sup>

#### 6.4 ENVIRONMENTAL RESPONSE TEAM (ERT) AND NATIONAL STRIKE FORCE

A group of highly specialized experts trained for hazmat emergencies is available through the EPA. Since its establishment in 1978, the ERT has participated in more than 500 hazmat incidents. Team members are trained in all aspects of hazmat emergencies, including:

1. treatment and monitoring of hazmats;

- 2. control, disposal, and contingency planning during hazmat emergencies:
- 3. instrumentation, sampling, and analysis activities; and
- 4. occupational health and safety.

The National Strike Force is the USCG's counterpart to the FRTs. Their expertise can be called on for shipboard and coastal hazmat emergencies, including the use of containment and removal equipment for responding to pollution incidents.

#### 6.5 ENVIRONMENTAL PROTECTION AGENCY

The EPA has developed and implemented a program designed to respond to cill and hazardous substance incidents, this program meets the goals of CERCEA and the Clean Water Act. When

a federal hazardous substance response is necessary, EPA takes steps to see that:

1. public health and environment are protected;

2. response personnel are prepared and supplied with proper equipment:

3. federal, state, and local resources are available and that their efforts are coordinated; and

4. response actions are timely and effective.

These steps include the sampling and monitoring of an actual or potential release, technical advice and assistance, and provision of mitigation and cleanup of released materials. EPA's roles at the NRT, RRT, and OSC levels during incident response have been described previously.

The EPA also provides site-specific technical advice and assistance through its Environmental Response Team (ERT). The ERT includes expertise in biology, chemistry, hydrology, geology, and engineering.

The EPA manages the trust fund (Superfund) established under CERCLA to cover the cost of hazardous substances response operations and is also responsible for enforcement actions against responsible parties. Under the new SARA provisions (see Sect. 5.7), EPA is to establish threshold limits for their list of "extremely hazardous chemicals" in the EPA's Chemical Emergency Preparedness Program (CEPP). If owners, operators of facilities have these materials in excess of the threshold limits, they are required to notify the state commission who will inform EPA. Thus, EPA is to be responsible for the data collection on fixed facility harmat operations in the United States. Under the Toxic Chemical Release Provision of SARA, EPA is required to establish an annual emissions inventory of hazardous chemicals released in excess of the threshold limits. The EPA is also authorized to carry out existing programs for emergency training with special emphasis on hazardous chemicals and to conduct a review of monitoring and detection device technology.

With respect to planning and prevention activities, the EPA initiated its CEPP in December 1985.<sup>5</sup> The CEPP addresses the sudden, accidental releases of acutely toxic chemicals into the atmosphere and the need to improve emergency preparedness and response capabilities at all levels of government to handle such an emergency. The CEPP is a voluntary, nonregulatory program

whose primary focus is on emergency planning and response capability at the local level. It consists of three basic components:

- 1. a list of acutely toxic chemicals, which EPA developed to provide a tocus for increasing community awareness and developing or improving contingency planning efforts, and is accompanied by individual chemical profiles containing information on each chemical;
- 2. guidance material to assist state and local communities in developing and exercising contingency plans; and
- 3. training and technical assistance to state officials and, through states, to local officials to help them identify potential chemical hazards and develop adequate contingency plans

Elements of the CEPP have been incorporated into the newly reauthorized amendments to CERCLA (SARA).

The EPA has preparedness coordinators in each of its ten federal regional offices who are responsible for focusing on preparedness efforts. These efforts include working with state and local officials to identify priority areas and conducting other preparedness activities such as contingency plan development and review, training, and simulations.

Along with five other federal agencies (FEMA, RSPA, USCG, HHS ATSDR, and DOL/OSHA) EPA participated in the development of the <u>Hazardous Materials Emergency Planning Guide</u>, originally known as FEM. v-10. In September 1986, the NRT endorsed the guide. It was officially reissued in April 1987 as an NRT Guide.<sup>13</sup>

The EPA also participates in preparedness initiatives with both private and public sector groups and such as the Chemical Manufacturers Association, the American Red Cross, and the National Governors Association. Overall, EPA has a predominant role in this area, one which continues to grow.

# 6.6 DEPARTMENT OF TRANSPORTATION RESEARCH AND SPECIAL PROGRAMS ADMINISTRATION

The DOT Research and Special Programs Administration (RSPA) has authority to issue regulations on many aspects of hazardous materials containers, except for bulk marine shipments, which are regulated by the U.S. Coast Guard. RSPA shares inspection and enforcement activities with the modal administrations, the Federal Highway Administration, the Federal Railroad Administration (FRA), the Federal Aviation Administration, the National Highway Traffic Safety Administration, and the Coast Guard, which also have authority over the vehicles or vessels themselves.<sup>23</sup> RSPA is responsible for the identification of hazardous materials as well as:

1. regulation of hazardous materials containers, handling, and shipments:

2. development of container standards and testing procedures;

3. inspection and enforcement for multimodal shippers and container manufacturers; and

4. data collection (Hazardous Materials Information System).

The (RSPA) develops, publishes, and distributes the <u>Emergency Response Guidebook</u> (ERG), a widely used publication in the emergency response community.<sup>26</sup> The guidebook is designed for use by firemen, police, and other emergency services personnel and provides initial emergency response guidance for virtually all hazardous materials transported in the United States. It enables persons who are unfamiliar with chemical names to identify hazardous materials by their four-digit identification number and determine safety measures to be taken. The distribution plan for the guidebook is to have one in each emergency response vehicle. However, distribution is also made to individual responders and training organizations upon request. The transportation industry is required by RSPA regulations to report incidents and or accidents that fall under specified criteria to the NRC. RSPA funds that portion of the operational cost of the NRC attributable to the administration mission, as well as the cost to the NRC for loading data into the RSPA data system. The interface between RSPA and state and local governments is achieved through this data system since states may retrieve data from the system, including the data entered by the NRC.

RSPA prepares and distributes emergency planning guidance primarily through two publications: <u>Community Teamwork<sup>21</sup></u> and <u>Lessons Learned</u>.<sup>22</sup> <u>Community Teamwork</u> provides ideas on how to develop a hazardous materials transportation safety program at the most economical cost by involving the different state and local agencies. It provides guidance on:

- 1. maximizing the use of available federal, state, and local resources, and increasing interagency cooperation;
- 2. consolidating hazardous materials transportation activities with other state and local programs;
- 3. expanding the use of mutual aid agreements;
- 4. maximizing the use of part-time and volunteer staff; and
- encouraging greater local industry involvement in hazardous materials incident prevention and emergency response activities.

Local industry is a valuable source of technological expertise, emergency response equipment, and containment materials.

Lessons Learned provides information on:

- 1. getting started in HAZMAT safety management;
- 2. surveying HAZMAT transportation and conducting a hazard analysis;
- 3. assessing incident prevention and response capabilities;
- 4. developing HAZMAT contingency plans; and
- 5. implementing and updating HAZMAT safety programs.

RSPA provides guidance to cities, counties, and regions for response and incident prevention planning involving hazardous materials, particularly transportation incidents.

6.7 U.S. COAST GUARD (USCG)

There is close connection between the USCG, the OSCs, and state and local agencies in incident response activities. OSCs develop Federal Local Contingency Plans (LCPs), which provide

for responses that are coordinated with state and local environmental, fire, emergency, and disaster agencies.

The USCG provides the National Strike Force (NSF) (see Sect. 6.4) and the Public Information Assist Team (PIAT). The NSF consists of three strike teams, which respond to both coastal and inland spills at the request of an OSC. The teams can provide technical assistance and advice, as well as specialized response equipment if adequate resources are not otherwise available. The PIAT consists of public affairs specialists who are available to assist OSCs and regional or district offices to meet the heavy demands for public information and participation which often accompany major incidents.

The National Response Center (see Sect. 6.2) established in 1974, is administered and staffed by the USCG. The FWPCA Spill Reporting Regulations and the NCP designate the NRC as the primary location for reporting pollution incidents. The NRC receives toll-free telephone reports trom every state, Puerto Rico, Guam, and the U.S. Virgin Islands and then relays the reports to the appropriate USCG or EPA OSC and other federal agencies by agreement. In addition to relaying notifications of pollution incidents, the NRC also provides limited advice (e.g., product information) and backup communications support to all response personnel through the OSC. Responders can also access four computer modeling data bases through the NRC. These data bases can be used to identify such things as the potential hazard zones resulting from a chemical spill. Additionally, the NRC is data-linked to CHEMTREC, a service of the Chemical Manufacturers Association, which is a centralized chemical emergency response information source (see Sect. 9.2).

The USCG also promulgates the Chemical Hazards Response Information System (CHRIS) manuals. Although the CHRIS Manuals were developed for use by USCG personnel, they are also used extensively by state and local responders and are available for public sale through the U.S. Government Printing Office.

The USCG is involved in a number of planning efforts to enhance federal, state, and local preparedness to respond to oil and hazardous substance incidents, including participation on the

National Response Team (see Sect. 6.3). The USCG's responsibilities in the federal response mechanism include development and or review of federal contingency plans at the national, regional, and local levels. Along with other members of the NRT, the USCG recommends and considers possible revisions to the NCP. Each RRT, for which the USCG provides the Co-chair, is responsible for maintaining a Federal Regional Contingency Plan (RCP). An RCP contains information on services and resources that are typically required by an OSC but are not necessarily available at the local level. The RRT is also charged with evaluating the effectiveness of the RCP and Federal Local Contingency Plans (LCPs) for pollution incidents. As discussed in the previous section on incident response, USCG OSCs develop LCPs within their zones of responsibility. An LCP is normally an action plan which addresses such matters as the most probable location for pollution incidents, the availability of local response equipment and personnel, and sensitive resources requiring protection.

# 6.8 DEPARTMENT OF LABOR OCCUPATIONAL HEALTH AND SAFETY ADMINISTRATION (OSHA)

The proposed OSHA employee protection standards (see Sect. 5.7.3) will, when finalized, cover an estimated 1.2 million workers who manage and clean up hazardous wastes and conduct emergency responses to hazardous substances. OSHA was required to promulgate a rule for these standards under Sect. 126 of SARA. The proposed rule includes provisions for the protection of workers engaged in hazardous operations, including provisions for safety and health programs, site control, training, medical surveillance, personal protective equipment, engineering control, information programs, decontamination procedures, and emergency response plans. When finalized, these standards will cover workers performing clean-up operations at hazardous waste sites, workers at RCRA-regulated treatment, storage, and disposal facilities, and members of private hazardous materials response teams. SARA, Sect. 126(f) also requires that EPA adopt standards identical to the OSHA standards to protect state and municipal employees (such as firetighters, police, and emergency medical teams) involved in hazardous substance operations in states that do not have

OSHA-approved job health and safety programs. States that do have these OSHA-approved programs must adopt standards comparable to the OSHA standards.

In January 1986, OSHA set up a pilot inspection program, the Chemical Special Emphasis Program (Chem SEP), which is focused on plants producing highly toxic chemicals.<sup>21</sup> The OSHA inspectors conduct more thorough inspections than the typical OSHA chemical plant inspection. However, since this is only a pilot project, only about 80 inspections were planned (1986), which is a small fraction of the total United States chemical plants (estimated at approximately 10,000). The actual plants inspected at the program completion numbered 40 since the OSHA inspection, resources were severely strained by the effort (each spent an average of 383 h per inspection).

Results of the inspections indicated that many of the problems in the plants discovered by the teams were not regulated by specific rules and had to be cited under the OSHA Act General Duty Clause. The number of general violations has resulted in an appraisal for additional regulations by OSHA. For example, a standard will be considered which will require facilities to monitor for releases of certain chemicals such as chlorine, carbon monoxide, and phosgene.

OSHA regards the Chem SEP project as successful from a policy standpoint, and they plan to take the following lines of action as a result:

- to develop a more system-wide approach to the short-term needs of the agency and the industry for preventing catastrophic hazmat releases; and
- 2. to develop over the long term, a set of regulations that "consider the dynamics of the chemical industry." OSHA believes that the availability of information on hazmats, employee training, and community awareness will be more effective than occasional OSHA inspections.

# 6.9 NATIONAL OCEANIC AND ATMOSPHERIC ADMINISTRATION (NOAA) HAZARDOUS MATERIALS RESPONSE BRANCH

NOAA is charged in the National Contingency Plan (see Sect. 5) with providing assistance to the U.S. Coast Guard (USCG) on-scene coordination (OSCs) during oil and hazardous material incidents.<sup>36</sup> This function is performed by a scientific support coordinator (SSC) who serves as a

member of the OSC's staff when requested during a response. The SSCs are available to act as the principal liaison between the OSC and the scientific community by coordinating responses to OSC requests for assistance from scientists. Most incidents handled by the USCG concern vessel collisions and port transfer accidents. However, the SSCs occasionally become involved as well in oil-well blowouts, railroad and industrial facility accidents, and problems at waste sites.

The NOAA Hazardous Materials Response Branch meets this responsibility with a team organized to meet OSC needs and questions 24 h per day. Regional SSCs based throughout the United States are supported by team specialists in computer communications, environmental resources - at risky physical process monitoring, chemical data interpretation, personal safety, and human health. Problems involving dangerous chemical substances require extensive use of all these specialties.

In order to provide rapid, yet complete, information on chemicals involved in spills, NOAA has developed a Chemical Advisory Report (CHEMREP) System. These standardized one-page reports are designed to provide the SSC and the OSC with a summary of relevant interpretations and conclusions from chemical data, as well as listings of selected data.

The system uses computer storage and electronic mailing technology to allow transmission of existing CHEMREP to the scene within minutes after notification. When a chemical release not included in the CHEMREP files occurs, a new report is compiled for transmission within 1 or 2 h.

The CHEMREP system has been used in many types of chemical accidents. A CHEMREP can either supplement other existing sources of information, such as CHEMTREC (see Sect. 9.2), or in some cases replace them. Some types of information are intentionally not included in a CHEMREP. Manufacturer contacts and details concerning a product's transportation history are available from CHEMTREC, so they are not included. Also, the detailed techniques for response mitigation are also omitted since they may be specific to each particular situation and rely on details available only to the on-scene responders. The system became operational in October 198<sup>3</sup> and since that time, the original file of 60 reports has been expanded at a rate of about 2 per week.

#### 7 STATE OF TENNESSEE

Most states currently have state emergency response organizations and are required to establish state emergency commissions under SARA Title III. Since the organizational picture at the state and local levels is in considerable flux, an overall assessment is not possible at present. However, to provide insight into one of the more aggressive and comprehensive state programs, we have selected the Tennessee Emergency Management Agency for detailed assessment.

The State of Tennessee instituted its Tennessee Emergency Management Agency (TEMA) in 1978 just after the railroad disaster at Waverly, Tennessee. This incident occurred on February 24, 1978, when a single jumbo railroad tank car carrying 27,871 gal of liquified propane gas ruptured, causing a boiling liquid expanding vapor explosion (BLEVE) in downtown Waverly. Although derailment of the car had occurred 40 h prior to the explosion, an almost completely ineffective evacuation was in force when the explosion took place. An initial evacuation of the area within 440 yd of the car had been ordered; but by the time the explosion occurred, only an area of three city blocks was barricaded. However, some businesses were allowed to operate in that area. For example, a tank truck unloaded 9000 gal of gasoline to an oil storage depot less than one block from the car shortly before the explosion. Consequently, the explosion killed 16 people and seriously injured more than 50 and has resulted in personal injury suits seeking in excess of \$362 million in compensatory and punitive damages.

At present, TEMA is considered one of the foremost state emergency operations in the country. One incentive for this is that Tennessee is located in the federal region (Region 4) experiencing the next-to-highest number of hazardous materials incidents during 1983-1984. (Region 5, midwest, had the greatest number of incidents.) Tennessee, which is a major producer of hazardous chemicals, is crossed by numerous interstate highways and rail lines used by the raw materials and bulk chemicals producers of the southern and southwestern. United States and by the chemical manufacturers and processors of the northeast. It is also an area of considerable growth. There is little doubt that Tennessee will continue to experience more than its share of potential for

hazardous materials emergencies. The following description of the TEMA organization and its activities was provided by TEMA.<sup>2128</sup>

TEMA has been given responsibility for hazardous materials emergency planning, training, response, coordination, and recovery at the state level. The aim of the program is to increase readiness op all levels of state and local government to a point where, in the event of a hazardous materials emergency, there will be no avoidable loss of life or injury and minimum property loss. To accomplish this aim, TEMA has established an extensive training program and has put into operation an emergency response plan which involves TEMA personnel, other state agencies, and local response teams.

The State Emergency Operations Center (SEOC) is maintained by TEMA and is manned 24 h per day. Through the state-wide communications net, the SEOC may be contacted by radio or iclephone from any point in the state. The SEOC duty officer is trained in the basics of hazardous materials chemistry and has access to an extensive reference library of hazardous materials information. There is a Ph.D. chemist on the TEMA staff who is on 24-h call for consultation. In addition, haison is maintained with physicians, toxicologists, other chemists, and state, federal, and industry experts for emergency consultation. The duty officer is also trained to locate chemical manufacturers and other parties directly concerned with the involved materials. Through these channels, the most complete information may be provided to the scene.

In many cases, local responders require more direct assistance. In these events, a TEMA Field Services Coordinator is dispatched to the scene. Field Services Coordinators are stationed throughout the state at locations that allow arrival at any scene within 1 h after notification. These Coordinators are certified hazardous materials technicians with more than 200 h of specialized training. They are equipped with personal protective gear and have access to hazardous materials vans which carry special equipment worth more than \$70,000. Once on the scene, the coordinator provides support and assistance, or at the request of the local commander, he will assume command and serve as the on-scene coordinator.

To implement the SARA Title III State and local government provisions, (see Sect. 7.1), Governor McWherter issued Executive Order No. 7 on April 1, 1987, which established the Tennessee Emergency Response Council (TCRC). TCRC is comprised of the Director of TEMA, who serves as chairman, and the commissioners of the Tennessee Department of Labor and the Department of Health and Environment. The organization of TERC is illustrated in Fig. 3.

The Hazardous Materials Advisory Committee is responsible for providing advice and guidance in the following functional areas: emergency planning and notification, community right-to-know, and toxic chemical release reporting. The Committee members will be provided a Title III progress report twice annually.

The Tennessee Emergency Management Agency is responsible under Title III Section 302(C) for receiving and processing the notification letters from the owners and operators of facilities that have extremely hazardous substances on their premises. A list of Section 302 facilities - by county - has been furnished to each local emergency planning committee. TEMA regional directors will be provided with a list of facilities in their respective regions to assist in the formation of local committees. As indicated in Fig. 3, TEMA's three regional offices will be responsible for the implementation of the Title III program at the local level.

In Tennessee, emergency planning districts are comprised of county boundaries, pending final examination of the number and distribution of facilities in the state. Each planning district (county) must be served by a local emergency planning committee. In the future, it may prove efficient to designate multicounty planning districts if there are relatively few facilities over a multicounty area. Planning boundaries are flexible and can change to accommodate unique characteristics and requirements. TERC is responsible for appointing members of a Local Emergency Planning Committee (LEPC) for each district. Title III, Sect. 302(C) of the law identifies the groups and organizations that should be represented on the local committee.

TERC is responsible for the coordination and supervision of emergency planning efforts at the local level, which will culminate in the completion, testing, evaluation and approval of local

emergency response plans by October 17, 1988. The LEPCs will prepare a local emergency response plan that incorporates, at a minimum, the nine planning elements that are set forth in Title III, Section 303(C). A Guidance Document for Title III, prepared by TEMA, is the reference document for local government and industry in the preparation of local plans.<sup>38</sup> The Guidance Document for Title III provides a six step process for preparing the local plan.

TEMA is responsible for managing state and local emergency preparedness, response, and recovery functions, as outlined in the Tennessee Emergency Management Plan (TEMP). The TEMP and local Emergency Operations Plans (EOPs) are the officially adopted documents that authorize and direct emergency operations in Tennessee.

The primary point of contact with LEPCs will be TEMA's three regional offices. Assistance is to be provide in the following areas: (1) planning; (2) training; (3) exercising; and (4) development of emergency notification procedures as required under Title III, Section 304. The LEPCs will submit their local emergency response plan to the TEMA Regional Director in their region for review, and the Tennessee Emergency Response Council will formally approve the local emergency response plans.

Implementation of the training provisions of Title III will involve input from a broad range of groups and disciplines, including state and local elected officials, emergency response personnel, media, environmental groups and business and industry. The Title III training program is designed to meet the needs of these groups.

Title III training is organized into four categories to reflect the requirements of various organizations:

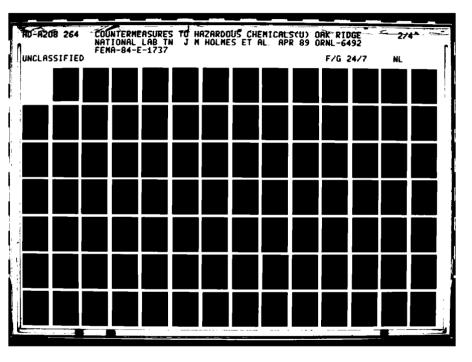
- Hazardous Materials Contingency Planning Course (32 hours) This course is targeted toward LEPC members and is designed to provide all the necessary tools for developing and testing local emergency response plans.
- 2. Title III Workshops A series of workshops (3 h) will be held in the three regions and will focus on the administrative and organizational aspects of Title III.

- Public Officials Conference (4 h) A series of Public Officials Conferences will be held across the state to examine the progress and opportunities associated with Title III.
- 4. Hazardous Materials Technical Training TEMA is currently undertaking a comprehensive reexamination of the state's hazardous materials preparedness and response for fixed facilities as well as transportation-related incidents. It is anticipated that a technically oriented, hazardous materials training program will be developed in the tall of 1988. The courses will incorporate existing training materials into a revised program that tocuses on the on-scene management of hazardous materials accidents.

Tennessee's 95 emergency planning districts have been placed into three categories of criticality: high medium, and low. The ranking of Tennessee's planning districts will allow a prioritization for training and education. Three considerations were used in determining a county's ranking: (1), the number of facilities responding to Title III reporting requirement, (2), the level of training in hazardous materials as determined by a study conducted by TEMA's regional offices, and (3), the number of reported incidents at fixed hazardous materials facilities.

Under Title III, Section 304, facilities must immediately notify the Community Emergency Coordinator of the LEPU and the State Commission if there is a release of a listed hazardous substance that exceeds the reportable quantity for the substance. In the event of a release of a reportable quantity of a hazardous substance, a facility owner must notify the Community Emergency scordinator for the LEPC in the county, as well as the Tennessee Emergency Management Agency. TEMA will maintain a file on emergency notifications from facility owners and operators, including the written follow up notice which is required.

The Title III Community Right-to-Know Provision (Section 311) requires that facilities within standard industrial Classification (StC) codes 20-39, which must prepare or have available Material Safety Data Sheets (MSDS) under the Occupational Safety and Health Administration (OSHA) regulations, to submit either copies of its MSDS or a list of MSDS chemicals to: (1) the State Commission, (2) the local committee, and (3) the local fire department. When Title III was



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1.1		2.0
		1.8
1.25	1.4	1.6

enacted, the OSHA HC Standard applied only to manufacturers and importers of hazardous chemicals within SIC codes 20-39. On August 24, 1987, OSHA, acting under court order, issued a final ruling extending the HC standard to all employers, thereby making nonmanufacturers subject to these requirements.

TEMA is responsible for the following aspects of Section 311: (1) receiving, processing, and storing Section 311; (2) distributing the Section 311 reports to local emergency planning committees and fire department; (3) answering inquiries from facility owners and the public on MSDSs and other aspects of Sect. 31, and (4) updating information on the Section 311 reports, as provided by facility owners and operators.

The Tennessee Department of Labor is responsible for the following: (1) Furnishing TEMA with a list of facility owners (SIC codes 20-39) and (2) answering inquiries from facility owners that are technical in nature, particularly questions related to specific chemicals.

In summary, response to the SARA Title III by the State of Tennessee has been established through the policies and procedures as outlined in TEMA's Policies and Procedures Guide.<sup>38</sup> The six functional areas of Title III comprise the Tennessee program include:

1. Program Management,

2. Emergency Planning,

3. Training,

4. Emergency Notification,

5. Community Right-to-Know, and

6. Toxic Chemical Release Reporting.

The responsibilities of TEMA, TERC, the LERCs, and facility owners and operators fall under the above six areas.

# 8 LOCAL/REGIONAL RESPONSIBILITIES - MEMPHIS/SHELBY COUNTY, TENNESSEE

The Memphis Shelby County area is the sixth largest distribution center in the United States; it is a major transportation hub. There are two major interstate highways and a number of U.S. highways that intersect at Memphis. Six major railroads maintain large switching and repair facilities in Memphis. The Mississippi River is utilized for 13,000,000 tons of cargo per year at the Port of Memphis and 122,000,000 tons of flow-by traffic. Because of the transportation facilities and geographic location, Memphis is a center for the manufacture and distribution of hazardous materials products. Sixty-eight major motor carriers have terminals in Memphis.<sup>29</sup>

The following description of the Memphis Shelby County programs was extracted from DOT's Lessons Learned.<sup>22</sup>

The major Memphis hazmat concern began in 1976 and 1977 with increasing transportation accidents involving hazmats. Some City Division of Fire Services personnel were trained on handling hazmat transportation incidents before the demonstration project was initiated, and two hazmat React Teams were organized and trained in 1978. A train derailment in Wynne, Arkansas, with toxic and flammable liquids proved to be a valuable learning experience. As a result of the Wynne incident, it was decided that the React Teams needed better training. Chief officers in the Division of Fire Services also needed to be trained, and a highly specialized group was needed within the division to serve as staff and resource officers at hazmat incidents. A liquefied petroleum gas explosion in Waverly, Tennessee, reaffirmed the conclusions reached after the Wynne incident.

As the numbers of incidents increased and a significant incident occurred within the city in 1979, local concern led to the formation of a volunteer task force. This group was charged to define hazardous materials problems that can affect the citizens of the Memphis/Shelby County area and to suggest strategies to further define, evaluate, and/or solve problems.

Task force findings showed that there are large amounts of hazardous materials in storage and transported through the area. While the air and river traffic seemed to be free of significant

incidents, problems were detected with materials transported by rail and highway. Recommendations of the task force led to a DOT-sponsored demonstration project, which included three broad phases:

- 1. Phase 1 was designed to determine the area's existing capability to prevent and respond to hazardous materials incidents.
- 2. Phase 2 included plans and strategies to prevent or respond to hazardous materials incidents.
- 3. Phase 3 encompassed the development and implementation of a hazardous materials management program.

Conceptually, this project relied on a basic research design of pretest, treatment, post test with a primary emphasis on emergency response capabilities. The operating mechanism for activities under this project was a local advisory council staffed by volunteers from industry, government, educational institutions, emergency response agencies, and a private consulting firm under subcontract to the Memphis Fire Services Division. The advisory council was called the Memphis Shelby County Hazardous Materials Advisory Council (HMAC). The HMAC was a reorganized and reactivated version of the original task force established prior to the demonstration project. The HMAC Chairman is a member of the Memphis City Council, and the Vice-Chairman is a member of the Shelby County Commission. Agencies represented include the Division of Fire Services, police department, County Civil Defense, the Memphis State Law School, University of Tennessee, local industry, and federal agencies. Six operation committees were organized under the HMAC for a total membership of 140 persons.

The HMAC plan identified actors and their roles in a hazmat emergency. Specific areas of responsibility were designated. The Division of Fire Services was given the lead responsibility in hazmat responses within the county; roles for the police department and the emergency medical services were also defined. The project also identified a model mutual-aid agreement that could be useful in other geographic areas. The pretest and post test activities were conducted in the form of county-wide drills involving a simulated derailment of tank cars of hazardous materials and

coordinated responses by the various emergency response organizations within the Memphis/Shelby County area.

The first county-wide drill involved over 400 people, 17 agencies, and 10 hospitals. It focused on three basic areas:

1. coordination of responses to the accident,

2. rescue and handling of victims, and

3. diagnosis and treatment of victims with acute chemical exposures.

Communications failures plagued all aspects of the drill and contributed to other failures to act. The drill pointed out the need for better communications capability, planning, training, cooperation, and coordination in hazardous materials emergency response activities.

Phase 3 of the Memphis HMAC Project focused on four major areas:

- 1. <u>Hazmat information system</u> Memphis established a hazardous materials information system which would serve as a reference for response staff in a hazmat incident. The information system contains information on the type of chemicals handled at stores and generator facilities and identifies the characteristics and properties of chemicals. The information system also identifies local, state, and federal resources for hazmat incidents.
- 2. <u>Training</u> Memphis conducted training sessions for the React Teams for 3.5 d. A general hazmat training program for 1450 emergency response personnel was conducted. Response personnel included: fire fighters, who used a 12-module self-study text; law enforcement personnel, who were trained by an instructor; and emergency medical services personnel, who were trained by a toxicologist.
- 3. <u>Public awareness</u> Memphis developed and implemented a public awareness campaign in this phase. Information on hazardous materials in the Memphis/Shelby County areas was presented to the media in a press conference and through participation in the second simulation drill, and to public groups through speeches by HMAC members.

4. <u>Second simulation</u> - A second simulation drill was conducted using a train derailment with hazardous chemicals. The simulation pointed out the need for a better communication system to transmit data on hazmat incidents to area agencies. It was also found that public awareness and the involvement of media in simulation are important aspects of a local hazmat transportation program.

Formation of the Memphis/Shelby County HMAC has coordinated organizational emergency response activities at the federal, state, and local levels, along with local industries such as DuPont, W. R. Grace, and others. Results of this program have produced significant improvements in public awareness, development of emergency response capabilities (REACT Teams), acquisition of emergency response equipment, development of mutual aid agreements, coordination of emergency responses, rescue and handling procedures, and treatment of exposed people during simulated emergency drills. Results and recommendations of the project can be summarized as follows:

- 1. The information system and data base inventory were crucial to planning a realistic mobilization plan.
- 2. As a result of the project recommendations, Tennessee has enacted a limited "good Samaritan" law that applies to incidents involving compressed gases.
- 3. The project determined that a planning structure that incorporates representatives of government agencies and private firms is very important (the advisory committee with an extensive committee system worked very well for Memphis).
- 4. The project team used the demonstration program to plan and conduct extensive training of emergency personnel React Teams, and the private sector (the city developed useful training materials for each major segment of the response team).
- 5. The two simulations were major achievements. Simulations are very useful to test planning, coordination, and responses to hazmat incidents. Memphis also designed an extensive evaluation system to judge the effectiveness of simulations.

- 6. The project team found it useful to cite the experiences and benefits of mutual-aid agreements in other areas when the city was trying to convince local governments and agencies to execute such agreements.
- 7. The second simulation drill showed very significant progress when compared with the first. Significant advances were noted in the areas of appropriate on-scene command and tactics, emergency medical operations, personnel protection, communications, and transport. Certainly the emphasis on training was one factor that contributed to this improvement.

In summary, the Memphis HMAC project is considered successful in that it has demonstrated positive improvements and the need for continuing efforts to maintain an effective response posture. The concepts used in this project are considered adaptable to other geographic regions. Of the materials developed in this project, some are readily transferable to other areas while some may need modification to suit another region's needs. The primary success factors in this project are, without question, adaptable to all geographic regions: planning, training, cooperation, and coordination.

The Memphis/Shelby County HMAC plan was finalized in December 1985 and the organization was involved in a number of activities in 1986, including several emergency simulations, a household hazardous materials collection program, and an extensive public relations program.

# 9 INDUSTRIAL AND PRIVATE INITIATIVES

An impressive effort with respect to emergency response planning, training, and coordination has been implemented by industry and private organizations including, but not limited to, the following:<sup>15,17</sup>

- 1. Chemical Manufacturers Association (CMA),
- 2. American Institute of Chemical Engineers (AIChE),
- Hazardous Materials Advisory Council (HMAC), (not the same as the Memphis/Shelby County HMAC),
- 4. American Petroleum Institute (API),
- 5. The Chlorine Institute,
- 6. American Association of Railroads (AAR), and
- 7. National Agricultural Chemicals Association (NACA).

# 9.1 CMA COMMUNITY AWARENESS AND EMERGENCY RESPONSE PROGRAM (CAER)

The Community Awareness and Emergency Response (CAER' Program of the CMA provides extensive technical assistance for local community and chemical plant emergency planning. The program is based on the CAER Program Handbook, which provides chemical plant managers with guidance on achieving community awareness; necessary elements of emergency response plans, including checklists of items to cover; and an evaluation matrix for identifying strengths and weaknesses of state, local, and other industry plans with which the plant's plan must be coordinated.<sup>30</sup> Key components of the handbook are these CMA position statements:

- CMA member companies have a responsibility to provide information on hazardous chemicals to the public. This information should be tailored to the needs of specific groups (e.g., emergency responders, physicians, general public).
- 2. Trade secrets must be protected while, at the same time, providing necessary hazard and health care information to the public.

 Industry, state, and local government leaders must work together in developing community right-to-know programs.

Other results of the program are distributions of letters and brochures describing plant operations to community residents, safety and environmental protection programs, community chemical information seminars, and one major corporation's mailing of CMA Handbooks to its 400 authorized distributors, along with a request that these distributors join the CAER program.

# 9.2 CMA CHEMICAL TRANSPORTATION EMERGENCY CENTER (CHEMTREC)

Since September 1971, the Chemical Manufacturers Association (CMA) has been operating a 24-h toll-free telephone service for providing technical information and operational support during chemical transportation emergencies. Although CHEMTREC's primary mission is to help during transportation incidents, it also provides support for chemical hazardous materials emergencies in nontransport (e.g., fixed-facility) situations.

CHEMTREC is establishing direct contact with chemical company medical personnel. These contacts will expand CHEMTREC's ability to provide medical advice to physicians who treat those exposed to chemicals. Another value of CHEMTREC is its link to the mutual-aid programs that exist for some products and materials. CHEMTREC receives many calls about radioactive materials transportation incidents and relays the assistance request to DOE regional response facilities. If an incident involves the chemicals of certain CMA companies that produce such materials as chlorine, or a pesticide, CHEMTREC calls emergency contacts in its own CHEMNET mutual-aid network, or those designated by the Chlorine Institute or the National Agricultural Chemicals Association. The emergency response networks of these organizations are described below.

# 9.3 CMA CHEMNET NETWORK

The CHEMNET mutual-aid network began operating on November 1, 1985, and is designed to provide prompt response, advice, and assistance at the scene of serious themical transportation incidents. It has more than 50 participating companies with emergency teams, 23 subscribers (who

receive services during an incident from a participant and then reimburse response and cleanup costs), and 4 emergency response contractors. CHEMNET currently has more than 170 geographically dispersed emergency response teams in the network and is expected to continue expanding. Participating companies include the nation's largest chemical producers and transporters (e.g., DuPont, Union Carbide, and Dow Chemical).

The CHEMNET network is activated when a member shipper cannot respond promptly to an incident involving that company's products(s) and requiring the presence of a chemical expert. If a member company cannot go to the scene of the incident, the shipper will authorize a CHEMNET-contracted emergency response company to proceed. Communications for the network are provided by CHEMTREC, with the shipper receiving notification and details about the incident from the CHEMTREC communicator.

## 9.4 CMA CHEMICAL REFERRAL CENTER (CRC)

Another technical assistance resource of the CMA is its Chemical Referral Center (CRC) for chemical users, chemical transporters, and the public. The CRC which began operation in December 1985, provides safety and health information that, for example, can be used by local emergency response planners in dealing with chemical companies who are not CAER members. The CRC operates daily from 8 a.m. to 9 p.m. (Eastern Standard Time). CRC operators determine the identity of the product being inquired about and use this information to provide a contact at the company. In most cases, the information is provided to the caller in the form of a material safety data sheet, plus more detailed product information when necessary. Initially the CRC can link callers to producers of over 100,000 products, but plans are in progress for the chemical information base to grow to over 500,000 products.

# 9.5 CHLORINE INSTITUTE EMERGENCY PLAN (CHLOREP)

Since its inception in 1972, the Chlorine Institute's Chlorine Emergency Plan (CHLOREP) has handled over 800 transportation and fixed-facility incidents. CHLOREP is a 24-h mutual-aid

program of 35 member companies and their 70 producing and packaging plants. Response is activated by a CHEMTREC call to the designated CHLOREP contact, who notifies the appropriate team leader, based on CHLOREP's geographical sector assignments for teams. The team leader, in turn, calls the emergency caller at the incident scene and determines what advice and assistance are needed.

# 9.6 NACA PESTICIDE SAFETY TEAM (PSTN)

The National Agricultural Chemicals Association Pesticide Safety Team Network (PSTN) was formed in 1970 to minimize environmental damage and injury arising from accidental pesticide spills or leaks. The network has 14 member companies and more than 45 safety teams with expert personnel and equipment for prompt and efficient cleanup of pesticides after a major incident.

PSTN has an area coordinator in each of its ten regions nationwide. These coordinators are available 24 h per day to receive pesticide incident notifications from CHEMTREC. Once notified, an area coordinator telephones the emergency caller, obtains necessary information regarding the incident, coordinates with the manufacturer of the pesticide to  $a_{e^{+}}$  ee on emergency procedures, and arranges for needed PSTN resources. The coordinator then recontacts the emergency caller and advises what immediate steps to take. If a safety team is needed from either the manufacturer or the roster of PSTN teams in the area, the team is mobilized and the coordinator notifies the caller that it is on the way.

# 9.7 ASSOCIATION OF AMERICAN RAILROADS FIELD FORCE

A quasi-mutual aid program for emergency response is the 19-member Field Force of the Association of American Railroads Bureau of Explosives. Team members, located throughout the United States and Canada, spend about 20% of their time responding to derailment and leaking car incidents. In addition, one primary responsibility of the Bureau Manager for Environmental Services is to assist rail carriers in the cleanup that follows an emergency. Although the Field Force is smaller than it was in the past, some railroads now have their own emergency response teams.

### 9.8 HAZARDOU3 MATERIALS ADVISORY COUNCIL - INFORMATION SERVICES

The Hazardous Materials Advisory Council (HMAC) is a nonprofit trade association that functions as a clearinghouse for safety information on hazardous materials transportation and a source of technical assistance for government agencies at all levels. HMAC's 216-incmber companies include carriers of all modes, shippers of varying size, container manufacturers and reconditioners, and emergency response and waste-cleanup contractors. HMAC publications are sent, on request, to about 8000 people and public sector organizations on its mailing list.

## 9.9 AICHE CENTER FOR PROCESS SAFETY

The American Institute of Chemical Engineers (AIChE), a professional society representing the chemical engineering profession, has been active in chemical-related activities. In January 1985, AIChE established the Center for Chemical Process Safety. The purpose of the center is to conduct research and provide objective technical information on issues related to the prevention of accidents in the manufacturing, handling, and storage of toxic and/or reactive materials. The center has budgeted \$1 million for these efforts per year and plans to supplement AIChE funding with grants from both private industry and the government.

is of January 1986, the center's efforts consisted of four projects:

- development of a document entitled <u>Guidelines for Hazard Evaluation Procedures</u>, which is currently in publication;<sup>31</sup>
- 2. a safety training program that probably will include developing self-study materials to sell to chemical processors (the center also plans to integrate safety issues into college level classes);
- 3. research in safety procedures for bulk storage and handling; and
- 4. research on vapor cloud dispersion models.

The AIChE is also working with EPA to implement its guidance for developing community preparedness programs. Since much of the guidance is highly technical, EPA has requested that AIChE provide personnel to help local communities develop response plans. As a result, AIChE is implementing a pilot program for a limited number of areas. As part of the pilot program, AIChE members living in these areas, many or whom are retired chemical engineers, will volunteer to assist the local communities in their planning efforts.

## 9.10 INSTITUTE OF HAZARDOU'S MATERIALS MANAGEMENT

The Institute of Hazardous Materials Management is a nonprofit corporation dedicated to upgrading professional practice in the field of hazardous materials management. Their Hazardous Materials Manager Certification Program has the following objectives:

- to provide credentialed recognition to those professionals engaged in the management and engineering control of hazardous materials who have attained the required level of education, experience, and competence;
- 2. to foster continued professional development of Certified Hazardous Materials Managers through continuing education, peer group interaction, and technological stimulation;
- to facilitate the transfer of knowledge and experience among professionals and organizations vitally concerned with hazardous materials management; and
- to provide government, industry, and academia with a mechanism for identifying hazardous materials management professionals who have fulfilled the requirements for certification by a professional peer group.

A Certified Hazardous Materials Manager (CHMM) Examination has been developed as a qualification requirement along with at least 3 years of professional hazmat-related experience in industry, government, or education. Major contributions and outstanding leadership in this field may also be credited toward meeting some of the requirements. The CHMM examination is offered periodically at universities located in various states. A training manual prepared by TVA personnel is available.<sup>44</sup>

# 10 SURVEY OF RESPONSIBILITY GAPS

In response to the work statement, significant gaps and overlaps identified during the evaluation of statutory and regulatory responsibilities are to be summarized. Empirical gaps and overlaps depend not only on existing statutes concerned with emergency response to hazmats but also on the extent that the federal, state, and local agencies have accepted these responsibilities, have received the necessary support to undertake extensive programs, and have coordinated with other organizations to avoid dysfunctional overlaps. Further, many community response programs have been conceived and developed through the direction and encouragement of private organizations such as the CMA CAER program and have not been the result of statutory rules. Therefore, it is important that the contributions made by these private programs toward the overall emergency response effort be adequately identified and evaluated. Many of these entities were formed in response to specific local needs; it is important that they be encouraged in their efforts, while any shortfall in compliance be flexibly corrected.

A review of numerous sources was made to identify important current gaps and overlaps in responsibilities. This review was performed to augment the review of the federal and state statutes presented in Sect. 5. The literature searched contained a significant number of issues; we have selected those which, in our judgment, appeared to be the most important and have categorized them according to the following areas: planning, prevention, response, and training.

### 10.1 PLANNING

As described in Sect. 6., contingency planning by federal agencies for emergencies is complex and the legislation is implemented by a variety of agencies. At the federal level, the statutes do not clearly define the roles and responsibilities of the various agencies with respect to response planning. Interagency coordination is accomplished through the National Response Team (NRT) as evidenced by NRTs guide entitled <u>Hazardous Materials Emergency Planning Guide</u>.<sup>13</sup> This is currently published in compliance with the SARA Title III provisions and will replace FEMA-10. The EPA has published interim technical guidance for its Chemical Emergency Preparedness Program

(CEPP),<sup>5</sup> and some of the material from this manual has been included in the NRT guide. EPA, FEMA, and DOT are also developing Emergency Planning Technical Guidance<sup>32</sup> documents for identifying acutely toxic chemicals, and for conducting vulnerability analysis and risk analysis. It is intended that local planners use both of these guides for developing emergency response plans. However, in our judgment, it is quite optimistic to assume that individual communities will have the resources and expertise to develop comprehensive emergency response plans without extensive support from government, industry, and concerned private citizens. Table 7 presents a list of the types of support that will probably be required. Since there are very great variations in local circumstances, this list can only reveal the general shape of the typical requirements. Many of the recommendations that follow in this section are based on these support requirements.

## 10.1.1 Federal/State Planning Coordination

With the establishment of EPAs Chemical Emergency Preparedness Program (CEPP), it is apparent that there may be an overlap between FEMAs and EPAs contacts with the various state emergency management organizations. Although SARA specifically states that the regional response teams are authorized to review the state and local plans, it is not clear what the roles of EPA and FEMA will be with respect to the planning process except through the NRT and RRT systems. Fisher<sup>33</sup> indicates that there is an ever-increasing need for federal agencies to coordinate their program development and implementation particularly through interagency projects such as the NRT.

With regard to state and local planning, SARA specifically authorizes the governors of each state to appoint emergency response commissions who are to designate emergency planning districts, appoint local emergency planning committees for the purpose of developing local emergency plans, and coordinate these plans with local facilities that handle hazmats such as chemical plants and storage facilities. Thus, this new statute clearly recognizes that community planning is the prerogative of the state and local governments. This is particularly true for planning activities, such as local area hazards evaluations, multiagency coordination agreements, and procurement of response

equipment, tailored to the particular needs of each local community.

A model response system, such as the Hazardous Materials Advisory Council in Memphis, Tennessee, was developed by local and regional jurisdictions, along with private organizations, with the support of a federal agency. Establishment of similar programs under SARA will probably depend on similar scenarios. However, the inadequate level of support offered by federal agencies has been one of the major impediments to local planning, as cited by the recent DOT-FEMA survey.<sup>35</sup> In a question asked of the respondents engaged in planning activities with respect to shortfalls resulting in unfulfilled major programmatic requirements, 70.4% mentioned finance and 62.2% mentioned training. In a FEMA survey concerned with the needs of local emergency management organizations during FY 1986-89, the major issues included training and planning deficiencies.<sup>36</sup> The number of organizations that agreed to address these deficiencies was only a fraction of the number designated as having the deficiencies, and the main reason given for this problem was lack of adequate funding.

Although several surveys concerning the current levels of state and local preparedness for emergency responses have been made, the NRT Preparedness Committee indicated that "no one survey provided a definitive indication of existing levels of preparedness, nor did all the surveys reviewed provide a comprehensive picture of existing preparedness.<sup>11</sup> Thus, it is again apparent that there is feedback from local organizations that their planning and training activities contain deficiencies due to inadequate funding, but comprehensive estimates are not available concerning the current levels of hazmat preparedness at the state and local levels.

#### 10.1.2 Planning Data Bank Requirements

A summary of specific areas where federal assistance could be implemented for local and regional planning includes the development of a "National Hazardous Materials Data Bank," which

Field of frequency requirements for local community emergency response planning

- 1. Technical assistance for the development of a hazards identification and analysis, the assessment of prevention and response capabilities, a title equipment and facilities required for the response organization
- 1. It leaf and financial support to implement and develop the energency plan and purchase the required emergency equipment and facilities.
- 1.1.1 resources that identify the facilities and transportation routes with respect to hazardous materials handled and their associated risks to the surrounding community.
- (c) appendion from the local industrial facilities, transportation compaties, government, and public service agencies to facilitate the planning organization in its evaluation of prevention and response reported s and capabilities
  - sequenation with nearby communities to coordinate their existing glans with the plan under development and to develop mutual-aid arresponts.
- Technical assistance in determining how hazmat releases are to be detected, warning the local population, the area and population that may be affected and the procedures to be used to protect the population (e.g., evacuation, sheltering, etc.).
- 2. Beview of the developed emergency plan by qualified experts as required by SARA Title III

could be made available to state and local planning committees for planning purposes. This data bank would include the following detailed information:

- production and storage facilities for hazmats in the United States, including capacities, locations, shipments, storage inventories, etc.;
- major shipping routes for hazmats as a function of hazmat type, location, carrier type, quantities shipped, etc.;
- 3. toxic property data for each hazmat listed, along with a listing of recent events where death or injury occurred as a result of the hazmat release; and
- 4. a ranking system for each hazmat to provide an indication of the relative risks of death/injury such as that described in Sect. 3 of this study.

An optimal arrangement would be for the planner to address this data base, which is organized such that, upon keying in the name of the community, county, or other subdivision, a listing of hazardous chemicals in the order of their danger to the community would be the response. Presumably the ranking for both fixed facilities and transportation would be given along with estimates of the annual quantities produced, passing through the community or in typical inventory. Starting from this raw information, a detailed assessment of the hazards could be assembled. Obviously, we are not yet prepared to invoke such a system, although a number of the elements of such a system exist at some level of development.

Past hazards analysis studies<sup>16</sup> have indicated that it was necessary to set up check points on major transportation routes to obtain data on hazmat shipments in the vicinity. By locating the sources of hazmat production, storage, and the major shipping routes, much of this data acquisition work could be circumvented thereby reducing the time and the cost of local planning studies. Sources of the data could be the information gathered under the "community right-to-know reporting" required under SARA. The property and past-event data are already available in various data bases.<sup>1,34</sup>

The development of a simplified risk assessment procedure would enable a local community to prepare a preliminary risk assessment based on data provided by the data base, the ranges of local weather conditions, and the geological characteristics of the region. Such a program could be made available through terminal connection to a mainframe computer by request of a local committee to FEMA. The results from this analysis should not be considered to be a complete high-level hazards risk assessment. It could be classified as a level 3 probability assessment (based on the classification levels proposed by A. D. Little<sup>38</sup>) to provide an understanding of the scope of hazmat risks for local planning committees. Results of such a study would provide the following to these committees:

- 1. an approximate indication of the risks from local hazmats to the community (high, medium, or low risks);
- a basis for planning for the types of emergency response equipment, procedures, and organizations to be involved;
- 3. a basis for determining whether cooperative emergency agreements with neighboring communities and local chemical companies are necessary; and
- 4. a basis for determining the levels of federal/state and other support required for more detailed planning at the 1 or 2 levels, if required.

Although SARA Title III calls for an inventory of facilities that handle extremely hazardous substances in excess of the allowable thresholds, it does not address the problem of hazmat transportation inventories. This is a major consideration for communities that do not have local hazmat facilities but are located near major transportation routes. Many communities fall in that category. These communities often may not be aware of the potential for extremely dangerous hazmat releases in their vicinity. In our judgment, this is one of the serious gaps in the current statutes, and it must be addressed if adequate levels of community planning for emergency response are to be achieved.

## 10.1.3 Planning Consultant Guidelines

The support requirements listed in Table 2 indicate that significant levels of technical assistance to the planning teams will be required. Most communities would not have the technical personnel available except in those cases where technical personnel were available from local industries, research, or educational institutions or the state emergency authorities. Therefore, the employment of consulting organizations to provide technical support to planning committees will probably become a widespread practice. Numerous engineering service organizations have recently added this capability and are prepared to offer their expertise under contract; however, to our knowledge, no guidelines currently exist to assist these committees in the selection of competent consultants. We recommend that FEMA consider the development and publication of a set of guidelines for emergency response consultation, which would include:

- 1. a list of FEMA-approved consulting organizations;
- criteria for estimating the levels of technical assistance required as a function of the desired plan scope;
- 3. minimum qualifications for consulting personnel;
- 4. methods for estimating the total time and the overall cost for consulting services as a function of the plan scope;
- 5. a definition of the extent of consulting responsibilities and liabilities of the consultant with respect to the planning scope; and
- 6. a definition of the liability aspects for volunteer consultants to the planning committee.

## 10.2 PREVENTION

Control of the release of hazmats throughout their entire lifecycle (production, storage, transportation, and final consumption) is a prime requisite for the prevention of emergency releases. In a recent address, L. Thomas, the Administrator of the EPA, indicated that the current federal effort has to focus particularly on prevention of chemical releases.<sup>36</sup> Included in the government's prevention program are: (1) the design and detailed engineering requirements for spill prevention,

particularly in the transportation section; (2) the information-sharing and response-planning efforts as required by SARA Title III; (3) expansion of the hazardous spills reporting process; and (4) increased efforts to ensure that response capabilities are available all the way from local levels, through higher levels, and are ultimately backed up by a federal response capability. However, the Federal effort recognizes that many of the motivating factors for prevention are outside the control of government and thus require "development of an integrated government and industry prevention effort." Responsibility for prevention of hazmat releases falls under the jurisdiction of many agencies and statutes. For example, during the manufacture, handling, and storage of hazardous materials, at least ten federal agencies have varying responsibilities for accident prevention.<sup>37</sup> When an accident has occurred, at least 14 agencies may be included in the accident reporting systems.<sup>37</sup> Our review of the data bases for hazardous materials accidents and materials flow (see Sect. 14.7.2) indicated that, although numerous data bases are available, coordination of the detailed information collected and the procedures for disseminating the data to planning organizations is sorely needed. In addition, there appears to be a need for coordination of the research and development programs concerned with hazmat prevention. This requirement has become more critical with the establishment of the new Hazardous Substance Research, Development and Demonstration Centers authorized by SARA Title I, Section 118, the ongoing testing conducted at DOE's Liquefied Gaseous Fuels Spill Test Facility (see Sect. 15.4), and other prevention research in progress at the national laboratories and federal research facilities. These issues suggest that there is a need for a federal coordinating organization for prevention activities comparable to the National Response Team, which coordinates emergency response and planning (see Sect. 6.3).

SARA Title II, Section 209, authorizes EPA to establish an Advisory Council to assist in the coordination of research and administration activities concerned with innovative waste treatment technologies and health effects. This council includes representatives of the relevant federal agencies, the chemical and toxic waste management industries, institutions of higher learning, state and local health and environmental agencies, and the general public. We recommend that the

following activities be considered as a framework for establishing "A Federal Prevention Coordinating Council":

- 1. coordination of the federal agency data base activities concerned with hazardous materials accidents, materials flows, right-to-know information, etc.;
- coordination of the federal information systems for use in hazards evaluations by state regional and local planning organizations;
- coordination and oversight of federal research and development programs concerned with the prevention of hazardous material accidents;
- coordination of the development of hazardous materials operator training and certification programs;
- 5. reviews of standards for siting and construction of facilities for the production and storage of hazardous materials; and
- 6. reviews of innovative new developments for the prevention of hazardous materials accidents.

The recommended membership for this coordinating council should include qualified representatives

from federal, state, industrial, and higher-education organizations.

### 10.2.1 Comparisons of Nuclear/Chemical Industry Responsibilities

A comparison of the jurisdictional responsibilities for nuclear and hazardous chemical materials is of interest. For the case of nuclear materials, prime responsibility resides with the Nuclear Regulatory Commission (NRC) as follows:<sup>38</sup>

In order to continue operations or to receive an operating license, an applicant/licensee will be required to submit its emergency plans, as well as state and local government emergency response plans to NRC. The NRC will then make a finding as to whether the state of onsite and offsite emergency preparedness provides reasonable assurance that adequate protection measures can and will be taken in the event of a radiological emergency. The NRC will base its findings on a review of the FEMA findings and determinations as to whether state and local emergency plans are adequate and capable of being implemented and on the NRC assessment as to whether the applicant's/licensee's emergency plans are adequate and capable of being implemented.

Other provisions of the NRC mandate the following:

1. specification of emergency action levels for each facility,

2. public dissemination of emergency planning information,

- 3. rapid notification of the public of a serious reactor emergency,
- 4. a licensed technical support center and a licensed near-site emergency operations facility,
- 5. redundant communications systems,
- 6. specialized training of personnel, and
- 7. up-to-date emergency plan maintenance.

In contrast for hazmats, the planning and public notification aspects are included in the SARA. Title III provisions, but the law requires only that planning districts be established, local emergency plans be prepared by the local committees for each district, and the plans be reviewed by the state emergency response commission and possibly the RRTs. This potentially allows considerable variations in approach from one state or local jurisdiction to another for exactly the same situation.

### 10.2.2 State Prevention Statutes

Probably the major activities concerning prevention are centered in the recently passed state statutes that require manufacturers of hazmats to develop risk analyses and emergency procedures for their facilities. As noted in Sect. 5.9, the state of New Jersey's "Toxic Prevention Catastrophe Act" requires hazardous chemical manufacturers to develop risk management programs. These programs must include design safety reviews, standard operating and preventive maintenance procedures, risk assessment of operating equipment, and emergency response planning. The importance of the risk assessment procedure in preventing chemical plant releases is emphasized in the AIChE's "Guidelines for Hazard Evaluation Procedures," which includes a selection of hazard evaluation procedures for identifying and evaluating chemical process hazards.<sup>34</sup> The document states:

The application of these procedures can be effective in the identification and subsequent management of process hazards, especially those with potential major consequences to the public. Actions based on the use of these procedures can lessen the probability of accidents with high consequences and reduce the consequences of the accidents that do happen. The primary emphasis is on qualitative procedures for hazard identification although some of the procedures can also be used for quantitative hazard analysis . . .the guidelines are intended to apply to process hazard analysis, although some of the methods can be applied in other areas such as transportation of hazardous chemicals. The procedures car be used for existing plants and for new plants.

In our judgment, if an adequate hazard evaluation program had been instituted at the Bhopal, India plant, the disaster that occurred on December 2, 1984, would have been prevented. Certainly, most of the equipment inadequacies and malfunctions would have been identified and corrected if a responsible effort had been made to carry out an effective hazards analysis program prior to the accident. [The disaster could have been averted if any one of the five safety devices had been functioning properly.<sup>30</sup>] More detailed descriptions and evaluations of hazards evaluation programs will be included as part of Task III of this program.

It is therefore apparent that certain state governments are beginning to accept prime responsibility for promoting emergency preparedness for hazmats, while the federal government through the NRC maintains prime responsibility for preparedness in the area of nuclear materials. This refers to fixed hazmat facilities and does not apply to their transportation, where responsibility resides in the Department of Transportation.

## 10.2.3 OSHA Prevention Initiatives

OSHA has proposed a rule to amend the OSHA standards for hazardous waste operations and emergency response personnel (see Sect. 5.7.3). The rule, when finalized, will essentially cover all workers connected with emergency response operations for releases or threats of releases of hazardous substances. Thus, anyone concerned with hazardous response operations at a production facility, involved in rail or highway transportation, or involved in response to incidents involving hazardous substances will be covered. Proposed provisions for emergency response at sites other than hazardous waste clean-up sites (79 CFR 1910.120 L) include:

1. training for response employers, and

2. procedures for handling emergency responses,

In addition, Hazmat team members are to be given the following [29 CFR 1910.120 (l) (4)]:

- 1. training or protective clothing and procedures for leaking vehicles or containers,
- 2. physical examinations and medical surveillance, and
- 3. chemical protective clothing.

Extension of the OSHA standards to hazardous substance responders, in addition to those employees covered at CERCLA and RCRA facilities, will broaden the emergency response capabilities of employees handling hazardous substances and could be a substantial step toward the mitigation of hazardous chemical emergencies. Further extension of these provisions to all workers handling hazardous chemicals is strongly recommended.

The OSHA Pilot Program (CHEMSEP), described in Sect. 6.8, could serve as an excellent model for future prevention programs that could have a significant impact on hazmat releases at industrial facilities. Results of CHEMSEP highlighted the need for more specific OSHA regulations with respect to items such as safety program management, development of maintenance schedules, provisions for emergency communications, and toxic chemical monitoring systems. The program also led some firms to reduce their hazmat storage inventories and possibly helped emphasize the need for programs such as the CMAs CAER Project.

We recommend that consideration be given to establishing a permanent OSHA program that would mandate periodic inspections of industrial chemical facilities to enforce rules developed for the prevention of hazmat releases. These inspections should encompass all of the company health and safety procedures and, in addition, evaluate the following:

- 1. company risk management programs,
- 2. company emergency response plans and management programs,
- 3. emergency equipment and facilities,
- 4. accident detection/warning/monitoring systems,
- 5. emergency communications systems,

- 6. command/control centers,
- 7. company maintenance programs,
- 8. coordination of plan with local and regional emergency response plans,
- 9. personnel training schedules,
- 10. hazmat risk reduction programs (inventory reduction, etc.),
- 11. security/access control systems,
- 12. meteorological measurement systems at the site,
- 13. prearranged mutual aid agreements with outside organizations, and
- 14. compliance with SARA Title III provisions.

Such a review would be time consuming, but the program could be operated with a relatively low frequency and remain effective.

## 10.2.4 OSHA Communications Standard Limitations

Limitations in the OSHA Communication Standard were identified during the OSHA oversight hearings before the House of Representatives Subcommittee on Health and Safety in 1985.<sup>40</sup> These limitations include:

- 1. Many sectors are not being covered, including farm workers, transportation, painters, and auto repairers. In fact, coverage extends only to the manufacturing sector.
- 2. Company discretion is allowed in the determination of which chemicals constitute hazards and the type of communication program used to comply with the standards. (The effect is that the chemical companies decide themselves which chemicals are to be considered hazardous and the communication procedures concerning their effects.)
- 3. If a material falls under the "trade secrets" section, the company is not required to identify the hazardous chemicals used in its manufacture.
- 4. There is an inadequate number of available inspectors.
- 5. Workers who attempt to obtain information on hazardous chemicals may jeopardize their jobs under the hazard communication standard.

The new SARA provisions of CERCLA (see Sect 5.7) require owners/operators of facilities where hazardous substances are handled to provide information on the manufacture, use, and storage of the substances. The facilities are required to prepare MSDS or a list of chemicals for which the MSDSs are required by the OSH Act. In addition, information required pertaining to these hazardous chemicals must include the following:

1. estimates of the maximum amounts of these chemicals present at the facility:

- 2. estimates of the average daily amounts of these chemicals handled by the facility; and
- 3. the general location of the chemicals.

This information is to be prepared for local planning committees, state emergency response commissions, and the fire departments having jurisdiction over the facility. Thus, the information will almost certainly be available to employees of the facility and will partially fulfill the requirements of the OSH Act, even though the hazardous chemicals may not have been classified in a final health standard by OSHA. However, SARA does not include provisions requiring monitoring equipment, warning labels, medical record keeping, and the allowable total exposure of personnel to these chemicals. The OSH Act is also inadequate with respect to requirement for equipment upkeep, backup safety equipment, and reliable instrumentation for the detection of hazardous chemical releases.

## 10.3 RESPONSE SYSTEMS

### 10.3.1 Notification of Releases

One of the most critical aspects of emergency response is the immediate notification of local, state, and federal authorities when a release of a hazmat has occurred. The release amounts that should be reported are tabulated as reportable quantities (RQ) as described in Sect. 5.7. Recently, Congress (in SARA Title III) mandated that owner/operators of hazmat facilities must report releases of both RQ chemicals and those listed in the EPA CEPP. The threshold release levels of the CEPP chemicals were published in November 1986.

The fact that delays in notification have occurred or at times releases were not reported is well.

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documented in the literature. For example, during the release of aldecarb oxime dissolved in methylene chloride at the Union Carbide Plant in Institute, West Virginia, notification was delayed for 20 min because the plant personnel were relying on a computerized dispersion-modeling system which predicted that the cloud would not be dangerous beyond the plant gates. It was subsequently evealed that the system was not programmed for these chemicals and that insufficient data were available on the effects of the chemicals in question on humans.

Cashman<sup>1</sup> illustrates how delays in response posed an extreme risk to the community of Hagerstown, Maryland, in 1979. As a remedial action following an incident in West Chester, Pennsylvania, involving a fire in a white phosphorus drum on March 22, 1979, the remainder of the drums were placed in larger 55-gal drums, filled with water, and sealed. The drums were then loaded onto two trailer trucks and driven to the carrier's terminal, 30 miles south in Hagerstown, Marvland. While at the terminal, the phosphorus manufacturer and the carrier haggled over who should take possession of the cargo because it had become apparent that the steel drums were reacting with the water/phosphorus mixture to form hydrogen and poisonous phosphine gas. Subsequently, the manufacturer informed the carrier that it was abandoning the cargo. Ultimately the State of Maryland took action and called in EPA's On-Scene Coordinator, who activated the They identified the most serious hazard as the potential explosion of the EPA ERT. hydrogen/phosphine mixture and release of the extremely toxic phosphine gas to residents within a 5- to 10-mile radius. A decision was made to transport the drums to a remote site for detonation, located 170 miles south at Fort A. D. Hill. However, it was not until April 6, 1979, that the drums left Hagerstown (5 d after their arrival). There is no indication of the time lost before the state learned of this extreme hazard, but it is apparent that immediate notification by either the carrier or manufacturer could have significantly reduced the risk to the local population.

Another example of delayed notification occurred on New Year's Eve in 1984 in North Little Rock, Arkansas,<sup>1</sup> when 3000 gal of ethylene oxide escaped from a tank car parked in a switching yard. Officials evacuated 2500 to 3000 residents of the area (ethylene oxide is highly toxic and also

very flammable). In a news article in the *Little Rock Democrat*, J. Burnett, Chairman of the National Transportation Safety Board, rated the accident as one of the worst involving hazardous materials on an American railroad in 1984. He also indicated that a "potentially disastrous delay" occurred between the time the leak was discovered and the time the North Little Rock Fire Department was notified. Again, there is no indication of the extent of the delay, but certainly, any delay in reporting a spill of this magnitude could have been catastrophic.

More stringent regulations are needed requiring <u>immediate</u> notification of significant releases from any storage vessel or other item of equipment or any transportation vehicle. Certainly, there is some reluctance for operators and supervisors to report spills until they have determined the magnitude or potential risk, but it is of utmost importance that the public's safety be given first priority whenever a question concerning notification arises. It is recommended that consideration be given to adopting regulations for notification that would include the following requirements:

- Notification should be made for any deviation from any facility normal operations that could have health, safety, or environmental significance to the surrounding community. This should apply not only to those materials listed as hazardous by federal agencies, but to any substance that could endanger the public health and safety.
- 2. Notification should be made immediately (within 15 min as required by nuclear regulations) upon discovery of a <u>release or imminent release</u> of hazardous materials or any situation that could adversely affect the surrounding community.
- 3. Notification should include, it practical, a statement of an appropriate "emergency action level" as proposed in Sect. 10.3.2.
- 4. Notification should be in accordance with previously approved emergency plans for the facility. This should also include emergencies in the local area that could have a possible impact on the subject facility.

With suitable heavy fines for failure to comply, the problem of deliberate delays in notification should almost disappear.

## 10.3.2 Emergency Action Levels for Hazmat Releases

The current statutes call for notification of hazmat releases in excess of reportable quantities or threshold values in the case of extremely hazardous substances specified by EPA;<sup>8</sup> however, the statutes do not address the issue of emergency classification, which refers to the gradation of emergency conditions from small incidents to catastrophic ones. The statutes also neglect the situation where there is imminent danger of a hazmat release but the event has not vet occurred. In each case, the public's welfare would be better served if the seriousness of the incident were classified so that response organizations could be alerted to an appropriate emergency action level. For example, nuclear power plants and some emergency organizations use the classification shown in Table 8. The advantages of this system are obvious: evacuation of an area would certainly not be required for an unusual event or a plant alert. Also, emergency notification of local organizations could be required; however, since the situation has been given a classification, the response level can be tailored to the class of the emergency. Of course, if the situation tended to worsen, the class would be changed as the situation developed. Had this type of notification been in effect at the Union Carbide plant in Institute, West Virginia, it is possible that local authorities would have been notified well in advance of the release and not after the release had occurred and dispersed.

Energency class	Plant criteria	Response
Unic call event	Indication of potential degradation; no release	Notification, information
Alert	Actual or potential degra- dation of plant safety; minor release	Same as above; alert emergency action teams
Site area epergency	Actual or likely failure of plant safety systems; small release within guidelines	Activate emergency center communications, deploy teams, monitoring
secterra l Cherrateriov	Actual 51 imminent substan- tial plant degradation; releases reasonably ex- pected to exceed guidelines	Recommend shelter/evac- uation

Table 8. Emergency classifications and responses

Many very hazardous materials such as gasoline, petroleum solvents, liquefied petroleum gas (LPG), and carbon monoxide are not included as CERCLA reportable material quantities, although they are extremely reactive and/or toxic. In contrast, during transportation, many of the materials are definitely classified as hazardous (see Sect. 5.2). As described in Sect. 2.2, LPG was the hazmat responsible for the deaths of 500 people and injuries to 2500 people reported in the 1984 PEMEX disaster in Mexico City. It is apparent that continuous evaluation and updating of the CERCLA "reportable quantity" list are needed in order to include hazmats not currently listed and develop more stringent requirements for listed hazmats where more recent data on hazmat releases indicate that additional protection is needed.

#### 10.4 TRAINING

Several federal statutes address the need for the development and careful overview of hazmat training systems. The 1984 Hazardous Materials Transportation Act required FEMA and DOT to survey training programs offered for hazmat emergency response and enforcement activities. The recent DOT-FEMA Survey<sup>18</sup> developed a list of training programs available from federal, state, local, and private organizations. SARA Title III specifically authorizes EPA and other appropriate agencies carrying out programs to provide emergency training with special emphasis on hazardous chemicals. In addition, FEMA will make grants to state and local governments and universities to improve emergency response preparedness. SARA also requires that response plans for the emergency planning districts include a description of the required training programs and schedules for response practice drills.

It might appear from the number of available training programs offered by various governmental and private organizations, in addition to the requirements for training specified by SARA, that the needs for support for this aspect of hazmat emergency response are being

adequately addressed. However, various sources<sup>15,16,31</sup> indicate that the effectiveness and extent of coverage of current training programs are uneven for the following reasons:

- 1. <u>Consensus standards for training</u> Consensus standards are needed for the competency levels required for each level of response personnel.
- <u>Course evaluation</u> The content and quality of existing courses are very diverse. Evaluation
  of these programs is needed to ensure consistency and provide for adequate training at all
  levels of response personnel.
- <u>Coordination of training courses</u> Numerous separate organizations offer courses, but there is little coordination so that programs are not evaluated and trainees have difficulty finding useful courses.
- Extent of coverage by training programs Only a portion of the wide range of response personnel needing training is actually receiving it. One reason for this is the lack of adequate support for training expenses.

## 10.4.1 Consensus Standards for Training

The DOT-FEMA Report to Congress (July 1986)<sup>15</sup> identified the need for developing consensus standards for the skills necessary to maintain levels of minimal competency and knowledge for each level of response personnel. Probably the most critical area is concerned with the needs of first responders since they are the most likely to be impacted by hazmat releases and are often poorly trained, if trained at all. The reasons for this include the high annual turnover rates within fire departments and the predominance of volunteers in these departments. However, the *NRT Planning Guide* indicates that personnel at all levels who coordinate or have responsibilities in a hazmat emergency, both directly and indirectly involved at the scene of an incident, must have appropriate training.<sup>13</sup>

The association of Bay Area Governments (San Francisco Bay area) proposed a training plan for emergency responders as part of their DOT Demonstration Project.<sup>42</sup> This study proposes a four-level training plan as follows:

1. problem awareness for local staff at hazmat incidents,

- 2. problem recognition for first-level supervisors at hazmat incidents,
- 3. hazard control for hazmat response team members, and
- 4. incident supervision for high-level agency supervisors.

Table 9 lists the various training items proposed for each of the above levels.

The state of Tennessee has one of the most extensive hazardous materials training programs in the United States. This program, established by the Tennessee Emergency Management Agency (TEMA), is called The Hazardous Materials Training Institute. It is directed by a full-time Ph.D.level chemist and is set up to train fire fighters, law enforcement officers, medical reserves personnel, as well as state and local personnel. It offers four levels of training as follows:

- 1. safety course for first responders (8 h),
- 2. basic chemistry and tactics for technician certification (2 weeks) and a recertification course (taken every 2 years),
- 3. advanced courses in select areas of specialization (four courses of 4 d each), and
- 4. incident management course for command-level personnel.

[Note: This program parallels, to a certain extent, the requirements for various response levels presented in Table 9.] Under this program since 1982, Tennessee has trained 2036 first responders, certified 287 technicians, recertified 137, and provided advanced training to 124 technicians. The success of this program can be judged, in part, by the record that shows no avoidable loss of life in Tennessee due to hazardous materials accidents since its inception.

Table 9. Recommended training requirements for various response personnel levels

#### Level 1: Problem Awareness for Location Staff

Assessment - harmat recognition and identification labeling, health and environmental hazards. Notification - location of harmats at fixed and transport facilities, protocols for notification of releases. Resources - response information source agencies, equipment, etc. Recommended extent of training - up to 24 h

#### Level 2: Problem Recognition for First-Level Supervisors

All of Level 1, plus the following:

Assessment - more extensive health and environmental impact analysis, hazmat identification and handling, protective equipment, incident investigation.

Resources and Notification - agency roles and responsibility, notification procedures/protocols, information data bases and organi zations, hazardous substance manuals

Containment and Control - methodology, incident supervision, command post procedures, evacuation, etc.

Recommended extent of training - 16 to 24 h after Level 1

#### Level 3: Hazard Control for Hazmat Response Team Members

All of Levels I and 2, plus the following:

In-depth hazmat courses, chemistry of hazmats, hazmat containment, hazmat drill exercises in response, containment, cleanup, etc., preplanning for target hazmats, hazmat problems for specific targets, identification of unknown substances

Recommended extent of training - 300 h

## Level 4: Incident Supervision for High-Level Agency Supervisors

All of Levels 1 and 2, plus the following:

Preplanning - development of response plans Assessment - investigation/documentation of events, personnel protection Notification/Response Coordination - operation of Emergency Response Centers, notification protocols, and followup Containment/Control - isolation/containment methodology, evacuation, response funding. Regulations - local, state/federal Statutes Media Relations/Public Information

#### 10.4.2 Course Evaluation

Currently, there is a need for the evaluation of the various federal, state, local, and private organization training programs with respect to the following questions:

- 1. Does the course adequately cover the basic material?
- 2. Does the program meet the consensus standards for the specified levels of emergency response personnel?
- 3. Are the instructors properly qualified?
- 4. Is adequate emergency response equipment available for training?
- 5. Are recertification courses provided? Are they tied to evaluations of the effectiveness of prior training?
- 6. How much time is devoted to simulated emergency situations?
- 7. Does the organization have adequate financial resources and a minimum number of instructors?
- 8. Are efforts made to keep costs within affordable limits commensurate with the levels of training required?
- 9. Is the curriculum oriented toward emergency response training or toward enforcement and compliance with current statutes?
- 10. Is adequate time scheduled to cover the course material at the required depth?
- 11. Is adequate notification of the courses given to reach a broad range of personnel who need the training?

The major goal of this recommendation would be the accreditation of those training programs that are judged to comply with the minimum standards established by the organization responsible for the reviews. Publication of a list of accredited programs would facilitate the selection of approved schools by personnel responsible for state and local training programs. It would also assist the various government agencies in their funding activities since each agency would not have to develop its own evaluation structure for the myriad of existing training facilities. It is suggested that the Accreditation Board for Engineering and Technology (ABET) be used as a model for such an evaluation organization.<sup>43</sup> ABET is currently concerned with accreditation of the U.S. engineering college departments and is recognized as the official accreditation agent by U.S. engineering societies. This is often one of the most significant criteria in the selection of an engineering school by prospective students.

Studies are recommended that would examine the current costs of training for hazmat personnel and ways of developing more cost effective training for small towns and communities who cannot afford training programs conducted by others for a fee. One aspect that could be examined is the use of volunteer personnel such as retired technical personnel and members of technical societies who are already involved in volunteer planning activities (see Sect. 9.9). Many communities currently utilize these types of volunteer services.

A private organization that might be used as a model for local volunteer training programs is the U.S. Power Squadron This organization, headquartered in Raleigh, North Carolina, is organized into power squadron districts and local power squadrons throughout the United States wherever there is significant boating activity. Its primary mission is to instruct boat owners in the safe handling of their equipment.<sup>47</sup> Although other courses are also offered, classes are conducted by trained volunteer instructors and the entire organization is supported by annual dues paid by its members.

Further study is also needed regarding the federal role in training activities. Should it be primarily developmental, support for accreditation, certification, and recertification standards, research and evaluation, training clearinghouses, etc.? An evaluation of where these activities should be done such as the federal, state, public, or private levels should also be included. The federal role is not spelled out explicitly at the present time.

## 10.4.3 Coordination of Training Information

A national organization is needed that would be responsible for the coordination of the following:

1. various available training courses,

2. additional training facilities and personnel, and

3. sources of governmental support for training activities.

This organization would act as a national clearing house for training information but would not be responsible for evaluation. It would keep track of accredited institutions and would serve as the source of information required by new or nonaccredited schools. New training curricula and emergency training equipment development could also be included as a responsibility of this organization. The need for a coordinating organization was highlighted by OTA's study of hazmat transportation, which stated, "In telephone interviews with OTA staff, state training officers voiced frustration at the lack of information they receive on the quality of available training resources and the lack of communication with their counterparts in other states. Moreover, some local officials are concerned that planned state programs are inadequate to meet the needs of local jurisdictions."

# 10.4.4 Extent of Coverage by Training Programs

The National Fire Academy estimated that there are 1,200,000 fire fighters nationwide (85% of whom are volunteers and 15% paid employees of local jurisdictions).<sup>41</sup> With respect to law enforcement personnel, the National Association of Chiefs of Police estimates a total of 480,000 to 500,000 law enforcement personnel employed by state and local governments.<sup>41</sup> In addition, there are 224,000 emergency medical technicians registered nationally. If other emergency response personnel involved in state and local programs are added to the above, a total of well over 2,000,000 people can be estimated as the target audience for training programs. Although a fraction of this audience has received some training, the recertification and training of new personnel (due to higher turnover rates) could overshadow the accomplishments to date. For example, a plan for training people to fill two million positions during 1989 to 1992 would require that a total of about 700,000

personnel be trained per year (assuming a 25% turnover of fire fighters/year). The September 1985 training activity, estimated at about 102,000 students/year<sup>15</sup> for all sectors, could not come close to this requirement. Thus, programs such as FEMA's "Train the Trainer" and on-the-job training through the use of videotapes, teleconferences, microcomputer programs, training reports, and pamphlets will be mandatory, particularly for the first responders. Ultimately, it is suggested that consideration be given to establishing courses at local high schools and colleges where response personnel would receive minimal levels of training utilizing the existing school personnel and facilities and would be tunded through state and regional SARA planning districts.

Finally, it is important that some form of certificate level be established which recognizes the achievement of various levels of training.

# 11 SURVEY OF TECHNICAL OPTIONS

The results from Task III in the work statement (Sect. 1), which includes a survey of the technical options for hazardous chemical countermeasures, are included in Sects. 12-18.

Section 12 reviews the principal methods to characterize the nature of hazardous chemical emergencies, and Sect. 13 identifies a technical basis for the countermeasures that are currently available, under development, or projected as future approaches. An evaluation of these countermeasures is developed in Sect. 14, and needs for improved response actions are identified. Section 15 includes existing and potential new approaches to reducing the risks and prevention of hazardous chemical releases. In particular, the need for new technical approaches that present opportunities for public and private sector programs are emphasized.

Although these sections are primarily concerned with technical options for emergency response operations, many of the countermeasures reviewed require statutory and/or institutional implementation, which is covered elsewhere in this report. Examples of this include the need for coordination in the areas of emergency response planning and training activities.

Sects. 16 and 17 are concerned with the development of a methodology for the ranking of hazardous chemicals and apply this procedure to a selected list of these materials. The establishment of a relative measure of the risk of one hazardous chemical relative to another is important for several reasons. It establishes a priority order for the establishment of procedures and the study of countermeasures. In addition, it helps expose materials which require more in-depth research. It will also raise the level of awareness of the dangers of the overall, most significant hazards.

## 12 CHARACTERIZATION OF EMERGENCY RELEASES

# 12.1 CHARACTERIZATION OF DISASTER LEVEL

No statutory classification criteria for airborne releases of hazardous chemicals exist. Numerous authors have proposed definitions based upon a wide range of criteria, including:

- 1. the quantity and toxic properties of the material released;
- 2. mode of release continuous vs instantaneous releases;
- 3. the area or population affected by the release;
- 4. the potential for additional release due to explosion; catastrophic failure, etc.,
- 5. the extent of emergency resources required for the response (local.state/federal response organizations, specialized response teams, etc.); and
- 6. meteorological conditions existing at the site proximity at the time of the release.

The National Response Team Planning Guide<sup>13</sup> defines three typical emergency response levels and recommends that these be provided to special facilities such as schools, day-care centers, hospitals, etc., who would abide by the recommendations conforming to the announced response level. Table 10 lists these response levels. A comparison of Table 10 with the levels specified for the nuclear industry (see Table 11) indicates an additional level called an "unusual event" in the nuclear levels. This is defined as an indication of potential degradation of the nuclear power system, but no release has occurred. The response required is notification for information purposes, but the alerting of emergency action teams does not occur until the next level, called "alert," is reached. Also, the nuclear system defines a "site-area emergency," which approximates the NRT "Level I - Potential Emergency Condition." The "General Emergency" nuclear classification, which would involve sheltering and evacuation, is covered by the two levels in the NRT classification called "Level II - Limited Emergency Condition" and "Level III - Full Emergency Condition." Thus, it appears that more stringent detail is placed on potential nuclear emergencies while chemical release levels include two emergency conditions: a "limited" condition that requires a possibly small-scale Table 10. Recommended NRT response levels to chemical releases

Response level	Description	Contact
I. Potential emergency condition	An incident or threat of a release which can be controlled by the first response agencies and does not require evacuation of other than the involved structure or the immediate outdoor area. The incident is confined to a small area and does not pose an immediate threat to life or property.	Fire Department Emergency Medical Services Police Department Partial EOC Staff Public Information Office CHEMTREC National Response Center
II. Limited emergency condition	An incident involving a greater hazard or larger area which poses a potential threat to life or property and which may require a limited evacuation of the surrounding area.	All Agencies in Level I Hazmat Teams EOC Staff Public Works Department Health Department Red Cross County Emergency Management Agency State Police Public Utilities
III. Full emergency condition	An incident involving a severe hazard or a large area which poses an extreme threat to life and property and will probably require a large-scale evacuation; or an incident requiring the expertise or resources of county, state, federal, or private agencies/ organizations.	All Level I and II Agencies plus the following as needed: Mutual Aid Fire, Police, Emergency Medical State Emergency Management Agency State Department of Environmental Resources State Department of Health EPA USCG ATSDR FEMA OSC/RRT

					16
Table 11.	Nuclear	emergency	classifications	and	responses <sup>40</sup>

Emergency class	Plant criteria	Response
Unusual event	Indication of potential degradation; no release	Notification, information
Alert	Actual or potential degradation of plant safety; minor release	Same as above; alert emergency action teams
Site area emergency	Actual or likely failure of plant safety systems; small release within guidelines	Activate emergency center communications, deploy teams, monitoring
General emergency	Actual or imminent substantial plant degradation; releases reasonably expected to exceed guidelines	Recommend shelter/ evacuation

evacuation along with local area response, and a "full" condition that requires a large-scale evacuation and possible response by a wide range of public and private organizations.

One prime criterion of any response level system, in our judgment, is that of simplicity such that first responders will understand the criterion and react very quickly to the emergency situation. However, this requires a certain level of technically informed judgment on the part of the first responder concerning the real potential for a major disaster. For example, what might appear as only a minor release could eventually become a major disaster if the responder was unfamiliar with the type and amounts of toxic material released, the possible pathway of the vapor cloud, the local population density, or other factors that could have a major impact on the surrounding community. Conversely, cases have occurred where gross overreaction resulted from releases such as the response to an acid tank car leak where a local fire department poured 100,000 gal of water on the car, fearing a BLEVE (boiling liquid expanding vapor explosion).<sup>7</sup> In another instance, a half-mile area was evacuated near an LPG tank car that had a minor leak in the valve seat.<sup>7</sup>

The above problems with classification of events by first responders suggest that an additional response level should be considered which could be classified as an "unusual event" similar to the nuclear classification, but not as yet an emergency situation. At this level, a first responder could state that the potential for an accident was present or that a release had occurred but lack of detailed information prevented specification of a higher response level. In any case, this would require immediate notification of the appropriate authorities, who would then alert the response system and dispatch a trained technician to the site for detailed evaluation and possible declaration of an emergency situation. It is well documented that the reporting of many dangerous releases has been delayed (see Sect. 10). The addition of this new level could help expedite notification of events where there is doubt concerning whether a serious accident situation has occurred or is about to take place. It would also help alleviate the situation where first responders hesitate to make judgments as to the actual emergency level yet provide for immediate notification, which is critical to the mitigation of toxic gas releases.

## 12.2 TYPES AND EXTENT OF RESPONSE REQUIRED

An indication of extent of response required for each of the NRT response levels is listed in column 3 of Table 10. As expected, the normcation levels are progressive, starting (for Level I) with the local emergency agencies, a partial emergency operations center (EOC) staff, CHEMTREC, and the National Response Center. Thus, a Level I response would involve the emergency services of the local police and fire departments but would probably not require an extensive evacuation or the services of hazmat teams.

For a Level II response, more extensive notification is required, including the county or district emergency management agency, the state police/health agencies/utilities, the setup of an emergency operations center, and the involvement of trained HAZMAT teams. A limited evacuation might also be placed in effect. These contacts for Level II would also include contacts specified for a Level I response. Since a Level II response is classified as only "limited," the callup of state and federal agency resources might not be required, but in Tennessee the FEMA emergency operations center would almost certainly be alerted and the regional emergency technicians would be dispatched to the emergency site.

For a full emergency condition (Level III), all of the Level I and II contacts would be made plus the extensive list of state and federal contacts shown in Table 10. Thus, for a full emergency all responsible agencies would be alerted and specialized response teams would be called upon by the state or federal on-scene coordinator (OSC) as needed. This could include local/state/federal and industrial teams as described in Sects. 6-9. Also, for a Level III incident, a large-scale evacuation would probably be required and would be implemented according to the emergency response system plans developed for the local area and the involved state. In Tennessee, the State Emergency Operations Center would be manned and the full state emergency plan would be implemented.

As indicated in the prior section, addition of a Level 0 response level is suggested to be used where the first responder is completely uncertain as to which classification should be applied to an

emergency or where there is a threat of a release but the risks involved are unknown. In this case, notification would require that a trained response technician be dispatched immediately to the site so that the proper response level could be established and the proper notification chain would be activated.

13 TECHNICAL BASIS FOR NEEDED COUNTERMEASURES

Although institutional, statutory, and social issues comprise a significant portion of the total needs for hazmat countermeasures, technical issues approach these other areas in importance. Certainly, implementation of the provisions in SARA Title III will require intense evaluation of the emergency response technology available to state and local planning committees. Items such as response equipment, hazards evaluations, atmospheric dispersion computer models, working communications equipment, etc., will become standard components of emergency response programs.

In order to categorize these various technical issues and define their technical basis, we have divided them into the following areas:

1. prevention,

2. planning,

3. response, and

4. training.

Probably the most important countermeasures involve the long-term methods for prevention of hazmat releases by manufacturers, storage facilities, and transporters.

Table 12 lists the preventive countermeasures evaluated along with their technical bases. Table 13 lists the planning countermeasures, Table 14 gives response countermeasures, and Table 15 presents the training measures required.

The technical bases cover a broad range of technical activities, including the following:

- 1. research and development of hazmat mitigation systems (foams, monitors, etc.);
- 2. mathematical modeling of hazmat emergencies;
- 3. emergency equipment specification, design, testing, inspection, and evaluation;
- 4. process safety evaluation;
- 5. plant citing criteria for emergencies;

	Countermeasure	Technical basis
1.	Transportation and faciliry reliability studies	Identification, evaluation, and correction of high-risk components in hazmat handling systems
2.	Terrorist attack and sabotage countermeasures	Same as No. l, except for potential terrorist targets, warning systems for political activities, operator training, human factors evaluation
3.	OSHA inspections	Enforcement of safety regulations for hazmats
÷.,	Reductions in plant inventories of hazmats	Process changes, storage changes, process substitutions
ò.	Hazards evaluations during plant design, construction, revisions, and maintenance	Improved design, specifications, and safety criteria
6.	Data-base development for hazmats	Facilities/transportation/storage accident reporting, accident frequency, etc.
7.	Hazmat containment systems	Design for process and storage systems
8.	Human error prevention	Human performance evaluation and the effects of human errors on performance

Table 12 Technical basis for countermeasures

Table 13 Planning
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Countermeasure	Technical basis		
Hamards or community risk analysis	Evaluation of risks from hazmats; accident probabilities and severity		
Definition of emergency planning zones	Definition of zones for possible emergencies, including evacuations, etc.		
Emergency response plan Participating agencies Facilities Equipment Communications Mutual aid agreements Notification	Technical aspects of emergency response plans		
Revision, updating, improvement of emergency plans	Plan; maintenance		
Public relations	Facilities for public information		
Financial support for planning	Estimate of costs vs scope of plan		

	Countermeasure	Technical basis
1.	Monitoring for hazmat releases	Equipment available or under development
2.	Evaluation of quantities released	Probabilities and spill quantity estimates
3.	Estimate of airborne dispersion	Dispersion models and computer applications
4.	Evacuation estimates	Estimate of evacuation zones
Ď.	Fire and explosion zone estimates	Models and computer simulations of fire and explosion zones
6.	Response equipment Fires and explosions Hazardous release containment Protective equipment Health-care equipment Communications Warning equipment	Types of response equipment
7.	Evacuations vs sealed shelters	Risk evaluation of evacuation vs remaining inside enclosed areas
8.	Population protective measures	Potential protective devices for the general population
9.	New technical approaches	

# Table 15. Training measures

	Countermeasure	Technical basis
1.	Plant operating personnel	Operator training and certification
1 + .	Transportation personnel	Driver training and licensing
3.	Emergency response personnel	Response training programs

6. accident risk and consequence evaluation;

7. Atmospheric dispersion modeling;

8. training of personnel for emergency response;

9. planning emergency response medical facilities;

10. emergency response planning at the federal/state/local community and production facility levels; and

11. development of information systems for emergency response.

Many of these activities are reviewed in Sect. However, chemical plant design safety features, site selection, and standard safety specifications are not included because they are specific to each type of chemical production process and ,therefore, beyond the scope of this study.

# 14 EVALUATION OF AVAILABLE RESOURCES

Technical countermeasures for the mitigation of hazardous materials releases include a wide variety of emergency equipment, mathematical models, probabilistic risk assessments, training programs, etc. This section provides an overview of the resources currently available to local response organizations and facilities that produce, store, or transport these materials. Some identification of the commercial sources of these resources is included; however, comprehensive identification and evaluation of all the organizations offering these resources in this rapidly changing field were not the goals of the evaluation. In cases where they add to the picture, cost data for some equipment are also included. The goal here is to provide an overview rather than an exhaustive handbook treatment.

#### 14.1 VAPOR HAZARD CONTROL

Control of the toxic vapors from a release is the first line of defense against the spread of toxic materials releases. Control of fires has equal priority because of possible dispersion of toxic chemicals and combustion products to the surrounding areas. Countermeasures included in this section include the following:

1. mechanical covers,

2. vapor curtains,

3. induced air movement,

4. gelling equipment, and

5. foam systems.

In addition, items of equipment that can be issued as preventative countermeasures to provide secondary containment and improvements to storage systems are included in Sect. 15.1.

#### 14.1.1 Mechanical Covers

Placing a lid over a spilled chemical is a direct approach for containing the toxic vapors with nearly 100% efficiency.<sup>46</sup> Three basic techniques have been considered: (1) total cover of the spill

area by cloth or other continuous material, (2) spray of a continuous cover such as urethane, and (3) buoyant particles (either spheres or polygonal shapes). Theoretically, such covers should contain essentially all the vapor release, but in practice some leakage is to be expected.

Several direct means for mechanically containing both the spill and the vapor hazards arisir, from it have been described by Robinson.<sup>47</sup> The covers that are presently available have the ability to contain most chemicals for subsequent removal or recycle. Vapors can be contained nearly completely over lagoons where off-gases are collected. Membranes capable of encapsulating floating hazardous chemicals are also available. On land, sealing may be a problem. In addition, the time required for installation and the deployment over large areas where separate sheets must be joined may be significant drawbacks.

Floating cover assemblies are presently being fabricated by suppliers for such purposes as protecting drinking water supplies, collecting methane gas from sewage waste lagoons, and sealing a broad range of chemicals for atmospheric isolation. A typical example of this concept is the Hypalon membrane fitted with polyurethane floats offered by Globe Linings, Inc. (Long Beach, California).<sup>47</sup> Covers up to 9750 m<sup>2</sup> have been installed, typically by two men within 2 d since normal installation uses 7.6-m-wide sections.

The selection of covering membranes and the method of deployment must consider factors such as the following:

- 1. probable spill size;
- 2. compatibility of the membrane with the spilled material;
- 3. weight and cost of the membrane;
- 4. portability, availability, and reuse requirements; and
- 5. interfacing with the vapor and liquid removal operations.

Depending upon the chemical resistance requirements, a number of synthetic materials such as butyl rubber, EPDM, neoprene, Hypalon, polyethylene, vinyl chloride, and polyurethane are available. Sheets can be provided with reinforcing fabrics for added strength. Large lengths are feasible, but larger sections are usually made by an appropriate joining method, which includes mechanical systems such as zippers, Velcro, etc.

Distribution of light particulates over a liquid s-rface is another means of developing a physical barrier to reduce evaporation losses. Evaporation is decreased by the presence of the densely packed layer of particles, which reduce convection currents and insulate the liquid surface. This technique is presently used for open storage tanks, ponds, and reaction vessels to restrict evaporative losses. Effective materials, in the form of hollow spheres or closed-cell pl. stic foams, include glass, polypropylene, and polyurethane. Polyurethane has been demonstrated to have the best combination of chemical resistance and mechanical integrity.<sup>16</sup>

Although particulate covers are potentially effective, cost and installation problems are deterrents to their use. The technique would require the dispersal of a minimum of 3000 particles per square meter of spill surface. At present prices, material costs would be approximately \$1000 per square meter (1982 U.S. S) and up to 1000 times this amount for equipment to disperse the particles.<sup>6</sup>

#### 14.1.2 Vapor Curtains

Accidental spillages of hazardous fluids from fixed storage installations or during transportation can give rise to toxic and/or flammable vapor clouds that create attendant risks to both exposed persons and property. Although the potential applications of water spray barriers have been recognized for some time, there appears to be little information available to assist a potential user. However, Prugh has published information on the design of water spray systems.<sup>38</sup>

Experiments have been performed with various water spray barrier configurations to disperse clouds of carbon dioxide.<sup>10</sup> Two different water spray barriers were necessary in order to investigate all the necessary configurations. A 3-m-high barrier employing a downward directed nozzle arrangement was constructed from mild steel water tubing. Also, a barrier for upward directed nozzle arrangement was constructed from rigid plastic water tubing. Carbon dioxide was used throughout the trials as a representative heavy gas. Most of the results were consistent with the

general theory that increasing the specific volume and momentum flow rates also increased a barrier's dispersive efficiency. Vapor reduction efficiencies in the range of 45 to 48% were achieved at water spray rates over the range of 5.1 to 7.6 L s<sup>-1</sup> m<sup>-3</sup>.

The wind direction is important in the performance of the water vapor curtains. Since the direction is rarely constant, barriers have to be made wider than the actual cloud, thus increasing their water consumption. Alternatively, they may need to be portable or easy to redeploy in case the wind direction should change suddenly.<sup>49</sup>

Nevertheless, accepting these practical problems for the present, it has been established that water spray barriers can achieve a worthwhile enhancement of the rate of dispersion and dilution of heavy gas spills.<sup>49</sup>

Other results have been reported in which water spray nozzles were utilized to mitigate LNG vapors.<sup>50</sup> The first few inches of the spray pattern were essentially a sheet of water. The remaining distance to the outer boundary of the spray consisted primarily of water droplets. These tests were made with wind that averaged 9 mph with gusts up to 17 mph. Tests indicated that concentration reductions do occur and demonstrate the mechanism causing the reduction. Two mechanisms appear to be likely candidates: heating the vapor plume, thereby causing it to rise; and increasing mechanical turbulence, which causes improved mixing. Both theoretical analysis and observation of the tests lead to the conclusion that the improved mixing is due to mechanical turbulence. Water spray systems should be designed to provide maximum turbulence in the vapor zone. Although a general basis of design cannot be developed based on this information alone, sprays can be effective in reductions in concentrations have been achieved, particularly where the gases are readily soluble in water such as ammonia and chlorine vapors. Prugh indicates that the use of water sprays is generally limited to protection against water-soluble, low-density, or nonflammable vapors.<sup>51</sup>

# 14.1.3 Induced Air Movement

Simple dilution provides a direct approach toward reduction of toxic vapor concentration. The dilution technique involves the transport and mixing of uncontaminated air with the vapors released from a chemical spill. The volume of uncontaminated air must be sufficiently large to maintain the concentration of hazardous chemical vapors below their threshold limit value or lower flammability limit.<sup>47</sup>

Performance specifications can be calculated from data generated using a natural dispersion model.<sup>46</sup> This model predicts the evaporation rates for spills of floating hazardous chemicals to be in the range of 1 to 3.5 m<sup>3</sup> of vapor released per hour per m<sup>2</sup> of spill surfaces (3.3 to 11.5 ft<sup>3</sup> h<sup>-1</sup> ft<sup>2</sup>).

Typical spills are anticipated to cover between 378 to 3780 m<sup>2</sup> and release between 378 and 13,230 m<sup>3</sup> of vapor per hour. If an average threshold limit value of 10 ppm is assumed, then between  $3.78 \times 10^7$  and  $1.3 \times 10^9$  m<sup>3</sup>/h of uncontaminated air must be added to maintain the concentration of the hazardous chemical vapor at this limit. If an average lower flammability limit of 1% by volume is assumed, then between  $3.78 \times 10^4$  and  $1.3 \times 10^9$  m<sup>3</sup>/h of uncontaminated air must be delivered each hour to prevent a vapor fire.<sup>47</sup>

One problem that must be considered when dispersion is used involves the increase in evaporation rates that may occur. If the release is a vaporizing liquid, the fan may significantly increase the total toxic or flammable vapor generated.

These maximum estimates indicate the necessity for using very large air-moving equipment. The dilution technique for responding to spills of hazardous chemicals may be considered to be a man-made wind. Such large gas volumes can be produced by blower equipment incorporating surplus jet engines. Such blowers are used by railroads to remove snow and by airports to remove fog.

Typical examples of this type of equipment are manufactured by the Railway Maintenance Corporation, Pittsburgh, Pennsylvania.<sup>47</sup> Their equipment is designed to remove snow from the road beds and switches to permit smooth operation in winter. An example of particular interest to this application is their Hurricane model blower, which utilizes an Allison J-35 jet engine. This blower can generate a 650-mph air blast, which would deliver approximately  $10^7$  ft<sup>3</sup>/h of diluting air over the spill. The Hurricane model jet blower is fabricated as a self-propelled railway car assembly complete with the accessories necessary for 5 to 6 hours of independent operation. It occupies a space of approximately 10 m2, weighs 12,250 kg, and costs approximately \$75,000 (1979 U.S. \$). Modifications, such as flat-bed mounting or skid assembly, for shipboard operation are conceived as resulting in a reduction of over 50% in weight and cost (47).

#### 14.1.4 Gelling Equipment

Gel formation involves the interaction between a high-molecular-weight molecule (macromolecule) and a liquid. It is one form of liquid-phase modification which has seen extensive development, but for liquid immobilization rather than for vapor hazard control. The gel structure is a combination of physical and chemical interaction that generally results in the formation of a two- or three-dimensional network of macro- molecular cages, entrapping the liquid phase.

The formation of a gel generally has some influence on the evaporation rate and hence on the vapor concentrations in the air over a spilled chemical.<sup>46</sup> Reduction of evaporation rate is achieved by forming a continuous cover of gelled material to encapsulate the more volatile spilled liquid. However, the primary benefit obtained from gelation is immobilization or confinement of the liquid. The time required for the gelling reactions to be completed is a limiting factor for this technique. There are a few gels that may be formed within minutes, but many gelling reactions can take hours.<sup>46</sup>

A "Universal Gelling Agent," developed under EPA sponsorship by the Calspan Corporation, contains a specific blend of gelling agents that combine the flexibility and rapid reaction rates required for treating spills of hazardous chemicals. A listing of the hazardous chemicals used to test the performance of this agent is shown in Table 16.° Currently, information is not available concerning the ability of these gels to suppress volatile chemical vaporization.

# 14.1.5 Vapor Hazard Controls

# 14.1.5.1 Foam Systems for Vapor Suppression

Foams consist of an agglomeration of air and water with a small amount of impurity in the water. (Typical foams are 95% air and 5% water.) The impurity present in the system is the source of the foam. Because of the chemical nature of the impurity, it has the ability to lower the surface tension of the water, which permits formation of the large surface areas characteristic of foams. Impurities with the ability to lower surface tension are called surfactants or surface-active agents. Foams must overcome the destructive forces of surface tensions to maintain their large interfacial surface areas. The mechanism of lowering the surface tension is dependent on the solubility differences in the surfactant chains. Surfactant molecules are usually alcohols or polymers. Their hydrophilic groups are very soluble in water and are typically OH, CO<sub>2</sub>Na, SO<sub>2</sub>Na, or SO<sub>3</sub>K. The highly insoluble group, or hydrophobic group, is a long hydrocarbon chain. The surfactant's surface activity is dependent on its solubility and length. Surface molecules orient themselves in a particular fashion in the bubble wall.<sup>52</sup>

The hydrophilic group has an affinity for the water and is submerged in the bubble wall or lamellae. The hydrophobic group prefers the air-water interface, and a portion of the hydrocarbon chain is probably located in the internal gas of the bubble. This position of the surfactant molecule is more energetically favorable than the water molecules; consequently, the surface tension is lowered.<sup>52</sup>

One of the major problems of the foams is their tendency to collapse. One mechanism by which foams collapse is foam drainage. The gravitational effects cause excess water from the foam to drain through a system of interconnected lamellae called plateau borders. This drainage causes instability because the lamellae are thinned to the point where they can be easily ruptured by vibrations, by disturbances from diffusing chemicals, or by physical limitations of the lamellae.<sup>52</sup>

Another mechanism of foam collapse is caused by the diffusion of air between adjacent bubbles. The internal pressure of a bubble is inversely proportional to the bubble radius. The pressure Table 16. Compounds for which Universal Gelling Agent has been shown to be effective

Acetone	Formaldehyde
Acetone cyanohydrin	Gasoline
Acrylonitrile	Isoprene
Ammonium hydroxide	Isopropyl alcohol
Aniline	Kerosene
Benzaldehyde	Methanol
Benzene	Methyl ethyl ketone
Butanol	Octane (2,2,4-trimethylpentone)
Carbon disulfide	Orthodichlorobenzene
Carbon tetrachloride	Petroleum ether
Chlorine water, saturated	Phenol (89%)
Chloroform	Pyridine
Cyclohexane	Sulfuric acid
Ethanol	Trichloroethylene
Ethyl acetate	Water
Ethylene dichloride	Xylcne
Ethviene glycol	·

difference between adjacent bubbles creates a driving force for the diffusion of gas between bubbles. Consequently, the gas from the smaller bubbles decreases and its pressure increases, creating larger driving forces.<sup>52</sup>

Surface-tension agents are utilized to avoid instability in foams. Additives aid in the foam stability by increasing the surface and bulk viscosity, which slows drainage.<sup>52</sup>

Some properties of foams are the expansion ratio, which is the ratio of the volume of expanded foam to the volume of foam solution, and the quarter-drainage time, which is the time required for 25% of the liquid in the foam to drain out.

Foam quality refers to the distribution of bubble sizes and the mixing of the foam concentrate with water. Foams with a broad distribution of bubble sizes do not suppress vapor as well as those with uniform small size bubbles. Good-quality foams are also represented by a homogenous mixture of foam concentrates and water. High-expansion foams are generally more efficient at suppressing vapor than lower-expansion foams. The expansion ratio is related to water drainage rates. For a given foam, increasing the expansion ratio will increase drainage time and thus improve vapor suppression efficiency.<sup>53</sup>

Applying foam to cryogenic materials or low-boiling-point materials may not be an effective method for <u>controlling</u> vapor release. Water drainage from the foam acts as a heat source, thus increasing vaporization. The rapid vaporization of the chemical can cause chimneys in the foam and the foam collapses. Improved vapor control may be accomplished by using slow-draining, high-expansion foams. The initial drainage from the foam will increase vaporization but then decreases as the drainage slows.<sup>53</sup>

Foam is produced by mixing foam concentrates in water in the range of 2 and 10%. The concentrates are generally made up of around 40% organic solvents and 40% surface-active agents. The organic solvents are usually glycol ethers such as butyl ethoxyethanol. The surface-active agents can be: sodium lauryl sulfonates, proteins, or synthetic fluorinated hydrocarbons. The remaining 20% are additives for foam stability and protection.

Figure 4 shows a nozzle apparatus, which is a basic method of combining water, air, and concentrate to produce the foam. Water under pressure is passed through a proportioner, which meters the proper amount of foam concentrate into the water stream. The resulting solution, under pressure (but with air not yet introduced), passes through additional hose to the foam nozzle. After the proportioner inducts the concentrate, the foam solution passes through the nozzle, where it creates a vacuum to induct air and mix the air and solution internally to form foam.

#### 14.1.5.2 Vapor Suppression Characteristics

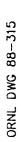
Foams have the ability to suppress vaporization when applied to a volatile chemical. Also, foam applied to the surface of a vaporizing chemical reduces the diffusion of air. The foam forms a barrier with a high resistance to both convective and molecular diffusion; it also has the ability to absorb vapors. Collectively, this results in a reduction in the concentration of the volatile components in the vapor space above the foam. The efficiency of vapor suppression depends on the vapor pressures and the solubilities in water of the vaporizing chemicals.<sup>52</sup>

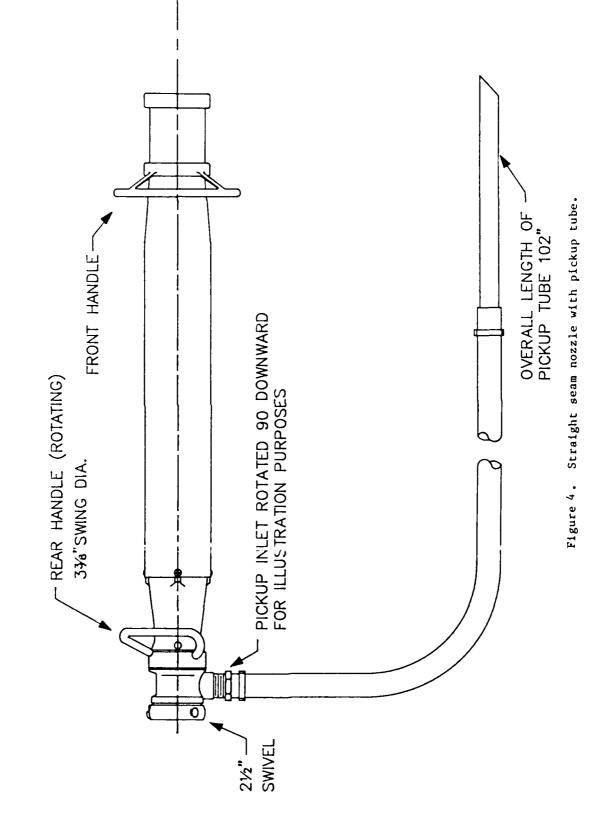
Three ways of mitigating vaporization can be attributed to foams:<sup>54</sup>

- 1. The foam blanket insulates the chemical from solar radiation and the ambient air, thereby reducing heat input, which in turn reduces vaporization.
- 2. The foam blanket physically suppresses vapors.
- 3. The foam blanket absorbs vapors.

As a spilled chemical vaporizes, the temperature of the chemical pool is lowered adiabatically. This results in a reduction of vaporization. If the spill is on land, the ground will initially serve as a heat source. The ground will quickly cool as the temperature of the chemical pool decreases and then aid in insulating the pool against the addition of heat from the ground. With foam, the pool is further insulated by blocking solar radiation and convective heat transfer from the surroundings.<sup>52</sup>

Foams lose their ability to suppress vapors due to aging or environmental effects (wind, temperature, humidity, or intensity of sunlight). If foam has lost its effectiveness, another layer of





foam must be applied to ensure the safety of response personnel. Foam can become saturated with vapors from the chemical and thus create the potential for ignition if the chemical is flammable.

#### 14.1.5.3 Types of Foams for Suppression of Toxic Vapors and Firefighting

Two basic foam types are currently available and in wide use by fire services: the protein-derived materials and surfactant- or detergent-based concentrates. Within the surfactant category there are two types of foams: hydrocarbon and fluorocarbon. The latter, marketed under the generic name of aqueous film-forming foams (AFFF), tend to be film formers rather than persistent foam formers. The AFFF foams are designed for fast knockdown of hydrocarbon fires. This film also impedes the escape of toxic and flammable vapors.<sup>46</sup>

Protein-base systems also have modifications. The fluoroproteins are combinations of fluorocarbon-surfactant materials with protein-base agents. The fluorinated surfactants have been added to improve properties such as fluidity and surface tension, while reducing the tendency of the protein base to absorb hydrocarbon liquids. The fluoroprotein foams demonstrate fast fire knockdown and long-term protection against the reappearance of flammable vapor concentration above a spilled liquid. The main uses of fluoroprotein foam are in hydrocarbon storage tanks. Fluoroprotein foams are available for 3 and 6% proportioning and can be used with fresh or sea water.<sup>55</sup>

The "alcohol foams" designed for use with polar compounds are normally protein-base types, although polar AFFF foams are now being made available.<sup>46</sup> The alcohol-type foams (ATF) are developed to extinguish hydrocarbon and polar solvent (water-miscible) fuel fires. They consist of an AFFF, regular protein-, surfactant-, or fluoroprotein-base concentrate with either a metal stearate additive or a polymer additive. When applied to polar solvents, the additive coalesces into a gel, forming an insoluble, low-permeability skin that inhibits vapor release. ATFs with a polysaccharide additive offer protection from polar or water-soluble chemicals.<sup>55</sup>

Foam concentrates derived from hydrolyzed protein are widely used in the control of hydrocarbon fuel fires. The regular protein foams are composed of animal protein containing

polyvalent cations and other stabilizing elements. They are the oldest of the firefighting foams. They display good resistance to reignition, poorer flowing ability, and slow fire knockdown for hydrocarbon fires.<sup>55</sup>

Protein foam systems have been long recognized by their ability to restrict vapor release.<sup>54</sup> ATF foams, when applied to polar solvents, form an insoluble, low-permeability skin that inhibits vapor release. ATFs have shown good results for the suppression of hazardous vapors.

#### 14.1.5.4 Commercial Foams

Available commercial foams have their own trade names but are equivalent to the general types of foams. National Foams offers two general classes of foam concentrate for firefighting: the regular protein-based type and the synthetic type.<sup>54</sup> National's NFPA 11, 11A, 11B, 409, and 16 define recommended minimum rates for most flammable liquid hazards. As a general rule, petroleum products, styrene monomer, benzene, and similar flammable liquids require a foam solution rate of at least 0.1 gpm/ft<sup>2</sup> for fixed systems where the foam can be flowed on, as from a chamber on a tank. Extinguishment of polar solvents such as alcohols, esters, ketones, aldehydes, etc., require a special type of foam because protein-based liquids and AFFF (aqeuous film-forming foams) are destroyed by these fuels.

National Foams also offers a "hazmat NF" foam series that is claimed to suppress vapors from hazardous material spills. They state that hazmat CHF-413 has been used very effectively to control anhydrous ammonia spilled into a pit. Vapor emission was reduced to the point that it was possible to stay nearby without breathing apparatus. National's CHF-784 foam was applied to suppress clouds of fumes coming from a tank that contained a dangerous mixture of nitric and hydrofluoric acids. An immediate reduction in fume evolution was apparent and it was then possible to add limestone to the tank without increasing fume evolution.<sup>56</sup> Experiments with National's CHF-784 produced a much greater reduction in vapor release than did those with fluoroprotein.

A new "stabilized" foam technology recently developed by the 3M Company is claimed to offer long-term suppression of hazardous, flammable and noxious vapors.<sup>57</sup> Using this technology, 3M has specifically designed products for both the hazardous spill and hazardous waste site markets.

Table 17 shows some chemicals whose vaporization can be suppressed by different foams. It includes foams that can be recommended for emergency response based on experience.<sup>55</sup>

## 14.1.5.5 Eoam Classification

Foam expansion is the volume of foam produced from a given volume of solution. For example, 10 expansion means ten volumes of foam from one volume of foam solution. There are three types of foams according to their expansion rate: (1) high-expansion foams, (2) medium-expansion foams, and (3) low-expansion foams.

#### Foam classification for firefighting

Low-expansion foams have expansions from 2 to about 15. These forms are useful for all types of flammable and combustible applications.<sup>15</sup> They are especially useful for controlling fires for fuels having a boiling temperature at or above ambient temperatures at atmospheric pressure. Test results show that low-expansion foams are useful for fires involving liquefied gases whose boiling point is only slightly below ambient temperature.<sup>16</sup>

Medium-expansion foams, which have expansions from about 15 to 100, show promise for spill firefighting.<sup>36</sup>

High-expansion foams range from 100 to 1000 or more. They are primarily for volumetric fill of areas that contain Class B fires where total flooding can be achieved and where low water damage can be tolerated.<sup>36</sup>

#### Foam classification for vapor mitigation

For vapor mitigation, low-expansion foams will provide the longest time delay before vapor breakthrough occurs. Low-expansion foams, by their nature, are less influenced by the atmospheric effects of wind, rain, or high temperature. However, they require larger volumes of water than high-

Product	Recommended	Satisfactory	Not recommended
Polat solvenis	Alcohol Joams		
Silicon (cirachloride) vapors	High expansion surfactant foams		
Octanoi	Alcohol	AFFF, fluoroprotein. protein	
LNG.	Surfactant H		AFFF
Vinvi acetate	Alcohol, fluoroprotein	AFFF	
Ethane	Surfactant H	Alcohol, fluoroprotein, protein, surfactant 1	
Ethylene	Surfactant H	Alcohol, fluoroprotein, protein, surfactant L	
Heptane	Alcohol	AFFF	
Octane	Alcohol	AFFF, fluoroprotein, protein, surfactant L, surfactant H	
Benzene	Alcohol	Fluoroprotein, protein, surfactant H	
Ethyl benzene	AFFF, fluoroprotein, alcohol, surfactant I.	Surfactant H	
Deface	Akohol, protein, Nuoroprotein	AFFF, surfactant L. surfactant H	
t valohevane	Alcohol.protein, fluoroprotein	AFFE, surfactant 1., surfactant H	
Gasoline	Alcohol, fluoroprotein, protein, surfactant H	AFFF	
Kerosene	Alcohol, fluoroprotein, protein, surfactant L	AFFF	
Naphtha	Alcohol, fluoroprotein, protein, surfactant L	AFFF	
Paint thinner	Alcohol, protein, fluoroprotein	AFFF, surfactant 1.	
Carbon disultide. Morganic	HAZMAT NF #2, MSA type V		
Hydrochloric acid	HAZMAT#2, MSA type V		
Ammonia	Surfactant H	AFFF, alcohol, protein, surfactant, fluoroprotein	
Ammonia anhydro	HAZMAT NF #1		
Friethylamine	Alcohol	Fluoroprotein	
Ethyl ether	Aconol		
n-butyl acetate	Alcohol	Fluoroprotein, AFFF. protein, low surfactant	
Methyl acrylate	Alcohol		
Cictane	Alcohol	Protein, fluoroprotein, low surfactant, AFFF	

Table 17. Recommended satisfactory toams based on experience

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Product	Recommended	Satisfactory	Not recommended
Benzene	Aiceboi	Protein, fluoroprotein, low surfactant, AFFF	
Cyclohexane	Protein, alcohol, fluoroprotein	Low surfactant, AFFF	
Ethylene oxide	Alcohol, polar liquid toams		
Vinvi chloride	Alcohol		
Atkaline spills	HAZMAL No. 1		
Void spills	HAZMAT No. 2		
Actylonitrile	Universal polar liquid toam		Regular protein
Vinvl acctate	Polar liquid toams. Nuoroprotein	4663	
Ethanol	Polar liquid toams		
Accione	Polar liquid toams		
Butane	Potar liquid toams	Eluoroprotein, protein	
Propulenc	l niverse		AFEE, protein. fluoroprotein

Table 17 continueds

expansion systems to effect a foam cover, and this can spread the spill or cause an overflow of impoundments.<sup>36</sup>

High-expansion foams use about one-half of the water volume required for the equivalent cover of low-expansion foams. Their use will be controlled by wind conditions, the containment of the spill, and the nature of the spilled material. With winds below 4.5 m/s, maintenance of an adequate high-expansion blanket should be possible. At higher wind speeds, some method of downward containment of the foam mass by fencing or other structure will be necessary.<sup>46</sup>

#### 14.1.5.6 Equipment to Produce Foams

Both low- and high-expansion foam equipment is available in fixed and portable units. Lowexpansion generators come in several forms: playpipes, applicators, air nozzles, etc. In each, the basic mechanism is the same air mechanically entrained into a foam solution by agitation within a nozzle system. Unit sizes range from as low as 5 gal to 4000 gal/min. The larger sizes are primarily marine monitors for shipboard use. In each type of system, output and foam projection are a function of water flow and pressure. The critical factor involves matching foam agent input to water flow so that an acceptable foam is made.<sup>56</sup>

#### Low-expansion equipment

Industrial equipment is offered by several foam manufacturing companies. For example, National Foams offers a large variety of nozzle and monitor combinations for use with virtually any flammable liquid hazard.<sup>54</sup> One of the simplest models is the "Model PC-31 Nozzle" that is available for producing a straight stream only or for a straight stream with spray attachment. It delivers 310 gpm at 150 psi. A pickup model for foam concentrate proportioning (with a fixed orifice, 3 or 6%) permits the PC-31 to be attached by its 2.5-in. female swivel connection to any existing water monitor, deluge gun, or hose. Foam concentrate may be supplied through the pickup tube from 55-gal containers.

When monitor-mounted nozzles of larger capacity are required. National Foams offers a range from 900- to 4000-gpm nominal flow rates at 150 psi inlet pressure.<sup>51</sup> The PC-90 through -200

series are available with either manually operated or hydraulically operated spray control. Figure 5 shows one of these models.

There are also mobile units (see Fig. 6). This type of unit is towed to the hazard area, and a fire hose is connected to the nearby foam truck or other suitable proportioning source. These units are available in 3-in, and 4-in, sizes for a range of flow rates from 150 to 1000 gpm.<sup>54</sup>

Technology developed by 3M illustrates the use of a typical stabilized-foam application system. It involves premixing a proprietary surfactant-based temporary foam concentrate at a 6% concentration in water and passing the pressurized premix through a hose line. A proprietary 3M agent is then injected or educted at about 6% concentration into the temporary foam concentrate. A stabilized foam is subsequently produced by passing this stream through a conventional air-aspiring or air-injecting foam nozzle. Immediately after generation, the stabilized foam exhibits the same fluidity as its precursor temporary foam, but within 1 to 4 min (depending on the temperature) transforms into a tough, elastomeric, nondraining foam. Stabilized foam systems have been formulated which exhibit excellent long-term vapor suppression over a wide variety of chemical hazards.<sup>56</sup> Low-expansion foams can be discharged for maximum distances of 30 to 200 ft, depending on the nozzle size and pressure used. These distances can also be achieved by using an eductor; however, water pressure must remain constant at the junction to the eductor. In general, foams should be directed to a point just in front of the spilled chemical or to a wall behind the spilled chemical. This ensures that the foam will flow across the surface of the chemical and maintain its structural integrity. The application rate of low-expansion foam for vapor control is not as critical as that for high-expansion foams because low-expansion foams can be applied rapidly with respect to mass time.56

# High-expansion foam equipment

High-expansion foams are made by spraying a foam solution against a screen while applying

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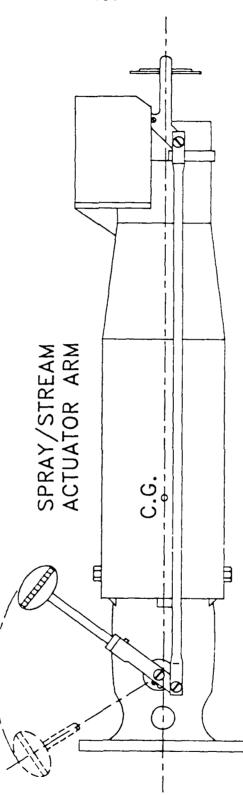
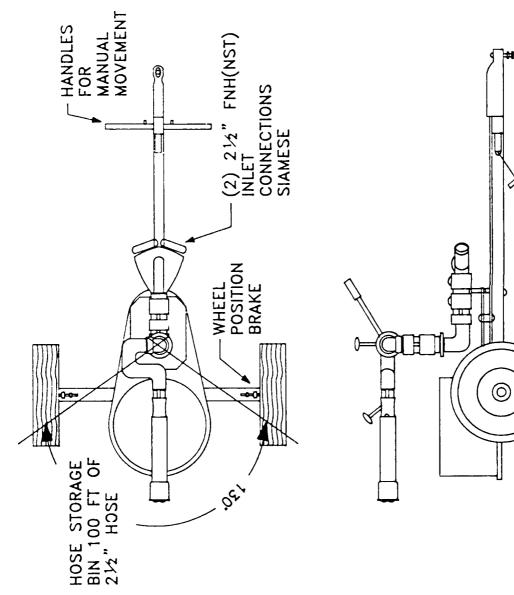


Figure 5. Manually operated spray nozzle.





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Figure 6. Roamin' Chariot.

blowing air from behind the screen. Foam generators range in size from 100 to 55,000 cfm output. The smaller units are usually the air-aspirating type of generators. In this form, there are no moving parts. The foam solution is forced at high pressure against the foam screen. The force of the water spray aspirates sufficient air to form foam. Since air aspiration is an inefficient process, expansion ratios are, by nature, on the low end of the high-expansion range. Small units start near 100:1, but even the larger, 1000-cfm unit does not exceed 450:1.<sup>46</sup>

With blower-type devices the water-foam solution is discharged onto the screens through which an air stream, developed by a fan or blower, is passing; as the air passes through the screens, wetted with foam solution, large masses of bubbles or foam are formed. The blower may be powered by compressed air or gas, by an electric motor, by an internal combustion engine, or by a hydraulic or water motor. This type produces foam of expansion up to 1000:1.<sup>59</sup>

Small air-aspirating units can produce up to 1000 cfm of foam and can be operated using a hose line. Portable or wheeled units operating off hose lines are available at outputs up to 6000 cfm. A few trucks have been built with 12,000-cfm water-driven units mounted integrally. Water pressures from 40 to 80 psi are required, with the higher pressures needed for water-driven units.<sup>46</sup> High-expansion foams must be directed onto the spill using a foam chute or other conveying device. The depth is sufficient to keep the concentration of most vapors beneath or within the lower explosive limit.

#### Medium-expansion foam equipment

The flooded plate generators have application in medium-expansion foams. A perforated metal plate is mounted midway in a rectangular enclosure. The plate surface is channeled with foam solution flowing down the channels. Air is introduced underneath the plate to generate the foam. Output and expansion are controlled by the size and distribution of the perforation, the rate of solution, and the air flow into the generator. Flooded-plate generators have application in that they are able to produce foams in the range of 100 to 200:1 with solutions too viscous to be suitable for normal high-expansion generators. Thus, medium-expansion foams can be made from solutions

containing high percentages of water-soluble polymers. This results in highly stable, slow collapsing, slow-drainage foams. The flooded plate can also be used where high percentages of solids have been slurried into the solution.<sup>46</sup>

### 14.1.5.7 Firefighting Foam Generation Equipment

Foam is generated with regular firefighting equipment using special air-aspiration nozzles or foam-generating equipment. For good-quality foam, the foam concentrate and the water must be mixed to form a homogeneous solution. If this is not accomplished, the resulting foam will have a poor bubble distribution, which will affect the efficiency of the vapor suppression.<sup>52</sup>

Foam should be applied indirectly to the spilled chemical surface to avoid mixing of the foam and chemical. With the use of a backboard, foam can be gently applied to the chemical. Foam generated the first 15 to 30 s of startup should not be used because it is poorly mixed and, therefore, its ability to suppress vapors is reduced.<sup>53</sup>

High-expansion foams are thinner than low- or medium-expansion foams and thus are more vulnerable to the wind. A 9-mph wind can displace a high-expansion foam layer of 4 in. A 5-mph wind can displace a 6-in. foam layer.<sup>55</sup>

# 14.1.5.8 Applying Vapor Suppression Foams

Assuming there is no fire and that the foam type is compatible with the spilled material, vapor suppression foam will be destroyed at a low rate, thus making the application rate less critical. However, response organizations should attempt to cover a spill as gently and as rapidly as their equipment will allow without creating turbulence because release of toxic and/or flammable gases will continue until the entire area is covered.

# 14.1.5.9 Quantitative Vapor Suppression by Foam

Experimental results using several foams on different chemicals are shown in Table 18. For

Chemical	. <b>.</b>	Total suppression time (min)
Toluene	Emulsiflame 2%	11
Cyclohexane	Emulsiflame 2%	20
Ethylbenzene	Emulsiflame 2%	11
Cyclohexane	Lorcon Full-Ex 2%	22
Benzene	Lorcon Full-Ex 2%	25
Toluene	Lorcon Full-Ex	40
Ethylbenzche	Lorcon Full-Ex	40
Cyclohexane	MSA Ultrafoam 2%	100
Benzene	MSA Ultrafoam 2%	40
Toluene	MSA Ultrafoam 2%	60
Ethylbenzene	MSA Ultrafoam 2%	100

# Table 18. Total vapor suppression time (20 in. of foam)

up to 20 min, ethylbenzene up to 11 min, etc.52

Other experimental data results show Rohm & Haas ASE 60/MSAR surfactants persisted for approximately 25 to 30 min when controlling  $N_2O_4$  vapors. The Rohm & Haas ASE 95 (polyacrylic)/MSAR surfactant persisted for more than 2 h when controlling amine fuel vapors.<sup>60</sup>

Data for the reduction of vaporization have also been collected.<sup>57</sup> Reduction in vaporization is measured as the ratio of actual concentration (using foam) with respect to the monitored concentration of free vaporization (no foam). Results are shown in Table 19.

## Flammability suppression by foam

Experimental data have been developed to determine the secure time to reach the lower explosive limit (LEL) (fixed at 20%) as a function of the depth of foam. For example, data utilizing alcohol-type concentrate (ATC) foam (6%) are shown in Table 20. In summary, these quantitative data indicate that substantial improvements in vapor suppression of many toxic chemicals must be achieved before this method can be considered as a viable countermeasure to hazardous chemical spills. Also, foams are useful only for releases of volatile liquids where the toxic or flammable vapors are evaporating to form a vapor cloud. In cases where very volatile materials have been released, the foams are useless since a vapor cloud is formed immediately and reduction of the vaporization rate is not possible.

#### 14.2 EMERGENCY EQUIPMENT

#### 14.2.1 Chlorine Emergency Kits

Severe exposure can occur whenever chlorine is handled or used. A person making or breaking a chlorine connection should have a suitable escape-type respirator immediately available. The following types of equipment are available:

1. Self-contained breathing apparatus is suitable for high concentrations of chlorine, and it is the preferred means of respiratory protection for the usual chlorine user. It provides protection for

Remical	Foam type		n (min)
Amronia	Komets Extract	50	120
Ammor: i kB	National Foams	55	120
Acrylonitrile	Universal Polar (10%)	50	40
Carbon	Universal (10%)	95	40
disulfide	Aer-O-Foam (3%)	90	40
	Aer-O-Foam Water Plus	90	40
	XL-3	75	75
Ethylene	PSL 10%	50 avera	ige 120
oxide	Universal	50 avera	ige 120
	Aer-O-Water Plus	40-50	120
Methvl	Universal (10%)	50	90
acrylate	Polar Liquid A	50	90
	PSL 10%	40	90
	Polar Liquid B	40	90
Ethanol	Universal (10%)	50	60
	PSL 10%	50	120
Vinyl acetate	Universal 10%	60-70	60
	PSL 10%	60-70	60
	Aer-O-Water Plus	40-50	60
Acetone	Universal 10%	40-50	40
	PSL 10%	80-60	40
Butane	PSL 10%	50	100
Propulene	Universal	40	10

# Table 19. Reduction in vaporization

Chemical	Secure time (min.)	Depth of foam (in.)
Dioxane	60	2.0
IPA	60	3.0
Acetic acid	60	3.5
Ethanol	60	3.7
Isopropyl ether	60	5.3
Heptane	60	5.6
МЕК	60	6.1
Toluene	60	6.5
Methanol	60	7.0
Ethyl acetate	60	7.8
THF	60	10.2
Acetone	60	10.5
Butylraldehyde	60	11.2
Aniline	30	2.0
Chlorobenzene	30	2.0
Butyl acetate	30	2.0

Table 20. Depth of foam to achieve a secure time (Alcohol-type concentrate, 20% LEL) a period that varies with the amount of air, oxygen, or oxygen-producing chemicals carried by the apparatus.

2. A hose mask having a full facepiece and with air supplied through a hose from a remote hand-operated blower is suitable for high concentrations of chlorine. The blower air supply must be free of air contaminants.

3. An industrial-canister-type mask, with a full facepiece and a chlorine canister, is suitable for moderate concentrations of chlorine, provided sufficient ambient oxygen is present. The mask should be used only for a relatively short exposure period.

About 30 years ago, a study of chlorine industry incidents revealed that a great majority of chlorine container leaks involved leaking valves, valve packings, gaskets, and similar equipment.<sup>46</sup> In response to this situation, the chlorine industry developed emergency kits. Kits for cylinders, ton containers, and tank cars were first made available. Today there are three standardized emergency kits for use with chlorine containers. These include the A kit for 45-kg (100 lb) and 68-kg (150 lb) cylinders, the B kit for 908-kg (ton) containers, and the C kit for railroad tank cars and highway trailers.

Emergency kit A for cylinders contains a clamp to control fusible-plug leaks, a hood to cover a leaking valve with means to hold it in place, and a patch to control leaks from small holes in the side of a cylinder. Emergency kit B for ton containers contains a hood to cover a leaking valve and a beam to hold it in place, a hood to cover leaks in a fusible plug, and a patch to control small leaks in the side of the container. Emergency kit C for tank cars and tank trucks contains an angle-valve hood, a safety-valve hood, and a beam to hold either hood in place against the manway cover, thus preventing leakage through the valve or the joint between the valve and the cover. There are no parts to handle leaks in the tank itself. All kits contain wrenches and other tools, but no respiratory equipment is included.

# 14.2.2 Commercially Available Off-Loading Pumping Systems

When a toxic or flammable liquid material is released during a spill, off-loading of the remaining contents of the tank or carrier is often one of the major mitigation procedures used. Also, if a patch or plug can be applied to stop the leak, this procedure is used to prevent further release and permit repair or disposal of the vessel.

Submersible pumping systems for off-loading petroleum products or for dewatering operations are commercially available. These pumps can be used for low-volatile hazardous materials; however, their application would probably not be practical for high-volatile materials.

The following list includes ten commercial pumps:

ADAPTS (Air Deliverable Anti-Pollution Transfer System)	The prime mover is a lightweight diesel- hydraulic unit of approximately 40 hp. The pump is a two-stage, mixed flow, 10-in. Byron Jackson with integral hydraulic motor.
APTS (Anti-Pollution Transfer System) STOPS (Self-Contained Tanker Off-Loading Pump System)	This is a lighter commercial version of ADAPTS, and it is single stage. This is almost identical to APTS.
Prosser 25-hp Pump	This is a 25-hp electrically driven pump with modified impellers to increase the flow rate when pumping high-viscosity oils.
Prosser 40-hp Pump	This is a 40-hp electrically driven pump similar to the 25-hp model.
Marco U100 Capsulpump	This is a pump of centrifugal design, which is rated at 28.4 hp and is hydraulically driven.
Sloan Model 6 Mixed Flow Pump	This is a mixed-flow pump, which is hydraulically driven and is rated at 90 hp.
Framo Model TK-4	This is a hydraulically driven pump, which is rated at approximately 60 hp. It is designed for emergency lighting.
Framo Model TK-6 Moyno Rotary Screw Pumping	This is a hydraulically driven pump, which is rated at 227 hp. This pump is capable of pumping No. 6
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oil without preheating; it is hydraulically powered at approximately 80 hp.

Hot Fluid Spray System

A hot-oil spray heating system (for use with centrifugal pumps) to reduce the viscosity of heavy oils, which is under development.

Removal of spilled material from groundwater often involves the use of separators and holding tanks. Skimming devices and pumping systems specially designed and constructed for the materials being handled should be utilized whenever possible. When this equipment is not available, the contaminated groundwater can be pumped into collection trenches or pools equipped with an impermeable liner or barrier. Vacuum equipment, such as a surface skimmer or pump and hose, may then be used to separate material in the trench or pool. In some cases, material from the trench or pool could be pumped into a gravity separator erected on-site. Water from the separator can be discharged to a wastewater treatment plant.<sup>61</sup>

#### 14.2.3 Inert-Gas Systems

Fire and explosions can be prevented by the creation of an atmosphere that will not support combustion by reducing the oxygen content of the normal air (contains 21% oxygen). The fire and explosion hazard of many materials can be safeguarded during storage and processing operations by the use of a suitable inert gas since combustion of most materials will not occur if there is an absence of atmospheric oxygen or if its concentration is reduced below certain specific limits. Typical examples are its use to make tanks inert prior to repair, to empty flammable liquid storage tanks by pressure, to prevent the formation of explosive mixtures in drying ovens, and to blanket flammable products in storage tanks or reaction equipment.

Any inert gas may be used for this purpose, but consideration of availability and costs limits such use to carbon dioxide, nitrogen, and mixtures of carbon dioxide and nitrogen produced by combustion (as in flue gas, internal combustion engine exhausts, and other inert-gas producers).

Other gases, such as argon, helium, and the chlorinated or fluorinated hydrocarbons (Halons), may satisfy special needs. In the fixed-volume method of application, the system to be protected is purged and the atmosphere is rendered inert by first reducing the pressure and then introducing inert gas. In the continuous method of application, the inert gas is added continuously in an amount sufficiently to supply peak requirements.

Inert gas from the internal-combustion engine type of producer consists of 13 to 14% carbon dioxide, zero oxygen, a trace of carbon monoxide, and the remainder nitrogen. The inert gas from this type of producer is stored under a pressure of 100 to 125 psi. Consideration must be given to the location and installation of producers, particularly of the flame type, in order not to introduce fire and explosion hazards.<sup>62</sup>

Carbon dioxide or nitrogen in cylinders is probably the best source of inert gas for small plants, or where the systems are of small volume and loss through leakage is relatively small. Carbon dioxide fire extinguishers should not be used since they are designed to discharge a liquid rather than a vapor.

Another inert gas can also be obtained by the catalytic oxidation of ammonia with air which forms NO gas. A further means of obtaining inerting media is by the liquefaction of air with subsequent fractionation to produce nitrogen. Package units of various capacities using this method are now commercially available.

#### 14.2.4 Patching and Plugging

Patching and plugging are methods used to prevent or reduce the discharge of hazardous chemicals from most types of chemical process equipment. Table 21 lists the results of a survey of patching-plugging techniques prepared by Battelle Memorial Institute.<sup>63</sup> The most promising conceptual approaches  $c_1 \Rightarrow -2$  listed in Table 3.12 proposed for development included the following:

Tech, name	Description
- Composite foam plug	A probe with an applicator tip consisting of a thin sheath of semiporous (silicone) or non- porous (polyurethane) rubber into which is injected a self-expanding polyurethane foam
Putty	A rigid concave form that provides temporary mechanical support for a putty (epoxy) patch until the patch material hardens. The putty is injected through the tubular handle on the form.
Folar Technique	Same as putty, except that polyurethane or polystyrene feam is substituted for epoxy putty
Wooder patch Decured by: Stud gan Bolts Exampts Suction cups Adhesives	Rigid plywood sheets placed over the damaged area and held in place as indicated; patch is made leak-proof with the gasketing material of foam/solid rubber or epoxy putty material
Tosted-fabric patch	Various fabrics such as neoprene, vinyl, or Hypalon-coated nylon placed over damaged area and held in place with explosively driven studs
Magacts (strips)	Can be located along the periphery of the coated fabric patch; molded suction cup seal strip, permanently bonded to the periphery of the fabric patch could also be used to hold the patch in place; other methods of holding the patch in place include bolted patches, adhesives, patches, etc.
Michanical patch	"Unbrella type", a coated-fabric rib-stiftened expandable patch, configured similar to an ordinary umbrella; the folded patch is inserted through the damaged hole and opened manually; a backup board and butterfly nut allow the patch to be pulled tightly against the inside surface of the damaged area.

Table 21. Patching-plugging techniques

# Table 1 . . . . . . inued)

1 - <sup>1</sup> - tratte	Description
Mesilari al'alsat Song	Frown as the "Magnetic Damage Control Blanket," It is a 9.045-in, thick layer of flexible permanent magnetic material made of subbers bended barium fermite composite, backed by a last? Sin, sheet of steel foil, which increases the physical strength of the blanket and increases its magnetic adherence
	Constant fabric on the informed heavy reflect Follows elike device which, in its deflated tate, is interted into the farated apening and inflated with gas to form a play.
one notaratin gaatoin Sono ootointeatoo aloo	A reated-fubric patch with a car-failated real permanently attached to the perichery of the patch: the patch is attached to the hull with hereing line out explosively drive astudy
ana da seria da an 1990 - Alanda 1990 - Alanda 1990 - Alanda Patrice a	Appelie ation of coastining seaterials lighted to Line of the enclosed
and later toget	Marina Diri applebed radie of wort april i to conactro car Terato
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	4. In the Point of the New Second first the expression from plant, in 1996 a low compare creation and twatering particulation in the Point of Second First Colleaped particulation of the parameter contract of Second pullifier as large and other calles first the theory of the expland.
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## Table 21 (continued)

Tech same	Description
Explosive pipe pincher concept	C clamp-shaped device that produces local deformation and flattening of a pipe with an explosively activated ram, thus pinching off the fluid flow
Hydraulic pipe pincher concept	As before except ram is activated by hydraulic cylinder and manual hydraulic pump
Bolted split clamp pipe repair	A split sleeve type coupling with bolted flange-type assembly; used to cover damaged areas of pipe
Velero "bandaíd"	A coated pipe patch using a Velero fastemer and an integral inflation blader in the manner of a medical doctor's blood pressure measuring device; the patch is wrapped around the damaged pipe and secured in place with the Velero fastemer

1. coated fabric patches applied by a stud gun or suction cups,

2. for leak stoppage,

3. air-inflated plugs,

4. hydraulic pipe-pincher concept for emergency shutoff, and

5. a Velcro "bandaid" concept for leak stoppage,

An explosive pipe-pincher concept also appears promising for small-diameter pipes from the standpoint of rapid installation and activation during emergencies releases. No vendors have been found for such a device, but the components are available and have been applied in the aerospace industry.<sup>64</sup> Another promising concept concerns the installation of explosive actuators on lever-operated block valves in critical chemical facility pipelines. Instantaneous closure of such valves could be achieved, particularly when the valves are located in remote locations. Technical Ordnance, Inc. (Minneapolis, Minnesota) produces a line of explosive actuators that could be employed for such an application; valve size would not be limiting since the force required would be very much lower than that required to pinch off a pipe or tube.<sup>54</sup>

#### 14.2.5 Response and Communications Equipment

An inventory of equipment of fire control, spill control, and decontamination should be included in an emergency plan. Some key pieces of equipment are booms, sorbent materials, detoxifying materials, fire-fighting equipment, alarm systems, and emergency telephones. All emergency equipment should be regularly tested and inspected, and appropriate records should be maintained.

An emergency converted "motor home" response van useful for providing fast initial response has been described by Lee.<sup>65</sup> Employment of this system could aid in the identification of released material, assessment of the incident, and initial containment and control of the incident until an industrial or government team arrives for containment and cleanup of the incident. This response unit will also handle the total management of small-scale incidents, if necessary. The unit must be staffed with trained professionals available on 24-h call. The unit should be fully loaded, equipped,

and self-contained.

The hazardous materials response unit should be a van that has the following equipment as a minimum: (1) monitoring equipment; (2) goggles and masks; (3) plugs and tools; (4) gloves; (5) first aid kit: (6) patching materials; (7) lights, water, and foam equipment; (8) tool storage; and (9) library, files, and desk.

The inventory of such a unit may comprise the items in Table 22, which are carried by the Houston Fire Department Hazardous Materials Response Vehicle.<sup>55</sup>

14.2.6 Equipment for Fires

The following classifications of fires are used for the selection of fire extinguishers:

<u>Class a</u>. Fires involving ordinary combustible materials (such as wood, cloth, paper, rubber, and many plastics) requiring the heat-absorbing (cooling) effects of water, water solutions, or the coating effects of certain dry chemicals which retard combustion.

<u>Class B</u>. Fires involving flammable or combustible liquids, flammable gases, greases, and similar materials, where extinguishment is most readily secured by excluding air (oxygen), inhibiting the release of combustible vapors, or interrupting the combustion chain reaction.

<u>Class C</u>. Fires involving live electrical equipment where safety to the operator requires the use of electrically nonconductive extinguishing agents.

<u>Class D</u>. Fires involving certain combustible metals (such as magnesium, titanium, zirconium, sodium, potassium, etc.) requiring a heat-absorbing extinguishing medium not reactive with the burning metals.

Some portable fire extinguishers are of primary value on only one class of fire; some are suitable for two or three classes; none is suitable for all four classes of fires.

Most currently manufactured extinguishers are labeled with a classification system so that users may quickly identify the class of fire for which a particular extinguisher may be used. The

Telly 22. Epigment and supplies carried on the Houston File Department Hazarbus Materials Response Vehille

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B. Energen y manualz

SFFA HM Carle Firefighters Handbock of HMs 2 H R I & Manual Energeniv Anti D Guile Farm Cherrials Handbock MAIX Tank Gir Manual Langer up Frigerties of Infortrial Materials Re Confirme and Management of Henry Tata Cherts Catety data Cherts

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Met 1 X extinuoushess
Met 2 Extinuoushess

1 <u>El mis poper t</u>

High-expansion fram generators AFFF volutions Frothin fram educators and mozzles

F. <u>Eligs and Patches</u>

CElerine Kits (A. E. and C Kits) Flart: Fags EE tank ar sing tryeto EE wild far glug

F. Erste tive epipment

irecoure lemand JIEA @rett 4 % and Type II, and and line) Acti souts Safety Larness bortable eye wash Terminal glove, kan souts Suggles Ear po tectors G <u>Supplies</u>

Lead wool T-bolt patches Toggle helts Sheet metal screws Pressure-sensitive tape Wester plugs Rubber stoppers Stainless pipe clamps Duct tape Quick-spray adhesive Foaming patch kits Red-rubber gasket material Neoprene gasket material Sheet lead Epexy kits Filerglass cloth Bungs and plugs Epoxy putty Duct sealing compliand File plugs (4 in. to 10 in. Coclamps (2 in to 3 in ... Silicone seal Form-argasket EB 35 sealant Stainless hose clamps Gas-line clamps High-expansion foam (25 gal) Protein foam (25 gal) Hydrocarbon emulsifier (30 gal) Sand (600 1b) Soda ash (300 lb) Dike Fak kits

H. <u>Tools</u>

Drum truck Air bags Wrenches and other small tools Vise and pipe cutter Jacks and chains Prace and bits Entrenching tools Chain hoists Ground rods Grounding and bonding cables

:\*:

classification system is contained in the NFPA Extinguisher Standard, which gives the applicable class symbol with supplementary words to recall the meaning of the letters.<sup>59</sup>

Numerals are used with the identifying letters for extinguishers labeled for Class A and Class B fires. The numeral indicates the relative extinguishing effectiveness of the device. For example, on an extinguisher rated for Class A fires, the rating and numeral that precede the letter "A" indicates the size of standard test fires the device is able to extinguish successfully under reproducible laboratory conditions. On an extinguisher rated for Class B fires, the rating numeral that precedes the "B" gives a proportionate indication of the maximum square foot area of a flammable liquid fire of appreciable depth (1/4 in.) which can be protected.

No rating numerals are used for extinguishers labeled for Class C fires since electrical equipment has either Class A or Class B combustibles, or both, as part of its construction.<sup>59</sup>

#### 14.2.6.1 Special Systems and Extinguishing Techniques

There are certain extinguishing and control systems, agents, devices, and techniques that are used with varying degrees of success when the fire category is not very common. These include: (1) systems using water or water solutions for particular fire control needs, (2) combustion gases used for extinguishment, (3) air agitation for oil tank fire control, (4) agents and techniques for controlling fuel and chemical spills, (5) steam-smothering systems, and (6) combined-agent systems.

## 14.2.6.2 Water or Water Solutions

Comprising the specialized systems utilizing water or water solutions, we have the ultrahigh-speed water spray systems, which are designed to handle extremely rapid fires of the type that can occur in the handling of solid propellants, sensitive chemicals, and any industrial process or oxygen-enriched environment possessing this type of fire potential. The wetting-agent systems (meeting the requirements of NFPA No. 8, standard for wetting agents) can utilize standard water spray, sprinkler, or foam system equipment. The viscous water systems may have the following basic systems for ground applications:

1. <u>Injector-recirculating ground tanker system</u>. This consists of a centrifugal pump and an injector-dispenser where the liquid and dry powder combine and flow into the tank.

2. <u>Demand viscous water tanker-mixer</u>. This consists of an auxiliary mixing tank, an auger feed mechanism, and a positive-displacement rotary meter acting as a power unit for the feed system.

3. <u>Slip-on chemical tanker-mixer</u>. This consists of a skid-mounted, all-metal unit for mounting onto a heavy-duty tractor-trailer for off-road assignments.<sup>59</sup>

#### 14.2.6.3 Air Agitation for Control of Oil Tank Fire

Under some conditions, a fire in an oil storage tank may be controlled or extinguished by introducing air under pressure near the bottom of the tank. The principle is founded upon the fact that flammable and combustible liquids require a temperature greater than their flash-point temperature to sustain burning. If a tank of oil having a flash point above the actual temperature of the liquid itself becomes ignited (when the temperature at the surface is raised above the flash point), the resulting fire may be controlled or extinguished by agitation of the oil mass. By agitating the oil mass, cool oil, circulated at a proper rate, decreases the temperature of the oil burning at the surface by displacement and mixing to a point below its flash point, thus slowing or inhibiting further combustion. This technique is not considered a standard method of combating oil tank fires.<sup>59</sup>

#### 14.2.6.4 Handling Spilled Fuels and Chemicals

Emulsifying agents-detergents have been used with varying degrees of success in extinguishing or controlling flammable liquid spill fires either on land or on water. A major problem with the use of emulsifying agents and detergents in lakes, rivers, harbors, etc., is that the resulting emulsions often have a more severe effect on aquatic forms of life than does oil alone.<sup>59</sup>

#### 14.2.6.5 Steam Smothering Systems

The principle by which steam may smother a fire is similar to the manner by which inert gases may achieve the same result (e.g., reducing the concentrations of oxygen and/or the gaseous phase of the fuel in the air to the point where combustion stops). The use of steam systems for fire extinguishment precedes the use of other modern smothering systems such as carbon dioxide and foam extinguishing systems and is rarely used today. It is clearly not a practical method to employ except in cases where a large steam supply is continuously available or where arrangements have been made so that this supply can be effectively and efficiently tapped when a fire emergency arises. The possible personal injury hazard of burns must be considered in any steam extinguishing installation.

Steam smothering systems used to be employed for the protection of cargo spaces and the holds of steamships. However, this method is no longer recommended. Tests indicating the relative inefficiency of such systems to control cotton cargo fires were conducted by the U.S. Coast Guard during the period 1944-1946.<sup>59</sup>

#### 14.2.6.6 Combined-Agent Systems

It is common practice in firefighting to use two or more agents simultaneously or in rapid sequence. Some common combinations used in manual fire control work include: (1) water and foam, (2) carbon dioxide and foam, and (3) certain dry chemicals and foam.<sup>54</sup>

## 14.2.7 Labels and Placards

Hazard labeling is a common governmental approach to warning the public of that hazard, and most federal agencies employ one form of labeling or another. Specifications for the appearatice of the labels are very particular and include the size, shape, hazard symbology, color, and written legend. Each label must be at least 4 in square and must be oriented on the package with the point up, giving the square a diamond configuration. Each label must have a solid line border at

least 3.5 in, long on each side. Except when having an outer border consisting of a dotted line, each label on a package must be on a background of contrasting color.<sup>46</sup>

The basic elements of the label are: the color, which is carefully prescribed in the regulations and is also part of the international labeling system; the symbol, which gives the name of the primary hazard of the product; and the verbal message or legend, which gives the name of the primary hazard for which the material is classified. The proper names and corresponding colors of today's labels are listed in Table 23.

Motor vehicles and freight containers containing 1000 lb or more (gross weight) of the hazardous materials classes are listed in Table 24 and must be placarded.

## 14.2.8 Personal Safety Equipment

### 14.2.8.1 Protective Clothing

The selection of items of protective clothing depends on the level of protection desired for emergency response personnel. The specific items that are available are boots, gloves, safety glasses, goggles, face shields, hard hats, aprons, splash suits, and fully encapsulated suits with independent air sources. Depending on the identity of the hazardous material spilled, the level of protection to prevent physical harm can vary from a minimum of boots, gloves, and hard hats to a maximum of a totally encapsulated suit. Selection and purchase of protective clothing depend on the behavior of the clothing's material when challenged by a spilled chemical.<sup>46</sup>

#### 14.2.8.2 Clothing Selection

The necessary protective clothing and equipment should be selected based on the assessment of the materials involved and the relative hazards and risks. Four types of clothing related to the needs of the fire-fighter are listed:<sup>\*\*</sup>

1. <u>Firefighter's protective clothing</u>. Full protective clothing for use at hazardous material emergencies is not the same as full protective clothing used in structural firefighting. According to NFPA,<sup>26</sup> full protective clothing is "protection to prevent gases, vapors, liquis, and solids from

Talle 23	Names and	colors	of	current	labels
	for hazardous materials				

Label Lame	Colors
	Grange, with a bomb-burst symbol: inscription and border in black
Numflammable gas	Green, with cylinder symbol, inscription, and border in black
Flammable gas	Red, with flame symbol, inscription, and border in black
Flammable light	Red, with flame symbol, inscription, and border in black
Slavnable solid	White, with vertical "candy stripes" in red, and with flame symbol, inscription, and borler in black: the words "Flammable Soli: must not touch any red stripe
lar Hizer	Yellow, with "flaming doughnut" symbol, inscription, and border in black
Organic jeroxide	Yellow, with "flaming doughnut" symbol, inscription, and border in black
Forson	White, with skull-and-crossbones symbol, inscription, and border in black
liritant	White, with no symbol, but an inscription on red and border in black; for import and export, the "Irritant" label may be white, with a skull-and-crossbones symbol and border in black
Aasiva tive White (	White, with radioactivity symbol, ins ription, and border in black, with a single overprinted vertical bar in red
Radicactive Yellow II	Upper half yellow and lower half white, with radioactivity symbol, inscription, and border in black, and with overprinted double vertical bars in red
kałichticy Yellow III	Upper half yellow and lower half white, with radioactivity symbol, inscription, and border in black, and with overprinted triple vertical bars in red
S ∶rosive	Epper half white, with Teaten hand" and metal Far symbols in black, lower 3-in. Aimension in black, with inscription in. white and outer 1/4-in. in white; dotted-line border in black
J} ntane uslv Jerattille	Typer half white and lower half red, with flame symbol, inscription, and border in black
Catigetto to wet	Blue, with flame symbol, inscription, and forder of the Y

Hazard classes	Class No.
Class C explosives	- · · · · · ·
Blasting agents	1
Nonflammable gas	÷,
Nonflammable gas (chlorine)	•
Nonflammable gas Oxygen, pressurized liquíds)	ý.
Flanmable gas	
Tombustible liquid	• •
Flammable liquid	
Flammable solid	• •
Gxidizer	
Organic peroxide	1.
Polson B	1.0
Corrosive material	1
Urritating material	18

Table 24. Hazardous materials classes for transportation

coming in contact with the skin." This includes the helmet; coat and pants; rubber boots; gloves; bands or duct tape around legs, arms, waist, and facepiece; as well as covering for the neck, ears, and other parts of the body not protected by the helmet, breathing apparatus, or face mask. This definition takes into account more protection that is normally considered as full protection by firefighters - and a great deal more than that normally provided for EMTs. Common firefighter's protective clothing does not previde adequate protection against chemical permeation or degradation due to chemical exposure. It may offer limited protection against solid materials and liquids; however, it is ineffective against gases and vapors.

2. <u>Nonencapsulating chemical protective clothing</u>. Chemical hazards and the potential harm from their release may require that specialized protective clothing be worn. Nonencapsulating chemical protective clothing is specialized clothing that does not offer a single, integral level of protection. It is commonly found as single-piece coveralls and two-piece overalls or pants worn in conjunction with a jacket.

Many different clothing materials are available, including neoprene, butyl rubber, polyväryl chloride (PVC), and chlorinated polyethylene (chloropel)."

3. <u>Encapsulating chemical protective clothing</u>. Encapsulating suits are specialized protective clothing that, when used with air-supplied respiratory protection devices, offers full-body protection trom a hostile chemical environment. Criteria for using these suits include:

- (a) When extremely hazardous substances are known or suspected to be present and skin contact is possible (cvanide compounds or toxic and infectious substances).
- (b) For potential contact with substances that destroy skin (corrosives).
- (c) For operations involving unknown or unidentified substances and requiring emergency response personnel. Common suit materials include butyl rubber, polyvinyl chloride, Viton, and chlorinated polyethylene (chloropel). In addition, disposable encapsulating suits constructed in Tyvek R, Saran R, and polyethylene coated or Saran-laminated Tyvek are available. Butyl rubber is compatible with approximately 70% of the chemicals listed.

4. <u>High-temperature protective clothing</u>. Specialized high-temperature protective clothing is used in situations where response personnel must operate in high-heat-flux and high-temperature environments and large flammable liquid and gas emergencies that exceed the protection factors of structural firefighting equipment.

Two types of aluminized protective clothing ensembles, each applicable to a specific environment, are commonly found. Of these, proximity suits such as those used by airport crash, fire, and rescue crews are most common.<sup> $\infty$ </sup>

Proper protective gloves should be worn whenever the potential for contact with corrosive or toxic materials and materials of unknown toxicity exists. Glove materials are eventually permeated by chemicals; however, they can be used safely for limited periods if specific use and glove characteristics are known (thickness and permeation rate and time).<sup>67</sup> Common glove materials include neoprene, polyvinyl chloride, nitrile, and butyl and natural rubbers.<sup>67</sup> Insulated gloves should be used when working at temperature extremes. Various synthetic materials such as Nomex(R) and Kevlar(R) can be used briefly up to 1000°F.

A variety of specialized clothing and equipment is commercially available for use in laboratories.

#### 14.2.8.3 General Eye Protection

Contact lenses and prescription glasses may be worn in hazardous situations when protected by additional safety equipment. The minimum acceptable eye protection requires the use of hardened-glass or plastic safety spectacles. Safety glasses should comply with the Standard for Occupational and Education Eye and Face Protection.<sup>67</sup> The American National Standard Institute specifies a minimum lens thickness of 3 mm, impact resistance requirements, passage of a flammability test, and lens-retaining frames. Side shields that attach to regular safety spectacles offer some protection from objects that approach from the side but do not provide adequate protection from splashes.

Goggles are intended for wear when there is danger of splashing chemicals or flying particles. Splash goggles that have splash-proof sides should be used when protection from harmful chemical splash is needed.

## Face shields

Goggles offer little protect on to the face and neck. Full-faced shields that protect the face and throat should always be worn when maximum protection from flying particles and harmful liquids is needed; for full protection, safety glasses should be worn with the shields.<sup>67</sup>

## 14.2.8.4 Respiratory Protective Equipment

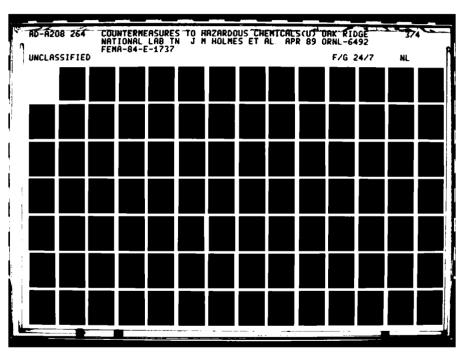
There are two basic types of respirators: air-purifying and atmosphere-supplying. The air-purifying respirator is dependent on the contaminated air and contains an air-purifying element (a filter, a sorbent materi, I, or a combination of both). The atmosphere-supplying respirator is independent of contaminated air and is either self-contained or uses an air-line and hose mask for air supply.<sup>67</sup> The choice of an appropriate respirator for a given situation will depend on the type of contamination, its estimated or measured concentration, its known exposure limits, and hazardous properties. Table 25 shows a guide for the selection of respirators.<sup>67</sup>

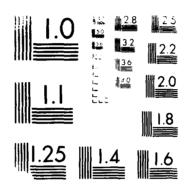
#### Chemical cartridge respirators

These are used only for protection against particular individual vapors or gases specified by the respirator manufacturer. Also, these respirators cannot be used if the oxygen content of the air is less than 19.5%. They function by the entrapment of toxic vapors and gases in a canister that contains adsorbent material. Activated charcoal is probably the most common adsorbent.

## Atmosphere-supplying respirators

The second main category of respirators is atmosphere-supplying. The hose-mask or air-line respirator has limited application and is not used for atmospheres immediately hazardous to health. This device provides the lowest level of protection for the atmosphere-supplying type of respirators. A continuous-flow, air-line respirator delivers breathable air at a constant flow, usually 45 ft<sup>3</sup>-min.





## Telle 26 - Sele time of respirators

Harar I	Respirator
lxygen Het, ren voormediatelv Janger, 2000 lite and health	Air-line, continuous-flow, pressure-demand type with escape provisions; air-line, continuous-flow helmet, hood or pait, with escape provisions; self-contained heatning apparatus (pressure-demand type, or positive- pressure, closed-circuit type)
lxvgen defi let v, t * turb itatelv talget sk * life and health	Self contained breathing apparatuat h se mask with blower; combination airtline respirator with auxiliary self-contained air supply
Rau ani mapir to ditadidadito nome Eratello dadue roduct lite and devalto	Self intained breathing applied in (pressure-formal type, open closed in positive-pressure, closed (product); powered air-purifying, full faceptere respirator with chemical canister; self-rescue monthpiece respirator; combination air-line respirator with adviliary self-contained air supply
Par and rap of distribution not conceduately Bander of to life and health	Airoline respirator: nose wouk with or without blower, and poritying respirator with costcal cattridge
Farticals - stanicanto not immediately dataerros to life and health	Airoparifying, respirator with particulate filter pad or cartribes aircline respirator; aircline, continuous-flow helmet, houd or puit: nose mask with or without blower
Combination gas, vapor, and particulate contaminants immediately langerous to life and health	Self-contained breathing apparatus; air-purifying, full facepiece respirator with chemical canister and appropriate filter; combination air-line respirator with auxiliary self-contained air supply
Colination gas, vapor, and particulate contaminants not immediately langerous to life and health	Nose-line respirator; nose mas', with or without blower; air- purifying reopirator with chemical cartridge and appropriate filter

The air-line respirator comes in two modes: demand and positive-pressure. In the demand mode, the air-line valve opens only when a slight negative pressure is produced inside the mask as a result of inhalation. In the positive-pressure mode, a slight positive pressure of air is maintained in the facepiece at all times.<sup>88</sup>

Another type of respirator in this category is the self-contained breathing apparatus (SCBA). A small SCBA for "emergency egress only" is available. It lasts from 3 to 15 min. This type usually has a high-pressure source of compressed air and plastic hood that covers the entire head.

Companies that manufacture open-circuit devices are: Mine Safety Appliances, Scott, Survivair, and Globe.<sup>n8</sup> "Open-circuit" means that the air you breathe comes from a compressed air source and is subsequently expelled into the surrounding atmosphere. These devices, with a 30-min air supply, weigh around 32 lb. They are mounted and can usually be switched between the demand mode and the positive-pressure mode.

Another type of SCBA uses recirculation to conserve the oxygen supply which comes from a compressed oxygen source. This type is called a rebreather.<sup>68</sup> The exhaled air is not expelled but, instead, passes through a  $CO_2$  absorber and enters a breathing bag to mix with fresh oxygen. The flow is then returned to the facepiece. This apparatus has definite advantages since its air supply duration is longer and it weighs considerably less (about 17 to 24 lb) than the open-circuit SCBA discussed above.

The oxygen generator uses a chemical source of oxygen that is liberated when carbon dioxide and moisture are absorbed from the exhaled air. A breathing bag is provided to mix the incoming oxygen and the purified exhaled air. It can be used for 30 min only; however, there is a potential problem involving water contamination: the canister can explode when the pressure levels exceed the rupture limits.<sup>56</sup>

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#### 14.3 EMERGENCY WARNING AND EVACUATION SYSTEMS

Emergency warning and evacuation systems are of utmost importance in the prevention of injuries and fatalities from releases of toxic chemicals. For fires and explosions, warnings and evacuations may be less effective due to the short lead times and the possible wide area effects. For flammable vapor clouds, the fire hazards are severe within the cloud and can extend well beyond the lower flammable concentration limits due to possible thermal radiation effects from a flammable vapor cloud fireball. For an explosion, the blast effects may extend hundreds of feet from the center and can be particularly severe on occupants of buildings not designed for blast protection. Therefore, unless adequate warning is given prior to a fire or explosion (preferably during the period when the event is impending), the probability of encape is quite low for those persons in the critical zone for these events. The disaster that occurred at Waverly, Tennessee, on Feb. 24, 1978, clearly demonstrated this.<sup>2</sup> A'though an official evacuation was in effect 40 h after a railroad tank car filled with LPG derailed in downtown Waverly, Tennessee, the actual evacuation extended only to the three-block vicinity of the car. Consequently, when the BLEVE (boiling liquid expanded vapor explosion) took place, there were 66 casualties, including many persons in nearby businesses. Obviously, warning and evacuation would have been futile after the onset of the explosion. Consequently, in our judgment, far more statutory emphasis should be placed on requiring immediate notification and evacuation in cases where there is imminent danger of a toxic cloud release, fire, or explosion even when no release of hazardous materials has occurred (see Sect. 16.3.1).

For toxic chemical releases, estimates have been made by EPA of the factors controlling the effectiveness of large-scale movements during evacuations. Prugh<sup>69</sup> suggests the application of these results to warnings and evacuations prompted by toxic vapor clouds. The effectiveness is a function of the area to be evacuated, the population density, and the warning time. Warning time (the interval between the start of a vapor cloud release and the arrival of the cloud at a point of interest) is a particularly important factor. For example, estimates indicate that evacuation of an

area of 1 square mile containing 5000 people would only be approximately 7% effective for a warning time of 0.1 h, 50% effective for a 1.0 h warning time, and greater than 99% effective for a 10-h warning time. Other factors that decrease the evacuation effectiveness include increases in both the area to be evacuated (square miles) and the population density (people per square mile). For example, for a warning time of 1 h, increasing the population density from 5000 people located in a 1 square mile area to 50,000 persons in the same area decreases the evacuation effectiveness from 50% to about 20%.<sup>69</sup>

Sorenson has addressed several issue (see Table 26) that enter into the effectiveness of evacuations for hazardous materials and other emergencies.<sup>70</sup> He concludes that many of these issues are valid points to consider in developing state-of-the-art evacuation plans.

Summarizing a review of public behavior during three major hazardous materials evacuations, Sorenson indicated that no major problems were encountered with getting people to evacuate except for the Love Canal situation.<sup>71</sup> People are more likely to evacuate their homes when they perceive the situation to be personally threatening. During one chlorine gas release in Canada,<sup>72</sup> a number of residents evacuated before official orders were issued; the impetus was provided by media reports and police requests. However, in the Love Canal situation, the ambiguity and lack of clarification of the perceived toxic chemicals threat over a period of time caused the residents to develop mistrust for both the officials and the experts, thus negating the perception that the situation was personally threatening. In a propane tank car derailment near Puget Sound, Washington,<sup>73</sup> the evacuation was determined in part by the public's belief in the warning and the level of perceived risk. Both of these factors were enhanced by the specificity of the warning received and the credibility of the warning source. Confirmation by other sources also contributed to belief in the warning.

Studies at the Disaster Research Center, Ohio State University,<sup>74</sup> indicate that most evacuations occurring in response to transportation releases are spontaneously aided by word-of-mouth warnings. The response is generally quick, usually spontaneous, and not based on formal evacuation plans.

#### Table 26. Evacuation issues

## I. Physical Hazard Characteristics

Uncertainty in ability to specify hazard parameters Uncertainty in ability to detect hazards Syudd of onset constrains evacuation effectiveness

II. Warning Characteristics

Uncertainty in ability to alert Information characteristics constrain evacuation

III. Social Issues

Social factors (denial of need, etc.) affect risk perceptions Cultural factors, etc. affect the ability to receive warnings Economic factors, etc. affect the ability to evacuate

IV. Organizational Issues

Planning elements are inadequate Training of evacuation personnel is inadequate Technical basis for evacuation planning is inadequate

V. Response Issues

Physical factors (population density, etc.) constrain evacuation Public behavior Emergency worker behavior Evacuation not accepted as beneficial by the public Problems are frequently encountered in these ad-hoc evacuations including the need to evacuate more than once to other areas and guidance upon reentry after the emergency.

Quarantelli<sup>24</sup> concludes that most communities are not well prepared for evacuations. He states that disaster preparedness for chemical emergencies, including evacuation, is: "neither accorded high community priority nor systematically addressed. . . . In particular, disaster preparedness for chemical emergencies is plagued by the public-private section division in our society, and also by the fact that the local community (which necessarily has to be the first response) has generally less capability and knowledge for dealing with chemical emergencies than extra- and supra-community social entities."

#### 14.3.1 Emergency Warning Systems

A public warning system for hazmat releases or potential imminent fires or explosions must essentially not only warn the community but also provide specific directions for evacuation and/or sheltering. Some systems consist of separate alerting components such as sirens and horns plus suitable communication components (e.g., public address, radio and TV broadcasts, etc.). Others such as telephone or door-to-door procedures accomplish both purposes at the same time. An effective system must alert and notify the public as soon as possible in an emergency situation and include a follow-up that checks to determine whether the message has been received by the entire population of the designated emergency response zone.

Audible warning devices are used most commonly for alerting the public of emergencies from fixed chemical plant of es. These include sirens, bells, bullhorns, whistles, and public address system announcements.<sup>75</sup> They typically are designed to emit warnings at least 10 dB above average noise levels at the location of the population at risk. They also must be distinctive for the intended alert and should not have sounds similar to other alarms in the vicinity. EPA indicates that the broad use of different tones for sirens for different purposes has not been effective since a large portion of the public is not able to clearly recognize different tones and does not remember what these tones signify. Gray<sup>76</sup> indicates that evacuation orders broadcast from helicopters and patrol cars

were not effective in reaching the public during a chemical plant explosion in a metropolitan area that released methyl parathion fumes.

Probably one of the most effective warning and evacuation events took place in Mississauga, Canada, in November 1979 following the derailment of a chlorine tank car.<sup>72</sup> Within 24 h, approximately 225,000 persons were warned and evacuated from 15 sequentially declared zones. About 95% of the population at risk received the evacuation warning before leaving, primarily through media warnings and police requests. A significant amount of voluntary evacuation took place before the official orders were issued. The success of the evacuation was attributed to unique institutional, social, and environmental factors and to extensive preplanning prior to the event.

Combined alert and notification systems are available commercially.<sup>75</sup> The most common are alert radio receivers, telephone alert/notification systems, and interruption of television programs. Alert radio receivers are activated by a radio signal followed by emergency instructions over the radio. Dow Chemical has installed monitor receivers in homes near their Plaquemine, Louisiana, facility for direct communication during emergencies.<sup>77</sup> Telephone alert/notification systems alert nearby residents by telephone followed by emergency instructions. Also available is an automatic telephone warning system which employs a personal computer as an automatic dialer and includes transmission of recorded instructions to the responder.<sup>75</sup>

#### 14.3.2 Emergency Evacuation

The steps and procedures recommended for emergency evacuation have been detailed in documents prepared for FEMA<sup>78</sup> and EPA/FEMA/DOT.<sup>32</sup> These recommended steps include:

- assignment of information tasks to evacuation personnel such as evacuation areas, instructions, protective gear, shelters, etc.;
- 2. evacuation warning and instructions;
- 3. provide movement assistance to evacuees such as transportation for those without private transportation and strict traffic control of the evacuated area.;
- 4. emergency medical case.;

- 5. security for evacuated area.;
- 6. sheltering of evacuces, and
- 7. decision for reentry to evacuated areas.

Prior experience indicates that in many cases the majority of people want to stay with friends and relatives or go to motels.<sup>79</sup> The remainder require emergency preplanning in order that the proper facilities and services are available when needed for an emergency. This includes identification of the potential shelters beyond potential evacuation zones and establishment of management and operational procedures in the preparedness plans.

The determination of the zone to be evacuated (or the emergency response zone - ERZ) involves complex procedures that are dependent on many factors. These procedures are listed in Sect. 14.4, which includes the basic considerations for modeling of airborne releases of toxic chemicals. Probably the most effective procedures for determining of the ERZ is to employ one of the computerized atmospheric dispersion/emergency response programs described in Sect. 14.4. Many of these programs can be utilized to develop scenarios for a large variety of possible emergencies for a fixed chemical facility. When an emergency occurs, an operator can estimate the evacuation requirements by choosing the preprogrammed scenario that approximates the actual situation and is keyed to the current average wind direction and possible speed.

In cases where the duration of a release from a fixed facility is of relatively long duration (hours), operation of the computer as a real-time dispersion model based on actual data involving the status of the release and meteorological conditions can be achieved. Thus, simulation of the actual release can be developed and updated as conditions change so that a more realistic determination of the ERZ can be made.

In the absence of an available computerized emergency response model or where a transportation emergency occurs in a remote area not covered by the computerized system, quick estimates of the ERZ can be developed using a variety of published methods. The simplest procedure would involve the use of the Evacuation Tables in the <u>DOT Emergency Response</u> <u>Guidebook</u>, assuming that the chemical released is known and that it is included in these tables.<sup>80</sup> These data are intended only for the initial phase of an accident, and reassessment of the accident must be made continuously to check on possible weather changes (e.g., wind changes). The tables list the recommended isolation distances for small spills and also for large spills from tanks, many containers, drums, etc. Also listed are the recommended downwind evacuation zone length and widths. For flammable or explosive materials, a 0.5-mile isolation <u>in all directions</u> is recommended because of potential fragmentation hazards. The individual pages in the guidebook for the respective materials should indicate whether this 0.5-mile requirement should be observed.

The <u>CHRIS Response Methods Handbook</u><sup>81</sup> contains a table of "Maximum Distances Over Which Hazardous Gases May Be Harmful," which can be used for estimates of evacuation zone length and width. The data are tabulated as a function of the respective chemical and the relative amounts released. The distances are based on the maximum distances over which the concentration of the gas in all may exceed its direshold limit value (TLV), the tolerable concentration for worker exposure. This assumption plus the use of low-turbulence weather conditions and the assumption of release onto water result in very conservative estimates for the ERZ.

Prugh<sup>82</sup> presents approximate expressions that can be used to estimate minimum distances downwind where no incapacitating injuries would occur and are thus an estimate of the ERZ distance limit based on the Immediately Dangerous to Life and Health (IDLH) level established by NIOSH. The equations assume that a "dangerous" dose can be obtained from the product of the IDLH and 30 min, which is: "correct for most materials."

The expressions are as follows:

For average conditions (neutral stability, wind = 10 mph)

For continuous release	X = 660(Z).60	
For puff release	X = 1250(Z).62	
For worst-case conditions (stable, wind = $2 \text{ mph}$ )		
For continuous release	X = 2300(Z).45	
For puff release	X = 4500(Z).63	

where

$$Z = \underbrace{}_{\text{IDLH X MW}}^{\text{W}};$$

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W = material release, kg;

IDLH = concentration that is immediately dangerous to life or health, ppm;

MW = molecular weight of the material;

X = downwind distance, m.

This method will give a first approximation to the outer radius of the evacuation zone. The width of the zone is not included, but a rough approximation has been suggested by Kahler<sup>83</sup> when no wind fluctuation data are available. When the wind speed is between 4 and 10 knots, the corridor width as an arc is assumed to be 90°; if the wind speed is greater than 10 knots, an arc of 45° is used; and anytime the wind is equal to or less than 4 knots, the toxic corridor is a circle around the spill with a radius equal to the corridor length, or a 120° arc for unstable conditions has been suggested. If wind shifts are expected, evacuation of the total 360° area has been recommended.

The Illinois Environmental Protection Agency (IEPA) has developed a simplified system for rapidly calculating safe evacuation distances.<sup>84</sup> It is based on the ground-level Gaussian dispersion equations developed by Turner.<sup>85</sup> A response guide has been developed which can be used to quickly determine downwind and crosswind evacuation distances based on the quantity released, the wind speed, the meteorological stability conditions, and the maximum allowable levels of the toxic

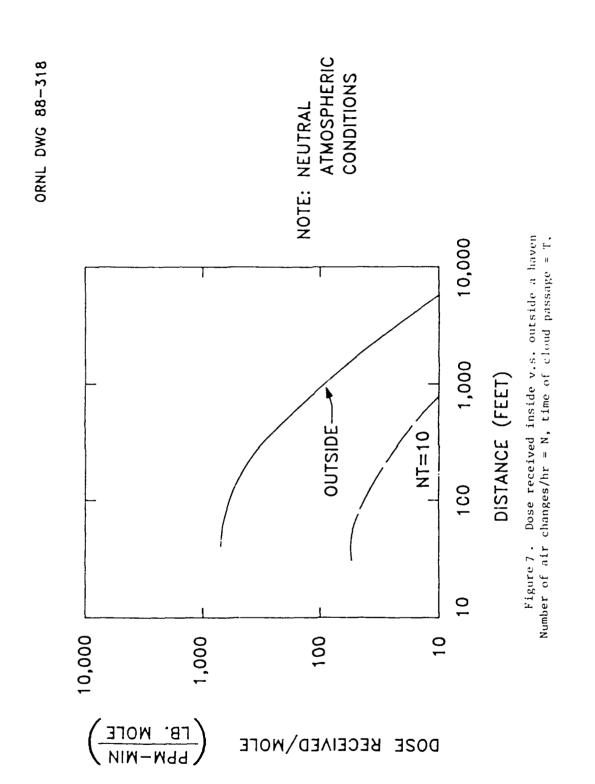
material as detertained by the IEPA. It is claimed that this system is "easy, fast, and reliable, and has been held-tested many times."

## 14.3.3 In-Place Sheltering

Prugh<sup>\*\*</sup> indicates that evacuation outside the emergency response zone may not always be necessary or desirable. He indicates that: "for materials which are toxic and flammable, havens may be viable means of self-protection at great distances downwind from the release point, where the concentration is well below the lower flammable limit but may still be toxic." He presents calculated curves (see Fig. 7) which indicate that for short-term puffs the dose (in ppm-min) to inhabitants of a typical closed dwelling (exchange rate = 1.0) would be one or two orders of magnitude less than that received by a person outside. Thus for short-term releases, it may be more prudent to have persons remain inside of their homes with the doors and windows closed and the heating and air conditioning systems off.

Harris<sup>56</sup> addresses the effects of very short time scales on the feasibility of evacuations. For example, a chlorine leak occurs in a plant situated 300 m from the site boundary and 600 to 1000 m from a local residential population. If the wind velocity is 5 m/s (10 mph) and blowing toward the population, the toxic cloud would reach the closest population boundary in 3 min and the population extremity in just over 6 min. Strong winds would halve these times. Under these circumstances, effective evacuation would probably be limited by one or more of the following circumstances:

- 1. Delays in detection and reporting of the leak,
- 2. Delays in analysis of the reported information and subsequent actions by the duty persons receiving the report,
- 3. Problems with the warning system implementation and the public reception and perception of the warning, and
- 4. delays in the public's response.



Under the above circumstances, it may be far more prudent for residents to remain inside their dwellings with the doors and windows closed, the heating and air conditioning systems shut off or placed on 100% recirculation, all exhaust fans and fireplace dampers shut off, and the gaps around doors and windows sealed with tape or wet toweling. Wilson<sup>87</sup> has shown that this procedure is particularly effective for toxic gases (e.g., hydrogen sulfide), where the prime hazard is proportional to the peak concentration during exposure rather than the total dose or the time integral of the concentration. He indicated that for short-term releases, sheltering not only effectively damps the outdoor concentration so that indoor concentrations are less than 10% of the mean outdoor concentration, but also damps out most of the momentary outdoor concentration fluctuations, which can be as high as 300% above the mean concentration. Wilson also points out that there are psychological problems associated with sheltering. Although the actual risk of mortality may be far less by staying indoors, the public is inclined to believe that it is better to react and do something than to assume a passive role and remain indoors. Education of response personnel and the public as to the relative risks involved may be the best solution to this problem.

Another problem associated with sheltering involves the effects of long-term exposure to the toxic gas while sheltered. Chester<sup>58</sup> developed a simplified mathematical model for the total dose (concentration-time integral) of toxic materials received by a sheltered individual as a function of time. He concludes that "for a tightly closed house, the concentration-time integral inside is exactly that outside if it is kept closed for times long compared to the infiltration time." For example, for a house with an air-change time of 1 h, the protection factor (ratio of outdoor to indoor dose) would only be about 1.1 after 8 h of staying indoors as compared with 10 after only 0.2 h (see Fig. 8). Thus, it is imperative that the house or enclosure be opened and flushed clean as soon as possible after the cloud passes and the outdoor toxic hazard returns to normal. If this is not possible, evacuation of the public from their contaminated shelters after the release may be necessary. Wilson<sup>87</sup> indicates that for gases such as hydrogen sulfide, where peak concentrations are

more deleterious to health than the total dose, long persistence of the gas indoors may not be as important a factor.

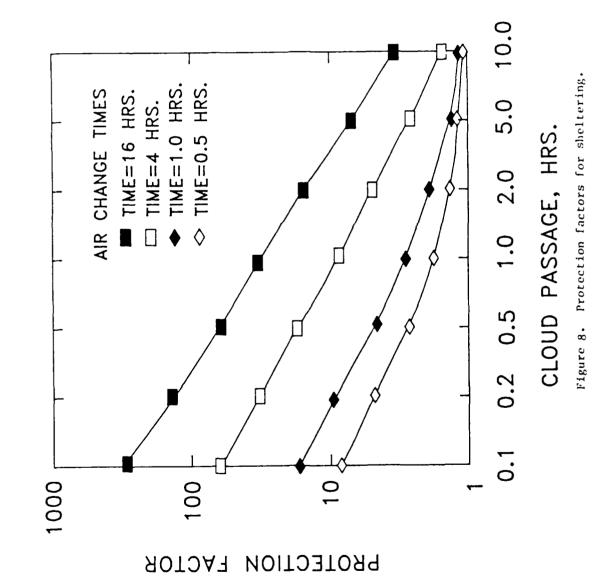
#### 14.3.4 Additional Countermeasures for Protection of the Public

Chester<sup>88</sup> also identified additional countermeasures that could be applied for the protection of the public as an alternative to shelters. These are discussed in the paragraphs that follow.

<u>Stored compressed air or oxygen</u>. Air or oxygen could be provided from compressed gas cylinders using appropriate regulator valves and a mouthpiece or mask. This equipment is used as a breathing apparatus by firefighters and other emergency personnel (see Sect. 14.2.8.4).

<u>Charcoal filtration</u>. Many toxic gases can be effectively removed from contaminated air by passing it through a bed or canister of activated charcoal. This is the principle utilized in chemical warfare or emergency response masks, but it could be used effectively for protecting the inhabitants of a shelter or room through the use of ventilation system charcoal filters. However, the logistic problems inherent in equipping the public with this equipment in areas of potential exposure would be expensive. Also, air filters capable of absorbing each toxic vapor that might be released in the area would be necessary and require larger and more expensive filters. However, for the population near fixed facilities, charcoal filters could be issued for the presumably fewer known hazardous substances produced at the plant.

<u>Collective protection</u>. This technique involves pressurizing a sheltered volume with air to prevent inleakage in winds up to 20 mph. This could be applied to an entire house or public building or to a single room in a building. Charcoal filtration of the inlet pressurizing air to remove contamination would also be required. Problems would be encountered with sheltering of large numbers of people in such a building similar to those experienced in evacuation since large numbers would have to be moved rapidly to the shelters.



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<u>Charcoal-cloth facelet mask</u>. The facelet mask is a British development consisting of a charcoal cloth bag held over the nose and mouth by clastic straps. This cloth is capable of absorbing chemical warfare agents and certain other toxic gases. It would not be quite as effective as a conventional charcoal canister but is far less expensive than a mask. Potential problems include a decrease in adsorptive capacity of the cloth due to moisture adsorption and a requirement for different types of charcoal for the various types of toxic gases.

<u>Mouthpiece respirator</u>. This is claimed to be an effective protective device against toxic gases for short periods of time (several minutes). It consists of a tube connected to an activated charcoal filter. The tube is held in the mouth, and the nose is closed by a separate nose clip. The wearer breathes in and out through the tube, and valves ensure that only inlet air is allowed through the charcoal. Advantages include the very low price and the ease with which it can be inserted in the mouth. This potentially could be a very effective countermeasure during an evacuation but it probably would equire that multiagent filters be available for the different types of toxic gases expected.

## 14.4 HAZMAT MONITORING AND AMBIENT-AIR DISPERSION MODELING SYSTEMS

Probably the most important countermeasure for mitigation of hazard materials releases once they have taken place involves the immediate detection of the hazardous material in the atmosphere plus spatial and temporal estimates of its dispersion pattern. Ideally, the detection of a hazardous material release could trigger an automatic warning system, activate an air dispersion modeling program, activate local and regional emergency response systems, and provide information for possible evacuations or in-place sheltering operations. However, the current state of the art has not been developed to the point where such a completely integrated automatic system is practical, and it would probably be far too expensive to install and maintain for most emergency districts. This section provides an overview of the various detection and monitoring systems that are commercially available and reviews their advantages and disadvantages.

#### 14.4.1 Types of Detectors for Toxic Gases

The development of sensors for detecting toxic gases has received significantly increased attention since the Bhopal disaster. Before Bhopal, attention was directed toward the monitoring of air pollution from stationary sources such as power and chemical plants. Various techniques such as longpath high-resolution infrared spectroscopy were used on a research basis to identify and measure concentrations of pollutants in the atmosphere. More recently, newer technology such as the use of laser-based systems has been applied to pollution measurements and is currently of broad interest for applications where monitoring the releases of toxic gases from chemical and other facilities is required.

The extent of monitoring for releases of chemical plants was investigated recently by the Chemical Manufacturers Association (CMA).<sup>54</sup> CMA members in three geographical areas (Baton Rouge/New Orleans, Philadelphia/Wilmington/South Jersey, and Niagara Falls/Buffalo) were asked a series of questions concerning their air monitoring systems in response to a request from Congressman John Dingell, Chairman of the Subcommittee on Oversight and Investigations.

Results of the survey indicated that over 45% of the CMA member responders routinely monitor emissions of chemicals from their facilities and over 90% of those employ two or more types of monitoring techniques. The systems used to monitor and detect emissions are tailored to the potential hazard of the process unit or facility or the chemicals being handled. The monitoring may vary from exposure readings taken from badges or sample tubes at the site to full-scale data collection and analyzing systems. Data obtained on monitoring activities (as a percentage of all process units) are as follows:

1.	Detection of odors by operating personnel	83%
2.	Industrial hygiene monitoring	79%
3.	Portable gas detectors	50%
4.	Detector tubes	43%
5.	Grab samples	38%

6.	Fixed-point continuous monitors	3177
7.	Personal dosimeters	31%

In reply to a question concerning whether detection systems are chemical specific or designed for the full range of chemicals present at a plant, the facilities indicated that they are designed and programmed to detect specific substances in specified concentration ranges. Typical substances detected directly are: chlorine, carbon monoxide, and vinyl chloride. However, systems can be designed to detect a range of similar compounds such as a series of chlorinated substances or a class of hydrocarbons. Although continuing progress is reported, the capability is not available for measuring all hazardous substances in the ambient air using one system. Various instruments are designed for different chemicals, but for the most part the chemical species and its expected concentration range must be specified before a reliable system can be installed.

Two types of monitors mentioned in the survey were threshold sensors and continuous monitors. Although the sensors in each type may be similar, the main differences are related to the method used for collecting and utilizing data and the ultimate cost of the instrument. Continuous monitors are more expensive because they are designed to quantify concentrations of the measured chemicals over a set range, whereas the threshold sensors are usually set to alarm at set concentrations and no other recording is made.

The location of monitoring instruments was also addressed by the survey:

	Frequency of monitoring
Within process unit areas	56
Elsewhere on plant property	26
At plant boundary	11
Off plant property	7
Total	100

It is apparent that most of the monitoring is performed within the process unit areas; little monitoring is performed at the plant boundaries or beyond.

Two main categories of monitors are currently available for chemical plant monitoring hazmat releases: point or contact sensors, which identify the toxic gas and its ambient concentration by analyzing the air at one or more locations in or around a facility site; and remote sensors, which are capable of continuously monitoring an entire plant area.

Point sensors are commonly located at critical points in a chemical plant according to the following criteria:<sup>90</sup>

- the probability of leakage of toxic materials at a particular place (pumps, valves, compressors, flanges, etc.);
- 2. the probability of human presence at that place; and
- 3. the most probable direction of the prevailing air stream.

However, it is impossible to predict all directions that air movements may take, and consequently it is not feasible to guarantee that unplanned emissions will be promptly detected. In many cases, multiple sampling points are located strategically around the plant and samples are piped to a central monitor such as a mass spectrometer for analysis. However, even though the central monitor may have a high sensitivity and speed of response, the long times for transmission of the sample and its introduction — into the monitor may be of concern to the safety designer. Also, some point sensors are sensitive to moisture and must be properly shielded from rain to ensure reliable performance.

Remote sensors can detect highly toxic materials from a distance and do not come in contact with the toxic target materials. They are essentially scanning instruments that can survey an entire area from inside the plant or on its perimeter.<sup>91</sup> Remote sensors can be further classified as active or passive. Active systems sense the perturbations of radiation from a controlled source such as an infrared beam to monitor for toxic gases. Passive systems consist only of a receiver and use natural radiation such as scattered sunlight for detection of the chemicals. Passive systems can be used to detect toxic chemicals in remote locations (e.g., clouds, stack plumes) or to monitoring for toxics from a helicopter.<sup>92</sup> Recent developments have produced a laser system that reflects a laser beam from normal plant equipment, the ground, or even from atmospheric dust particles. Comparison of the reflected beam with a reference beam enables the detection of toxic materials in the vicinity of the laser pathway.

Portable detection instruments have been developed for locating toxic leaks in a plant. These are normally used for routine monitoring of critical equipment or to pinpoint leaks discovered by area-point or remote sensors. Several types of portable leak monitors are commercially available, although consideration must be given to their application in areas containing flammable or explosive vapors.

Miniature sensors which can be worn by operators, are commercially available for monitoring for toxic vapors such as carbon monoxide, phosgene, hydrogen sulfide, and chiorine. These devices, which are usually based on electrochemical technology, will provide immediate warning to personnel working in areas containing hazardous chemicals. They are used to signal for the evacuation of an area or the mandatory use of gas masks or self-contained breathing apparatus. Personal monitors are very effective but require careful maintenance because of an enhanced risk of accidental or willful damage.

An overview of commercially available point and remote sensors, leak detectors, and personal monitors follows.

14.4.2 Point Sensors

### 14.4.2.1 Ion Mobility Spectrometry (IMS)

A sample of air contaminated with a certain toxic gas is introduced into a reaction region by means of a carrier gas where beta particles released by a radioactive source generate reactant ions. These ions, in the presence of the sample, undergo ion/molecular reactions to produce product ions according to a variety of ion/molecular reactions. As the ions are formed, an electric field drives the positive or negative ions, depending on the polarity of the field, to a shutter grid where they

are pulsed periodically into a "drift" region. The drift region maintains a drift electric field so that ions can be separated from each other due to their different velocities in the drift field. Measurement of the times that the various ions require to travel a drift field of known length at standard temperature and pressure permits the identification of the sample constituents. A microprocessor is used to process the input data and provide control functions to the IMS equipment. Interfering gases include water vapor, ammonia, and the oxides of nitrogen.

A compact, portable IMS detection system has been built and operated by the U.S. Army on a limited number of toxic vapors,<sup>33</sup> but a much broader list of chemicals has been analyzed by this technique as recorded in the literature. A military version of this IMS detector is offered by Bendix<sup>44</sup> for chemical warfare agents such as nerve and blister agents. This portable instrument, called ACADA, is reported to have a sensitivity of 0.1 mg/m<sup>3</sup> for the warfare agents. Honeywell<sup>46</sup> and Bronewick Corporation<sup>46</sup> also manufacture IMS detectors designated M43A1 for the military. Their sensitivity is also 0.1 mg/m<sup>3</sup> for nerve-gas agents. Contacts with Bendix, Honeywell, and Brunswick indicate that none of these organizations has done extensive development of the IMS for hazardous chemical civilian applications, but all of them are interested in possible future markets for their products. Honeywell also markets a military IMS for measuring surface contamination which includes a more sensitive type of flight detector that is claimed to provide improved discrimination between molecules but is projected to cost an order of magnitude more than the M43A1. It is recommended that all of these instruments be reviewed for possible future application in fixed-point monitoring of hazmats based on their sensitivity, simplicity, and very reasonable costs.

### 14.4.2.2 Amperometric and Voltametric Methods

Voltametric analyzers serve as detectors for certain hazmats by measuring the current induced by the electrochemical oxidation of the chemical at a sensing electrode. Depending on the composition of the hazmat, a polarizing (or retarding) voltage is applied such that the reaction at the sensing electrode is specific for the hazmat being measured. A simplified diagram of the polarographic analyzer is shown in Fig. 9. For example, for SO<sub>2</sub> analysis the oxidation that occurs at ti  $\downarrow$  sensing electrode after the SO<sub>2</sub> has diffused through the semipermeable membrane is as follows:

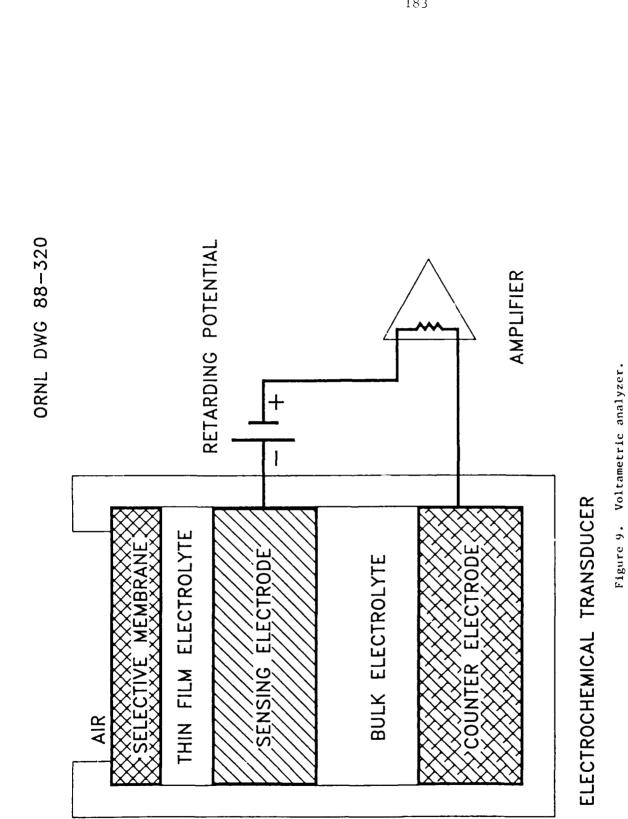
$$SO_{4} + 2H_{2}O = SO_{4}^{-2} + 4H^{+} + 2e_{-}$$

The flow of electrons to the counter electrode is measured, and the amount of current is proportional to the sample  $SO_2$  concentration. Other cells can be used for the detection of various hazmats.

Amperometric analyzers measure the current across the electrodes due to the reaction of the hazardous gas and the cell electrolyte. Commercial monitoring versions of this type of instrument are available from Sensidyne, Environmental Products Companies, and Anacon. Sensidyne produces instruments based on detection of the following gases by a potential change of the sensing electrode:<sup>97</sup> (1) ammonia, (2) amines, and (3) hydrogen cyanide. A current change between the electrodes is used to detect these additional gases:

Chlorine	Arsine
Hydrogen	Phosphene
Hydrogen chloride	Silane
Chlorine dioxide	Fluorine
Hydrogen sulfide	Iodine
Sulfur dioxide	Nitrogen dioxide
Carbon monoxide	Hydrogen fluoride

The response time for most of these gases is <20 (except for hydrogen where it is <60 to 90% of concentration). Each gas requires a separate detector, and up to two similar detectors could be connected to a Sensidyne controller or many sensors could be monitored by a computer dedicated to the monitoring system. Location of multiple detectors at a plant boundary is also an alternative.



The current cost averages about \$1600 to \$1800 per sensor point.

Anacon<sup>98</sup> offers a similar system for the following gases:

Chlorine	Boron trichloride
Hydrogen chloride	Sulfur peroxide
Bromine	Hydrogen cyanide
Hydrogen fluoride	Hydrogen sulfide

The Anacon system permits connection of up to 10 probes to a local processing unit which multiplexes each probe every 3 s and also warns if the probe becomes inactive. Single and hand-held point monitors are also available.

# 14.4.2.3 Colorimetric Analyzers

Colorimetric analyzers measure the optical absorbance of a solution or dry-reagent spectrophotometrically as an indication of the presence and concentration of hazardous gases in an air sample. In general, the advantages of colorimetric analyzers are simplicity, high sensitivity, good specificity, and rapid response.

For dry-reagent colorimetric systems, the reagents are applied as a substrate on a paper tape which is continuously exposed to the ambient air. The reagents are individually formulated to produce color changes for each specific hazardous gas or group of gases. The reagents are claimed to be nontoxic and act as both a gas trapping and an analysis medium which can detect nanogram amounts of the hazardous gas.

Commercial paper-tape colorimetric analyzers are available from MDA Scientific, Inc., for monitoring the following gases:<sup>99</sup>

Ammonia	Germane	Phosgene
Arsine	Hydrogen halides	Phosphine
Bromine	Hydrogen selenide	Silane
Chlorine	Hydrogen sulfide	Stibine
Chlorine dioxide	Nitrogen dioxide	Sulfur dioxide
Diborane	Ozone	

The MDA multipoint monitoring system (PSM-8E) can monitor up to eight locations and provide alarm and control systems for control of toxic gas releases. Personal monitors with alarms are also available for some of the above hazmats.

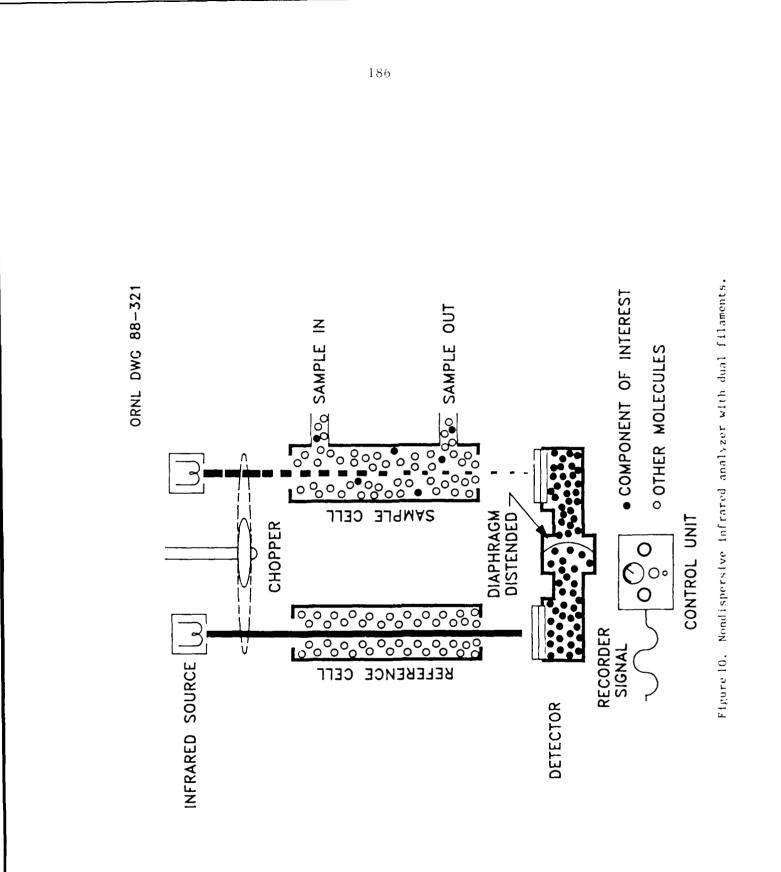
# 14.4.2.4 Flame Photometric Analyzers

For sulfur compounds such as H<sub>2</sub>S, SO<sub>2</sub>, and CH<sub>3</sub>SH, a flame photometric detector (FPD) may be employed for monitoring the ambient air. These instruments use a photomultiplier tube to measure the emissions from sulfur compounds introduced into a hydrogen-rich flame. Advantages of this analyzer include low maintenance, high sensitivity, fast response, and excellent sensitivity for sulfur compounds. Disadvantages include the need for compressed hydrogen and its specificity for sulfur compounds; other instruments must be provided for nonsulfur-containing gases.

Commercial FPD monitors are available from the Columbia Scientific Industries Corporation. They can monitor for SO<sub>2</sub> levels as low as 0.5 ppb in air with a fast response time. Differentiation between the various sulfur compounds can be achieved through the use of a coupled gas chromatograph-flame photometric.<sup>100</sup> Also, through changes in the optical system the Columbia instrument can monitor for gaseous phosphorus compounds such as phosphorus trichloride.

# 14.4.2.5 Nondispersive Absorption Spectrometers

Nondispersive absorption spectrometers are based on broad-band spectral absorption, which is sensitized for a particular gas by means of a detector, a special cell, or an optical filter. Both nondispersive infrared (NDIR) and ultraviolet (NDUV) monitors are available. Figure 10 shows



an example of a NDIR that uses a double-beam arrangement where one beam is directed through a reference cell containing a non-IR absorbing gas and the other through the sample cell where the hazmat gas absorbs part of the radiation. The two split beams are then totally absorbed in the detector cell which is filled with the hazmat gas. The difference in the heating effects on either side of the detector serves as a measure of the levels of hazmat present in the sample cells. It should be noted that this analyzer is specific for only one hazmat gas. Introduction of multiple cell sets would be required for sampling for other species. Also, NDIR instruments are usually subject to interference because frequently other gases absorb close to the wavelengths for the sampled hazmat gas.

Nondispersive ultraviolet analyzers are somewhat more sensitive than the NDIR and are not as sensitive to interfering gases as the NDIR. However, both  $NO_2$  and particulate matter can be serious interferents in the ultraviolet (UV) range. NDUV monitors are also specific for a hazmat gas since a filter must provide source radiation at the UV-absorbing wavelength of the hazmat gas, which is compared with another nonabsorbing wavelength beam split from the same source.

NDIR analyzers are available from Beckman<sup>101</sup> and other vendors. DuPont offers NDUV analyzers, but they have not yet been employed as area monitors for hazmat gases.<sup>102</sup> Costs for these instruments are in the range of \$5,000 to \$20,000, depending on the sensitivity and components monitored.

# 14.4.2.6 Dispersive Absorption Spectrometers

A dispersive absorption spectrometer can be set at any wavelength within its range. It differs from a nondispersive spectrometer, which looks at a broad spectral region, but must be sensitized for each particular gas of interest. The main disadvantage of the dispersive spectrometer is concerned with multicomponent mixtures where it may be difficult to locate an absorption wavelength for the hazmat gas that is in a spectral region where other gases such as water vapor do not absorb.

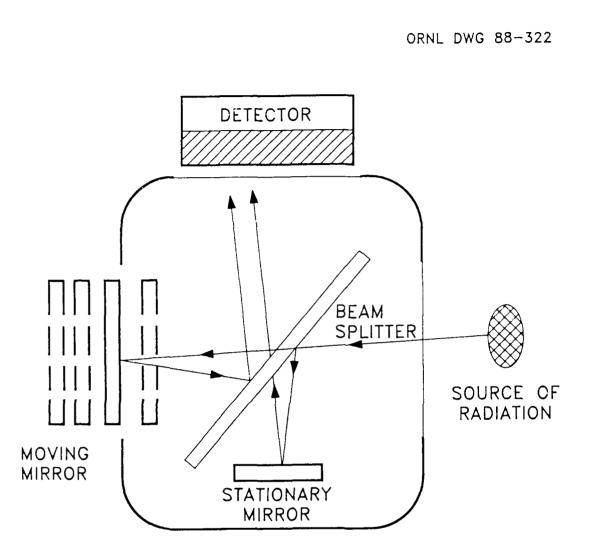
The Foxboro Company<sup>103</sup> offers a multipoint ambient air monitoring system (MIRAN 981),

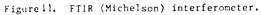
which incorporates a single-beam microprocessor-controlled infrared spectrometer and uses a 20m variable-pathlength gas cell. It can monitor up to five components in air at as many as 24 locations, with each location up to 1000 ft from the monitor. Response times depend upon the number of hazmats monitored and the distance of the sample locations. For five hazmats and a 500-ft sample point location, the analysis time for each point is about 54 s. Therefore, if ten locations were sampled, the response would be less than 5 min for the entire system. The monitor also provides documentation and an alarm system. Hazmat gases that are monitored efficiently by this system include many of the organics and organic halocarbons, ammonia, and hydrocarbons. However, it will not monitor for chlorine, low levels of hydrogen sulfide, hydrogen fluoride, and sulfur dioxide. The cost of a MIRAN 981 is currently in the vicinity of \$40,000.

# 14.4.2.7 Fourier Transform Infrared Spectrometers

A Fourier transform infrared spectrometer (FTIR) utilizes an instrument known as a Michelson interferometer in place of the conventional diffraction grating used in dispersive spectrometers. Although both instruments produce infrared (IR) spectra, the methods of measurement are quite different. The dispersive spectrometer measures a spectrum one wavelength at a time, whereas the interferometer is designed to measure optical interference of all wavelengths at the same time and the resulting interferogram is Fourier-transformed by a computer to produce the spectrum of the sample.

The optical components of a FTIR are shown in Fig. 11. The light from the IR source is projected by a spherical mirror into a scanning interferometer where it is split into two beams. One goes to a scanning mirror and the other to a fixed mirror. The scanning mirror places a sine-wave modulation on each frequency of the recombined beam as it passes out of the interferometer to the sample. The superposition of these waves constitutes the interferogram, which is then transformed in the computer to the infrared spectrum after passing through the sample.





In order to remove the effects of interfering materials, a reference spectrum is made (scan without the sample) and Fourier transformed. The sample is then inserted and another interferogram generated, followed by Fourier transformation. The two transmission spectra are then ratioed to produce the desired spectrum without the interferences.

The primary advantage of the FTIR over a dispersive spectrometer lies in its speed. Since the Fourier transform is performed by the computer, the spectrum is of comparable quality but is accomplished in about one-thousandth of the time that it would take a grating spectrometer to scan the entire spectrum. Another advantage concerns the ability of the computer to add the data from a number of successive scans, thereby averaging the noise but building up the signal. Also, the computer output can be manipulated and plotted in various modes. Although FTIR instruments have been rapidly accepted for laboratory applications, they have only recently been adapted to monitoring applications due to their susceptibility to vibration and temperature effects<sup>104</sup> and the need for highly accurate alignment of the moving mirror.

A commercial FTIR instrument designed for monitoring hazardous chemicals is available from Alnalect Instruments, Inc., Utica, New York. Their model PCM-80 is an on-line instrument capable of FTIR monitoring of gaseous streams and ambient air samples. Operation is based on their TRANSEPT interferometer principle, where pathlength scanning occurs by movement of one of two matched wedges of transparent material to change the thickness of this material in one area of the interferometer. This design is reputed to eliminate the drawbacks of conventional FTIR systems, which encounter angular alignment, vibration, and temperature effects. A military version of the FTIR, called the XM21, has been developed by the military avionics division of Honeywell, Inc., for the detection of chemical warfare agents. However, it is a passive remote sensor type of system.

# 14.4.2.8 Mass Spectrometers

Mass spectrometers are designed to separate ions of a particular material by their mass/charge ratios. The instrument produces charged ions from the original molecule of gas and sorts these ions by their mass/charge ratios. Several methods for obtaining a mass spectrum have been developed

but most involve components such as: (1) a sample inlet system; (2) an ion source; (3) an electrostatic accelerating system; and (4.) an ion detection system. A high vacuum is maintained in the instrument. Ionization is effected by the collision of electrons produced by a filament and the molecules as they pass through the ion source. However, other methods of ionization may also be utilized. The positive ions produced are accelerated and are then passed into a chamber where their separation occurs. The most common method utilizes magnetic-deflection systems to classify and segregate them according to their mass-to-charge ratio. A mass spectrum is obtained by varying either the ion accelerating field voltage or the magnetic field strength, which serves to focus each beam of specific mass/charge ratio on the detector.

In a time-of-flight spectrometer, ions of different mass/charge ratio are separated by the difference in time required for their travel from the ion source to the detector. Using an oscilloscope, which measures the time required for a pulse of ions to drift down the evacuated tube, a complete mass spectrum can be scanned in microseconds. This response speed is a major advantage of this type of instrument.

Perkin Elmer Corp. (Norwalk, Conn.) offers a mass spectrometer (ICAMS) specifically designed for plant perimeter monitoring applications. It can centrally monitor up to 50 locations as far as 1000 ft away and analyze up to 25 hazardous compounds.<sup>105</sup> The cost is in the range of \$3000 to \$4000 per monitored point.<sup>106</sup>

### 14.4.3 Remote Scanning Monitors

Since the Bhopal release, the chemical industry has shown significant interest in the development of remote sensing instruments for the detection of highly toxic materials at the periphery of their plants.<sup>52</sup> Ideally, a remote sensor could scan the plant area for gaseous releases without coming in contact with the gas by using either an active or passive sensor arrangement. Systems that have been developed utilize laser adsorption, laser-induced Raman scattering, and IR or UV absorption. Future improvements will probably integrate remote monitors with computerized versions that predict the direction and future location of releases. This would provide a rapid

complete prediction of hazardous gas releases, including their species, amounts, direction, and concentrations at any point in time and could also take into account the effects of wind changes during a release.

A major advantage of remote sensors is that they can improve upon the detection ability of a large number of direct-contact-point sensors even though their sensitivity is not as high. A group of commercially available remote sensors is described below.

### 14.4.3.1 Differential Absorption Light Detection and Ranging (DIAL)

The development of lasers that can produce light of high spectral brightness (high intensity over a narrow spectral range) has improved detection of certain hazmat gases significantly. In a DIAL system, we carbon dioxide lasers are used. One is tuned to the wavelength where the hazmat gas is absorbed and the other to a wavelength close by where it is not. Figure 12 shows the arrangement of this system. The hazmat-absorbing laser A and nonabsorbing laser B are directed at a single detector about 100 m away. For plant applications, reflection by either a mirror or from plant buildings or process equipment can be used to direct the radiation back to the detector. The relative return-signal strengths are metered to determine the presence and concentration of the hazmat gas monitored. When the hazmat is absent, the beams have the same levels. By using a reference beam, the effects of other gases, moisture, dust, and temperature are automatically canceled out. The instrument meters the total quantity of gas over the beam length; thus, a 1-ppm concentration read over a 1-m length will produce the same reading as a 0.1-ppm concentration over a 10 meters length.

It is claimed that most industrial gases (except those that are not IR absorbers such as chlorine) can be monitored. However, it will be necessary to use tunable lasers or multiple laser sources for detection of multicomponents in the atmosphere. Carbon dioxide lasers emit over 100

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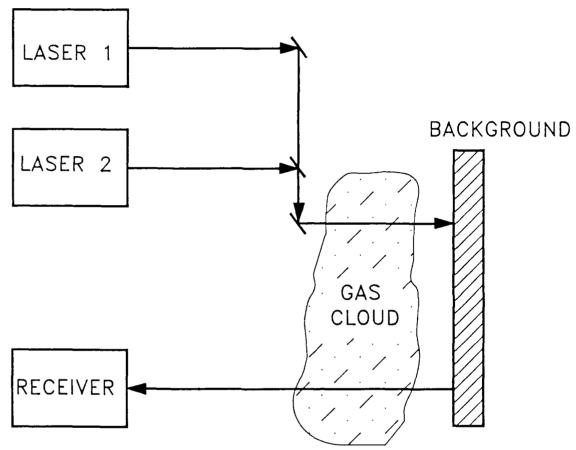


Figure 12. DIAL system for gas detection.

wavelengths in the 9- to 11-micron region while CO lasers emit over 50 throughout the 5- to 6.6micron region.

A DIAL system for the detection of ethylene has been in use by the Imperial Chemical Industries in Great Britain.<sup>107</sup> It is claimed to be accurate to 1.0 ppm for many gases and has a response time in milliseconds. A modification called "Lasersafe" is being marketed in the United States by Environmental Laser Systems, Atlanta, Georgia, for between S125,000 and S175,000.<sup>52</sup> Table 27 indicates the gases that can be detected by a CO<sub>2</sub> laser and other lasers using this instrument.

# 14.4.3.2 Lidar Systems

Lidar (light detection and ranging) operates on the principle of the Raman effect. This is a measure of the increase or decrease of the scattered radiation frequency when a gas is excited by monochromatic radiation from a laser. To observe the effect, the laser radiation produces an intense illumination in the test sample and the scattered radiation is detected spectroscopically. The scattered lines in the Raman spectrum are characteristic of the vibrational modes of the sample molecule and therefore are unique to that molecule. Diatomic molecules such as  $H_2$  and  $Cl_2$ , which do not give IR spectra, do have a Raman spectra.

Computer Genetics (Wakefield, Mass.) offers a Lidar system for the measurement of plume opacity and for hazardous gases. However, the cost of the system is very high - \$400,000 to \$700,000 for a custom-built mobile unit, which would probably be considered excessive for most applications.<sup>109</sup>

### 14.4.4 Portable Instruments for On-Site Detection

Portable instruments for immediate detection of toxic or flammable chemical leaks and releases are important for many reasons. First, many of these detectors are inexpensive and, therefore, would probably be readily available to plant operating, maintenance, and emergency personnel. They are also common equipment for emergency response teams. Second, the use of these instruments

# Table 27 . Cases capable of being detected by correctly available laters

<u>Nari u li xile la er</u>

# <u>laiten min xide laser</u>

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Amonia Acetaldehyle Betzone Bradiele Betene Ethylete Nitric oxide Nitrigen dioxide Fropylene Fropylene Fropylene Vinyl chloride Water

### <u>Desterior fluoride lasei</u>

n Butane Isa butane Carbon drixi le Bydrogen chloride Methane Irag me Nitric oxi le Nitric oxi le Nitricen dioxide Nitrous oxide Sulfir dioxide

#### <u>Helium-neon\_laser</u>

Methane Propane General hydrocarbons LFG

### <u>Hydrogen fluoride laser</u>

Hyirogen fluoride Nitrogen dioxide Nitrous oxide Carbon dioxide Carbon monoxide

······

# Culfur dioxide

140102 Laser

Ethylene oxide

 $\frac{12_{\rm C}\log_21_{\rm AGe1}}{12_{\rm C}\log_21_{\rm AGe1}}$ 

Photoseter

would not normally require a high degree of technical training, so most plant operators or first responders could quickly determine the species of gas present and an approximate concentration of a toxic gas or the lower explosive limit (LEL) if the material is a flammable gas. Third, these detectors function in remote locations even though power may not be available; this is of significance particularly for transportation accidents.

In many cases, a spill may involve many releases where the detectors must analyze for a wide range of toxic or flammable materials. This is especially true in the case of railroad accidents where many tankcars or boxcars loaded with drums or cylinders may be involved. Many portable monitors are capable of detecting a wide variety of chemicals and, thus, are very useful for providing guidance on respiratory protection requirements for emergency personnel and information as to whether an area should be evacuated.

# 14.4.4.1 Gas Detector Tubes

Detector tubes are used to detect approximate toxic levels of hazardous gases in air. A typical tube detector kit contains a pump, spare parts, instructions, a data sheet, and up to 20 packages of detector tubes or reagent kits. The pump is used to draw an accurate volume of air through the detector tube. The air volume is controlled by the distance the pump handle is withdrawn. The concentration of the particular toxic gas metered is determined according to the length of stain on the detector tube. Calibration charts of concentration vs stain length as a function of the number of pump strokes are available in the kit. Special accessories can be used to detect halogenated hydrocarbons, or special chemically treated filter papers can be used to detect certain gases colorimetrically.

Many companies produce gas detector tube kits, including the Mine Safety Appliances Company, Pittsburgh, Pennsylvania (Samplain Pump); Enmet Corporation, Ann Arbor, Michigan; and Sensidyne, Largo, Florida (Gastree Detector Tubes).

# 14.4.4.2 Combustible Gas Detectors

Combustible gas detection analyzers are commonly used to monitor for flammable gaseous mixtures in the air around chemical plants and utility stations. Many portable instruments for detecting gases such as carbon monoxide, hydrogen, methane, and hydrocarbons are available. Most of these operate using a catalytic sensor which is one arm of a resistance bridge. Another arm is desensitized to combustible gases by chemical treatment. The two arms are heated electrically where, in the presence of combustible gas, oxidation occurs at the sensitive element raising its temperature and hence its resistance. The voltage generated as a result of the bridge imbalance is, therefore, proportional to the combustible gas concentration.

Solid-state semiconductor technology has also been used for the detection of combustible gases. Detection of the gases involves embedding two electrodes in a solid-state sensor cell and applying a voltage to the cell. The gas molecules ionize at the sensor and change its resistance, which in turn changes the cell output proportional to the gas concentration. Sensors can be made sensitive to one gas or group of gases and insensitive to others. Fouletier<sup>100</sup> gives a list of gases that can be monitored by solid-state sensors. They include many which are not combustible; hence this technology is applicable to a wide range of toxic gases.

Industrial models of portable combustible gas analyzers are available from many vendors. A few examples include the Mine Safety Appliances Company, Pittsburgh, Pennsylvania (Explosimeter, Minibard Gas Indicator, Gascope, Tankscope, LEL Spatter); Energetics Science, Hawthorne, New York (Ecolyzer Portable Monitors); and Bacharach Instruments, Pittsburgh, Pennsylvania (Digital Minnie Canary Monitor). International Sensor Technology, Irvine, California, offers solid-state sensors for a wide variety of gases. They offer three portable instruments and larger fixed models capable of handling up to 255 sensors (model AG512) in one system. The cost for the portable instruments is in the \$900 to \$1500 range.<sup>110</sup>

# 14.4.4.3 Portable Gas Chromatographs

Portable gas chromatographs that can quantitatively analyze toxic gases are commercially available. Chromatographic columns of various designs are used along with detectors that utilize thermal conductivity or flame ionization technology for analysis. These instruments are capable of monitoring multichemical mixtures of compounds because of the chromatographic separation; however, they are not usually designed for application in explosive atmospheres. Sentex Sensing Technology, Ridgefield, New Jersey, offers a Scentor portable chromatograph capable of monitoring for 16 different compounds. Detector systems offered include argon ionization, electron capture, and photoionization. Argon is used as the carrier gas. Internal calibration, which utilizes calibration gases stored in gas cylinders, is included.

# 14.5 TOXIC GAS DISPERSION MODELING

Prompt prediction of the direction, speed, and the impacted area during the dispersion of a toxic vapor release is a critical step in initiating the consequences of the accident. As soon as the downwind pattern of the spill has been determined either by computer or using hand calculations, safe evacuation distances can be determined and the local emergency plan can be placed into effect. This procedure is certainly far more efficient and, in some cases, safer than instituting a over-evacuation based on a "worst-case" assumption. At times, overreaction in the past events has created public safety problems that were compounded by a lack of satisfactory guidelines for an accurate determination of realistic and safe evacuation distances.<sup>54</sup> A further advantage of rapid modeling concerns the possible procedure where people in certain areas of the emergency zone are safer if they remain indoors as the toxic cloud passes by. This alternative is developed in Sect. 14.3.3 but is mentioned here because it can be an essential part of the modeling program.

Many dispersion models have been developed ranging in complexity from simple formulas and numerical tables or graphs to comprehensive computer-based models that can rapidly predict evacuation zones based upon more complex dispersion models. These systems can be programmed for a wide variety of toxic materials and often include the following factors that are important for characterizing the initial gas cloud and the emergency response zone:

- initial release features such as release height, total quantity or rates of release, and initial gas dilution;
- effects of chemical type, toxicity, and storage conditions on the dispersion pattern and the emergency zone;
- 3. differences in dispersion due to continuous vs instantaneous releases;
- 4. effects of meteorological conditions during the release on the dispersion pattern; and
- 5. effects of local geographical objects such as buildings; mountains, etc., on the dispersion pattern;

Additional features available in certain computer models include the following:

- inclusion of local emergency action plan modules capable of displaying the predicted plume pattern, evacuation areas, evacuation routes, etc.;
- display of the emergency evacuation zone with an overlay showing the areas of siren sound propagation;
- a special population-needs data base that identifies critical facilities (hospitals, schools, dependent care homes, etc.) within the emergency zone and details for the evacuation of these facilities;
- 4. special facility on-site features that display the manufacturing process and enables an operator to zoom in the location of a release and obtain detailed information on the various components involved; and
- 5. provisions for emergency plan checklists to monitor the progress of the response and determine whether specific benchmarks have been achieved.

An overview of the types of systems that have been developed for dispersion modeling and a brief comparison of several commercially available computer programs follows.

Consideration of the amounts, release type, and the eventual formation of a vapor cloud must take into account the types of materials and their physical condition prior to release. Generalized categories for these releases that have been proposed are summarized in the paragraphs that follow.

Bouyant gases - Gases that are buoyant upon release and experience buoyant plume rise, plume dilution, and subsequent Gaussian dispersion.

<u>High-molecular-weight-gases</u> - These gases may experience gravity spreading with entrainment and turbulent mixing in the atmosphere if the release rate is high enough and dilution with initial ambient air is minimal.

<u>Pressurized, liquefied gases</u> - These gases, stored as liquids at ambient temperatures and elevated pressures, will be released as a gas by two means: (1) flash evaporation due to a reduction of pressure to reach equilibrium with the atmosphere and (2) pool evaporation resulting from heat transfer to the cold escaped liquid pool. Gravity spread and dispersion of the cold gas are also

influenced by surface heating of the cloud since the vapors emitted are at the boiling temperature of the gas. As a result, cloud mixing is enhanced with heating along the cloud path.

<u>Refrigerated, liquefied gases</u> - Gases such as LNG vapor emanate from pool evaporation after a spill. The resulting vapor is denser than air and disperses with a gravity spread component until mixing and cloud heating cause the gas to become neutrally or positively buoyant with respect to air.

<u>Refrigerated</u>, <u>pressurized</u>, <u>liquefied gases</u> - This category combines pressurization and cooling gases stored as liquid. Accidental releases of such liquids would combine flash and pool evaporation and cloud heating.

For modeling purposes, releases are usually subdivided according to duration and are categorized as continuous or instantaneous. Releases from storage vessels that have a duration greater than the specified simulation period (usually about 10 to 15 min. depending on the travel time to key receptors) are treated as continuous sources. All other sources are treated as instantaneous sources. Selecting models for specific situations or specifying the length of the simulation period always requires some judgment.

Release features such as the phase of the release (vapor, liquid, suspended aerosol, or combined); leak size; the type, area, and composition of the surface that received the escaped liquid; the extent of flashing of a liquid near its boiling point; and possible fires or explosions during release are also important considerations necessary for characterizing the initial vapor cloud.

Comprehensive models have been developed to take these factors into account and to provide estimates of the hazardous vapor source term for many types of hazardous substances. However, since the actual conditions of release of volatile liquids is seldom well defined during most accident situations, numerous assumptions are usually made. For example, Gudiksen<sup>111</sup> describes the simulation of accidental chlorine releases from various capacity liquid chlorine storage tanks using a comprehensive computer system at Lawrence Livermore National Laboratory. Assumptions made included the time of release (3 to 12 min) and the amounts released, the fraction of the liquid

flashed to vapor during the release (15 to 20%), the amount of acrosol produced (relatively minor), and a range of chlorine evaporation rates from the liquid pool on the ground. Although the latter factor could be calculated by the program based on the rate of heat transfer from the ground and atmosphere, the pool size, the surface composition, and its temperature were not well known so a range of evaporation rates were assumed (2.4 to 215 kg/s).

Initial estimates of a vapor cloud source term during an emergency will usually depend on the first responders at the scene. Prugh<sup>82</sup> indicates that, for toxic chemicals, the "dangerous dose" area covered by a continuous vapor cloud release is primarily dependent on the total amount released and is essentially independent of the release rate. However, for vapor-cloud explosions, the release rate for continuous releases is important because it determines the mass of vapor in the cloud, which in turn establishes whether the lower flammable limit for the particular material is exceeded.

When only the total quantity of a volatile liquid in a container is known and the release rate or total released is unknown, Ryckwan<sup>112</sup> recommends that one assumes a complete release of the entire contents over a 10-min period. For fires involving volatile liquids, he recommends that the source strength be estimated by selecting the most toxic combustion product and assuming that it is emitted over a 60-minute period. Kelty (84) presents estimates of the vapor source strengths for volatile liquids in kilograms per second as a function of their vapor pressure at 20°C.

Major advances have been made recently in modeling of the atmospheric dispersion of large-scale spills. It is often not sufficient to use conventional air pollution models for predicting the dispersion of heavy gases that have higher molecular weights than air or are possibly more dense due to temperature effects. Simplified air pollution models (Gaussian dispersion) assume that the toxic materials in a cloud disperse without losses and have no effect on the atmosphere in which they are dispersed. For heavy gases, buoyancy effects as well as turbulent forces affect the dispersion patterns significantly and the neutral buoyancy models are not appropriate until the cloud becomes neutrally buoyant with respect to air. For example, because of the high molecular weight of chlorine and its low temperature relative to the ambient atmosphere, the liquid from a chlorine spill

evaporates to form vapor clouds that are heavier than air. This heavy cloud spreads horizontally while being transported down-wind by ambient winds and, with time, is diluted by the atmosphere and will eventually become a neutrally buoyant mixture. Therefore, computer models must take into account the following effects: (1) the heavy gas gravity flow (slumping and horizontal spreading), (2) turbulence damping (reduced mixing of the vapor cloud with the atmosphere), and (3) heat flow effects if the heavy gas is cold. Subsequently, when neutral buoyancy is reached, the Gaussian dispersion models can be used to model the dispersion patterns.

Although complex computer programs such as the FEM3 model used by Lawrence Livermore Laboratory in the chlorine simulations<sup>72</sup> are available, they are not practical for use in emergency response situations. The three-dimensional numerical procedures used require large, fast computers.

A recent review of a group of emergency response models was developed by TRC Environmental Consultants, Inc., for the Chemical Manufacturers Association.<sup>113</sup> Eighty source and dispersion models or modeling systems were identified. Of the 80 models identified, 10 were commercial emergency response systems. Of these 10 models, a group of four emergency response systems and one emergency response nomogram were evaluated. All of the four response systems included integrated source and dispersion models, and all except one were capable of simulating the dispersion of heavy gases. The evaluation included a comparison of results simulated by the models to those observed during actual heavy-gas experiments performed in Great Britain at Thorney Island.<sup>114</sup>

Results of these comparisons showed reasonable agreement for several models and identified potential problem areas in others. The models studied included provisions for the most frequently expected chemical release situations but did not include the following parameters:

- 1. chemical reactions, fire, and explosion after release,
- 2. multicomponent liquid vaporization,
- 3. material losses to the soil,
- 4. spreading of evaporating liquids on land,
- 5. dispersion in the presence of buildings and other obstacles, and
- 6. terrain effects on gravity spreading.

Smith<sup>115</sup> identified a group of computer system features necessary for effective real-time assessment of chemical release emergencies:

- automatic acquisition of chemical inventory and meteorological data that permit rapid review by the program;
- 2. graphical display methods that permit rapid identification of the vapor cloud and the emergency action zone;
- 3. simple initial operations procedures required of the user which utilize default scenarios and limit requirements for new information prior to displaying tentative results;
- 4. user flexibility which permits input of a wide variety of modifications to the model data;
- 5. incorporation of the highlights of the emergency plan procedures, particularly notification protocols; and
- 6. location of the system so as to be accessible to emergency personnel with provision for remote or duplicate access to the systems information in case the prime location was uninhabitable.

Table 28 lists a group of commercial response models currently available as a sampling rather than an exhaustive list of available systems. Included are the vendors, an overview of important features such as visual data displays, integrated real-time meteorological data, computer emergency response notification systems, etc. When available, an approximate estimate of system price is included, but these data will probably vary over significant ranges based on the complexity of the systems specified.

Features included in this overview include the following:

<u>Computer</u>. The type of computer system required for the program [microcomputer (PC) or minicomputer (VAX, etc.)].

Integrated release and dispersion system. The program determines the release rate based on predetermined release scenarios or the physical characteristics of the container, hole size, and the material characteristics. The program also determines whether the release is continuous or instantaneous and if an evaporating pool of liquid is formed.

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Table 28. Commercial computer-based emergency response modea

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"Adapted from nuclear models. Primatik for planning use but would be modified for real-time emergency response  $\ell$  an predict location of lower explosion time boundary.

<u>Acquisition of meteorological data</u>. The meteorological data are input manually or automatically from the metering equipment.

<u>Heavy gas-dispersion</u>. Does the program include models for the dispersion of gases more dense than the surrounding air?

<u>Display of dispersion pattern and emergency action zones</u>. Does the model include a graphical display of the plume or puff superimposed on a local area map and does it graphically define the limits of the response action zones?

Determination of fire and explosion consequences. Does the model take into account the potential fire and explosion spatial and temporal consequences?

Building downwash effects. Are the effects of buildings and other terrain effects included?

Inclusion of emergy plan procedures. Are the local emergency plan procedures displayed by the model?

<u>Trajectory modifications during modeling</u>. Can modifications due to changes in meteorological conditions be made during real-time response modeling?

Log of user entry information. Is a log of information entered by the users kept during each modeling run?

In some cases, model features included in the literature are not adequately described and, consequently, are listed as unknown in Table 28. Since this overview is intended only to identify and list the features of several well-known commercially available models, the reader is advised to obtain further detailed up-to-date information from the vendors.

# 14.6 HAZARDS EVALUATIONS OF PROCESSING FACILITIES HANDLING TOXIC MATERIALS

A very important group of procedures used for the prevention of toxic chemical releases and for process safety evaluation, in general, in processing facilities is classified under the title of "Hazards Evaluation." These procedures are used to identify and evaluate chemical process hazards throughout all phases of the life of a facility: design, construction, startup and shutdown, normal operation, and plant revisions. They have been developed and used extensively over the past 10 years by chemical, petrochemical, and petroleum refineries throughout the world. Although the existing federal regulations do not require the specific application of these procedures to hazmat facilities, the New Jersey Toxic Catastrophe Prevention Act enacted in 1986 requires chemical manufacturers in that state to institute risk management programs that include many of the hazard evaluation procedures described below. Specifically, the statute requires facilities to perform an Extraordinary Hazardous Substance Accident Risk Assessment (EHSARA) on those operations that generate, store, handle, or safeguard extraordinary hazmats. A work plan for this assessment is to include the following elements:

1. reporting of the identities and quantities of all extraordinary hazmats that are generated, stored, handled, or that could accidentally be produced by the facility;

2. reporting of the nature, age, and condition of all hazmat handling components plus schedules for their maintenance and testing;

3. an analysis of possible hazmat discharges and procedures and equipment designed to prevent such events;

4. reporting of the training or management practices used to communicate hazmat information to personnel and safety training to promote safe operation and prepare for unanticipated releases; and

5. reporting of other preventive maintenance measures, on-site emergency response capabilities, or other internal systems to safeguard against releases.

The EHSARA is to be conducted according to a work plan developed by an independent consultant or by the New Jersey Department of Environmental Health. Quite probably, other states will emulate the New Jersey statute in the foreseeable future.

The AIChE Center for Chemical Plant Safety has categorized the basic approaches to hazard evaluation.<sup>116</sup> Essentially there are two basic approaches: (1) adherence to good practice and (2) predictive hazard evaluation procedures. Many of these approaches address the proper procedures

that operating personnel must use during startup, normal operations, shutdown, and emergencies but do not include evaluation of the factors leading to human errors. This area is known as Human Error Analysis, and its purposes are to identify potential human errors and their effects and to analyze the causes of observed human errors in processing facilities. The results of Human Error Analysis are often incorporated in the predictive hazard evaluation procedures in order to evaluate the probabilities of human errors prior to and during emergency situations. Techniques used in Human Error Analysis are normally applied by professionals trained in human-performance technology.

# 14.6.1 Adherence to Good Practice

Adherence-to-good-practice techniques has been in effect in the process industry for many years and include observance of safety rules and regulations, adherence to accepted standards and procedures, and following proven practices based on years of operating experience. The procedures that are used most frequently for identifying deviations from good practice include checklists, safety reviews, and the use of Dow and Mond Hazard Indices. Brief summaries of these methods are included below.

# 14.6.1.1 "What-If" Hazards Analysis

A "what if" analysis is intended to be a less structured procedure than methods such as Failure Modes and Effects or Hazop Studies. Its purpose is to examine and analyze the consequences of deviations from the design, installation, modifications, maintenance, and normal operation of a process plant. In operation, a group of two or three experienced technical personnel determine what would happen if events occurred that are not within the intent of the plant design or normal operations.

# 14.6.1.2 Checklists

This is an inexpensive screening procedure to identify the hazards involved in a process and the recommended means for their correction. In many cases, it is used to identify deviations from good

engineering practice and standards. It generally is concerned with the plant equipment and facilities, including all safety and personnel protection systems. Checklists are used during design, construction, startup, operation, plant modification, and shutdown. For an existing plant, the time that must be allotted for this activity is usually about 1 week and requires the services of one or more experienced cagineers.

### 14.6.1.3 Dow and Mond Hazard Studies

The Dow and Mond Indices provide a convenient way to prepare a relative ranking of the various chemical plant features such to chemical reactions, process materials, fire and explosions risks, etc.<sup>117118</sup> Penalties are assigned to those features which could contribute to an accident, and credits are applied for safety features that could mitigate the consequences of an event. The penalties and credits are combined to develop an index that represents the relative risk of each group of processing units (a processing unit is a primary item of process equipment) in a chemical plant. Conditionation of the indexes for all the process units leads to an overall rating of the plant hazard potential. One drawback to this procedure is that material toxicity is not separately ranked. Also, the procedure requires one qualified technical analyst who can usually complete rating two to three average process unit evaluations per week.

# 14.6.1.4 Safety Review

A "safety review" is essentially an intensive plant inspection to identify plant conditions or procedures that pose a significant risk in terms of events that could cause losses of life or facilities. It is also called a process safety review, loss prevention review, or a periodic safety review since it is often performed at one or more yearly intervals. A team of two to five persons of varied backgrounds and responsibilities may perform the review over a weekly period or more. The goal is to identify major risk situations through plant staff interviews; review the plant drawings, emergency plans, codes and standards, and all applicable procedures; inspect the plant and equipment; and prepare a detailed report of the findings and recommendations. The review may

also include a mock emergency to provide insight into the facilities' response during emergency operations.

### 14.6.2 Predictive Hazard Evaluation Procedures

Predictive hazard evaluation procedures essentially involve an in-depth analysis of the processes, systems, and operations and may not be based on prior experience. Included in these evaluations is a definitive series of steps to be followed. First, the system is described completely, which permits the identification of any hazards inherent in the process as its equipment. After a hazard has been identified, the probabilities of its occurrence can be estimated along with its consequences on life and property in the vicinity. Overall risk can then be determined by assuming that the consequences can be expressed in quantitative terms. An assessment of the risk then permits a decision as to its acceptance; if not, the system must be modified so as to lower the risk and permit normal operations to be pursued. Application of predictive hazard evaluation to all processes and process equipment items in a facility enables the management to develop an overall risk analysis. However, this must include the identification of possible accident sequences that involve multiple events, including an initiating event, intermediate events in the sequence, and the nature of the final consequences. During the analysis, opportunities to reduce risks by lowering the probabilities of the initial and/or intermediate events and decreasing the consequences must be taken in order to reduce the overall risk to acceptable levels.

Actions taken to reduce the overall risk include:

- 1. changes in the physical design layout or control system;
- 2. changes in operating/management procedures;
- 3. process changes (pressure, temperature, process materials);
- 4. changes in materials of construction;
- 5. changes in testing and inspection/calibration procedures; and
- 6. additions and/or changes in the safety equipment.

A list of predictive hazard evaluation methods developed by Henley is presented in Table 29.<sup>119</sup> Brief descriptions of each of these methods are presented in the subsections that follow.

### 14.6.2.1 Preliminary Hazards Analysis (PHA)

This is a preliminary analysis whose purpose is to recognize hazards early in the initial design or renovation of a processing facility. It is patterned after the U.S. Military Standard System Safety Program Requirements. Since it is normally applied during the conceptual design phase, few details on the plant components are available; therefore, only qualitative information regarding the projected process and equipment, numbers and types of hazardous operations, operating conditions, system component interfaces, and prior experience with similar processes is available. The prime purpose is to provide guidance to designers concerning the safety aspects of the final plant design and provide incentive for consideration of alternatives if major safety problem areas become apparent.

# 14.6.2.2 Failure Modes, Effects, and Criticality Analysis

A Failure Modes and Effects Analysis (FMEA) is a tabulation of potential plant component failures and how these failures can affect the normal operation of the plant. Usually single failure modes are examined and operator errors are generally not examined; however, the effects of misoperation are usually described by an equipment failure mode (116).

The addition to a FMEA of a ranking system concerning how critical the consequence of each failure mode qualifies it as a Failure, Modes, Effects and Criticality Analysis (FMECA). The criticality or consequences ranking scale of 1 to 4 usually includes:<sup>45</sup>

1. no effect,

2. minor process upset,

- 3. major upset normal shutdown, and
- 4. extreme hazard emergency shutdown.

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FMECA is used during all phases of a plant's life: design, construction and operations. The results are essentially qualitative, but a relative ranking of the following can be made based on the consequences of each failure and the failure probabilities or frequencies.

As indicated in Table 29, a major effort is not required unless a large facility is studied. For example, Harrington describes a FMEA study of a refinery where 1017 component failures were identified.<sup>120</sup> However, it does require personnel experienced in the safety analysis of processes.

# 14.6.2.3 Fault-Tree Analysis

A fault tree analysis (FTA) involves evaluation of the cause-consequence relationships for each particular accident event. The fault tree is usually developed as a graphic model showing the various combinations of equipment failure as shown in Fig. 13.<sup>121</sup> The accident is defined as the top event and the happenings (and their related probabilities) leading up to this event are shown on the logic diagram. The probability of the top event can be estimated using mathematical manipulation of the probabilities for each event. For a complicated chemical or refinery process, it is necessary to develop many fault trees, which requires extensive time and effort by experienced technical personnel. Also, determination of the probabilities for each event, including the processing equipment, instrumentation, electrical gear, safety equipment, etc.

# 14.6.2.4 Event-Tree Analysis

An event tree involves the identification of potential initiating events (such as the top events from fault-tree analysis) and determines a potential accident sequence and the probable consequences. The accident sequences include operator or safety system response to the initiating events and applying probability factos to each of these responses. The results define the chronological series of failures or errors that lead to the final accident. The event-tree also estimates the accident consequence and its probability. Event-trees are used during plant design to assess potential accidents and during plant operation to determine the adequacy of existing safety equipment and estimate the potential consequences of equipment failure and/or operator errors. Extensive time and effort is required for a large or complex process unit. Also, an extensive data base concerning equipment failures is needed if the probabilities of each sequence are to be quantified.

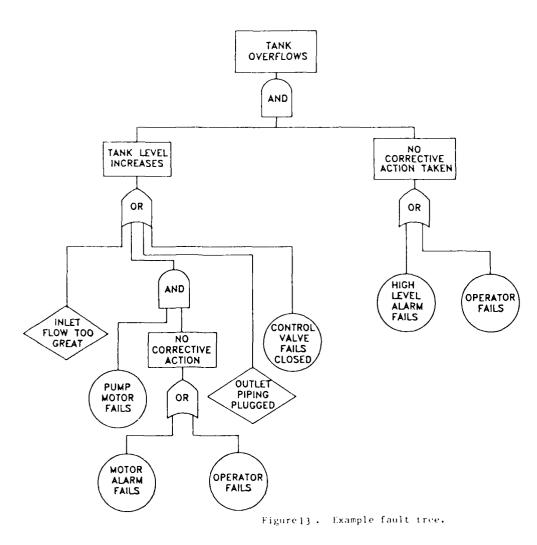
# 14.6.2.5 Cause-Consequence Analysis

Cause-consequence analysis incorporates elements of both the fault-tree and the event-tree methods. It utilizes the forward flow structure of the event-tree analysis, which starts with an initiating event and develops the potential accident sequence plus the fault-tree structure that examines the causes leading to the initiating event. Thus, it goes all the way back to the "root" causes of the accident and can estimate the expected frequency of occurrence if the appropriate data are available. The time and costs for a cause-consequence analysis are significant since the analysis is a complex procedure. Also, an experienced team of analysis is required.

# 14.6.2.6 Hazards and Operability Studies (HAZOP)

The HAZOP method is an extended FMEA procedure for identifying hazards in a process design, their possible cause, their potential consequences, and the actions required for correction of the causes. The method utilizes a multidisciplinary team that meets to review the plant design in detail. Each line and vessel in the design are identified, and certain predefined guidewords such





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as temperature, pressure, flow, etc., are applied to the process variables at that point. The following guidewords are normally used:

Guideword	Definition
No	Reverse of design intent
Less	Quantitative decrease
More	Quantitative increase
Part of	Qualitative decrease
As well as	Qualitative increase
Reverse	Opposite of the design intent
Other than	Complete substitution

The guidewords are applied to flow, temperature, pressure, level, composition, or any other variables; initial causes for each deviation are listed; the consequences are slated; actions required to provide solutions to the problem are listed; and the actual recommendations of the team are included. This method provides an in-depth qualitative analysis of a plant during its conceptual design and is very effective in identifying and correcting potential hazards. Generally, events requiring simultaneous and independent occurrences of three or more equipment malfunctions or operational errors are not considered credible. The optimum times for HAZOP studies are during the plant conceptual design, design freeze, plant startup, and normal operation periods.

A HAZOP study team should be made up of five to seven professionals, but the number could be fewer for a small plant design. AIChE estimates that each major equipment item could require about 3 h of effort; hence, a significant expenditure of time and money would be required for a large, complex plant.<sup>116</sup> In addition, meetings of the team would usually be limited to a few hours per day due to the intense effort required for the analysis. Results of the HAZOP study will include a list of critical events that would require more detailed analysis before the ultimate consequences could be determined. These events are typically expressed in terms of the amounts of toxic and/or flammable materials released from the equipment component. Release rates and

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their duration are then estimated for use in a detailed consequence model.

Once the release rate information has been developed, computer based dispersion models such as those described in Sect. 14.5 can be employed to quantify the following parameters:

- 1. the expected extent of toxic and/or flammable vapor cloud travel under varying weather conditions,
- 2. thermal radiation fields around vapor and liquid pool fires,

3. overpressure and impulse fields from equipment explosions,

- 4. the extent of missile or fragmentation activity resulting from explosions,
- 5. geographical areas to be evacuated, and
- 6. the levels of response equipment and personnel required in terms of medical, fire, police, ambulance, rescue, etc., assistance.

For highly hazardous events, a complete cause-consequence analysis may be required (see Sect. 4.6.2.5).

### 14.6.3 Overview of Hazard Evaluation Techniques

The two basic approaches for hazard evaluation include (1) adherence to good practice and (2) predictive hazard evaluation. Both approaches are considered to be valuable for the prevention of chemical plant releases, but the former is essentially a minimum requirement during the design, construction, and operation of all process plants. Accepted standards and proven safety practices have been in effect for many years and have been responsible, in part, for the excellent safety experience at many chemical plants. Additional procedures such as checklists and safety reviews are also included under this category and are common procedures in most chemical facilities.

Predictive hazard evaluation procedures include additional steps that enable the evaluation of chemical processes where new, different, or extremely hazardous systems and materials are being considered. They also enable the evaluation of very-low-frequency/high-consequence events where there is little or no prior experience available. These procedures range from simple and relatively inexpensive preliminary hazards analysis to very detailed, complex, and expensive systems such as

fault-tree analysis and cause-consequence analysis. Computerized systems that include provisions for predicting human failure are available for the development of these analyses.<sup>122,123</sup>

Acceptance by the chemical industry of these predictive hazard evaluation systems varies considerably among the various methods. Widespread acceptance has occurred for the Preliminary Hazard Analysis, the Failure Modes, Effects, and Criticality and the HAZOP procedures. They are primarily quantitative procedures that force the plant designer/operators to review the process in detail and identify those areas where significant risks exist. Risk in this context is the product of the expected frequency of an event and its expected consequences in the plant and its surrounding area. The main purpose of these procedures is to reduce the risk of chemical releases through prevention of equipment failure and the subsequent loss of plant containment.

Many organizations use the HAZOP procedure as the initial method for identifying and characterizing hazards for subsequent quantitative analysis such as the fault-tree method. Bendixen<sup>124</sup> indicates that an ideal hazard identification approach should accomplish the following:

- 1. detect all significant hazards in the chemical process plant,
- 2. yield accurate descriptions of these hazards in a form suitable for subsequent qualitative analysis,
- 3. consume a minimal amount of time, yet permit judgments as to those hazards considered serious and those which can be classified as insignificant failure modes.

The most efficient methods in terms of time and costs for initial hazard identification are those which consider and document the following:

- 1. man/machine interactions;
- 2. operator oversight ettects;
- 3. effects of process condition variations;
- 4. self-mitigating effects of certain hazards;

- 5. data on composition, rates or quantity velocity, direction, location, and initial conditions of hazardous materials releases; and
- 6. qualitative ranking as to their potential seriousness of the hazards identified.

Several organizations experienced in chemical plant risk assessment recommend the HAZOP approach as a very effective method for achieving the above criteria.<sup>123-125</sup> A. D. Little surveyed the chemical industry recently and found that between one-third and one-half of the major chemical companies have used the HAZOP technique in their facilities. Other hazard identification methods such as a "what if" analysis, although thorough, may be inefficient because a complete listing of all hazards is attempted without screening out those failure modes that are insignificant process risks. Checklists, on the other hand, may fail to identify significant hazards, particularly when new process technology is under consideration.

Quantitative methods such as fault-tree and event-tree analyses have been the subject of extensive recent reappraisal. The prime reasons for the concern are related to the time, expense, and extensive data required for detailed quantification of the risks in chemical plants. Freeman<sup>126</sup> addressed the results of an extensive process risk study recently completed for the Rymond area of the Rhine River delta north of Rotterdam. The results of this study illustrate some of the limitations of current probabilistic risk assessment/methods. The goal of the study was to "decide what role the methodology of risk assessment can play for the formulation of a safety policy." Three toxic chemical storage facilities, two flammable chemical storage facilities, and a chemical separation process handling toxic chemicals were studied. Several important conclusions reached by the study were:

- The estimated probabilities of accidents examined had uncertainties of one or two orders of magnitude.
- The estimated consequences of the accidents examined had uncertainties of one order of magnitude.

- 3. For facilities whose useful life is only 30 years, results that estimate accident frequencies of once per  $1 \times 10^7$  years had little physical meaning.
- 4. Risk assessment studies are very expensive and time consuming.

A major recommendation of the study was that risk assessment be used selectively on problems where the existing technical knowledge is inadequate to provide insight into the disks. Joschek<sup>127</sup> also indicates that these quantitative probabilistic methods provide a rough order of magnitude of the overall risk for a new technology or processing activity such as that found in the nuclear industry. He recommends that overall risks for chemical processing plants using known technology be determined from operating experience alone. Uncertainties in probabilistic risk assessment studies of the chemical industry in Germany can be summarized as follows:

1. The process plants utilize a large variety of process operations and a wide range of operating conditions; therefore, obtaining reliable data on the large number of equipment items under identical or similar conditions is not possible.

2. Legal problems concerned with current chemical plant licensing procedures in West Germany could be formidable for this technology. So far, licensing has not been based on failure probabilities due to the inaccuracy of the results, the difficulty in reviewing the results in the courts, and the fact that legal authorities have yet to define acceptable risks in a probabilistic manner.

3. Current hazards evaluation procedures of BASF Corporation, which include a three-step safety evaluation, are deemed adequate for their risk assessment of new facilities. Consequently, in their judgment, there is no need for probabilistic risk assessment. They do include extensive HAZOP studies as part of third-stage steps in the safety evaluation.

Consequently, BASF recommends that probabilistic risk assessments such as fault-tree analysis be applied only to hardware-oriented systems with a small number of components where adequate reliable failure data are available. They also suggest that these procedures be used only as a backup for normal design procedures.

A review of DuPont's Process Hazards Management (PHM) program indicates that analytical methods used include checklists, failure modes and effect, HAZOP, and fault-tree analysis.<sup>128</sup> The methods used vary, depending on the capability of the review team, prior company operating experience, process complexity, and other factors. Process hazard reviews are made during design, construction, before startup, and during operation at periodic intervals. During the periodic reviews, emphasis is placed on those processes or process steps where an event could lead to serious injuries, release of significant quantities of a flammable or toxic material, or result in a major fire or explosion. The frequency of the reviews is based on the hazards present but range between 2 and 7 years.

The extensive use of fault tree analysis by DuPont has been described by Helmers.<sup>129</sup> Their principal criteria used to characterize risk through fault trees include:

- 1. <u>Interval Between Incidents (IBI)</u> interval in years between serious incidents for a chemical process or process component.
- 2. <u>Process Hazards Index (PHI)</u> the most probable time interval in years between individual fatalities caused by a chemical process.
- 3. <u>Individual Hazard Index (IHI)</u> number of fatal injuries in 1 x 10<sup>6</sup> h of exposure to a particular process hazard.

Guidelines for using these three definitions of risk determined by fault-tree analysis are:

- 1. They are useful for supplementing other methods used for process hazard management.
- 2. Target values of PHI and IHI are used in setting priorities for process risk reduction.
- 3. Alternatives are identified for increasing the PHI to above initial values.
- 4. If the PHI is less than 10,000 years, consider improvements to the system.

The prime usefulness of DuPont's program for quantifying the process risks is to set priorities for safety improvements, make better decisions, and optimize the benefits achieved from their allocation of safety resources.

# 14.6.4 Availability of Hazards Evaluation Services

Table 30 lists some of the commercial firms who offer hazards evaluation services. The list was developed from information presented in the literature and does not purport to include all the vendors of these services. The costs of these services vary widely, depending on the type of analysis, complexity of the plant to be evaluated, and level of resolution required. However, Fussell indicated in 1984 that "an entire plant can be analyzed for less than \$250,000 . . . a unit analysis can run as low as \$20,000."<sup>130</sup> However, this range is judged to be somewhat low, particularly when viewed within the context of current professional salaries.

# 14.7 EMERGENCY RESPONSE INFORMATION AND DATA BASES

Information requirements for the development of local community and facility emergency response plans can be very extensive and can consume significant amounts of time and resources. In fact, the NRT Planning Guide states that: "Developing a complete hazards analysis that examines all hazards, vulnerabilities, and risks may be neither possible nor desirable. This may be particularly 'rue for smaller communities that have less expertise and fewer resources to contribute to the task. The planning team must determine the level of thoroughness that is appropriate." Identification of the major data sources in this section should assist planners in their tasks of developing the necessary information about the hazardous materials of concern to their locality or site. The types of hazmat information bases to be considered include:

- 1. hazardous materials properties (toxicity, flammability, reactivity);
- 2. historical data on hazmat accidents, and
- 3 inventories and materials flow of hazardous materials.

Information on the sources of these bases is presented below.

	Organization	Location	Reference
1.	JBF Associates	Knoxville, Tennessee	9
. <sup>`</sup> .	Arthur D. Little	Cambridge, Massachusetts	9
; ; .	Battelle Columbus Division	Columbus. Ohio	Q
۰.	Design Services	Pittsburgh, Pennsylvania	Ċj.
Э.	Hercules, Inc.	Rocket Center, West Virginia	10
÷	Stone & Webster Engineering Corp.	Boston, Massachusetts	11
	Pickard, Lowe, and Garrick, Inc.	Newport Beach, California	1.2

# Table 30. Commercial vendors of chemical plant hazards evaluations services

# 14.7.1 Hazardous Materials Properties Data Bases

# 14.7.1.1 Extremely Hazardous Substance Data Base

The data base for the identification of an "Extremely Hazardous Substance" under SARA Title III Section 302 is the list of 402 extremely hazardous substances prepared by EPA.<sup>131</sup> This list includes the 402 chemicals published in the "CEPP Interim Guidance List"<sup>8</sup> plus 4 other chemicals added as a result of new information. EPA adopted the criteria shown in Table 31 to identify those substances which may present severe health risks to humans exposed during hazmat releases. These criteria are consistent with toxicity values judged by the scientific community to be indicative of the potential for acute toxicity and are lower than those in the OSHA health hazard definitions. In addition, EPA also included some chemicals that do not meet the acute toxicity criteria but may pose threats due to their large volume production, acute lethality values, and known risks (as indicated by their history as the cause of deaths and injury in accidents).

To develop the acutely toxic chemicals data base, EPA applied the criteria shown in Table 31 to the Registry of Toxic Effects of Chemical Substances<sup>120</sup> (RTECS) data base maintained by NIOSH. This data base is the largest computerized set of acute toxicity information available and includes information on more than 79,000 chemicals. EPA selected only those chemicals in current production as listed in the "1977 Toxic Substance Control Act Inventory" and the current EPA list of active pesticide ingredients. Chemical substances starting production since 1977 were also included. Substances not considered for inclusion were research-and-development-stage chemicals, chemicals used as food additives, drugs, or cosmetics, and nontoxic flammable or reactive substances. Toxic or reactive nontoxic materials were not included because SARA Title III initially addressed only acutely toxic hazardous chemicals.

Table 31		th hazards to humans exposed
Route of Exposure <sup>a</sup>	Acute toxicity measure <sup>b</sup>	Value
Inhalation	Median lethal concentration in air (LC, )	Less than or equal to 0.5 milligrams per liter of air
Dermal	Median lethal dose $(LD_{12})$	Less than or equal to 30 milligrams per kilogram of body weight
eral.	Median lethal dose (LD.)	Less than or equal to 25 milligrams per kilogram of body weight
	· · · · · · · · · · · · · · · · · · ·	

<sup>a</sup>The route by which the test animals absorbed the chemical, i.e., by breathing it in air (inhalation), by absorbing it through the skin (dermal), or by ingestion (oral).

<sup>12</sup>LC50: The concentration of the chemical in air at which 50% of the test animals died.  $LD_{50}$ : The dose that killed 50% of the test animals. In the absence of  $LC_{50}$  or  $LD_{50}$  data,  $LC_{10}$  or  $LD_{10}$  data should be used.  $LC_{10}$ : Lethal Concentration Low, the lowest concentration in air at which any test animals died.  $LD_{10}$ : Lethal Dose Low, the lowest dose at which any test animals died.

A summary of the publicly available information on each of the substances listed under the "Extremely Hazardous Substances" is available from EPA. These are called "EPA Chemical Profiles" and have the same recommended formats as the Material Safety Data Sheets described later. The profile on each chemical includes information on synonyms, recommended exposure limits, physical/chemical characteristics, fire and explosion hazards and firefighting procedures, reactivity, health hazards, use, and precautions. Profiles for each extremely hazardous substance are available in hard copy and on IBM-compatible floppy disks. The profiles are being updated with additional information.

# 14.7.1.2 Material Safety Data Sheets

SARA Title III Section 301 specified that the owners or operators of facilities that are required by the OSH Act of 1970<sup>131</sup> to prepare Material Safety Data Sheets (MSDSs) must make them available to local and state emergency response organizations. The MSDSs are data sheets on individual chemicals or mixtures containing hazardous chemicals. Chemical manufacturers and importers are required to develop an MSDS for each hazardous material that they produce or import under the Hazard/Communication Rule of the Occupational Safety and Health Act of 1970.<sup>133</sup> Employees are required to have an MSDS for each hazardous chemical that they use. Included in each MSDS is the following information:

- 1. the chemical name and other identification;
- 2. Physical/chemical characteristics;
- 3. Toxicity, corrosivity, reactivity data;
- 4. Basic precautions in handling, storage, and use;
- 5. Basic countermeasures to be taken in the event of an accident; and
- 6. Basic protective equipment to minimize exposure to the chemical.

It is important to note that the MSDS materials do not include only toxic chemicals since, according to the OSHA definition, "a hazardous chemical means any chemical which is a physical hazard or a health hazard." A physical hazard is defined as; "a chemical for which there is

scientifically valid evidence that it is a combustible liquid, a compressed gas, explosive, flammable or organic peroxide, an oxidizer, pyrophoric unstable (reactive) or water reactive." Thus, the Title III Section 311 definition of a "hazardous material" extends beyond that for an "Extremely Hazardous Substance" given in Section 302 since it also includes physical hazards in addition to health hazards.

Material Safety Data Sheets are available from the manufacturer of each hazardous chemical in accordance with the OSH Act. They are also available from the sources listed in Table 32.<sup>134</sup> The Information Research and Analysis Section of Oak Ridge National Laboratory has developed a computerized information system for MSDS in conjunction with Martin Marietta Energy Systems, Inc. Approximately 1400 MSDSs have been prepared for chemicals in use at Energy Systems installations. Although the system is intended for use by Energy Systems employees authorized users can access it using off-site modems.<sup>135</sup>

#### 14.7.1.3 The MEDLARS Data Base

The National Library of Medicine's MEDLARS Data Bases contain several valuable information sources concerning toxic substances.<sup>136</sup> They include the following:

1. CHEMLINE - An on-line interactive dictionary of chemical substances which provides information on over 650,000 chemical substances. It contains CAS Registry Numbers, molecular fermulas, and other data that assist in locating additional information in other MEDLARS files.

2. RTECS (Registry of Toxic Effects of Chemical Substances) - This file currently contains toxicity data for more than 70,000 substances and is an on-line version of the National Institute for Occupational Safety and Health's (NIOSH's) annual compilation of substances with toxic activity. The information in RTECS is structured around chemical substances with toxic action, and, thus, provides a single source for basic toxicity information. Also included in RTECS are threshold limit values, air standards, NTP carcinogenic review information, status under various federal regulations, compound classification, and NIOSH Criteria Document availability. The file can be searched by chemical identifiers, type of effect, or other criteria.

Name	Source	Type of data	Number of substances	i
:	Occupational Health Services 470 Seventh Avenue New York, New York	Data sheets and PC software	())))),<	1
;	Information Handling Services P.O. Box 1154 Englewood, California	Microfilm or magnetic tape	))))), ()))), ())),	
Material Data Sheets	Genuim Publishing Corp. Schenectady, New York	Published data sheets	>125()	
Compendium of Safety Data Sheets for Research and Industrial Chemicals	VCH Publishers Deerfield Beach Florida	Three-volume collection of MSDS	Current = 867 Planned = 411	230
Hazardous Materials Information Service	Dynamic Corp. Center (Operated for DOD) U.S. Government Printing Office Washington, D.C.	MSDS data on microfiche	;	
MSDS Collection	Chem Service, Inc. West Chester, Pennsylvania	PC software diskettes	> 16(X)	
<u>CHEMTOX</u>	VNR Information Services 115 Fifth Avenue New York, New York	PC software package	4(KK)	

Table 32. Available collections of MSDS information

Fable 32 (Continued)

TOXIC ALERT	HAZOX P.O. Box 6.37 Chadds Ford, Pennsylvania	PC software package	()());+<
The Sigma-Aldrich Library of Chemical Safety Data	Milwaukee Wisconsin	Large-volume data collection	> 26())
Combined Data Bases	Canadian Centre for Occupational Health and Safety Hamilton, Ontario, CANADA	Collection of MSDS	:
;	MSDS Inc, Ventura California	Collections/Software under development	;
1	Research Alternatives Rockville, MD	Collections/Software under development	;

3. TOXNET (Toxicology Data Network) - TOXNET is a computerized system of toxicologically-oriented data banks operated by the National Library of Medicine as part of the MEDLARS system. This minicomputer-based system includes a variety of modules used by NLM to build and review records. For outside users, TOXNET offers a search-and-retrieval package, which permits efficient access to valuable data, drawn from numerous sources, on toxic and otherwise hazardous chemicals. Currently operating on TOXNET are the following files:

<u>CCRIS</u> (Chemical Carcinogenesis Research Information System) - CCRIS is a scientifically evaluated data bank, developed and maintained by the National Cancer Institute (NCI), that contains carcinogenicity, tumor promotion, and mutagenicity test results. The data are derived from a set of core sources plus primary journals and special reports. Organized by chemical name, the file currently contains some 1200 records.

HSDB (Hazardous Substances Data Bank) - HSDB is a scientifically reviewed and edited data bank containing toxicological information enhanced with additional data related to the environment, emergency situations, and regulatory issues. The data are derived from a variety of publications, including government documents and special reports. Organized by chemical name, the file contains over 4100 records.

# 14.7.1.4 CHRIS Hazardous Chemical Data

The Chemicals Hazards Response Information System (CHRIS) was developed to provide information for decision-making by U.S. Coast Guard personnel during emergencies that occur during the water transportation of hazardous chemicals.<sup>137</sup> The Hazardous Chemical Data compilation lists the specific chemical, physical, and biological data needed to assess hazards in the calculation procedures developed for CHRIS. Each chemical is listed separately, along with its chemical and physical properties, its topic, flammable water pollution, its reactivity properties, the response procedures recommended during a release, shipping information, and chemical designations. Both health and physical hazards are listed.

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# 14.7.1.5 Association of American Railroads, Bureau of Explosives Data Base

The Bureau of Explosives of the Association of American Railroads has published a comprehensive data base for use in surface transportation applications.<sup>136</sup> The information is primarily directed toward recommendations for response to releases or hazmate from railroad vehicles. Methods for controlling fires, preventing fires, personnel protection, area evacuation, and environmental considerations are included for each material listed. General rules for response to the materials in each type of DOT Hazard Classification are also presented.

# 14.7.1.6 Fire Prevention Guide on Hazardous Materials

The National Fire Protection Association (NFPA) has prepared an information guide on the hazardous properties of industrial chemicals for those using the chemicals and for those confronted with emergencies involving them.<sup>119</sup> The individual NFPA documents that make up the manual include the following:

1. FIRE HAZARD PROPERTIES OF FLAMMABLE LIQUIDS, GASES, AND VOLATILE SOLIDS (NFPA 325M)

The fire hazard properties of more than 1300 flammable substances are listed alphabetically by chemical name. The values elected are representative figures suitable for general use. Hazard Index markings are included for most entries.

# 2. HAZARDOUS CHEMICALS DATA (NFPA 49)

Data are given for approximately 416 chemicals on their fire, explosion, and toxicity hazards. Recommendations on storage and firefighting. Hazard Index markings for all entries. Chemicals arranged alphabetically by names and synonyms.

# 3. MANUAL OF HAZARDOUS CHEMICAL REACTIONS (NFPA 491M)

Includes 3550 mixtures of two or more chemicals reported to be potentially dangerous in that they may cause fires, explosions, or detonations at ordinary or moderately elevated temperatures. Arranged alphabetically by chemical name. Reactions referenced.

# 4. RECOMMENDED SYSTEM FOR THE IDENTIFICATION OF THE FIRE HAZARDS OF MATER!ALS (NFPA 704)

This identification system simplifies determining the degree of health, flammability, and reactivity hazard of materials. The system also permits identification of reactivity with water, radioactivity hazards, and fire control problems.

The Hazard Index marking refers to a suggested hazard identification marking system which informs of the general hazards as they relate to health, flammability, and reactivity hazards. In addition, the marking also indicates unusual reactivity with water to alert firefighting personnel to possible risks. The marking system is described in NFPA 704 referenced above.

# 14.7.2 Historical Data on Hazmat Incidents

Historical data can be very valuable for planning purposes when evaluating the probabilities and consequences of hazardous materials accidents, particularly for those materials of interest to the local planning committees. Tabulations of prior accidents for each hazmat can also serve as an initial point of reference when more in-depth information concerning a particular event is required. The data bases discussed in Sects. 14.7.2.1 - 14.7.2.4 have been developed.

# 14.7.2.1 Acute Hazardous Events Data Base

EPA has formed an Acute Hazards List Workgroup to investigate the safety-related characteristics of U.S. industry with regard to accidental chemical releases that could pose exceptional risks to human health and to identify those chemicals which appear to represent unusually high risks. As a result, the Acute Hazardous Events (AHE) Data Base was assembled.<sup>1</sup> The AHE Data Base was not constructed to serve as a basis for nationwide estimates of frequencies of events, quantities released, or their consequences. Emphasis was placed on acquiring a measure of the scope of events rather than on estimating quantities precisely or frequencies of releases. Incidents that involved death or injury were given highest priority. EPA further directed that priority be given to incidents involving chemicals released into air.

The AHE Data Base indicated that four high-volume industrial inorganic chemicals (chlorine,

ammonia, hydrochloric acid, and sulfuric acid) together were reported to have been released in over 25% of the events recording human casualties. Neither great quantity nor high inherent toxicity alone produced the conditions for human casualties. When the characteristics of the released substances are examined, toxicity appears to be the cause of most of the injuries recorded, while flammability and explosivity were the mechanisms associated with most of the fatalities in the data base.

For events reporting quantity released, the quantities approximated a log normal distribution. The amounts released exceeded 1000 lb for over 38% of the recorded events. Releases over 100,000 pounds occurred in less than 3% of the events, but these events account for 93% of the total quantity of materials released. More than 80% of the events in the data base reported that at least one of the substances released was a liquid; 16% of the events involved the release of a gas.

### 14.7.2.2 Hazardous Materials Information System

By law, the Research and Special Programs Administration (RSPA) of DOT must report to Congress annually on the safety of hazardous materials transportation. This requirement, at a minimum, necessitates good records of hazardous materials accidents and spills.

Hazardous materials incidents or releases, defined as any unintentional release during interstate transportation, loading, unloading, or temporary storage related to transportation, must be reported to RSPA in writing within 15 d. The written reports serve as the basis for the Hazardous Materials Information System (HMIS), which is the sole DOT data base that specifically records information on releases, casualties, associated damages, and related information on the material, container, cause, and location of the release.

Numerous modal hazardous materials release and accident reporting systems had been developed prior to 1971, when HMIS became the official recordkeeping system for release data. The U.S. Coast Guard, the National Highway Traffic Safety Administration, the Federal Railroad Administration (FRA), and the Bureau of Motor Carrier Safety (BMCS) continue to require reports of modal accidents. The Coast Guard reporting requirements are particularly extensive, and most

water releases are reported to the Coast Guard system.

Although reporting releases is a regulatory requirement, the Office of Technology Assessment (OTA) found evidence that the compliance rate is low.<sup>23</sup> To assess the completeness and accuracy of the HMIS, OTA contractors compared it with relevant federal modal data bases, the National Transportation Safety Board (NTSB) data, and state data collections. All of these resources are available to DOT, with many of them housed at the Transportation System Center (TSC). The comparisons showed that for air and marine transport, the number of releases is underrepresented in the HMIS by factors of 10 and 20, respectively. For rail and interstate highway transport, the number of releases is underrepresented by factors of 3 and at least 2, respectively.

# 14.7.2.3 National Response Center Data Base

Under the Comprehensive Environmental Response, Compensation, and Liability Act of 1950 (CERCLA) and SARA Title III, the releases of hazardous materials above certain specified quantities must be reported to the National Response Center (NRC) in Washington, D.C. The NRC, operated by the U.S. Coast Guard, handles the reporting of all significant hazardous materials spills under agreement with DOT and EPA. The reports must be made by telephone immediately after the release and by written notice as soon as practicable after the release. The written reports are used as the basis for the NRC data base, which includes incidents, casualties, associated damages, and a multitude of descriptors related to the materials released, containers, cause, and location of the release. Although reporting releases is a regulatory requirement, OTA found that the compliance is quite low.<sup>23</sup> EPA uses the NRC reports, in addition to spills reported to its regional offices and other sources to formulate regulatory policy.

# 14.7.2.4 Material Flow Data Base

As a result of the problems inherent in the collection of hazardous material flow data, the Commodity Transportation Survey (CTS) is the only federal multimodal data base available. Other organizations, such as state and local governments, normally do not collect similar information.

However, separate, relatively complete data bases are available for rail and marine transport. Because the sample waybill data collected by the Interstate Commerce Commission (ICC) has recently been increased, it has been adequate for determining flows of commodities by rail. Additionally, although costly and difficult to obtain, the proprietary TRAIN II data, kept by the Association of American Railroads (AAR), provides much more complete information representing data on at least 80% of the rail shipments.

CTS data for truck and air shipments are much less helpful than the railroad data. Data from the Bureau of Census and the Federal Highway Administration's Bureau of Motor Carrier Safety (BMCS) provide some useful information.

The OTA study concluded that, although no federal resource can provide shipment and materials flow information with the specificity required for state and local planning needs, the annual DOT summaries of aggregate regional shipments can provide useful regional and state commodity flow information. They also indicate that the locally conducted collection of data concerning hazmat facilities and transport is very valuable for planning purposes and has the additional benefit of enlightening the concerned personnel on the local hazardous materials problems.<sup>23</sup>

# 14.8 COMMUNITY AND FACILITY PLANNING FOR TOXIC CHEMICAL EMERGENCIES

Probably one of the most important aspects of emergency response mitigation is concerned with the planning for possible events at various levels of government (federal/state and local). Past experiences have demonstrated that poor or inadequate planning for hazmat emergencies has led to disastrous consequences in terms of lives lost, injuries sustained, and property damage. The disaster at Waverly, Tennessee, in 1978, where an ineffective evacuation was attempted is a good example.<sup>7</sup> After the Bhopal disaster, it became very apparent that adequate planning is essential, and as a result, several federal and private organizations have developed guidance documents for community planning.

Community planning was entirely voluntary prior to the Superfund Amendments and

Reauthoriza ion Act of 1986 (SARA), but with its advent, Congress mandated the establishment of state emergency response commissions, emergency planning districts, and local emergency planning committees. The local emergency planning committees must include representatives of: (1) state and local officials; (2) law enforcement, civil defense, firefighting, health, environmental and transportation personnel; (3) media personnel; (4) community groups; and (5) representatives of facilities who produce, store, or consume hazardous materials subject to SARA, Title III requirements. Facilities subject to SARA, Title III are also subject to the emergency planning requirements. Other regulations that require emergency contingency planning include the Resource Conservation and Recovery Act (for hazardous waste producers), the FEMA Emergency Operations Plan (for states and local governments receiving tunding from this plan), OSHA regulations (for operators involved in hazardous waste operations), and individual laws and regulations currently in force in many states.<sup>10</sup>

Many guides, planning procedure handbooks, and reports of planning projects have been developed under the sponsorship of the federal government, industrial trade organizations, and private engineering organizations. To attempt a review of these systems is beyond the scope of this study; therefore, a brief description will be included of a group made available to ORNL. The various features of these planning systems are compared.

# 14.8.1 National Response Team's "Hazardous Materials Emergency Planning Guide"

This planning guide was developed as a cooperative effort of the 14 federal agency members of the National Response Team to comply with Section 303(f) of SARA, Title III (13). It replaces the guide developed by FEMA, usually referred to as FEMA-10. It includes the following sections concerned with developing emergency community plans:

1. selecting and organizing the planning team,

- 2. tasks of the planning team,
- 3. developing the plan,
- 4. hazmat planning elements, and

5. plan appraisal and continued planning.

This document is recommended as the basic text for implementation of community planning for chemical emergencies.

# 14.8.2 FEMA's Integrated Emergency Management System

FEMA's "Guide for Development of State and Local Emergency Operations Plans" (CPG 1-8) provides information for emergency management planners and for state and local government officials about FEMA's concept of emergency operations planning under the Integrated Emergency Management System (IEMS). IEMS emphasizes the integration of planning to provide for all hazards discovered in a community's hazards identification process. CPG 1-8 provides extensive guidance in the coordination, development, review, validation, and revision of EOPs (see Sect. 14.2).

This guide for hazardous materials emergency planning is deliberately meant to complement CPG 1-8. Chapter 4 describes how a community can incorporate hazardous materials planning into an existing multihazard EOP or how it can develop a multihazard EOP while addressing possible hazardous materials incidents. In either case, communities should obtain a copy of CPG 1-8 from FEMA and follow its guidance carefully. All communities, even those with sophisticated multihazard EOPs, should consult Chap. 5 of this guide to ensure adequate consideration of hazardous materials issues.

# 14.8.3 EPA's Chemical Emergency Preparedness Program

In June 1985, EPA announced a comprehensive strategy to deal with planning for the problem of toxics released to the air. One section of this strategy, the Chemical Emergency Preparedness Program (CEPP), was designed to address accidental releases of acutely toxic chemicals.<sup>8</sup> This program has two goals: to increase community awareness of chemical hazards and to enhance state and local emergency planning for dealing with chemical accidents. Many of the CEPP goals and objectives are included in Title III of SARA. EPA's CEPP materials (including technical guidance,

criteria for identifying extremely hazardous substances, chemical profiles, and lists) are designed to complement this guidance and to help communities perform hazards identification and analysis.

A recent addition to the CEPP includes a document entitled "Site Specific Technical Guidance for Hazard Analysis: Emergency Planning for Extremely Hazardous Substances".<sup>92</sup> The purpose of this guide is to help emergency planners conduct a hazards analysis for airborne releases of extremely hazardous substances. A hazards analysis helps to define potential problems and serves as the foundation of planning and prevention efforts. (See Sect. 1.3 for a definition and brief description of "hazards analysis.") While this guide can be useful to all community and industry planners, it is intended especially for local emergency planning committees (LEPCs) established under the provisions of Title III of SARA. This document represents a joint effort by EPA, FEMA, and the Department of Transportation (DOT) to provide coordinated, coherent technical guidance to aid LEPCs in meeting SARA statutory requirements.

# 14.8.4 DOT Reports and Guides

The U.S. DOT's "Community Teamwork" is a guide to help local communities develop a cost-effective hazardous materials transportation safety program. It discusses hazards assessment and risk analysis, the development of an emergency plan, enforcement, training, and legal authority for planning. Communities preparing an emergency plan for transportation-related hazards might use "Community Teamwork" in conjunction with other guides <sup>146</sup>

"Lessons Learned"<sup>22</sup> is a report on seven hazardous materials safety planning projects funded by DOT. The projects included local plans for Memphis, Indianapolis, New Orleans, and Niagara County, New York; regional plans for Puget Sound and the Oakland/San Francisco Bay area; and a state plan for Massachusetts. The "Lessons Learned" report synthesizes the actual experiences of these projects during each phase of the planning process. A major conclusion of this study was that local political leadership and support from both the executive and legislative branches are important factors throughout the planning process.

DOT has also published a four-volume guide for small towns and rural areas to use in writing

a hazardous materials emergency plan.<sup>121</sup> DOT's objectives were to alert officials of those communities to the threat to life, property, and the environment from the transportation of hazardous materials and to provide simplified guidance for those with little or no technical expertise. Titles of the volumes are: "Volume I, A Community Model for Handling Hazardous Materials Transportation Emergencies"; "Volume II, Risk Assessment Users' Manual for Small Communities and Rural Areas"; "Volume III, Risk Assessment Vulnerability Model Validation"; and "Volume IV, Manual for Small Towns and Rural Areas to Develop a Hazardous Materials Emergency Plan."

# 14.8.5 <u>Chemical Manutacturers Association's Community Awareness</u> and <u>Emergency Response Program (CMA/CAER)</u>

The Chemical Manufacturers Association's (CMAs) Community Awareness and Emergency Response (CAER) program encourages chemical plant managers to take the initiative in cooperating with local communities to develop integrated emergency plans for responding to hazardous materials incidents.<sup>36</sup> Because chemical industry representatives can be especially knowledgeable during the planning process, and because many chemical plant officials are willing and able to share equipment and personnel during response operations, community planners should seek out local CMA/CAER participants. Even if no such local initiative is in place, community planners can approach chemical plant managers or contact CMA and ask for assistance in the spirit of the CAER program.

# 14.8.6 AIChE Emergency Planning Training

The American Institute of Chemical Engineers (AIChE) offers a course directed toward chemical plant safety personnel entitled "Emergency Response Planning for Fixed Chemical Facilities."<sup>th</sup> The course is offered at each of the four AIChE meetings as part of their "AIChE Today Series." Included in the curriculum are topics covering

- 1. chemical emergency planning philosophy,
- 2. organizing for emergency preparedness,
- 3. planning for emergencies,
- 4. examples of proper planning and response actions, and

5. emergency response "table-top" exercise.

# 14.8.7 Consultant Organizations Offering Emergency Planning

There are various industrial consulting organizations that offer emergency planning assistance to state, local, and chemical plant processing committees. Table 33 presents a partial list of these organizations. The field is currently expanding very rapidly; thus, our list is necessarily incomplete.

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# **15 NEW TECHNICAL APPROACHES**

As a result of the Bhopal disaster in 1984, novel approaches are under investigation along with improvements in existing technology. The advent of SARA Title III has resulted in significant increases in development funding, particularly in the area of monitoring devices.<sup>2</sup>

# 15.1 PREVENTION OF CHEMICAL ACCIDENTS

Increased emphasis has been placed recently on the technical aspects involved in the prevention of chemical accidents and the interaction between the prevention and the emergency response aspects. Both the federal government and private industry have been involved. L. Thomas, the EPA Administrator, emphasized this recently: "As we have dealt with the U.S. effort during the last couple of years, we particularly tried to focus on prevention. As we look at this area, you find there are multiple causative factors for chemical accidents." design factors, human factors, and many others, all associated as causative factors for chemical accidents."

A review of new and proposed technical approaches in the area of prevention addressed below includes:

- 1. human factors for accident prevention,
- 2. prevention at chemical production and storage facilities,
- 3. prevention through education and certification, and
- 4. community awareness programs.

# 15.1.1 Human Factors in Accident Prevention

The prime research need proposed for the area of human factors as applied to accident prevention at chemical plants is the application of proven analytical techniques to identify the potential for human errors, and the relative contribution of these errors to the public risk.<sup>49</sup> Technical statts in chemical organizations usually do not include human factor experts; their involvement should result in process systems and procedures that one significantly improve with

respect to reliable operation and the prevention of chemical disasters. To avoid potential accidents in chemical process plants, human factors must be incorporated in all phases of plant design and operation and must be systematically included in all risk assessments performed on the facility. Justification for this may be found in the historical records, which indicate that fewer than 50% of the accidents in chemical plants were caused by equipment failure. Although the record indicates that about 11.4% were due to operator error, the "unknown" causes are indicated at 21.5%, which certainly includes many failures due to human factors.<sup>1</sup>

Bell stated that it is feasible to identify those human errors which will impact plant performance, to assess the likelihood of those errors and to evaluate their effects both on and off the plant site.<sup>13</sup> Identification of human errors involves a review of past plant records to determine the types of errors and the circumstances under which they occurred. When such records are not available, detailed task-analysis techniques can be utilized to identify and describe the human tasks required by the process system and to determine how the performance of these tasks under both normal and emergency situations impacts on the overall operation of the plant. Task analysis information can be obtained by several methods, including job performance reviews, interviews, questionnaires, and design reviews. It can also be developed by actual performance of the task by experienced analysts.

Evaluation of human performance and the effects of human errors on plant operating systems involves combining the information from the task analysis with psychological and physiological models of human performance. The results are a description of what can be expected of average operating personnel under a number of circumstances. These range from normal operations to maintenance, trouble-shooting, accident response, and emergency response. Results of the human error evaluation can be of a qualitative nature (descriptive analysis of the tasks, comparison of options for performing the tasks, a ranking of options under consideration, etc.), a quantitative nature where quantified error-probability estimates are developed, or both a qualitative and a quantitative nature. Quantitative estimates can be utilized as a necessary input to comprehensive facility risk assessment such as fault-tree analysis. However, the value of qualitative results lies in the relative values when comparison is made between various tasks rather than in their absolute values, which are often suspect due to insufficient input data for most human error situations.

Assistance to plant operators and other personnel during other than normal plant operations can be effected through an expert system computer program.<sup>111</sup> This program, named "Plant Risk Status Information Management System" (PRISM), is capable of determining an appropriate response to a given plant status, including abnormal situations when key plant components are out of service. Identification by the user of the components that are out of service prompts an estimation of the increase in plant risk over the average plant risk during normal operation. This enables the operator to take prompt corrective action when relatively unsafe conditions are indicated. The program also develops and ranks accident scenarios concurrently in order to identify critical operator errors and weak links in the system. When a known process abnormality occurs, the operators can use PRISM to identify the corrective emergency procedures; and when upsets of unknown origin occur, the operators can diagnose the problem and obtain the corrective action from the program. It is claimed that this program can be effective in training personnel for off-normal events and can serve as a valuable tool for response to upsets during normal operations.

# 15 i.2 Prevention at Chemical Production and Storage Facilities

The prevention of hazardous chemical releases and accidents must begin at the source of the hazards – the production and storage facilities that process, produce, and store the dangerous chemicals. Transportation must also be included and is considered as a separate topic. Consideration of prevention features can be divided into two areas of concern: prevention at existing facilities and inclusion of adequate safety provisions during the design, installation, and startup of new facilities and additions to existing plants. Many of the countermeasures such as the risk analysis procedures mentioned below will be common to both. The countermeasures that the areas have in common will be discussed first, tollowed by a review of specific procedures that have been recommended during the design, installation, and startup phases of new plants.

The need for prevention programs at existing facilities at chemical plants was emphasized by Caputo,<sup>10</sup> who described the following factors that could contribute to increase in hazmat events in the United States:

- 1. The average age of the facilities has been increasing due to the high cost and lack of capital for replacement plants. Current plants are subject to deterioration and potential increases in equipment failure.
- Reductions in the numbers of highly trained and experienced senior personnel due to layoffs and early retirement programs.
- 3. Increased competition from lower-cost imported products and a worldwide surplus of capacity have decreased the investment in current plant improvements as well as the employment of additional manpower.

Although it has been demonstrated that the cost of safe operation of chemical plants pays for itself (India is suing Union Carbide for \$3.3 billion in connection with the Bhopal disaster in 1984<sup>146</sup>), consideration of the trade-offs between closing a plant and investing additional capital in safety may lead to decisions that select the most expedient solutions to the problem.

# 15.1.2.1 Plant Risk Analysis

As discussed in Sect. 4.5, plant risk analysis is probably one of the most important methods for the prevention of accidents involving the release of hazardous materials. The initial step involves identification and establishment of the credible sources of hazards in the process or storage facility. By employing the knowledge base of physical, chemical, and toxic properties of the materials used by or stored at the facility, a systematic investigation of the plant will lead to a comprehensive list of potential hazardous events. To determine the consequences of these events, it is necessary to examine both normal and abnormal operating conditions. Both single and multiple failures must be included along with situations that occur outside the facility such as floods, seismic activity, severe weather, and power failures. Methods developed for hazard identification are described in Sect. 14.5. They include HAZOP, Checklists, Failure Modes and Effects Analysis, and the Dow and Mond Indices.

Once the sources of hazards in a facility have been identified, quantitative mathematical models can be developed for judging the risks associated with plant operations under both normal and abnormal operating conditions. It is then necessary to develop scenarios are developed which begin with an initiating event and continue through chains of plausible events to an end point, which identifies the overall consequences of the accident. Human factors such as operator response to a particular situation are also included. Probabilities of failure at each step in the chain of events are assigned this permits evaluation of the expected frequency for each chain in the scenario. The result of this type of analysis is typically an estimate of the total risk, which is the product of the consequences and the expected frequency. With these results, management of the facility can select plant and operating improvements that achieve the lowest risk levels commensurate with the resources available. Procedures that have been developed for this type of analysis are described in Sect. 14.5 and include event trees, fault trees, and cause-consequence analysis.

Application of plant risk analysis should also be utilized during the design, construction, and startup of new facilities. Safe engineering of process and storage facilities will minimize both the probabilities of accidents and the consequences to the operating personnel, the general public, and the operating system. Caputo<sup>138</sup> recommends a comprehensive program applied during all stages of new plant activity, including:

1. process Collgn,

2. conceptual design,

3. detailed design,

4. preparation of operating manuals, and

5. pre-startup.

Comprehensive reviews at the completion of each of these stages are also recommended.

# 15.1.2.2 Isolation to Limit Quantities Released

Prugh<sup>32</sup> recommends that isolating devices be installed in process equipment to stop flow of

a leaking fluid to the leak point before the entire inventory of connected equipment can be discharged. Devices suggested include remote-controlled valves, remote shutdown for pumps, check valves, and the use of positive displacement pumps. The latter type of pumps can effectively stop the flow of fluids when shut down because of their installed check valves.

# 15.1.2.3 Depressurizing

In the event of equipment leakage, depressurizing of the system should be employed to decrease the leak rate. This can be accomplished by venting the equipment, cooling or removing volatile liquids, cooling equipment exposed to external fires, etc. Consideration should be given during the design phase to depressurizing or emptying all equipment in a plant.

# 15.1.2.4 Secondary Containment Systems

All nuclear reprocessing facilities must install secondary containment around equipment that is used to process hazardous radioactive chemicals. This includes buildings, shells, or other structures that would effectively seal off leakage from the primary equipment in case of an accident. The Resource Conservation and Recovery Act requirements published on July 14, 1986, requires that secondary containment with some type of monitoring must be provided for all new hazardous waste tanks.<sup>107</sup> Secondary containment is judged to be the only generally applicable mechanism that will allow detection and response to releases from hazardous waste storage tank systems before they reach the groundwater and/or surface waters.

For toxic gases and volatile vapors, secondary containment systems such as building structures, containment tanks, and containment pipelines must be vented to equipment suitable for removal, condensation, destruction, or storage of the toxic materials.<sup>111</sup> Processes that can be used for this include:

1. physical absorption using a solvent in which the material is soluble;

2. physical adsorption using an adsorbent such as activated earbon, etc.;

3. condensation of the vapors to below their dewpoint using a cooling system;

- 4. destruction of organic vapors in a flare or incinerator;
- 5. storage of noncondensible gases under pressure in an auxiliary vessel; and
- 6. transfer of liquids or condensed vapors to auxiliary vessels.

Harris discusses the advantages and disadvantages of rooms or structures built around process equipment that serve as double containment for hazmats such as chlorine.<sup>148</sup> This is done frequently in Europe, where many chemical plants are built inside buildings that are vented directly to an exhaust or destruction facility. In some cases, storage tanks are also constructed inside buildings. Advantages of this system include the following:

- 1. heat gains from insolation and wind effects are designed out of the process system. Thus, the room can be cooled, lowering the vapor pressure of released materials.
- 2. The emergency exhaust can be vented directly to a destruction or removal facility.
- 3. Toxic gas detectors can be effectively used to monitor and warn of releases.
- 4. The room can be kept dry and maintenance standards improved in many cases. Potential disadvantages of this type of double containment include:
- 1. Startup of the emergency exhaust system may be delayed.
- 2. Large gas releases may exceed the capacity of the exhaust system, thus resulting in failure of the containment.
- 3. Fire or explosion in the process equipment could breach the containment structure.
- 4. Additional costs may be incurred.

# 15.1.2.5 Reduction of Toxic Material Inventories

In considering reductions in the probabilities of catastrophic toxic materials releases, it is apparent that reduction in the inventories of these materials would provide significant improvments. Wade<sup>149</sup> indicates that Monsanto defines the minimum inventories desirable from a safety standpoint as follows:

The minimum safety inventory is the minimum inventory or quantity that is consistent with safe, stable operation. This is normally the lowest inventory with which the process could operate without safety concerns.

One example cited by Wade involved the storage of crude acrylonitrile from a reaction area prior to purification in a purification area. The crude acrylonitrile is a hazardous chemical itself, but in addition, it contains relatively high levels of dissolved hydrogen cyanide (HCN). The reaction area operates about four times longer than the purification area before shutdown, so accumulation takes place when the purification area is shut down for maintenance. Reduction in this inventory accumulation was achieved by operating the reaction area throughput at the lowest safe rate when the purification area was inoperative, thus effectively reducing the product inventory of the crude acrylonitrile. Another example involved negotiating with suppliers of toxic materials to ensure that before are made only when needed. This effectively reduced the inventories of rail cars containing hazardous materials at the plant.

The Monsanto Company and Hercules, Inc., have altered the ways in which their chlorine invent thas are stored. <sup>10</sup> They now keep the materials in 150-and 350-lb containers rather than in 10,000 Tb tanks in order to minimize the chances of a large release. Dow Chemical Company had cat its worldwide chlorine inventories by 20 to 25% by November 1986.<sup>100</sup> They also reduced their phoseene inventory at 1 a Porte, Texas, by 95% by operating their satellite process units directly from the phoseene field unit instead of drawing phoseene from storage. In other cases, the transportation of methyl isocytonate from one plant to another has been completely eliminated through changes in the process at the receiving plant.

in a 1986 report issued by the National Institute for Chemical Studies (NICS), the results from various hazardous chemical inventory reduction programs at several chemical plants in the Kanawha Valley. West Virginia, were as follows:

Plant	Location	Total plant inventory reduction (lb)
t mon Carbide	Institute WV	5.020,000
Union Carbade	South Charieston, WV	6,640,000
T MC	Nitro, WV	50,000
Monsanto	N(Iro), WV	410.000

DuPont	Belle, WV	17,703,000
Occidental	Belle, WV	400,000
FMC	Spring Hill, WV	340,000

The above companies have in place a corporate policy endorsing hazardous chemical reductions at plants, which is backed up with specific performance requirements for company personnel. Each company has performed an in-plant audit of chemical use and waste generation and established cost accounting systems that enable management to determine the cost of raw materials, material losses, and various inventory options.

Inventories of the following hazardous chemicals were reduced.

Methyl isocyanate	Chlorosilanes
Phosgene	Hydrogen chloride
Chlorine	Sulfuric acid
Acrolein	Silicon tetrachloride
Vinyl methyl ether	Mesityl oxide
Acetone	Diacetone alcohol
Butyl chloride	Methanol
Phosphorus trichloride	

Twelve chemicals that were judged to constitute the most salient potential hazards to surrounding communities in the Kanawha Valley of West Virginia were as follows:

Chlorine	Phosphorus trichloride
Bromine	Phosphorus oxychloride
Hydrogen cyanide	Sulfur trioxide
Phosgene	Hydrogen fluoride
Methyl isocyanate	Hydrogen fluoride (anhydrous)
Ammonia	Hydrogen fluoride

These compounds were selected by the NICS out of a total of 46 potentially dangerous

chemicals, as defined by the EPA, located at 13 Kanawha Valley chemical facilities. They were chosen as having properties that make them especially dangerous to the public in terms of their potential to form a toxic cloud and migrate off-plant into the surrounding communities. The list was reviewed by the appropriate plant managers and discussed with consultants from Bechtel National, Inc., independent experts from EPA, and the American Institute of Chemical Engineers. All of these chemicals are included in our rating system, which is described in Sect. 17.

### 15.1.2.6 Substitutes for Hazardous Materials

The literature indicates that several major chemical manufacturers are exploring the feasibility of, or have already instituted programs for, substituting less hazardous materials for some of the very toxic chemicals utilized in or produced by their processes. Several examples have been identified by Zanetti:<sup>150</sup>

- 1. Hoffman la Roche, Nutley, New Jersey, has substituted ethyl chloroformate for the phosgene used in small volume applications.
- PDG Industries, Chicago, Illinois, has developed carbonyl diimidazole as a substitute for phosgene in the syntheses of pharmaceutical products. This substitute is about 100 times more expensive than phosgene.
- 3. Bayer, AG, in West Germany and Belgium has substituted several nontoxic solid chemicals for the phosgene used in the manufacture of methyl isocyanate insecticides.
- 4. Aqueous ammonia solutions can be substituted for anhydrous ammonia, muriatic acid for anhydrous hydrogen chloride, and wet benzoyl peroxide for dry benzoyl peroxide. In each case the solutions are less hazardous than the anhydrous material.
- 5. Ethylene dichloride solvent reacted with sodium hydroxide produces small, but hazardous, quantities of vinyl chloride. The use of alternative solvents can eliminate this hazard.

These are just a few examples of potential substitutes for hazardous chemicals in chemical plant operations. Development of a comprehensive data base of substitutes for all the major hazmats is recommended as a prime countermeasure. The economics of hazmat substitution should also be addressed because the toxic material will probably not be replaced if the substitution makes the process conomically impossible. Research concerning the characterization of reactive chemicals, as proposed by Kohibrand,<sup>1,2</sup> should also be included in order to identify potential hazardous chemical reactivity associated with these substitutes.

# 15.1.2.7 Explosion Suppression Systems

Equipment for use in explosion suppression systems for process vessels is as follows:

<u>Detectors</u>. The most commonly used detector is a very sensitive and stable type of pressure switch designed to close electrical contacts very early in the pressure growth. This may be set to setter a pressure as low as 0.1 psig, depending on plant conditions. Detectors are used in the matchest with suppressors and other types of midgation devices.

Surveyors - Suppressors provide the automatic dispersal of a mitigating agent upon detection to a cyplosion. Two types are used, frangible and pressurized, with the selection dependent on the explosion characteristics and the process variables encountered. Frangible suppressors consist of than-walled reservoirs filled with the suppressing agent into which a small explosive charge such as a blasting defonator is inserted. Since disside device is not pressurized, the force to disperse the agent its supplied by the explosive charge, which also ruptures the wall of the reservoir. Pressurized uppressors, known as "high-rate discharge extinguishers," contain the agent under the nitrogen pressure, and opening of the container is accomplished with an explosive charge. A very large bore is used in order to allow dispersal of the agent in a minimum period of time.

Explosion suppression has been too expensive and unproven for larger applications (>100 cubic matters) — However, experiments have been performed with a 10 cubic meters vessel to evaluate, in a first phase, explosion suppression systems using threshold pressure detectors and "6-mm-diam-ordict high rate discharge (HRD) suppressors. The HRD suppressors were charged with ammonium ph sphate powder suppressant and pressurized with dry nitrogen to 60 bar. It was found that increasing the size of the HRD explosion suppressor by a factor greater than 2 (from 20 1 to 45 L) did not result in a corresponding halving of the number of explosion suppressors required for

effective suppression of the explosions. The suppressant discharge rate was obviously one of the limiting factors.

In the second phase of the experimental program, the effectiveness of explosion suppression systems was evaluated against the same explosion threats using HRD suppressors with a capacity of 45 L and an outlet diameter of 127 mm. This culminated in a series of large-volume explosion suppression tests in the 250-m<sup>3</sup> vessel.

Volumes of 6.2, 10, and 25 m<sup>3</sup> were considered small, and it was demonstrated that the 45 L 127-mm-diam HRD suppressor was considerably more effective than the 45 L, 76-mm-diam unit.

Explosion suppression tests were carried out in the large volume of 250 m<sup>3</sup> using the 45 L, 127mm-diam unit. The results of these tests were comparable in the 10-m<sup>3</sup> and 25-m<sup>3</sup> vessels with the same HRD suppressor. Thus, the efficacy of explosion protection by suppression for large plant components was established. Consequently, the authors claimed that the technique of dust explosion suppression is viable, up to volumes of 1000 m<sup>3</sup>.

### 15.1.2.8 Machinery Vibration Programs

Prevention of catastrophic failures of rotating machinery in chemical plants is of prime importance in reducing process upsets and safety hazards to a minimum. The acute Hazardous Events Database indicates that 43.3% of a total number of 5179 in-plant events were caused by equipment failure. Although the fraction of these failures due to rotating machinery breakdown is not indicated, it is well known that pumps, compressors, turbines, blowers, and fans are more subnerable to failure than other types of operating equipment. The failures are also critical because they impact on the flows of process fluids, heating and cooling media, power sources, and the other utilities in the plant. In addition, failure in other process equipment has been known to precipitate tailure of the rotating machinery because of temporary overloading. Le Blane presents an example of the destructive effects resulting from a chlorine compressor failure.<sup>122</sup> This centrifugal chlorine compressor was known to be a problem since chlorine leakage had contaminated its lubricating oil

supply, which resulted in excessive vibration at the compressor bearings. Nevertheless, operation was continued when it was discovered that maintaining adequate speed on the unit and purifying the lubricating oil apparently stopped the vibration. However, the compressor was later inadvertently allowed to slow down, resulting in severe vibrations. It was then manually shut down and removed for repairs. Subsequent inspection showed that the vibration resulted in an iron chlorine life within the compressor, and portions of the compressor rotor were burned away.

Fortunately, prompt operator response prevented more extensive machine damage and thus avoided op-extremely hazardous asmospheric chlorine release.

A predictive maintenance program to effectively survey, analyze, and respond to rotating machinery vibration at a petrochemical plant has been described by Le Blane.<sup>354</sup>. It includes the following steps:

1. Periodic (montily) field vibration testing of all rotating equipment.

2 Continuous surveillance of critical components using control room vibration monitors.

3. Analysis to determine the causes of machinery vibration and methods to correct the problems. This includes held diagnosis by trained analysis for simple problems and the use of sophisticated computerized programs for more complex situations.

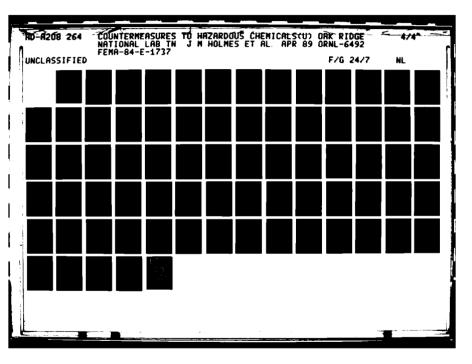
4. A comprehensive program to assist in correction and prevention of rotating equipment problems. This is particularly important during equipment startup and component changes.

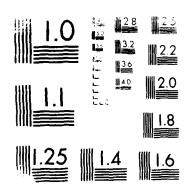
Machinery vibration programs are a basic component of process plant loss-prevention systems. Their primary goal is to avoid extensive damage and safety hazards by detecting and analyzing preddems and proceeding corrective actions before complete failure of the component occurs.

15.1.3 Improvements to Storage Systems

Storage systems are particularly vulnerable to releases of toxic and or flammable materials for the following reasons:

1. Jarge inventories of hazardous materials,





- 2. less operator attention since tanks are often located in more remote areas of plants,
- 3. fewer detection instruments used in storage areas to warn of hazardous releases,
- 4. higher probabilities of accidents during loading to and unloading from transportation vehicles, and
- 5. higher probabilities of failure due to external events such as collision by vehicles, fires in adjacent installations, and sabotage.

Al-Abdulally<sup>35</sup> discusses preventive measures taken on a large fertilizer complex located in Ahmadi, Kuwait Many of these measures could also be applied to the storage of other hazardous chemicals. Measures used for their ammonia storage system include the following:

- 1. Provision of a concreted containment area under the storage tanks with a dike wall of sufficient height to contain all of the contents of any given tank.
- Equipment of each storage tank with safety devices to warn of or prevent a major rupture of the tank. The safety relief valves are connected to a flare system to prevent releases due to overpressurization.
- 3. Use of a common refrigeration system to maintain all the tanks at -33°C.
- 4. Provisions for collecting released ammonia to drains and pumps to direct the spilled liquid to another tank.
- 5. An ammonia leak detection system and alarm indicators located in the control room.
- 6. Installation of a foam station to reduce the evaporation rate of ammonia from the diked area.

Consideration was given to the construction of a bund wall (or dike wall) around each tank to the full height of the tank. Thus, there would be an annular space about 2.5 m wide around each tank with the top left open for ventilation. The prime advantage of the bund would be the reduction in the ground area under each tank by a factor of about 49, which was estimated to decrease the continuous evaporation rate of a spill also by a factor of about 49. The bund would also provide some protection from external events such as sabotage, vehicle collision, etc. A decision against the bund wall was made due to high capital costs, construction problems, and only a slight reduction in the disaster potential due to tank failure (the maximum distance traveled by the toxic vapor cloud was reduced slightly).

# 15.1.4 Prevention Through Education and Certification

One basic preventive measure that has been almost completely neglected concerns the teaching of chemical process safety to undergraduate chemical engineering students. During their preparation to fill positions as researchers, designers, operators, and managers of chemical processes and facilities, chemical engineers in most universities are not required to take any formal safety courses, and in many cases their only exposure to process safety occurs during their process design courses. However, this is usually left to the discretion of the professor teaching the course. The members of the Accreditation Board for Engineering and Technology (ABET), who are responsible for accreditation of the U.S. Engineering Colleges, do not currently have any requirements for process safety in chemical engineering curricula. However, they do plan to add these requirements in the near future.<sup>156</sup>

The American Institute of Chemical Engineers (AIChE) has recognized this deficiency and recently moved toward developing educational modules in support of the undergraduate chemical engineering curriculum.<sup>125</sup> These modules, which are designed to introduce safety into undergraduate engineering programs, will include all facets of safety: prevention and mitigation of accidental releases of hazmats, personal safety, occupational safety, industrial hygiene, toxicology, etc. The modules will be designed so that they can be added to the current chemical engineering curriculum.

For graduate engineers, the AIChE has a goal of sponsoring meetings primarily concerned with process safety and developing countermeasures for the release of hazmats.<sup>157</sup> Their objectives are to develop a dialogue on concerning identification of the problems and obtain a consensus on directions that research in this area should take.

Training and certification of graduate engineers and other technical personnel have been undertaken by the Institute of Hazardous Materials Management. Their Certified Hazardous Materials Manager (CHMM) examination has been developed as a qualification requirement along

with at least three years of professional hazmat-related experience in industry, government, or education. Major contributions and outstanding leadership in this field may also be credited toward meeting some of the requirements. The CHMM examination is offered periodically at universities. A training manual prepared by TVA personnel is available.<sup>158</sup>

### 15.1.5 Community Awareness Programs

The public is concerned that hazmats produced, stored, or transported through their communities may have an adverse effect on their health and safety. This concern is becoming more widespread and emotional, particularly since the Bhopal disaster in 1984. The Chemical Manufacturers Association (CMA) states that the public perceives that information on hazardous chemicals is being hidden from them, and this perception has precipitated the right-to-know legislation at the state levels as well as the federal level (SARA, Title III statutes). To counteract this increased public concern trend, the CMA has established their community awareness and emergency response program.<sup>30</sup> CMA proposes that the basis of any effective community awareness and emergency response program is an informed public familiar with the operations of local chemical plants. Such a public will be better able to understand the emergency response plans that plant managers will help communicate to it. One of the first steps is to go into the community and contact the people who are needed to participate in emergency planning. This initial contact will include a description of the facility, its safety and accident prevention programs, its emergency response capability, and its safe operating history.

Therefore, chemical plant managers are advised to consider outreach programs as a general response to the public's demand for information and as a means to create an educated community that is able to participate effectively in the emergency response program. The plant manager's role as a catalyst in any planning effort will be easier if the community knows what goes on inside facilities, what safety measures are in place, and what emergency preparedness measures are taken. The public's fears about chemical hazards will also be diminished. Outreach programs could include speaking at community meetings (e.g., school and church groups, service clubs, and City Council

meetings), plant tours, and brochures explaining the facility.

The Louisiana Chemical Association Community Awareness Project is a good example of an outreach program. It includes the following elements:

1. <u>Chemical Operations Awareness Seminar</u> - On-site seminars at chemical plants which include accident prevention, design and engineering safeguards, emergency response, and community protection systems.

2. <u>Booklet, "Protecting People and the Environment."</u> - A concise booklet developed to familiarize the public with chemical operations and procedures.

3. <u>Chemical Emergency Preparedness Symposium</u> - A symposium to promote awareness of emergency procedures and precautions already in place at a chemical facility.

4. <u>Program Evaluation and Monitoring</u> - Opinion surveys of media, officials, and community leaders to evaluate the effectiveness of the Chemical Operations Awareness Seminars.

In summary, a well-conducted community awareness program should develop a better public understanding of hazardous chemical processing and help to establish two-way communications between the facility and its community, which will serve as the basis for the effective development of emergency response planning and implementation.

### 15.2 DETECTION AND WARNING SYSTEMS

Atallah<sup>159</sup> reviewed systems currently under development for the detection of hydrocarbon leaks such as methane and other hydrocarbons. They include the following:

- A Raman light detection and ranging (LIDAR) system under development by the Computer Genetics Corporation, can detect hydrocarbons throughout an entire facility continuously at a scan rate of °2s. The projected LIDAR beam can scan to a distance of 500 m for localized leaks of 5000 ppm concentrated over 1 to 2 m. The system has an estimated cost is about \$750,000 and could be adapted for use with other toxic gases.
- 2. A (DIAL) type system (see Sect. 14.5) is under development by SRI International (Menlo Park, California), supported by Gas Research Institute (GRI) for the detection of natural gas leaks from buried pipelines. It actually senses ethane in the natural gas in order to prevent false alarms from other sources of methane. It can be vehicle-mounted and has a sensitivity of 3.5 ppm-m for ethane over a range of 150 to 1000 m. As outlined in Sect. 14.5, tunable lasers could be applied to a wide range of toxic gases. The technology appears to be applicable not only to fixed facilities and storage sites, but also to areas where large population centers are at risk or to transportation centers such as railroad yards or truck centers. The high cost of these instruments is probably the prime obstacle to their application at the community level.
- 3. The Columbia Gas Service Corporation (Columbus, Ohio) is also developing a DIAL-type detecting device under the sponsorship of GRI. Helium-neon lasers are to be used. The instrument is shoulder-mounted and has a detection limit of 3 ppm/m over a range of 11 to 17 m. Prototypes developed thus far were priced at \$20,000 per instrument.

Prugh<sup>51</sup> reviewed the various types of detectors and suggested methods other than toxic gas sensors such as odor, color, or fog detection. Most chemical substances have a characteristic odor which could serve as a warning, provided that the detection threshold is sufficiently below the immediately dangerous to life and health (IDLH) level. However, odor detection may not be adequate if the chemials produce olfactory fatigue, where the small sensitivity is lost after prolonged

exposure. Also, every person has a different sensitivity to various classes of materials. (Some persons may be very sensitive to a smell, while others would detect it weakly or not at all).

Instrumentation is not available for the detection of odorous materials ii: the atmosphere. The prime method for detection is the human nose. However, other techniques can be applied for estimating the quantitative levels of concentration in the atmosphere, and gas chromatographs can then be used to select the odor source from among several potential sources by comparing the concentrations of the odorous components with their threshold levels. odor characteristics, and concentrations at different locations in a plant.<sup>160</sup> This technique would probably be too slow and cumbersome for use as an emergency response tool. However, spiking toxic chemicals with an odorous tracer such as that used to identify natural gas is one possible method for detecting emergency spills. Such a tracer must be nontoxic, nonradioactive, have low background levels, be chemically and thermally stable, and be amenable to rapid detection by analytical instruments. Also, release to the atmosphere should not create deleterious environmental problems.

A few gases and vapors have characteristic color which could aid in identifying sources of leaks and also approximate concentrations if the observer is trained for such an observation. However, these materials are noticeable only at significant concentrations, so this method is useful only near the source.

Some gases become visible when mixed with moist air because of reaction with the moisture or the formation of aerosols after extracting the water-vapor from the air. Low-temperature vapors can cause fog by condensing moisture from the air. Thus, observation of these plumes can assist in locating the source of leakage and also serve as a detection measure. However, one would have to differentiate between a toxic fog and the normal releases of steam and other vapors from most chemical plants. Prugh<sup>51</sup> suggests the use of closed-circuit television systems for monitoring plant sites for fog-indicated releases.

Probably one of the most promising countermeasures for fixed facilities is the direct tie-in between the toxic material detector and an efficient warning system such as a siren, telephones to transmit prerecorded messages, and computers programmed to dial preselected telephones in the vicinity. Radio and television messages may also be an effective measure. Prugh<sup>51</sup> further suggests that "process computers could be programmed to detect leakage by changes in pressures, flows, and levels, to support, verify, or combine with the alarms generated by the leak detectors. As confidence is developed concerning reliability and absence of false alarms, the area-alarm, site-wide-alarm, and off-site warning actions could be made automatic." Certainly such systems could reduce the warning and evacuation starting times by as much as an order of magnitude.

For vehicles used to transport hazmats, such as chemical tank trucks and railroad cars, we recommend that an automatic radio warning system be developed that would be ariggered by a major impact, such as a collision or overturn, or by a signal from the driver or train engineer. A system of this type could be tuned to a common emergency communications channel and would broadcast a warning message concerning the materials spilled and instructions for the countermeasures to be taken. If many tank cars on a train were involved, a timed sequence of messages might be required. Such a system would provide very rapid notification to arriving response personnel; it would identify the materials released and their position in the train from a distance, thus circumventing close observation of the accompanying labels and providing instructions to the responders who might not have the proper emergency response guidebooks. Costs of such a system should not be excessive unless a high degree of sophistication is required.

A promising recent development concerning the use of satellites to track trucks carrying hazardous materials is being tested by several trucklines.<sup>161</sup> The system, offered by the Geostar Corporation, Washington, D.C., utilizes transmission of coded signals that are sent to a satellite and then beamed back to a stub antenna on the truck. The truck then automatically responds with a signal to the satellite, which is relayed to the ground station. Triangulation can then be used to determine the location of the truck using a LORAN navigation system. Geostar claims that with

two satellites in orbit, the truck position can be determined to within 30 ft. The truckline users can obtain the information on the truck position by checking the screen of a personal computer located at their headquarters. Communication between the PC and the ground station is maintained by telephone. Also, in case of an emergency, a driver can relay a call for help by punching a button in the cab which relays a message back through the satellite link. The current cost of the system (S165'month per truck) is stated as justified by minimizing the number of stops required by the driver to phone his position back to the truck headquarters. For hazardous materials shipments, prompt response to major spills would probably be adequate justification for this cost.

### 15.3 MINIMIZING TRANSPORTATION RISKS

A recent review by the Congressional Office of Technology Assessment (OTA) concerning the transportation of hazardous materials provides insight into needed technical countermeasures.<sup>103</sup> These include data collection and information needs, containers for hazardous materials, bulk packaging and intermodal containers (containers that hold 4 to 6000 gal of material and are supported by a metal frame locked into special fittings on a vehicle).

# 15.3.1 Data and Information Needs

The Office of Technology Accessment (OTA) reviewed the federal data-collection activities (as of 1986) concerning hazardous materials transportation and concluded that they "present a sound basis for additional state and local commodity flow data collection." However, city officials and planning committees have expressed a need for a national flow data resource, and some requests have been made for a real-time notification system for hazardous shipments. Many emergency response committees prefer to develop their own local inventories and transport surveys to assist in their planning. The time delays in utilizing federal annual summaries of shipments may render the data obsolete. Also, a real-time information system could overwhelm the response organizations tracking the masses of current data. However, the state of Colorado now requires permits for all hazardous materials shipments through the state, and these permits could serve — an excellent data

base for planning purposes.

OTA concluded that, although the federal information resources cannot provide the specific shipment information required by the state and local planning organizations, the annual DOT summaries of aggregate regional shipments can provide useful regional and state flows of hazardous commodities. Locally conducted data collection on hazmat facilities inventories and transportation surveys is encouraged. Data provided by SARA Title III, if rigorously enforced, should be of real value to these locally conducted surveys (see Sect. 15.1.2).

# 15.3.2 Containers for Hazardous Materials

Containers used for shiping hazardous materials include tank truck: railroad tank cars, barges, bottles, boxes, drums, and intermodal containers. DOT's Research and Special Programs Administration is responsible for the packaging and hazard communication regulations for all hazmat containers except bulk marine containers, which come under the jurisdiction of the U.S. Coast Guard. Studies conducted by DOT show that many of the releases from tank trucks come from discharge valves, pressure relief valves, and manhole covers and that poor maintenance and inspection of the trucks contribute to the problem. An OTA study<sup>23</sup> revealed that cargo tank trucks carrying gasoline are involved in more deaths and damages than all other hazardous materials accidents combined. OTA indicates that adoption of the proposed rule changes concerning the

"Requirements for Cargo Tanks"<sup>162</sup> would significantly improve the reliability of tank trucks. This proposal includes a number of revisions to the regulations including the following:

- construct and certify cargo tanks according to the American Society of Mechanical Engineers (ASME) Code,
- 2. specify accident damage protection for tank trucks,
- 3. require retesting and annual inspection of specification cargo tanks,
- 4. require corrosion testing of unlined cargo tanks at least every 2 years,
- 5. specify additional safety control measures for cargo tanks used to transport materials having more than one hazard class,
- 6. require that tanks used for certain hazmats have a minimum design pressure of 25 psig,
- 7. require that major repairs to cargo tanks be performed by qualified facilities, and
- 8. require certain recordkeeping of owners of hazmat transportation vehicles.

The proposal resulted from long-term research that evaluated the records of past cargo truck accidents and examined the existing Hazardous Materials Regulations pertaining to cargo tanks. Results indicated that the MC306-type cargo tanks used to transport flammable liquids were "highly susceptible to leakage and presents a substantial fire risk when overturned." The MC331-type cargo tank used to transport ammonia an 1 CPG is not, in some instances, properly maintained and requalified. Also, external corrosion, failure of a large percentage of relief valves, and substantial stress corrosion cracking were observed.

Cargo tanks used to transport high-vapor-pressure hazardous materials (MC307-type tanks) were found to have problems with poor maintenance, repair, requalification, and both external and internal corrosion. Also, leakage from malfunctioning valves during loading and unloading is a serious problem. DOT recommends that adoption of these proposed changes and additions in the Hazardous Materials Regulations would significantly improve cargo tank integrity during hazmat transportation.<sup>23</sup> An additional recommendation contained in the OTA study concerns the safety of intermodal containers, which are defined above. The United State has few manufacturers of these tanks, but their numbers in service are increasing rapidly. The problem with these containers involves the truck chassis used and the methods for securing the tanks to the truck chassis. Most of the available chassis in the United States for this type of container are "deficient either in length, securement devices, or overall design, which typically incorporates a high center of gravity," OTA recommends intensive study of the vehicle chassis and securement methods for intermodal tank transportation.<sup>23</sup>

Kletz<sup>261</sup> reviewed various transportation hazmat countermeasures in effect in the 1'nited Kingdom with those in the United States. Relief valves are cited as beneficial for prevention of tatk rupture because of overtilling; but often they do not prevent a burst during fires because the tank wall metal failed from high-temperature exposure. Also, relief valves are prone to leakage, can be knocked off during an accident, are difficult to maintain, and may discharge liquids (with no pressure relief) if the tank overturns. Kletz recommends a review concerning the safety aspects of relief valves and suggests their possible elimination on tankers carrying liquefied toxic gases. He also indicates that a study was made recently of the possible transportation of liquefied flammable gases (such as LPG) in retrigerated tanks at atmospheric pressure and temperatures below their boiling points. Possible increased safety would be achieved during a rupture, but insulation would reduce the overall payload and require more trips for the same quantities transported. More extensive investigation of this option appears to be warranted.

Kletz also addressed possible reasons why the U.S. railroad hazmat record was so much worse than that experienced in the United Kingdom (U.K.). Several of the possible reasons included:

1. poorer state of the U.S. trackage,

- 2. free shunting of tank cars in the U.S. railroad yards,
- 3. longer U.S. trains with heavier tank cars,
- 4. more segregation of loads in the U.K.,
- 5. more axle box inspection in the U.K.,
- 6. differences in the metallurgy of tank cars, and
- rail trips are longer in the United States with more sharp bends, higher centers of gravity for the tank cars, and more variations in the ambient temperature.

Improvements in U.S. railroad tank car design has been partially responsible for the decline in reported incidents since 1979. These features included the use of improved couplers, head shields to prevent couplers from piercing the ends of the tankers, and insulation to protect the tank cars from fire.

Olson<sup>164</sup> reviewed the major causes for train derailments and suggested a possible method for reducing the damage caused during derailment, which could in turn reduce the damage to tank cars carrying hazardous materials. The method involves installation of on-train derailment monitors that would activate the brake systems automatically on all cars carrying these materials. The monitors open the brake line on a derailed car at the instant of derailment and thereby actuate the emergency brakes on the train to reduce the damage of the derailment. A device to actuate the brakes at both the point of derailment and at the end of the train is claimed to prevent the cars at the end of the train from crushing the derailed car due to the delays in brake application.

A countermeasure that could mitigate hazmat releases during rail transport involves the installation of automatic sensors and warning devices at large railroad yards. An example illustrating this need concerns an acetaldehyde release from a ruptured tank car at the Conrail Corporation railyard in Avon, Indiana, on July 25, 1987.<sup>165</sup> About 20,000 gal of acetaldehyde were

released, forcing the evacuation of 2500 people, fifteen persons who were exposed to the fumes were treated at local hospitals. The first evacuation of East Avon, started 35 to 50 min after the release (depending on the time of the release according to different sources) and required about 55 min to complete. It is apparent that an immediate warning device could have decreased the delay of the start of evacuation significantly and possibly reduced the evacuation time too, since notification was primarily by local police patrol cars. Consideration should also be given to the installation of sensors and warning devices at all major transportation centers, including railroad yards, truck stops, inspection stations, truck terminals, etc.

### 15.3.3 Human Error Effects in Transportation Accidents

Analysis of transport accident causes recorded by DOT's Hazardous Materials Information System between 1976 and 1984 indicates that human error has been recorded as the primary cause (62%) followed by package failure (26.8%) and vehicular accidents (6.1%).<sup>23</sup> Therefore, consideration of improvements in human performance training and reliability must be given top priority when considering improvements to transportation safety. Kletz<sup>166</sup> classified human errors in the following four different categories:

1. <u>Accidents due to a moment's forgetfulness</u>. These often occur in spite of extensive training and long-term experience and probably can be avoided by better equipment designs that provide safeguards and alarms for nonstandard operations.

### 2. Accidents that could be prevented by better training and instruction.

This is particularly relevant to transportation where inadequate training of truck drivers, driver inexperience, and the absence of requirements for a national truck driver's license (requiring special training) are all major causes of accidents. The OTA study suggests the development of a national driver's license with special requirements for all hazardous materials, including gasoline.

3. <u>Accidents due to lack of ability</u>. These accidents are not as common but do occur in some cases because workers are required to perform more than they are capable of, physically or mentally. A common example of this would be the problem of driver fatigue, which is caused by drivers'

attempts to lengthen their (oad times through the use of stimulants, pep pills, etc.

4. <u>Accidents that would have been prevented by better supervision or regulations</u>. Although this category applies more clearly to production facilities where constant supervision is required, it has been applied effectively to the trucking industries through the use of checklists for hazardous materials shipments developed by the American Trucking Association.<sup>167</sup> The checklists, which are essentially the responsibility of the shippers' supervision, include three phases of inspection:

- Preinspection checklist checks compliance with shipping documents, vehicle markings/placards/specifications, vessel material of construction, and previous cargo identification.
- Preload checklist check on residual materials from prior loads, inspection of vessel and its fixtures, and check on vehicle cleanliness.
- <u>Postload checklist</u> check for leaks, closure of valves, installation of covers/caps/plugs, installation of placards, and a final check on the shipping documents, including the Material Safety Data Sheets and dangerous cargo manifests.

Experience indicates that shippers can effectively prevent or reduce the number of releases during transport. Comparable supervision during vehicle unloading operations is also extremely important.

One of the most effective methods for preventing human errors is through adequate training of operators, including periodic retraining to maintain their skills. OTA<sup>23</sup> recommends that: "special operator training specifically related to hazmats, and training for shipper and cargo personnel responsible for loading and unloading, fastening, blocking, and bracing nonbulk loads could increase safety substantially." OTA suggests that Congress consider mandating the development of specific training guidelines for all aspects of hazmat transportation, including the transfer operations. As an example of extensive inspection and training, the ICI Plant at Wilton, U.K., requires that all chemical haulers be evaluated every 2 years and their management, vehicles, driver training, whose control, and maintenance standards be examined in detail by a two-man team. If they are found to be below standard, the hauler is not allowed to operate for at least 3 months.<sup>163</sup>

# 15.4 LARGE-SCALE TEST FACILITIES

The Liquefied Gaseous Fuels (LGF) Spills Test Facility began operations in the summer of 1986. The facility, which was built at Frenchman's Flat as part of the DOE nuclear test site in Nevada,<sup>168</sup> is designed to test materials from each of the generic categories: cryogenic, aerosol forming, chemically reactive, isothermal (high pressure), and with some minor modifications, superheated liquids.<sup>169</sup> The design of the plant includes the following facilities:

1. The nitrogen storage and supply system provides drive, cooldown, and purge gas to the entire plant. The source of nitrogen gas is a liquid nitrogen (low-pressure) storage tank with a high-pressure cryogenic discharge pump. The vaporizer is an atmospherically heated unit. The liquid nitrogen or cold nitrogen gas is used to precool the cryogenic piping and tankage prior to introduction of fluids into the system.

2. The cryogenic spill system consists of means for receiving and storing cryogenic fluids and for discharge of the fluids at the spill point. Each of the two cryogenic tanks has a capacity of 26,000 gal. The cryogenic storage tanks are provided with valves and piping used for unloading test fluid into the storage tanks and transferring fluids from one tank to another.

3. The noncryogenic fluid spill system is used to test fluids that are not stored at cryogenic conditions. The storage tank reserved for this purpose is a 24,000-gal vessel of carbon steel construction and works at a pressure of 300 psig.

4. The vent system consists of a gathering header and a 400-ft-long transport header that discharge into the base of a 40-ft-high vent stack. This system is designed and sized to transport vented gases from any of the test fluids systems at the maximum flow rate anticipated during off-normal conditions.

5. The command, control, and data acquisition system serves as the overall control center for the spill facility, including the data acquisition system. The system consists of modern industrial control computer hardware and software of proven reliability and performance, plus the liquefied

gas facility acquisition system.

The facility has been designed to have the capabilities necessary to meet the testing needs of its potential users and is capable of reproducing actual sizes and rates of accidental releases as closely as possible using the actual materials of concern. The facility will allow tests such as pool fires (on water) and rapid phase transitions, which require the discharge of test fluids on water. The facility will accommodate, with some modifications, those tests of liquid gaseous fueld (LGFs) which, by their nature, require an extremely rapid or explosive release of test fluids into the atmosphere.

Two tests were conducted (September 1986) there by the Amoco Corporation, and DOE expected more companies to use the facility in 1987.<sup>168</sup> Amoco completed two tests releasing anhydrous hydrogen fluoride into the air. In each test, a controlled spill of 1000 gal was made, one lasting 3 minutes and the other 6 min. According to DOE, the vapors dispersed rapidly and traveled only about 1900 ft before completely disappearing well within the boundaries of the test site.

The weather conditions will allow tests at the facility only from the beginning of April until the end of September. Since a major purpose for the construction of the test facility is to provide a site for private sector-funded research and development, industrial involvement is mandatory. Individual corporations may participate through trade association-user groups or on an individual basis.

## 15.5 MISCELLANEOUS COUNTERMEASURES

Adaptations of equipment and procedures under development for other applications could be potential solutions to the problem of hazardous substances. Several examples such as remotely operated equipment, advanced computer programs based on artificial intelligence technology, and controlled burning of escaped chemicals are described.

#### 15.5.1 Remotely Operated Response Equipment

The automation and remote control technology that has been common and essential in handling hazardous materials for years is now just beginning to appear in firefighting technology.<sup>47</sup> The Snail is typical of a new generation of remote control firefighting devices, frequently dubbed robots, that are being developed for the firefighters of today. The Snail is a tracked, battery-operated device controlled by an umbilical cable on which is mounted a similarly remote controlled nozzle. The nozzle can operate through a full range of patterns from "on" and "off" to a straight stream or any fog pattern. At present, its capability includes the ability to drag 400 ft of charged 2-in, hose. The operator controls it from a belt-carryable console strapped to his waist through an umbilical cable; he can stand about 150 ft away from the Snail itself. This is far enough away to be shielded from the usual effects of heat but not far enough for some blast effects unless he has additional shielding. The Snail has the advantage of being lightweight and flexible. It would also be an economical unit to construct, being potentially available at a price many fire departments could afford.<sup>47</sup>

Another unit, the Fire Cat, which is now commercially available, it can drag 1500 ft of hose and can be operated by radio from a similar distance. Maneuverable up to a 60° grade and able to travel 5 mph, it can achieve a water discharge of 1200 gal/min.<sup>47</sup>

The usefulness of these two devices to responders of hazardous material emergencies could include many tasks that require closeup manipulations such as mechanical cover installation. In these two devices, the Fire Cat appears to be considerably more powerful in terms of water application, safe distance between the operator and machine, and speed. The Snail, on the other hand, has an enhanced portability due to its lighter weight and is less costly to build. It is not yet on the market, although it can be leased through its builder. Foreign devices, such as the one developed for the Yokohama, Japan, Fire Department, are wheeled instead of tracked and have a generally vertical rather than horizontal configuration. Television viewing capability has been installed.

Another unit under construction in Frankfurt, Germany, resembles a tanker with a cab at both ends. Underneath the truck in the center are two compartments that are used to house remotely controlled devices. The remote devices are intended to be primarily foam handling units but could also handle water.

The robots of the United States, Germany, and Japan are only one phase of the automated control devices that are being developed and will be of great assistance in handling of hazardous materials spills. Guided vehicles have been fabricated in the United States to improve manufacturing productivity that could very well be suited for use as remote units during hazardous material accidents. Examples of this type of vehicle are cited in the literature.<sup>180</sup>

Although not yet commercially available for hazardous accident control, a robot arm mounted on a computerized mobile unit could be utilized for patching and plugging purposes. The elements that comprise this module are in an advanced state of development. There are several models of electronic arms as well as mobile units that have reached commercial availability.<sup>180</sup> Little additional effort would be necessary to put these modules together to produce the first prototype of a hazmat remote vehicle.

### 15.5.2 Advanced Computer Systems

One of the major recent developments in technology is the accessibility of small efficient computers. Personal computers have become a prominent aid to problem solving. Many different software packages have been developed. In particular, small expert programs could be developed that would provide rapid preliminary solutions to particular emergency situations. Small computers in emergency vans could be also connected to a large central computer having a central expert system that would indicate, in a brief period of time, the emergency response measures to be taken immediately to mitigate a large variety of situations.

### 15.5.3 Controlled Burning of Hazardous Substance Releases

Although controlled burning of hazardous vapors from volatile chemical spills is a known countermeasure, information concerning the methodology and the situations where it can be applied is scarce. The CHRIS Manual<sup>81</sup> which was developed for waterways spills states that:

Burning-off is one of the most dangerous treatment operations. Burning should only be considered when it can be determined that the risks to people would be greater if burning were not attempted. Changing meteorological conditions or water surface currents can create hazardous conditions during burnoff.

Conditions where burning may be considered include:

- 1. during the disposal of floating flammable liquids,
- 2. when the travel of flammable gases must be stopped in order to localize the hazard.
- 3. in cases where well-established plans for burning have been developed prior to the accident, and
- 4. when the potential for an explosion, BLEVE, or generation of lethal combustion gases has been clearly ruled out under all possible circumstances.

The CHRIS Manual indicates that there is a lack of knowledge and experience concerning controlled burning and that assistance from experts should be obtained prior to any intentional ignition attempt.<sup>81</sup> Thus, it appears that investigation of this technique for a variety of extremely high risk chemicals should be implemented. Results of such a study could include:

- 1. guidance as to which chemicals can be safely burned under emergency spill conditions,
- 2. conditions under which the above chemicals can be safely burned, under controlled conditions,
- 3. procedures for igniting and controlling the combustion during a controlled burn,
- 4. A review of the types of location and the meteorological conditions when controlled burns should never be attempted,
- 5. A review of current industrial practices and standards for controlled burns, and
- 6. Development of mechanical devices for improving the safety of controlled burns.

7 Procedures for interrupting controlled burning if circumstances change during an emergency or controlled non-emergency.

In our judgment, implementation of the above recommendations should help establish whether this technology is a feasible countermeasure for hazardous chemical releases.

### 16 METHODOLOGY FOR RANKING OF CHEMICAL HAZARDS

A system for developing a uniform approach to the measurement of the relative threat from various hazardous chemicals was a principal element in the work statement (Sect. 1). This approach is needed because of the wide diversity in these materials with respect to:

1. toxicity level as airborne gases, vapors, or aerosols;

2. fire and explosive potential;

3. mobility of the substance after release;

4. domestic production and location of major production plants; and

5. domestic shipments.

Numerous attempts have been made to rank hazardous chemicals with respect to one or more of the above criteria, but to our knowledge, none has included all of them. The Comprehensive Environmental Response and Liability Act of 1980 (CERCLA) established methodology for setting priorities for remedial action at chemical waste sites in the United States.<sup>170</sup> Included among the criteria established was the hazard potential of the stored chemicals and the relative risk to nearby population. This "Hazard Ranking System" for determining the relative risks of the stored chemicals included the following criteria for "air route releases":

1. substance reactivity and incompatibility,

2. substance toxicity,

3. hazardous-waste quantity, and

4. targets population within a 4-mile radius.

Although this method of ranking is applicable only to CERCLA waste sites, portions of the methodology were used in developing our proposed system.

The EPA Industrial Research Laboratory developed a "Hazard Potential" system for comparing chemical spills on a scale of 1 to 10. This system included consideration of quantities of material released and the toxicity of the material; however, it did not include measures for the relative mobility or fire and explosive characteristics of the substance. The importance of the latter two

measures is emphasized by data that indicate that flammability and explosivity are associated with most of the fatalities in the AHE data base.

In the private sector, the Dow Chemical Company has developed a procedure for estimating the risk in terms of the maximum probable property damage that might occur from a chemical plant fire or explosion. Included in the methodology is a method for determining a "material factor" for various chemicals which is a measure of the intensity of energy release from a chemical compound during a fire or explosion. Consideration of its chemical toxicity is not included because the procedure is concerned only with property damage. The procedure involves using the National Fire Protection Agency's (NFPA) flammability factor (Nf) and reactivity factor (NR) for the chemicals to determine the material factors denoted by a number ranging from 1 to 40. For materials with unknown NFPA factors, the flammability can be derived from the flash point and the reactivity from the decomposition temperature or other properties. For this analysis, a decision was made to use the NFPA flammability (Nf), reactivity (NR), and health (NH) ratings for the various chemicals examined. Details of the definitions for each of these ratings are discussed below.

### 16.1 TOXICITY LEVEL

Recently, EPA published a list of 405 acutely toxic chemicals<sup>8</sup> as part of their Emergency Preparedness Plan intended to help communities to become aware of the toxic chemicals produced or transported through their areas. The criteria used to select this list are tabulated in Table 31 (Sect. 14.7.1.1).

EPA also included 26 chemicals that did not meet these criteria but are produced and transported in such large quantities as to constitute significant hazards. All of the volatile compounds in this group are included in the chemicals selected for ranking in Sect. 7. This EPA listing is probably the most comprehensive tabulation of acutely toxic chemicals produced on an industrial scale in the United States and has served as the basis for selection of the chemicals in Sect. 7 for ranking purposes.

The rating scheme proposed for toxicity in this study is that developed by the NFPA. An abbreviated description of the ratings follows:<sup>139</sup>

Rating	Description for materials within rating
0	No health hazard beyond that of ordinary combustible
	materials
1	Slightly hazardous to health; self-contained breathing
	apparatus desirable
2	Hazardous to health; use self-contained breathing
	apparatus
3	Extremely hazardous to health; use full protective
	clothing and self-contained breathing apparatus
4	A few whiffs of material cause death; normal protective
	clothing not adequate; use special equipment designed
	for specific chemical

Levels of the NFPA ratings and the associated toxicity data for the chemicals selected for rating are presented in Sect. 7.

### 16.2 FIRE AND EXPLOSIVE HAZARDS

The NFPA flammability ratings used for the fire hazard are described as follows:<sup>139</sup>

Rating	Description of materials within rating
0	Normally stable even in a fire and not reactive with water
1	Normally stable but become reactive at high temperature
	and pressures, or react with water
2	Normally unstable and will explode but does not detonate
3	Capable of detonation or explosive decomposition but
	requires strong initiating source or must be heated
	when confined before initiation
-4	Capable of detonation or explosive decomposition at normal
	temperature and pressures; sensitive to mechanical or
	localized thermal shock

The NFPA flammability and reactivity ratings for the selected chemicals are tabulated in Sect. 7.

# 16.3 MOBILITY IN THE ATMOSPHERE

In order for a hazardous chemical to be dispersed from a source, it would either have to be volatilized as a vapor or dispersed as a mist, aerosol, or dust by an explosion, fire, rapid reaction, or rapid pressure release when mixed with a volatile gas. The latter situation occurred at Institute, West Virginia, on August 11, 1985 (see Sect. 2.3), when aldecarb oxime was dispersed in volatile methylene chloride vapor as it was accidentally released from a storage vessel. Fires such as the pesticide fire that occurred at the Drexel Chemical Company near Memphis, Tennessee, can spread nonvolatile toxic chemicals in the smoke plume.<sup>29</sup>

The following is proposed for the mobility rating of volatile substances that could form gases or vapors upon release:

<u>Rating</u>	Mobility
0	Very low volatility; normal B.P. > 300°F
1	Low volatility; normal B.P. $< 300^{\circ}F > 150^{\circ}F$
2	Moderately volatile; B.P. $< 150^{\circ}F > 90^{\circ}F$
3	Very volatile; B.P. $< 90^{\circ}F > 20^{\circ}F$
4	Normally a gas; B.P. $< 20^{\circ}F$

This rating must also account for mobility in cases where the substance has a low volatility but might scatter acrosols via a fire or explosion. This is accomplished by setting the mobility rating equal to the maximum rating value of either the mobility value via volatility or the fire value or the reactivity values. For example, if a substance had a low volatility (rating = 1) and an explosion rating of 3, then the mobility rating would also be set at 3. If it had a fire rating of 4, then the mobility rating would also be set at 4.

### 16.4 DOMESTIC PRODUCTION/LOCATION

The actual threat from domestic production of hazardous chemicals is related primarily to the average amounts held in inventory at each plant site times the number of operating plants close to population centers. However, in the absence of operating plant inventory data, information on the total domestic capacity, average plant size, and location must be used to develop ratings for production. In Fig. 1 (Sect. 3.5), the frequency data for 28 chemicals show a trend of increasing numbers of releases with annual production. Based on this observation, the following arbitrary rating scale for production is proposed:

Rating	1984 production, Millions of Ib/year
1	<10
2	11 to 1000
3	1001 to 10,000
4	>10,000

To account for plant site, it would be necessary to locate each production facility with respect to its proximity to major clusters of population. Although data are available for many of the selected chemical plant addresses, detailed site maps will be required and these are not currently available. A major survey of hazardous chemical plant sites, surrounding areas, and transportation modes is recommended as an extension of this preliminary study.

#### **16.5 DOMESTIC SHIPMENTS**

In a manner similar to the production and storage of hazardous chemicals at plant sites, shipments presently constitute comparable risks but are more complex to evaluate. Exactly where and how much is being transported and on what type of vehicle are not known at present. The Office of Technology Assessment estimates that the number of hazardous shipments by land, sea, and air amount to about 500,000 per day.<sup>41</sup> Since very few data are available on shipments of hazardous chemicals, the full range of the quantitative risks involved cannot be determined.

However, an approximate ranking system can be developed for order-of-magnitude estimates of the quantities shipped, based on the following sources:

- 1. <u>Domestic production of the chemical</u> shipments should approximate some fraction of total production (e.g., about one-half of the chlorine produced is shipped).
- 2. <u>Import/export data</u> since both must be shipped, this provides minimum values for shipment.
- 3. <u>Data on "captive" production plants</u> certain sources indicate whether a few products are for captive use or are marketed.
- <u>Data from the United States Bureau of the Census (USBC)</u> publishes data on major chemical shipments such as ammonia and chlorine.<sup>171</sup> However, the degree of aggregation negates its utility for most chemicals.

Since bulk shipments for ammonia and chlorine are known to be at least 50% of the annual production, an upper limit value of 4 can be assigned to these shipment quantities and ranges for other materials scaled as follows:

Rating	Annual shipments (millions lbs/year)	
1	<10	
2	11 to 1000	
3	1001 to 10,000	
4	>10,000	

Since data concerning U.S. shipments of individual chemicals are not available in the literature, the following assumptions were made to establish the ratings for shipments:

### production-exports

1. Shipments (1984) = exports + imports + 2

This essentially assumes that all exports and imports (for which some data are available) are shipped and that about 50% of the annual production (less exports) is also shipped. This method usually results in a shipping ranking equal to the production rating. 2. Where data were available for production, import, and export rates prior to 1984, a 2% annual increase was assumed to determine the values for 1984.

Although these assumptions represent only rough approximations, they are used only for establishing relative levels between the chemical production and shipping rates and thus appear justified.

# 16.6 OVERALL RATING PROCEDURE

The expression developed for the overall ranking of the selected chemicals is:

$$OR = [NH * MH + Nf * Mf + NR * MR]$$

where

OR = overall rating for each chemical.

<u>Factor</u>	Individual rating	Multiplier
Toxicity	NH	MH = 2
Fire	Nf	Mf = 1
Explosive	NR	MR = 1
Mobility	Max(NM, Nf, NR)	MM = 1
Production	NP	MP = 1
Shipment	NS	MS = 1

This procedure represents an entirely arbitrary ranking system. The methodology expresses the overall ranking as a product of the intensive hazard ratings (toxicity, fire, and explosion) and the extensive quantity ratings (production and shipment). The mobility rating times its multiplier serves as an adjustment to the quantity ratings. Also, since mobility can be achieved by either high volatility or a fire or explosion which could scatter the material as as aerosol, the mobility rating used is the maximum of NM (mobility via volatility) or NR (explosive rating) or Nf (fire rating).

After determination of the overall ranking (OR) values for all the chemicals, the maximum value of OR is selected and normalized percentage values (based on maximum value  $\approx$  100) for the remaining materials are calculated. The chemicals are then arranged in four groups having a descending order of overall ranking as described in Sect. 7.

## 17 PROPOSED HAZARDOUS MATERIALS RATING SYSTEM

In order to test the rating system for hazardous materials described in Sect. 6, hazardous chemicals were selected from the EPA list of 405 toxic chemicals and from other sources of hazardous materials data such as the AHE.<sup>1</sup> A data base for these materials was then developed, and the proposed procedure was used to rank them into four groups having a descending order of relative risk.

### 17.1 SELECTION OF HAZARDOUS MATERIALS

Table 34 lists the chemicals selected for the ranking procedure along with their ratings for each category. All of these chemicals are considered toxic; however, some were included in the EPA list as "compounds considered hazardous but do not meet the criteria for acute poisons" and are so designated. Many materials such as methyl chloride, MIBK solvent, carbon monoxide, liquid oxygen, gasoline, propane, etc., were not included in the EPA list. A number of these materials were shown to be hazardous in the AHE report but were not included in the EPA list of 405 toxic chemicals.

The range of variables used as criteria for selection of these materials is as follows:

- 1. very acute to low toxicity,
- 2. large bulk industrial chemicals to low annual production rate chemicals,
- 3. highly flammable/explosive to relatively nonflammable/reactive materials,
- 4. materials listed in the AHE as causes of gross to zero numbers of injuries or death during 1980 and 1985, and
- 5. very volatile (mobile) to slightly volatile chemicals.

Data for the various NFPA ratings and production rates were obtained from the ORNL Toxicology Data Base,<sup>172</sup> the <u>SRI 1984 Directory of Chemical Producers</u>,<sup>143</sup> <u>Shreve's Chemical Process</u> <u>Industries</u>,<sup>174</sup> <u>Chemical and Engineering News</u>,<sup>175</sup> and the <u>Census of Manufacturers</u>.<sup>171</sup> Dow Chemical developed a list of "material factors" for most of the chemicals selected.<sup>117</sup> This list also includes NFPA ratings for health, flammability, and reactivity; however, in some cases, these ratings were increased, based on Dow's experience, and for this study the higher ratings were selected.

Table 34. Hazardoos che aicals selected for ranking procedure	
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		••••			Rankar	 Эк	
Chemical in the	Lowelly	Fue	Exposive	Mobility	Production	Shipment	Overall
Acetodervác	2		2	1	3	1	120
Accione	1	3	U.	٦	3	3	45
Acerviene	1	1	1	4	2	2	50
Arrolein	3		:	•	?	?	88
Adviced	3	2	1	2	2	2	36
$A_{i}(\alpha) = m^{(i)}(\alpha)$	1		1	ŧ	3	3	180
A(x) = 2	3	\$	11	3	3	2	65
Anviethende	1	3	1	3	2	2	(al.)
Amm. No.	3	2	0	1	1	-1	112
Amalon um	2	0	0	4	2	2	32
nvdervide Ammen om	0	t)	3	3	-1	3	32
niti de Benvene	2	3	0	1	3	3	63
Batad ene	2	1	2	1	3	3	120
But the	:	ĩ	ct	4	3	3	72
Barsheetine	;	3	U	;	2	2	30
Cartelland	1	11	0	1	2	1	12
Carbon do Xido	I	1)	u	4	3	3	21
Carbon disattor	2	3	41	3	2	2	42
Carbon	2	1	0	-1	4	2	Чю,
mon vade Carbon (etca	3	0	0	1	2	2	12
chiordane	3	3	1	3	1	-	30
Chlorine	3	1	1	1	-1	4	128
Chioroform	0	0	0	2		2	0
Chloropenn	1	0	1	-	1	1	33
	1	3	0	3	-1	4	365
Crude on							
Cumene	2	1	0	3	3	3	63
Cumenc hydro peroside	1	2	3	1	3	3	*1
Cylobexane	1	3	0	1	3	3	48
Cyclobexanone	1	2	0	2	2	2	16
Dazinon	.1	0	0	1	l	1	8
Dichior-methane	2	1	0	2	2	2	20
Dimethylamine	3	4	0	4	2	2	80
Epichloromyden	3	2	2	2	2	2	<b>1</b> ()
i tisyl acrylate	2	3	2	3	2	2	54
Eduction and the	11	1	0	1	3	3	27
Funzi persene	2	i	0	3	٦	1	63
Fither Fride	2	1	0	1	2	2	61
Erby' ether	2	i	1	1	2	2	ŗ,
Erm mercepter	2	1	0	I.	1	1	32
CENTER	I	4	2	1	3	3	Wi
infisiene chierade	2	3	0	٦	,	3	63

	200
Line 3+ controled	Prizedous chemicals selected for ranking procedure

			· · · · · · · · · · · · · · · · · · ·				
a Marina na Ka		tas	P Marshe	Mobility	Production	Shepment	Overall
n na sana ang ta	2	4	·		3		132
the state of the	2	0	u	u	2	2	41
the state	1	0	3	1	2	1	(st)
1999 - J. A.D.	2	;	0	-1	`	3	9m
	i	ì	U	3	2	r	<b>`</b> 0
diversions.		3	2	3	2	2	( sf.
with the standard	1	0	0	3	2	2	18
National Sector	ii.	;	11	1	3	2	413
n kultur an te Tim tan	\$	n	n	1	3	3	22
ಾರ್ಷ-೧೯೯೮ ಕಾರ್ಯಕ್ರ	1	1	2	1	2	2	112
nd i znit n Xiz	2	u.	ĩ	3	2	2	42
Ne e unar	;	:	13	1	3	2	\$400)
	:	1	н	1	3	2	60
1. 1. 1. 1. 1. 1. 1. 1. 1. 1. 1. 1. 1. 1	2	1	2	1	2	2	50
is proteins accure	:	,	:	3	2	2	34,
septerix <sup>1</sup> and mar	;	3	П	3	3	2	38
Sec. Sec.	0	2	и	2	1	1	1es
fracial witten	:	11	11	1	1	1	32
N: 38	2	3	0	3	2	2	42
Marian A	:	ţ	17	1	2	1	Li
Morenna	1	1	u	3	3	3	45
$\mathbf{M}_{\mathbf{g}}(\mathbf{m}) = (\mathbf{m}_{\mathbf{g}}) \mathbf{m}_{\mathbf{g}}$	<b>X</b> .	3	2	3	2	2	51
Marine mig	3		u.	3	3	3	63
$\mathbf{V}_{0}(\mathbf{x}_{0}, \mathbf{r}) = \mathbf{r}_{0}$	2	t	ų	-1	2	2	64
Methyl enyl Ketone	1	3	0	3	2	2	30
Methyl old me	1	П	1	2	1	1	1 \$
Merrar	2	\$	3	3	2	2	est (
is issuede Methyl	2	ł	()	i	۱	l	32
mercapian		,	,	3		,	
Methyl mythiadviare	2	ĩ	2		1	2	11
Meri svienu In verde	2	:	11	2	2	2	20
Martin and States and	2	;	11	t	1	2	32
Nactival petrolo Numeroter	1	1	0	1	3	3	72
Neppitulenc	2	2	0	2	2	2	24
$N \approx g_0 n = (q_0) d_0$	1	11	0	ĩ	1	1	`
New as walk	:	ì	43	\$	2	2	23
Owen is	:	*1	0	1	1	4	32
Participant	1		0	0	2	2	0
Parati in	ı	-	2	2	1	1	

					Rankir	אָר	
Chemicie name	Lower	hire	Explosive	Mobility	Production	Shipment	Overail
Peprocht in sphere of div	3	48	0			?	0
entane	1	3	u .	1	2	2	18
08 Dec.	X	2	14	2	3	3	48
n same	1	4	11	3	3	2	641
wish few search	<b>、</b>	:	2	2	2	2	341
nt el Nesprencies	;	11	2	2	2	2	5
Webber (1996) Both Else	2	:	a.	1	2	2	10
nnval a pilolote	:	1		1	٦	3	.j
n și vi che	1	;	l	1	:	3	45
opvine zven	п	1	ti	1	3	3	3
hi py ene uncle	2	1	2	4	3	3	120
tad	n	1	1	1	2	2	1
bisspecial cases Note zoniem 22	1	П	Ð	;	2	2	12
inter.	:	1	2	1	1	-	22
u di Jan	3	1	2	2		2	še.
ed att Alexan	;		-	-		-	U U
ed aminis ee		U.	11	0	2	-	
ores I d'aministe	1	0	0		-	-	0
u ur de Nde	,	u		1	-	-	0
eraener var	2	3	"		2	2	37
stoline 11.2.2			2	3	3	3	8)
1,2.2. Letra . http://www.hanc	1	0	0	1	2	2	10
etrich if ethylene	2	0	0	1	2	2	8
etraethyl lead	1	3	, <b>t</b>	3	2	2	72
etrahvdre (gren	2	3	1	ĩ	2	2	48
emamethy: lead	1	i	ĩ	3	2	2	72
runium zrach stale	1	0	1	I	2	2	14
duene	2	3	11	3	3	3	63
oluene 2.4. isocsanate	3	1	1	1	2	2	[n
richler ictuate 1.1.1		1	1	1	2	2	16
richloroethane- 1.1.2	3	3	0	3	2	2	54
1.1- Tri aloroethane	3	I	1	1	2	2	16
1.2 Tri- shloroethune	3	0	0	1	I	1	6
richloroethstene	2	1	(r	I	2	2	10
m actin	1	1	3	1	3	3	108
mil there	2	t	1	a	3	3	108
inșt de ni	2	i	2	1	2	2	NI
tooride (hite	1	3	i	3	2	2	eals.

classic 34 contract. Have the coordinate weeded for ranking procedure

Consideration was also given to the inclusion of perfluoroisobutylene (PFIB) as an extremely toxic chemical ten times as toxic as phosgene as a pulmonary irritant.<sup>176</sup> It is not listed in the EPA acutely toxic chemical list is included in  $Sax^{177}$  as having an  $LC_{LO}$  of 0.5 ppm/6 h for rats. Arito<sup>178</sup> has identified PFIB as a pyrolysis product of polytetrafluoroethylene (Teflon) when heated in a nitrogen stream at a temperature of 500°C or higher; however, heating in an air stream did not produce measurable levels of PFIB. Thermal degradation of Teflon has been known to cause "polymer fume fever," an influenza-like syndrome, due to inhalation of the pyrolysis products. Nevertheless, whether PFIB is partially responsible for this reaction has not been established.

Data on industrial production of PFIB are not available. <u>Chem Sources - USA (1984)</u><sup>179</sup> lists one supplier, SCM Specialty Chemicals, Gainesville, Florida, but a phone call revealed that they no longer sell it and did not know of any other suppliers in the United States. Therefore, it was not possible to include PFIB in the rating system.

## 17.2 OVERALL CATEGORIZATION OF HAZARDOUS MATERIALS

The rating system for hazardous materials described in Sect. 16 is useful to either rank the materials with respect to their relative risks or to group them into categories that represent decreasing levels of risk to the general public. The latter method was selected because it relieves local planning committees from forming judgments as to the real levels of risk for chemicals when they are simply ranked in a descending order of relative risk. The following categories were selected for this procedure:

	Overall rating range
Very high risk	72 - Max.
High risk	48 - <72
Moderate risk	32 - <48
Lesser risk	0 - <32

#### 17.2.1 Very High Risk Materials

This category includes those chemicals with high individual ratings for toxicity and/or fire and explosion, large production and shipment levels, and high mobility when released from confinement. For example, chlorine has individual ratings of 3, 1, 1, 4, 4, and 4 for toxicity, fire, explosion, mobility, production, and shipment, respectively, which results in an overall rating of 128. Propane has an overall rating of 72 resulting from individual ratings of 1, 4, 0, 4, 3, and 3 as described above. Most of the materials in this category are either extremely dangerous and/or are produced and shipped in large quantities.

## 17.2.2 High Risk Materials

This category also includes chemicals that are either produced and shipped in large quantities but have lower rating values for toxicity, fire, and/or explosion, or have lower production and shipping levels but high values for the hazards ratings (toxicity, fire, and explosion). An example of the latter is tetraethyl lead, which has ratings of 3, 3, 3, 3, 2, and 2 for toxicity, fire, explosion, mobility, production, and shipment, respectively.

### 17.2.3 Moderate Risk Materials

This category has a range of overall ratings from 32 to <48. Included are materials that have the lowest levels of production and shipment but high hazards levels. Several very high production and shipment materials are also included, but their hazards levels are quite low.

## 17.2.4 Lesser Risk Materials

This category includes those materials with an overall rating from 0 to <32. It includes those chemicals that have one or more hazards ratings above 0, and production/shipment ratings that generally range in the 1 to 2 levels. In some cases, the overall ratings are 0 because they are relatively nonvolatile (mobility rating = 0) even though they may have a significant toxicity rating.

### 17.3 RESULTS OF MATERIAL CATEGORIZATION

Categorization of the 121 materials selected into the four categories described in Sect. 17.2 is presented in Table 35. No attempt is made to rank the individual materials in their descending order of risk within – each category because in our judgment the data are not adequate for such a refinement.

Inclusion of all the chemicals listed in the EPA CEPP, along with other materials that are hazardous because of flammability and/or reactivity (that have not yet been included), is recommended as a further extension of this procedure. Although the number of hazardous materials listed under each category is about the same for this preliminary study, extension of the complete EPA list of 402 chemicals would probably increase the number of moderate risk and lower risk materials substantially. This initial effort attempted primarily to identify those high production/highly toxic materials that were more probable candidates for the very high and high risk categories. Benefits to be derived from an extension of this system include the following:

- 1. Local and regional planning committees would be able to prioritize their planning efforts around those materials which represented the highest risks to the local population.
- 2. Facilities that produce, consume, or store the higher risk materials could concentrate their efforts toward reducing the risks by countermeasures such as inventory reduction, substitute materials, improved containment, etc. (see Sect. 15.2).
- 3. Manufacturers of equipment for hazardous material mitigation could concentrate their development efforts on those materials shown to be the most risky to the population.
- 4. This system would provide a rational basis for determining the relative basis of population risk for new chemicals entering the market place.
- 5. This proposed system would focus attention on those materials in the data base which have the highest probabilities for major accidents over longer periods of time. Although the AHE data base records past experience for most of the hazardous materials examined here, many of the frequencies are low since occurrence of serious events follows a random pattern.

Table 35. Categorization of hazardous materials according to relative risk

1

Accident device and a schore accident activity accident activity accident activity activity activitient activity activity activitient activitient activity activitient activitient activity activitient activity activitient activity activitient activity activitient activitient activity activitient activitita activitient activitient activitient activitient ac	Very high risk materials (Overall rating = 72-max)	High risk materials (Overall rating = 48-<72)	Moderate risk materials (Overall rating = 32-<48)	l esser risk materials (Uverall rating = 0 - <32)	
Allyl alcohol Benzene Cumene Eihyl henzene Eihyl henzene Eihyl henzene Eihyl henzene Eihyl henzene Hydrofluoric acid Isobutane Methyl acrylate Methyl socyanate acctone Penane Phenol Ph	Acetaldehvde	Allvi chloride	Acetone	Butyl acctate	
Benzene Cumene Ethyl acrylate Ethyl acrylate Ethyl henzene Ethyl henzene Ethyl henzene Hydrazine Hydrazine Hydrazine Hydrazine Methyl acrylate Methyl acrylate Methyl socyanate actione Pennanc Pennac Pennanc Pennac Pennanc Pennanc	Acetylene	Allyl alcohol	Acrylic acid	Carbofuran	
Cumene Ethyl acrylate Ethyl henzene Ethyl henzene Ethyl henzene Ethyl henzene Ethyl henzene Gasoline Gasoline Methyl bromide Methyl socyanate actione Penanc	Acrolein	Benzene	Ammonium hydroxide	Carbon dioxide	
Eithyl acrylate Eithyl henzene Eithyl henzene Eithyl henzene Hydrofluoric acid asolina Hydrofluoric acid Isoburane Methyl acrylate Methyl isocyanate actione Penane Penane Penane Prenane Toluene White phosphorous Xylene (p-xylene)	Acrylonitrile	Cumene	Ammonium nitrate	Carbon tetrachloride	
Eithyl benzene Eithyl chloride Fluorine Gasoline Hydrazine Hydrazine Hydrazine Hydrazine Bobutane Methyl isocyanate actione Methyl isocyanate actione Penanc Phenol Phenol Phenol Touene Touene Touene White phosphorous Xylene (p-xylene)	Ammonia	Ethyl acrylate	Carbon disulfide	Chlordane	
Eithyl chloride Fluorine Gasoline Gasoline HydraZine Hydrafluoric acid Isodura Methyl acrylate Methyl socyanate actione Methyl isocyanate actione Phenol Phenol Phenol Phosphorous Xylene (p-xylene) te	Butadiene	Ethyl benzene	Chloropicnn	Chloroform	
Allorine Gasoline Gasoline Gasoline Gasoline Bytrofluoric acid Isobutane Methyl bromide Methyl bromide Methyl isocyanate acrone Phenol	Butane	Ethyl chloride	Crude oil	Cyclohexanone	
Gasoline Hydrazine Hydrofluoric acid Isobutane Methyl acrylate Methyl bromide Methyl isocyanate actone Penlanc Phenol Phe	Carbon monoxide	Fluorine	Cyclohexane	Diazinon	
Hydrofluoric acid Hydrofluoric acid Isobutane Methyl bromide Methyl bromide Methyl isocyanate actone Phenol Phenol Phose Prenar Tousene White phosphorous Xylene (p-xylene)	Chlorine	Gasoline	Epichlorohydrin	Dichloromethane	
Hydrofluoric acid Isobutane Methyl acrylate Methyl bromide Methyl bromide Methyl isocyanate acctone Phenol	Cumene hydroperoxide	Hydrazine	Ethyl mercaptan	Ethyl alcohol	
lsobutane Methyl acrylate Methyl bromide Methyl isocyanate actone Phenol	Dimethylamine	Hydrofluoric acid	Ethylenediamine	Ferric chloride	
e Methyl acrylate Methyl bromide Methyl bromide Methyl isocyanate acctone Pentane Phenol Phosene Prosphene White phosphorous Xylene (p-xylene)	Ethyl ether	Isobutane	Hydrogen	llexane	
Methyl bromide Methyl chloride Methyl isocyanate acctone Pennanc Phenol Phosene Toluene Toluene Toraphene White phosphorous Xylene (p-xylene)	Ethylene	Methyl acrylate	Hydrogen peroxide	Kerosene	
Rethyl chloride Methyl isocyanate acctone Peniane Phenol Phosene Tetrahydrofuran Toluene Toxaphene White phosphorous Xylene (p-xylene)	Ethylene oxide	Methyl bromide	Isopropyl acetate	Malathion	
entanc Penanc Penanc Phenol Phosene Totrahydrofuran Toluenc Toxaphene White phosphorous Xylene (p-xylene)	Formaldehyde	Methyl chloride	Isopropyl alcohol	Methyl ethyl ketone	L
Penlanc Phenol Phenol Phosgene Tetrahydrofuran Toluenc Toxaphene White phosphorous Xylenc (p-xylene) k	Hydrogen chloride	Methyl isocyanate acetone	Liquid oxygen	Methyl iodide	92
de Phenol Ieum etter) Tetrahydrofuran Toluene Toxaphene White phosphorous Xylene (p-xylene) ad aride	Hydrogen cyanide	Pentane	MIBK	Methylene chloride	
ileum etter) Phosgene Tetrahydrofuran Toluene Toxaphene White phosphorous Xylene (p-xylene) ad ride	Hydrogen sulfide	Phenol	Methanol	Naphthalene	
ileum etter) Tetrahydrofuran Toluene Toxaphene White phosphorous Xylene (p-xylene) ad ride	lsoprene	Phosgene	Methyl mercaptan	Nitrogen (liquid)	
e Toluene Toxaphene White phosphorous Xylene (p.xylene) ad rride	Naphtha (petroleum ether)	Tetrahydrofuran	Methyl methacrylate	Nitrous oxide	
e Toxaphene White phosphorous Xylene (p.xylene) ad rride	Propane	Toluene	Monochlorobenzene	Paraquat	
c White phosphorous Xylene (p-xylene) ad aride	Propylene	Toxaphene	Oxygen (gas)	Parathion	
Xylene ( <u>p</u> .xylene) ad ride	Propylene oxide	White phosphorous	Phos. pentasulf. (fire)	Pentachlorophenol dry	
Ide	Styrene	Xylene ( <u>p</u> -xylene)	Phosphorous oxychloride	Phthalic anhydride	
÷	Tetraethyl lead		Silane	Propylene glycol	
	Tetramethyl lead		Sodium	Red phosphorous	
	Vinyl chloride		Sulfur dioxide	Refrigerant 22	
Vinyl actate	Vinylidene chloride		Xylene ( <u>m</u> -xylene)	Sodium cyanide	
	Vinyl acetate			Sodium nitrate (fire)	
				Sodium nitrite	
				Tetrachloroethane-1,1,2,2	
				Tetrachloroethylene	
				Titanium tetrachloride	
				Toluene 2,4-diisocyanate	
				Toluene diisocyanate	
				I nchloroethane-1,1,1	
				Inchloroethane-1,1,2	
				I richloroethylene	

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#### 18 SUMMARY AND CONCLUSIONS FOR TECHNICAL OPTIONS

## 18.1 CHARACTERIZATION OF EMERGENCY RELEASES

A review of the principal methods currently used for characterizing the nature of emergencies produced a wide range of proposed definitions. The three typical response levels - a potential emergency, a limited emergency, or a full emergency condition - defined by the <u>NRT Planning</u> <u>Guide</u> provide guidelines to the public for determining the extent of the emergency. Response recommendations in terms of the emergency contacts to be made are also included. A comparison of the NRT Response Levels with the Nuclear Emergency Classifications reveals that the latter contains four levels of classification, including an unusual-event category. This alerts responders of potential degradation in the system but no release of radioactivity. Consideration of the addition of this level to hazardous materials emergencies is proposed in order to provide notification in cases where a potential emergency exists or where the first responder is unable to specify the level of response when an actual release has occurred. The types and extent of response required are also included in the NRT Response Level definitions.

#### 18.2 TECHNICAL BASIS FOR NEEDED COUNTERMEASURES

The technical issues are categorized, and their technical basis is defined for four areas: (1) prevention, (2) planning, (3) response, and (4) training. The technical bases cover a broad range of technical activities that will involve experts from a wide variety of disciplines, including engineering, mathematics, physics and chemistry, education, social science, and medicine.

## 18.3 EVALUATION OF AVAILABLE RESOURCES

Technical countermeasures for the mitigation of hazardous materials releases include a wide variety of considerations, such as emergency equipment, mathematical models, probabilistic risk assessments, and training programs. An overview of the resources currently available to local response organizations and chemical facilities that produce, store, or transport hazardous materials has been developed along with a partial identification of commercial sources.

#### 18.3.1 Vapor Hazard Control

Control of toxic vapors from a release is the initial line of defense against the spread and eventual damage to the public health that would occur. Control of fires and explosions has equal priority because of possible dispersion of toxic chemicals and the general safety of the surrounding community. Countermeasures evaluated include mechanical covers, vapor curtains, induced air movement, gelling equipment, and foam systems.

Three basic mechanical cover techniques are considered: (1) total cover of the spill area by cloth or other continuous material, (2) spray of a continuous cover such as urethane, and (3) buoyant particles that can be floated on the surface to reduce vaporization. Floating cover assemblies as well as particulate covers but are available commercially, cost may be a deterrent to the latter technique.

Water spray barriers can achieve worthwhile enhancement of the rate of dispersion and dilution of heavy gas spills, but these are practical problems with this technique. Wind direction changes necessitate the use of barriers wider than the actual vapor cloud and may require frequent redeployment of the equipment. Sprays have been shown to be effective in reducing the flammable plume size downwind of LNG spills.

Simple dilution provides a direct approach toward the reduction of toxic and flammable vapor concentration. This involves the transport and mixing of uncontaminated air with the released vapors. Large blower equipment, such as surplus jet engines, is available commercially and is currently being used by railroads to remove snow and by airports to disperse fog.

Gel formation on the surface of toxic spills has been used for liquid immobilization but not for vapor hazard control. The formation of a gel can generally reduce the vapor concentrations in the air over a spill; however, the time required for the gelling reactions to be completed is a limiting factor in the application of this technique for volatile toxic liquid releases. It is not applicable for releases of toxic gases.

Foams have the ability to suppress vaporization when applied over the surface of a volatile

chemical. The foam forms a barrier with a high resistance to both convective and molecular diffusion; in addition, it has the ability to absorb the vapors to a certain extent. The efficiency of vapor suppression depends on the vapor pressure and the solubility of the vaporizing chemical in water. Foams also reduce vaporization by insulating the chemical from solar radiation and the ambient air. However, foams lose their effectiveness for vapor suppression due to aging and the effects of wind, temperature, humidity, or intensity of sunlight. Additional layers of foam must be applied when this occurs.

Results of vaporization reduction tests (vaporization reduction is the ratio of actual concentration in the ambient air using foam to the monitored concentrations for free vaporization) indicate reductions that vary between 40 and 90% over duration periods up to 120 min. The data for ammonia showed reductions of about 50% for periods up to 120 min. Results for the flammability suppression by foams were measured in terms of the secure time before ambient air concentrations reached the lower explosive limit for particular flammable chemicals. Secure times of 60 min were achieved using foam depths of up to 10 in. In summary, we conclude that substantial improvements in vapor suppression of many toxic chemicals must be improved before this method can be considered as a viable countermeasure; however, foams do appear to be quite effective in preventing fires during the release of certain flammable chemicals.

## 18.3.2 Emergency Equipment

A wide variety of equipment is available for use in preventing toxic materials spills and in responding to emergencies that involve these materials. Many of these items are included in the equipment and supplies carried by emergency response teams responsible for mitigating the effects of chemical spills. The inventory of emergency equipment carried by the Houston Fire Department Hazardous Materials Response Vehicle is included for reference.

Items described include the following:

1. chlorine emergency kits,

2. off-loading pumping systems,

- 3. patching and plugging equipment,
- 4. response and communications equipment,
- 5. equipment for fires,
- 6. personal safety equipment, and
- 7. labels and placards.

In addition to the above items, inert-gas systems for the prevention of fires and explosions in vessels and storage tanks are also included.

#### 18.3.3 Emergency Warning and Evacuation Systems

Emergency warning and evacuation systems are of utmost importance in the prevention of injuries and fatalities from releases of toxic chemicals. In the case of fires and explosions, warnings and evacuations may be less effective due to the short lead times and the possible wide area effects. More statutory emphasis should be placed on requiring immediate notification and evacuation in instances where there is imminent danger of a fire or explosion even when no release of hazardous materials has occurred. For toxic chemical releases, the effectiveness of large-scale evacuations has been shown to be a function of the area to be evacuated, the population density, and the warning time. Warning time is a particularly important factor. Other issues that impact the effectiveness of evacuations include uncertainties in the physical hazards, uncertainties in the warnings, social factors, organizational factors, and certain behavioral factors. In general, the general population is more likely to proceed with evacuation when they perceive the situation to be personally threatening. However, most local communities are not well prepared for evacuations, and disaster preparedness for chemical emergencies is not currently accorded high priority or systematically addressed.

Public warning systems for the types of events considered must not only warn the community but should also provide specific directions for evacuation and/or sheltering. Systems that are available include alerting components such as sirens, bells, whistles, and horns plus communication components such as public address, telephone, radio and TV broadcasts. Combined alert and

notification systems are available and are used at certain chemical plants.

The determination of the zone to be evacuated during an emergency involves complex procedures that are dependent on many factors. Probably the most effective systems for this determination are the computerized atmospheric dispersion-emergency response programs available commercially. This judgment assumes that the release is of sufficient duration to allow operation of the computer system. Further, operation of the computer in a real-time mode enables periodic updating of the vapor cloud location, composition, and predicted direction of transport.

In the absence of available computerized systems or in cases where time will not permit their application, quick estimates of the emergency response zone can be developed by using a variety of published methods. These include evacuation tables, tables of maximum distances over which hazardous gases may be harmful, simple mathematical formula for estimating an evacuation zone, and charts based on Gaussian dispersion equation calculations. Development of a simple low-cost hand calculator that could be used by emergency response personnel to determine emergency response zones is recommended.

As an alternative to evacuation, in-place sheltering may be a viable means of self-protection at large distances downwind from the release point where the concentration of hazardous material is well below the flammable limits but may still be toxic. Calculations indicate that for short-time puffs of toxic gases, the dose to inhabitants of typical dwellings would be one or two orders or magnitude less than if they were exposed to the vapor cloud outside. Although the dose to the inhabitants short-term is low, over a long period (hours) the dose would be the same as that outside if the dwelling is not opened and flushed clean as soon as possible after the cloud has passed. If this is not possible, evacuation from the contaminated area may be necessary.

## 18.3.4 Hazmat Monitoring and Ambient-Air Dispersion Modeling

Response to a recent survey of monitoring activities by various chemical plants indicated that over 45% of the respondents routinely monitor emission of chemicals from their plants. The following methods are used:

- 1. detection of odors by operating personnel,
- 2. industrial hygiene monitoring,
- 3. portable gas detectors,
- 4. detector tubes,
- 5. grab samples,
- 6. fixed point continuous monitors, and
- 7. personal dosimeters.

Although advances in technology are in progress, the capability is not currently available for measuring all hazardous substances in the ambient air using a single system. Various instruments are designed for different chemicals, but for the most part the chemical species and its expected concentration range must be specified before a reliable system can be installed for emergency detection and monitoring. The survey also revealed that most of the monitoring done by chemical facilities is performed within the process unit areas; little monitoring is done at the plant boundaries or beyond.

The two major categories of monitors are point sensors, which analyze the air at one or more locations in or around a facility, and remote sensors, which are capable of continuously monitoring an entire plant area. Point sensors that were reviewed include the following:

- 1. ion mobility spectrometers,
- 2. amperometric and voltometric analyzers,
- 3. colorimetric analyzers,
- 4. flame photometric analyzers,
- 5. nondispersive absorption spectrometers,
- 6. dispersive absorption spectrometers,
- 7. fourier transform infrared spectrometers, and
- 8. mass spectrometers.

Remote scanning monitors considered include the following:

- 1. differential absorption light detection and ranging (DIAL), and
- 2. lidar systems.

Portable instruments for the detection of toxic or flammable chemical leaks that were also identified include:

- 1. gas detector tubes,
- 2. combustible gas detectors, and
- 3. portable gas chromatographs.

Many computer-based dispersion models for predicting the spatial and temporal dispersion of toxic and flammable vapor clouds have been developed and are now commercially available. In addition to their dispersion capabilities, certain models include features such as; inclusion of local emergency action plans, graphical displays of emergency action zones, special population (hospitals, etc.) needs information, facility on-site features to indicated process features at the leak location, and emergency plan checklists to monitor the progress of an emergency response.

A recent review of a group of 80 emergency response models identified ten commercial emergency response systems. Four of these systems were then subjected to detailed evaluations, which included simulations of actual dispersion tests. Results of these comparisons showed reasonable agreement for several models and identified potential problem areas in others. A major deficiency in all the models was the exclusion of simulations for chemical reactions, fires, and explosions. Seven commercially available emergency systems are identified, and their features and approximate costs are compared.

## 18.3.5 Hazards Evaluations of Processing Facilities

Predictive Hazards Evaluations (PHE) is the title given to a group of procedures used for detailed qualitative and quantitative safety studies performed on chemical processing facilities. They are used to identify and evaluate process hazards throughout all phases of the life of a facility:

design, construction, startup and shutdown, normal operations, and plant revisions. PHE have been

developed and used extensively over the past 10 years by chemical, petrochemical, and petroleum refineries throughout the world.

The procedures that have been developed may be divided into two categories: (1) those which provide identification of the specific hazards in a process plant and (2) a group of quantitative mathematical models capable of estimating the risks associated with both normal and abnormal plant operations.

Predictive Hazards Analyses (PHA) range from simple relatively inexpensive identification studies to very detailed, complex, and expensive systems. Decisions as to which systems are to be employed by a particular plant depend primarily on the levels of risk existing at the plant, the complexity of the process, the potential for serious consequences from an accident to the plant personnel and the local community, and the technical and financial resources available to the plant management.

Acceptance of PHA systems by the chemical industry varies considerably for the different methods. Widespread acceptance has occurred for Preliminary Hazard Analysis; Failure, Modes, Effects, and Criticality Analysis; and the HAZOP procedure. These are primarily procedures that force the plant designer/operators to review the process in intensive detail, identify those areas where significant risks exist, and provide information to management concerning the corrective actions required. A partial list of contractors who offer PHA services to the chemical industry is included.

#### 18.3.6 Emergency Response Information and Data Bases

The information required for developing of local community emergency response plans is very extensive, and obtaining it can consume significant amounts of time and resources. The types of information bases to be developed include:

1. hazardous materials properties (toxicity, flammability, reactivity, physical properties, etc.);

- 2. historical data on hazmat accidents; and
- 3. inventories and materials flow for hazmats.

Several excellent data bases are available for the properties of hazardous materials, including the EPA List of "Extremely Hazardous Substances," the Material Safety Data Sheets (MSDS), the MEDLARS Data Base, the CHRIS Hazardous Chemical Data Base, the Association of American Railroads Data Base, DOT's Guidebook for Hazardous Materials Incidents, and NFPA's Fire Prevention Guide on Hazardous Materials.

For historical data on major hazmat incidents, the most complete resource is the EPA Acute Hazardous Events Data Base. Transportation events are recorded under the DOT Hazardous Materials Information System; and, by law, all significant hazmat events are to be reported to and recorded in the National Response Center Data Base. This data base will probably improve significantly under the reporting provisions of the new SARA Title III statute.

The only federal materials flow data base for transportation of hazmats is the Commodity Transportation Survey. However, this information is usually aggregated and not useful for specific materials flows. Data concerning hazmat transportation by rail or by water are available, but data for truck transport are far less plentiful. Local surveys are usually required to determine the flows of hazmats through local communities for emergency planning purposes.

## 18.3.7 Community and Facility Planning for Toxic Chemical Emergencies

Guides, planning procedure handbooks, and reports of successful planning projects have been developed under the sponsorship of the federal government, industry, trade organizations, and private engineering organizations. Descriptions of the various documents available for planning operations, along with a partial list of organizations available for consulting in this area, are included.

#### **18.4 NEW TECHNICAL APPROACHES**

#### 18.4.1 Prevention of Chemical Accidents

Increased emphasis has been placed recently on the technical countermeasures involved in the prevention of chemical accidents and the interaction between the prevention and the emergency response aspects. Technical approaches reviewed in the area of prevention include the following:

- 1. human factors in accident prevention,
- 2. prevention at chemical production and storage facilities,
- 3. prevention through education and certification, and
- 4. community awareness programs.

Prevention countermeasures that appear promising for existing plants include:

- 1. plant risk analysis (HAZOP, Failure Mode and Effects, etc.),
- 2. equipment depressurization during emergencies,
- 3. secondary containment systems,
- 4. reduction of toxic material inventories,
- 5. substitutes for hazardous materials,
- 6. explosion suppression systems,
- 7. machinery vibration programs, and
- 8. improvements to storage systems.

Many of these countermeasures have already been implemented in certain chemical plants. Their adoption by the entire sector would almost certainly improve the overall safety and reliability of the processing industry and significantly reduce the frequency of chemical releases.

#### 18.4.2 Detection and Warning Systems

Probably the most critical need with respect to detection systems concerns the requirement for a remote sensing instrument that will detect releases of a wide range of chemicals over the entire area or boundary of a plant site. Instruments are currently available to perform this task for one or perhaps several chemicals but not for a broad range of materials. Also, they are not currently capable of detecting a mixture of hazardous materials in the ambient air. Costs for the available instruments for remote sensing are very high and probably beyond the range of most communities concerned with monitoring local highways, truck stops, and rail yards. The only realistic detection systems for local monitoring appear to be low-cost point sensors for particular chemicals such as ammonia, chlorine, hydrogen sulfide, etc. Selection of the hazards to be monitored can be accomplished by performing a hazards evaluation for a particular community and by identifying those chemicals that are most likely to present a risk to the community.

## 18.4.3 Minimizing Transportation Risks

Improved data and information systems concerning highway and rail transportation of hazardous materials are probably the most critical countermeasures needed by local planning committees. Data are not currently available for the flow of these materials throughout the nation; in most cases they can only be developed through local surveys. Many communities have followed this approach, but the costs are high - probably beyond the resources of most local areas. It may be feasible to utilize the data required by the new SARA Title III statute to develop a materials flow data base, and studies of this potential resource are recommended. The installation of adequate monitoring and warning equipment at transportation vehicle concentration points such as rail yards and truck stops appears to be a critical need. Recent experience has demonstrated that these areas are probable locations of toxic releases, and they represent significant risks to the nearby populations.

Another proposed countermeasure concerns the use of radio warning systems installed in vehicles carrying hazmats. These radios would be activated during an accident and would give first responders a description of the cargo and provide recommended response procedures from a remote position. It is suggested that this countermeasure would permit identification of the cargo much more rapidly and remove most doubts concerning the proper procedures to be used in response to chemical transportation accidents.

Development of remotely operated emergency response equipment, advanced computer programs that utilize artificial intelligence for emergency response situations, and investigation of the feasibility of controlled burning during hazardous chemical releases are also recommended.

## 18.5 METHODOLOGY FOR RANKING OF CHEMICAL HAZARDS

A procedure for ensuring a uniform approach to the measurement of the relative threat from various chemicals has been developed. Such as approach is needed because of the wide diversity in these materials. The procedure takes this diversity into account by assigning ratings for toxicity, fire, reactivity, mobility, domestic production, and domestic shipments to each material. Each rating is then multiplied by an importance factor, and the results are combined mathematically to obtain an overall ranking that can be used to compare the relative risks for each material.

The rating system was tested on 120 hazardous materials selected from the EPA list of "Extremely Hazardous Substances" and other sources. A broad range of variables was used as the criterion for selection of these materials, including the following:

1. very acute to low toxicity,

2. bulk industrial chemicals to low annual production rate chemicals,

- 3. highly flammable/explosive to nonflammable/nonreactive materials,
- 4. chemicals that have caused casualties to many injuries or deaths during 1980-85, and
- 5. very volatile (mobile) to slightly volatile chemicals.

Results of this rating system are tabulated in the following four categories, representing descending levels of relative risk: (1) very high risk materials, (2) high risk materials, (3) moderate risk materials, and (4) lesser risk materials. No attempt was made toward ranking the individual materials within their individual categories. The 120 chemicals selected were spread roughly equally among the four categories.

In our judgment this ranking system should be of value to planners responsible for selecting those materials which represent the maximum danger to their local communities and also for

determining the hazard ranking of new chemicals entering the market. Extension of this procedure to the entire list of "Extremely Hazardous Materials" is recommended.

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# 20 APPENDIX

# Glossary of Acronyms

AAR	American Association of Railroads
ABET	Accreditation Board for Engineering Technology
AIChE	American Institute of Chemical Engineers
API	American Petroleum Institute
BLEVE	Boiling Liquid Exponding Vapor Explosion
CAER	CMA's Community Awareness and Emergency Response Program
CEPP	EPA's Chemical Emergency Preparedness Program
CERCLA	Comprehensive Environmental Response, Compensation and Recovery Act (of 1976)
CFR	U.S. Code of Federal Regulations
CHEMNET	A mutual aid network of chemical shippers and contractors. CHEMNET has more than fifty participating companies with emergency teams, twenty-three subscribers, and several emergency response contractors.
CHEMSEP	OSHA Chemical Special Emphasis Program
CHEMTREC	Chemical Transportation Emergency Center operated by the Chemical Manufacturers Association
CHLOREP	Chlorine Emergency Plan operated by the Chlorine Institute
CHRIS/HACS	Chemical Hazards Response Information System/Hazard Assessment Computer System developed by the U.S. Coast Guard. HMACS is a computerized model of the four CHRIS manuals that contain chemical-specific data.
СМА	Chemical Manufacturers Association
CPG 1-3	Federal Assistance Handbook: Emergency Management, Direction and Control Programs, prepared by FEMA
CPG 1-8	Guide for Development of State and Local Emergency Operations Plans, prepared by FEMA
CPG 1-8A	Guide for the Review of State and Local Emergency Operations Plans, prepared by FEMA
CRC	CMA's Chemical Referral Center

CWA	Clean Water Act
DOC	U.S. Department of Commerce
DOD	U.S. Department of Defense
DOE	U.S. Department of Energy
DOI	U.S. Department of the Interior
DOJ	U.S. Department of Justice
DOL	U.S. Department of Labor
DOS	U.S. Department of State
DOT	U.S. Department of Transportation
EMA	FEMA's Emergency Management Assistance Program
ЕМІ	The Emergency Management Institute is a component of FEMA's National Emergency Training Center.
EOP	Emergency Operations Plan developed in accord with the guidance in CPG 1-8
EP	Extraction Procedure in RCRA
EPA	U.S. Environmental Protection Agency
ERG	DOT's Emergency Response Guidebook
ERT	EPA's Enviornmental Response Team
FEMA	U.S. Federal Emergency Management Agency
FEMA-10	Planning guide and checklist for Hazardous Materials Contingency Plans, forerunner of present Hazardous Materials Emergency Planning Guide
FWPCA	Federal Water Pollution Control Act
HAZMAT	Refers generally to hazardous substances, petroleum, natural gas, synthetic gas, acutely toxic chemicals, and other toxic chemicals.
HAZTOP	Hazard and operability study, a systematic technique for identifying hazards or operability problems throughout an entire facility
HHS	U.S. Department of Health and Human Services
НІТ	Hazard Information Transmission program provides a digital transmission of the CHEMTREC emergency chemical report to first

	responders at the scene of a hazardous materials incident.
HMAC (P)	Hazardous Materials Advisory Council
HMAC (P)	Memphis/Shelby County, Tennessee, Hazardous Materials Advisory Council
НМТА	Hazardous Materials Transportation Act
HSWDA	Hazardous and Solid Waste Disposal Amendments (1984) to RCRA
IEMIS	FEMA's Integrated Emergency Management Information System
IEMS	Integrated Emergency Management System, developed by FEMA
JRT	Joint Response Team efforts between the U.S., Mexico and Canada
LPG	Liquified Petroleum Gas
MSDS	Material Safety Data Sheets specified by SARA Title III
МТВ	Material Transportation Board of DOT
NACA	National Agricultural Chemicals Association
NCP	National Contingency Plan
NCP	National Oil and Hazardous Substances Pollution Contingency Plan
NEMS	FEMA's National Emergency Management System
NESHAP	National Emission Standards for Hazardous Air Pollutants
NETC	FEMA's National Emergency Training Center
NFA	The National Fire Academy, component of FEMA's National Emergency Training Center
NIOSH	National Institute for Occupational Safety and Health
NOAA	U.S. National Oceanic and Atmospheric Administration
NRC	National Response Center
NRT	National Response Team, consisting of representatives of 14 government agencies (DOD, DOI, DOT/RSPA, DOT/USCG, EPA, DOC, FEMA, USDA, DOJ, HHS, DOL, Nuclear Regulatory Commission, and DOE)
NSF	National Strike Force (under USCG)
OSC	On-Scene Coordinator, the Federal official predesignated by EPA or USCG to coordinate and direct Federal responses and removals

under the NCP

OSHA PL PMN	DOL Occupational Safety and Health Administration U.S. Public Law Premanufacturing Notification provision in TSCA
PSTN	Pesticide Satety Team Network (National Agricultural Chemicals Association)
RCRA	Resource Compensation and Recovery Act (of 1976)
RDDT	Research, Development, Demonstration and Training Provisions of SARA
RPM	Remedial Project Managers
RRT	Regional Response Teams composed of representatives of Federal agencies and a representative from each State in the Federal region
RQ	Reportable Quantities of hazardous chemicals (from CERCLA plus recent revisions)
RSPA	DOT Research and Special Programs Administration
SARA	The "Superfund Amendments and Reauthorization Act of 1986." Title III of SARA includes detailed provisions for community planning.
SARA Title III	The "Emergency Planning and Community Right-to-Know Act of 1986" (included in SARA)
SEOC	State Emergency Operations Center (Tennessee)
SSC	Scientific Support Coordinators (NOAA or EPA)
TEMA	Tennessee Emergency Management Agency
TSCA	Toxic Substance Control Act
USCG	U.S. Coast Guard (Department of Transportation)

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