PDHonline Course M282 (4 PDH)

Fire Dynamics Series: Fire Protection Fundamentals

Instructor: Lawrence J. Marchetti, PE, CFPS

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PDH Online | PDH Center

5272 Meadow Estates Drive
Fairfax, VA 22030-6658
Phone: 703-988-0088
www.PDHonline.com

APPENDIX B. FUNDAMENTALS OF FIRE PROTECTION

This appendix reviews some selected fundamentals and most relevant characteristics of fire chemistry and physics (temperature, combustion products, smoke, toxicity, and fire extinguishing agents, etc.). Those inspectors who have never been exposed to fire protection will benefit from studying these fundamentals.

B.1 T-Squared (t^2) Fire Power Law Heat Release Rate

B.1.1 Introduction

The primary mechanism driving the growth of a fire is the flame spreading across a fuel item or between multiple fuel items. This growing fire will continue until one or more of the following conditions exist(s):

- Flashover occurs and all combustible materials are involved simultaneously.
- The fire cannot spread further due to lack of combustible materials.
- The fire uses all available oxygen for combustion.
- The fire is extinguished by intervention.

B.1.2 t^2 Heat Release Rate

Fire development varies depending on the combustion characteristics of the fuel(s) involved, the physical configuration of the fuel(s), the availability of combustion air, and the influences associated with the compartment. Once a stable flame is attained, most fires grow in an accelerating pattern, reach a steady state characterized by a maximum heat release rate (HRR), and then enter into a decay period as the availability of either fuel or combustion air becomes limited. Fire growth and development are limited by factors such as the quantity and arrangement of fuel, quantity of oxygen, and effect of manual and automatic suppression systems.

The primary parameter for describing fire growth is the HRR of the fire and how it changes with time. The fire growth rate depends on the ignition process; flame spread, which defines its perimeter; and the mass burning flux over the area involved. Once a combustible surface has ignited, the fire size increases as the flame spreads across the surface or as additional items in the room become involved. An important aspect is that the time required for the fire to grow is driven by the ignition source and the combustible or flammable materials present.

For most materials, a local ignition eventually involves the entire fuel item by flame-spreading processes. A typical sofa, for example, involves some combustion of horizontal, upward vertical, and downward vertical flame spread. For furniture and commodities, this complex fire growth process cannot be predicted by a simple formula. However, each item can have a characteristic growth time consistent with its composition and configuration. For example, a given item is ignited, it may achieve a heat release of 1 MW (1,000 kW) in 130 seconds, while another object might take 80 seconds. A complete mathematical description of this process is quite involved and relatively unpredictable given the range of ignition scenarios and the complexity of describing the burning item(s).

Nonetheless, testing has shown, that the overall HRR during the fire growth phase of many fires can often be characterized by simple-time dependent polynomial or exponential functions (Heskestad, 1997). The total heat release of fuel packages can be well approximated by the power law fire growth model for both single item burning and multiple items involved in a fire. Testing has also indicated that most growing fires can be expected to grow indefinitely until intervention by fire fighters, and the fires have an early incubation period where fire does not conform to a power law approximation, as shown in Figure B.1-1. That figure illustrates that following an incubation period, the HRR of the fire grows continuously, proportional to the square of time.

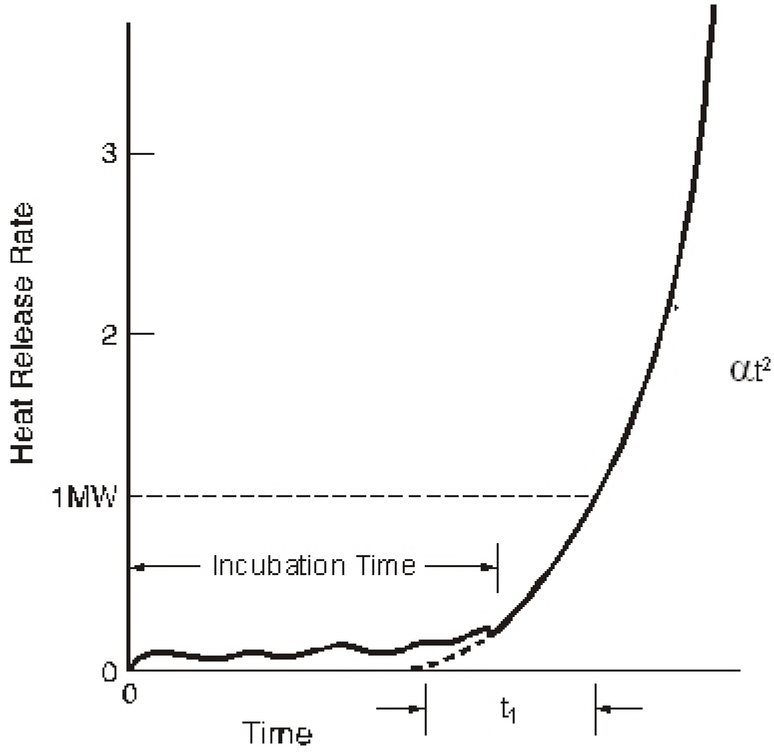

Figure B.1-1 Fire Growth of t^2 Fitted to Data
(Heskestad, 1997, © NFPA. With permission.)

The proposed model of the environment generated by fire in an enclosure is dependent on the assumption that the fire grows according to the following equation:

$$\dot{Q} = \alpha t^2 \qquad \text{(B-1)}$$

Where:

$\dot{Q}$ = the heat release rate (HRR) of fire (kW)
= a constant governing the speed of fire growth (kW/sec^2)
t = the time (sec)

The proposed model of the environment generated by fire in an enclosure is dependent on the assumption that the fire grows according to the following equation:

$$\dot{Q} = \alpha t^2 \qquad \text{(B-2)}$$

Where:

$\dot{Q}$ = the rate of heat release of fire (kW)
= a constant governing the speed of fire growth (kW/sec^2)
t = the time (sec)

The growth rate approximately follows a relationship proportional to time squared for flaming and radially spreading fires, which are consequently called t-squared (t^2) fires. Such fires are classed by the speed of growth, identified as ultra-fast, fast, medium, and slow. Where these classes are used, they are defined on the basis of the time required for the fire to grow to a heat release rate (HRR) of 1,000 kW (1 MW). Table B.1-1 summarizes the fire intensity constant ( ) and the growth time (t_g) for each of these classes.

Table B.1-1. Summary of t^2 Fire Parameters

Class of Fire Growth	**Intensity Constant (kW/sec^2)**	**Growth Time t_g (sec)**
Slow	0.00293	600
Medium	0.01172	300
Fast	0.0469	150
Ultra-Fast	0.1876	75

Figure B.1-2 plots the t^2 fire growth rate curves that have been developed. The t^2 relationship has proven useful and has therefore been adopted into NFPA 72, “National Fire Alarm Code®,” to categorize fires for siting of detectors as well as NFPA 92B “Guide for Smoke Management Systems in Mall, Atria, and Large Areas,” for design of smoke control systems.

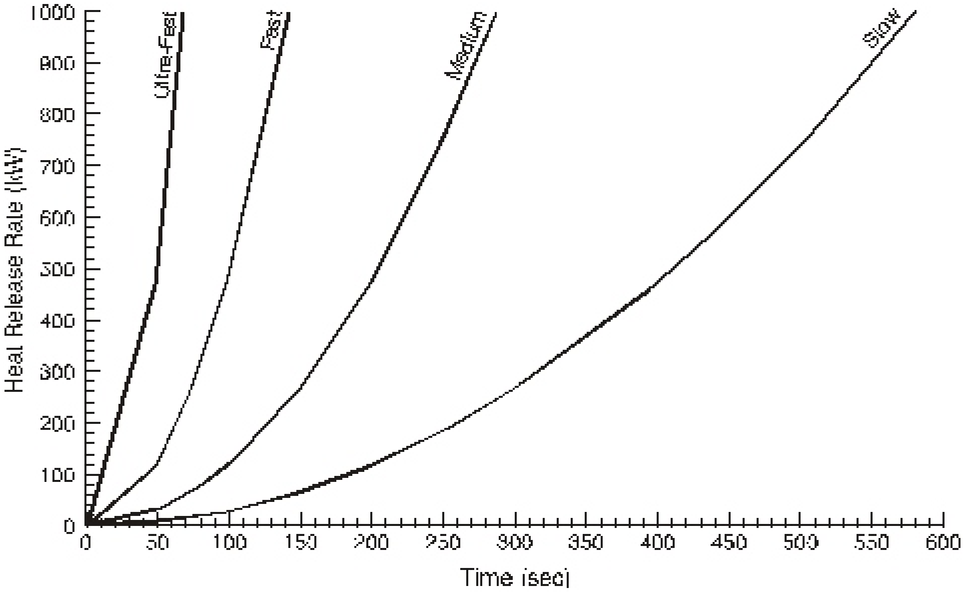

Figure B.1-2 Growth Rate Curves for t^2 Fire (NFPA, 72 and NFPA, 92B)

A t^2 fire can be viewed as one in which the HRR per unit area is constant over the entire ignited surface and the fire spreads as a circle with a steadily increasing radius. In such cases, the burning area increases in proportion to the square of the steadily increasing fire radius. Of course, fires that do not have such a conveniently regular fuel array and consistent burning rate might or might not actually produce a t^2 curve, but the t^2 approximation appears to be close enough for reasonable design decisions.

Figure B.1-3 provides the HRR results of various full-scale free burn tests performed at Factory Mutual Research Corporation (FMRC) (also reported by Nelson, 1987), superimposed on the t^2 HRR curves, using various standard test commodities for fuel arrays. Figure B.1-4 relates the classes of t^2 fire growth curves to a selection of actual fuel arrays. Figure B.1-5 plots the HRR curves for various upholstered furniture items. Figures B.1-3 to B.1-5 show that the actual fire growth curves for many common fuel arrays tend to be greater than the medium fire growth curve.

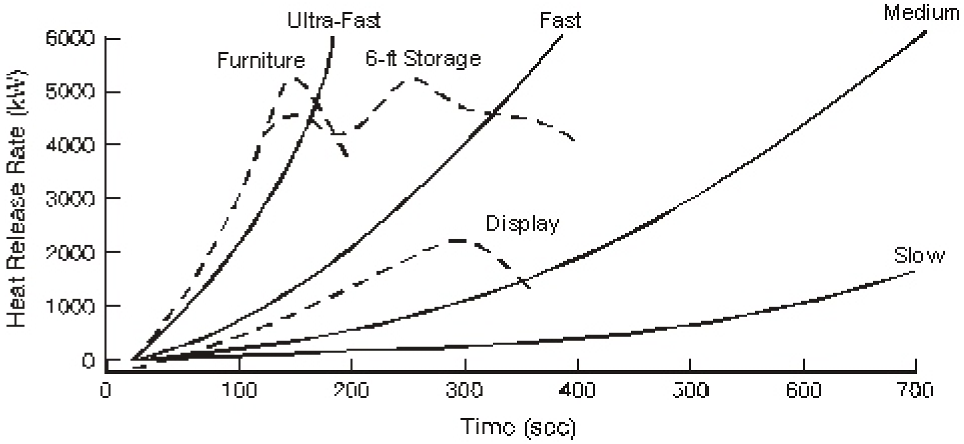

Figure B.1-3 Comparison of t^2 Heat Release Rate with Full-Scale Free-Burn Heat Release Rate (Nelson, 1987)

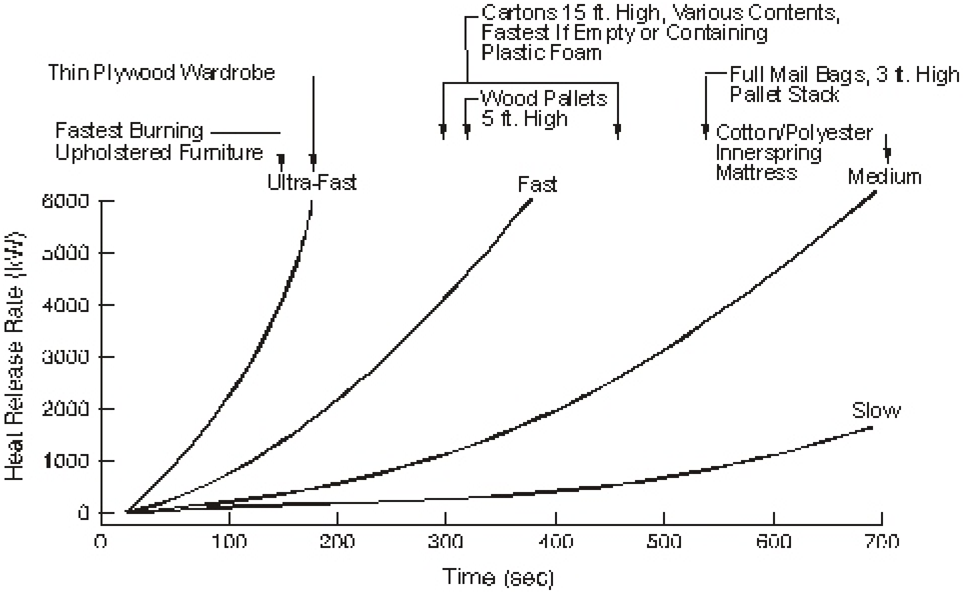

Figure B.1-4 Relation of t^2 Heat Release Rate to Some Fire Tests (Nelson, 1987)

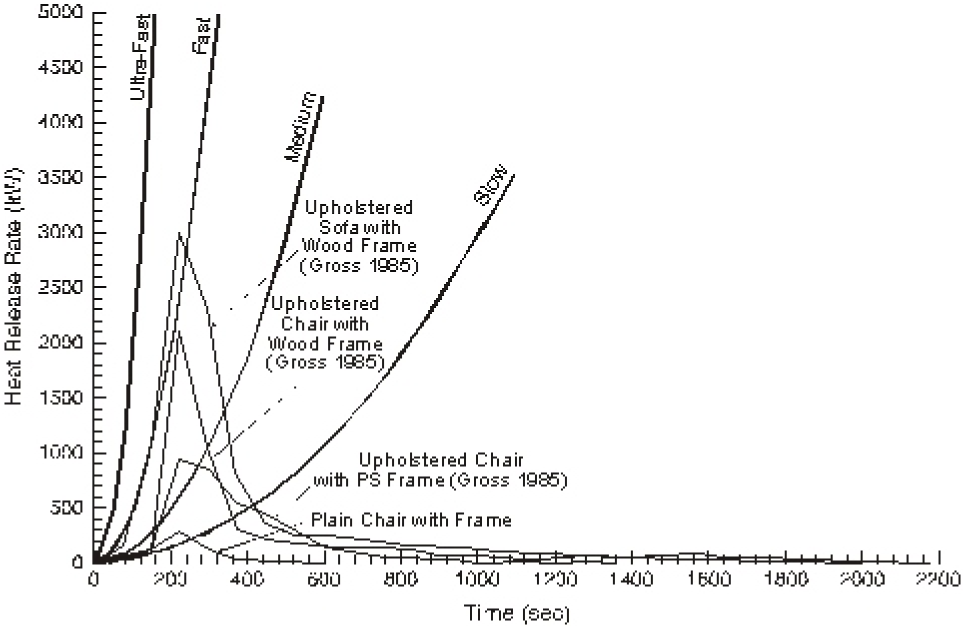

Figure B.1-5 Comparison of t^2 Heat Release Rates with Full-Scale Furniture Heat Release Rate

Table B.1-2 tabulates the maximum HRR for various warehouse materials. As shown, the majority of these materials exhibit fire growth rates in the fast or ultra-fast ranges. The preponderance of actual fire testing over the 1990's has shown that common fuel arrays exhibit fire growth rates that tend to exceed the medium t^2 fire growth rate.

Table B.1-2. Maximum Heat Release Rates of Warehouse Materials (NFPA 72, 1999 Edition, Appendix B)

Warehouse Material (See Notes 1 and 2)	**Growth Time (sec)**	**Heat Release Rate ($\dot{Q}$) (Btu/sec-ft^2) (See Note 3)**	**Fire Growth Classification**
Wood pallets, stacked, 1½ ft high (6%–12% moisture)	150–310	110	Fast-Medium
Wood pallets, stacked, 5 ft high (6%–12% moisture)	90–190	330	Fast
Wood pallets, stacked, 10 ft high (6%–12% moisture)	80–110	600	Fast
Wood pallets, stacked, 16 ft high (6%–12% moisture)	75–105	900	Fast
Mail bags, filled and stored 5 ft high	190	35	Medium
Cartons, compartmented and stacked 15 ft high	60	200	Fast

Table B.1-2. Maximum Heat Release Rates of Warehouse Materials
(NFPA 72, 1999 Edition, Appendix B)

Warehouse Material (See Notes 1 and 2)	**Growth Time (sec)**	**Heat Release Rate ($\dot{Q}$) (Btu/sec-ft^2) (See Note 3)**	**Fire Growth Classification**
Paper, vertical rolls, stacked 20 ft high	15–28	-	(See Note 4)
Cotton (also PE, PE/cot, acrylic/nylon/PE), garments in 12 ft high racks	20–42	-	(See Note 4)
Cartons on pallets, rack storage, 15 ft–30 ft high	40–280	-	Fast-Medium
Paper products, densely packed in cartons, rack storage, 20 ft high	470	-	Slow
PE letter trays, filled and stacked 5 ft high on cart	190	750	Medium
PE trash barrels in cartons, stacked 15 ft high	55	250	Fast
FRP shower stalls in cartons, stacked 15 ft high	85	110	Fast
PE bottles, packed in item 6	85	550	Fast
PE bottles in cartons, stacked 15 ft high	75	170	Fast
PE pallets, stacked 3 ft high	130	-	Fast
PE pallets, stacked 6 ft–8 ft high	30–55	-	Fast
Methyl alcohol	-	65	-
Gasoline	-	200	-
Kerosene	-	200	-
Diesel oil	-	180	-

Notes:
(1) For SI units, 1 ft = 0.305 m.
(2) FRP = fiberglass-reinforced polyester; PE = polyethylene; PS = polystyrene; PP = polypropylene; PU = polyurethane; PVC = polyvinyl chloride.
(3) The HRRs per unit floor area are for fully involved combustibles, assuming 100-percent combustion efficiency. The growth times shown are those required to exceed 1,000 Btu/sec HRR for developing fires, assuming 100-percent combustion efficiency.
(4) Fire growth rate exceeds design data.

Madrzykowski (1996), compared HRR data for office work stations with standard t^2 HRR fire curves. Figure B.1-6 shows the HRR time history of the fire growth of a three-sided office work station compared to t^2 fire curves. Notice how the fire begins as a slow-medium growth rate fire, and then the slope increases to be representative of a fast-ultra-fast fire. As shown in Figure B.1-6, one can use the t^2 fire growth model to determine the HRR of similar fuel packages.

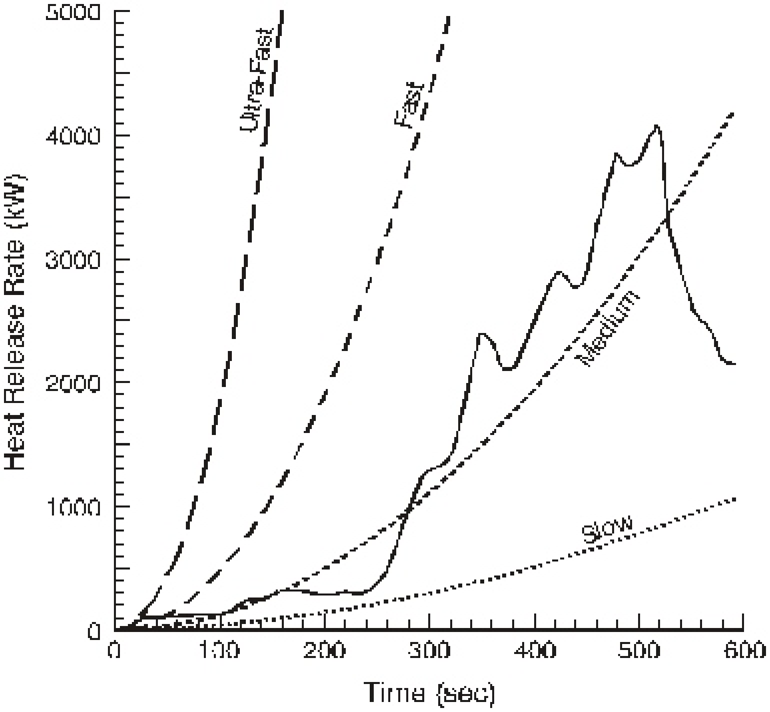

Figure B.1-6 Three-Sided Work Station Heat Release Rate Curve Compared with t^2 Curves (Madrzykowski, 1996)

Figure B.1-7 shows the relationship between t^2 fire curves and six 1.2-m (4-ft) high stacks of mixed wooden pallets (8 to 9 pallets per stack) arranged in two rows of three stacks, with the three stacks in each row forming an unbroken line with 100-mm between the front and back rows. Figure B.1-7 shows that both tests exhibited there was an incubation period following which the fire growth rate was approximately parallel to the t^2 fast fire growth curve.

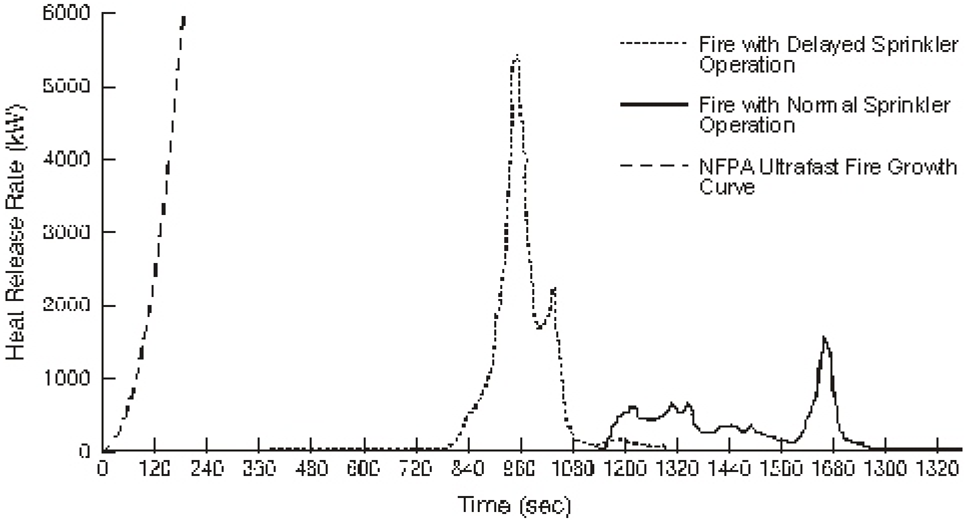

Figure B.1-7 Heat Release Rate Curve for Idle Pallets Compared with t^2 Curves (Garred and Smith, 1999, Interscience and Interflam. With permission.)

Figure B.1-8 shows the relationship between t^2 fire curves and six 12-m (4-ft) high stacks of cardboard boxes arranged in two rows of three stacks, with no gaps between the stacks. The boxes were ignited by setting light to a ball of crumpled newspaper pushed 100 mm under the front of the central stack in the front row of the array. Figure B.1-8 shows that both tests exhibited a long incubation period, as the ball of newspaper proved to be slow burning. However, the fire did break into the boxes immediately above the ignition source, and the flames eventually burst from the front of those boxes and then rapidly up the front of the central (ignition) stack. Thereafter the fire growth rate was similar to the ultra-fast t^2 fire curve.

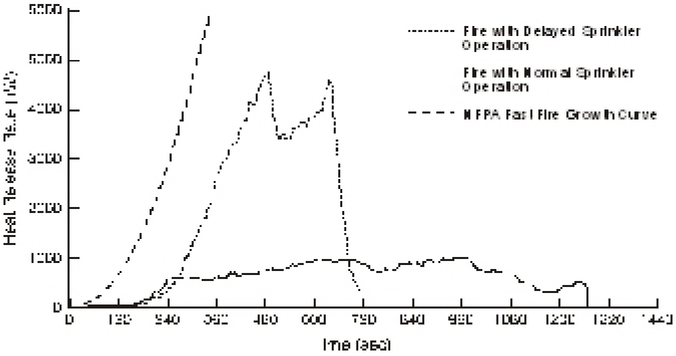

Figure B.1-8 Heat Release Rate for Stacked Box Fires Compared with t^2 Curves
(Garred and Smith, 1999, Interscience and Interflam. With permission.)

B.1.3 References

Garred, G., and D.A. Smith, "The Characterization of Fires for Design," Interflam 1999, Conference Proceedings of the 8th International Interflam Conference, Interscience Communication Limited, England, pp. 555–566, June-July 1999.

Gross, D., "Data Sources for Parameter Used in Predictive Modeling of Fire Growth and Smoke Spread," NBSIR 85-3223, U.S. Department of Commerce, National Bureau of Standards (NBS), Gaithersburg, Maryland, 1985.

Heskestad, G. "Venting Practice," Section 7, Chapter 7, *NFPA Fire Protection Handbook*, 18th Edition, A.E. Cote, Editor-in-Chief, National Fire Protection Association, Quincy, Massachusetts, pp. 7–105, 1997.

Madrzykowski, D., "Office Station Heat Release Study: Full Scale vs. Bench Scale," Interflam 1996, Conference Proceedings of the 7th International Interflam Conference, Interscience Communication Limited, England, Compiled by C.A. Franks, pp. 47–55, 1996.

Nelson, H.E., "An Engineering Analysis of the Early Stages of Fire Development: The Fire at the Dupont Plaza Hotel and Casino on December 31, 1986," NBSIR 87-3560, U.S. Department of Commerce, National Bureau of Standards (NBS), Gaithersburg, Maryland, May 1987.

NFPA 72, "National Fire Alarm Code," 1999 Edition, National Fire Protection Association, Quincy, Massachusetts.

NFPA 92B, "Guide for Smoke Management Systems in Malls, Atria, and Large Areas," 2000 Edition, National Fire Protection Association, Quincy, Massachusetts.

B.2 Elements of Hydraulic and Electrical Systems

Table B.2-1 provides the basic elements of a hydraulic system along with the corresponding elements of an electrical system.

Table B.2-1. Corresponding Elements of Hydraulic and Electrical Systems
(NFPA 921, 2002 Edition)

Elements of a Hydraulic System	**Elements of an Electrical System**
Pump	Generator
Pressure	Voltage (potential or electromotive force)
Pounds per square inch (psi)	Volts (V)
Pressure gauge	Voltmeter
Water	Electrons
Flow	Current
Gallons per minute (gpm)	Amperes (A)
Flowmeter	Ammeter
Valve	Switch
Friction	Resistance (Ohms)
Friction loss	Voltage drop
Pipe size (inside diameter)	Conductor size (AWG No.)

Hydraulic systems use a pump to create the hydraulic pressure necessary to force water through pipes. The amount of hydraulic pressure is expressed in pounds per square inch (psi) and can be measured with a pressure gauge. By contrast, electrical systems use a generator to create the necessary electrical pressure (voltage) to force electrons through a conductor. The amount of electrical pressure is expressed in volts and can be measured with a voltmeter.

In hydraulic systems, water flows in a useful way. The amount of water flow is expressed in gallons per minute (gpm) and may be measured with a flowmeter. By contrast, electrical systems, it is electrons that flow in a useful way in the form of electrical current. The amount of electrical current is expressed in amperes (A) and may be measured with an ammeter. Electric current can be either direct current (dc), such as supplied by a battery, or alternating current (ac), such as supplied by an electrical utility company.

In hydraulic systems, water pipes provide the pathway for the water to flow. By contrast, electrical systems, conductors such as wires provide the pathway for the current to flow.

In a closed circulating hydraulic system (as opposed to a fire hose delivery system, where water is discharged out of the end of the hose), water flows in a loop, returning to the pump, where it again circulates through the loop. When the valve is closed, the flow stops everywhere in the system. When the valve is opened, the flow resumes. By contrast, an electrical system *must* be a closed system, in that the current must flow in a loop known as a complete circuit. When the switch is turned on, the circuit is completed and the current flows. When the switch is turned off, the circuit is open (incomplete) and the current flow stops everywhere in the circuit. This voltage drop is called the potential or electromotive force.

Friction losses in the pipes of a hydraulic system result in pressure drops. By contrast, electrical friction (i.e., resistance) in conductors and other parts of an electrical system results in electrical pressure drops or voltage drops. Ohm's law must be used to express resistance as a voltage drop.

When electricity flows through a conducting material, such as a conductor, a pipe, or any piece of metal, heat is generated. The amount of heat depends on the resistance of the material through which the current is flowing and the amount of current. Some electrical equipment, such as heating units, are designed with appropriate resistance to convert electricity to heat.

The flow of water in a pipe at a given pressure drop is controlled by the pipe size. A larger pipe allows a greater volume (more gallons per minute) of water to flow than a smaller pipe at a given pressure drop. Similarly, larger conductors allow more current to flow than smaller conductors. Conductor sizes are given in American Wire Gauge (AWG) numbers. The larger the number, the smaller the conductor diameter. The larger the diameter (and hence the larger the cross-sectional area) of the conductor, the lower the AWG number and the less resistance the conductor has.

B.2.1 Reference

NFPA 921, "Guide for Fire and Explosion Investigations," 2001 Edition, National Fire Protection Association, Quincy, Massachusetts.

B.3 Classes of Fires

Generally the purpose of a letter designation given to a particular fire category is to classify it according to the type of fuel and possible spread of the fire. The letter classification also provides a general indication of the severity and type of the hazard. NFPA 10, “Standard for Portable Fire Extinguishers,” classifies fires as either Class A, Class B, Class C, Class D, or Class K according to the fuel involved.

Class A Fires

Fires in ordinary combustible materials, such as wood, cloth, paper, rubber, and many plastics.

Class B Fires

Fires in flammable or combustible liquids, petroleum greases, tars, oils, oil-based paints, solvents, lacquers, alcohols, and flammable gases.

Class C Fires

Fires that involve energized electrical equipment where the electrical nonconductivity of the extinguishing media is of importance. (When electrical equipment is de-energized, fire extinguishers designed for Class A or Class B fires can be safely used).

Class D Fires

Fires in combustible metals, such as magnesium, titanium, zirconium, sodium, lithium, and potassium.

Class K Fires

Fires in cooking appliances that involve combustible cooking media (vegetable or animal oils and fats).

B.3.1 Reference

NFPA 10, “Standard for Portable Fire Extinguishers,” 2002 Edition, National Fire Protection Association, Quincy, Massachusetts.

B.4 Classification of Hazards

B.4.1 Light (Low) Hazard

Light hazard occupancies are locations where the total amount of Class A combustible materials (including furnishings, decorations, and content), is a minor quantity. This can include some buildings or rooms occupied as offices, classrooms, churches, assembly halls, guest room areas of hotels/motels, and so forth. This classification anticipates that the majority of content items are either noncombustible or so arranged that a fire is not likely to spread rapidly. Small amounts of Class B flammables used for duplicating machines, art departments, and so forth, are included, provided that they are kept in closed containers and safely stored (Conroy, 1997 and NFPA 10).

B.4.2 Ordinary (Moderate) Hazard

Ordinary hazard occupancies are locations where of Class A combustibles and Class B flammables are present in greater total amounts than expected under light (low) hazard occupancies. These occupancies could consist of dining areas, mercantile shops, and allied storage; light manufacturing, research operations, auto showrooms, parking garages, workshop or support service areas of light (low) hazard occupancies; and warehouses containing Class I or Class II commodities as defined by NFPA 231, "Standard for General Storage," (Conroy, 1997 and NFPA 10).

B.4.3 Extra (High) Hazard

Extra hazard occupancies are locations where the total amount of Class A combustibles and Class B flammable (in storage, production, use, finished product, or combination thereof) is over and above those expected in occupancies classed as ordinary (moderate) hazard. These occupancies could consist of woodworking, vehicle repair, aircraft and boat servicing, cooking areas, individual product display showrooms, product convention center displays, and storage and manufacturing processes such as painting, dipping, and coating, including flammable liquid handling. Also included is warehousing or in-process storage of other than Class I or Class II commodities (Conroy, 1997 and NFPA 10).

B.4.4 References

Conroy, M.T. "Fire Extinguisher Use and Maintenance," Section 6, Chapter 23, *NFPA Fire Protection Handbook*, 18th Edition, A.E. Cote, Editor-in-Chief, National Fire Protection Association, Quincy, Massachusetts. 1997.

NFPA 10, "Standard for Portable Fire Extinguishers," 2002 Edition, National Fire Protection Association, Quincy, Massachusetts.

NFPA 231, "Standard for General Storage," National Fire Protection Association, Quincy, Massachusetts.

B.5 Classes of Fires and Extinguishing Agents

One or more of the following mechanisms—more often, several of them simultaneously—can be used to extinguish fire:

- Physically separating the combustible substance from the flame
- Removing or diluting the oxygen supply
- Reducing the temperature of the combustible or of the flame
- Introducing chemicals that modify the combustion chemistry

For example, when water is applied to a fire of a solid combustible burning in air, several extinguishing mechanisms are involved simultaneously. The solid is cooled by the contact with water, causing its rate of pyrolysis, or gasification, to decrease. The gaseous flame is cooled, causing a reduction in heat feedback to the combustible solid and a corresponding reduction in the endothermic pyrolysis rate. Steam is generated, which, under some confined conditions, may prevent oxygen from reaching the fire. Water in the form of fog may block radiative heat transfer.

As another example, consider the application of a blanket of aqueous foam to a burning pool of flammable liquid. Several mechanisms may be operative. The foam prevents the fire's radiant heat from reaching the surface and supplying the needed heat of vaporization. If the fire point of the flammable liquid is higher than the temperature of the foam, the liquid is cooled and its vapor pressure decrease. If the flammable liquid is water soluble, such as alcohol, then, by a third mechanism, it will become diluted by water from the foam, and the vapor pressure of the combustible will be reduced.

As yet an example, when dry chemical is applied to a fire, the following extinguishing mechanisms may be involved:

- Chemical interaction with the flame
- Coating of the combustible surface
- Cooling of the flame
- Blocking of radiative energy transfer

The agent mentioned above—water, foam, and dry chemicals—each work by a combination of several mechanisms, and the relative importance of the various contributions varies with circumstances. Table B.5-1 provides the classes of fires with examples and extinguishing agent.

Table B.5-1. Fire Classes with Extinguishing Agents

Fire Class	**Description**	**Examples**	**Extinguishing Agents**
A	Ordinary combustibles	Wood, cloth, paper, rubber, and many plastics	Water, dry chemicals, foam, some Halon
B	Flammable liquids, gases, and liquid-derived solids	Gasoline, oils, LPG, paraffin or heavy lubricants, grease	CO_2, dry chemical agents, Halon, foam (Class B extinguishers isolate the fuel from the heat by cutting off oxygen to the combustion zone or by inhibiting and interrupting the formation of molecular chain reactions)
C	The same fuels as Class A and B fires, together with energized electrical equipment	Energized Class A material, such as household appliances	CO_2, dry chemical agents, Halon (Extinguishers for Class C fires are rated according to the nonconductive properties of the extinguishing agent)
D	Combustible metals or metallic alloy elements with combustible metal components	Magnesium, sodium, potassium, titanium, zirconium, and lithium	Dry chemical agents (Water and water-based extinguishers should never be used on Class D fires. To be effective on a Class D fire, an extinguisher must suppress the fire without reacting physically or chemically with the combustible metal materials)
K	Cooking appliances that involve combustible cooking media	Vegetable or animal oils and fats	Dry chemical agents, CO_2, wet chemical agents

B.6 Classification of Flammable and Combustible Liquids

In common usage, *flammable* refers to a liquid that is readily ignited, burns rapidly and vigorously, and produces a lot of thermal energy—in other words, heat. *Combustible* usually refers to a liquid that is less easily ignited, burns less rapidly, and is, therefore, relatively safer. In simple terms, *flammable liquids* produce vapors at normal room temperature in concentrations that can be easily ignited by a small spark or flame. *Combustible liquids* ***do not*** produce vapors that can be ignited at normal room temperature. However, if a combustible liquid is heated up to or above its flash point, the vapors generated by the now-heated liquid can be ignited. In these cases, combustible liquids can be just as dangerous as flammable liquids. And, some of them, hydrocarbon fuels for examples, can burn just rapidly and evolve just much heat once they are ignited. Some common combustible liquids—mineral spirits and paint thinners, for example—are blended so they are just above the accepted dividing line between flammable and combustible. So, moderate heating of these liquids or storing them in a very warm environment can also present a fire hazard.

B.6.1 Flammable Liquid

According to most fire safety codes (NFPA 30, "Flammable Combustible Liquids Code"), a flammable liquid is generally defined as any liquid that has a closed-cup flash point below 37.8 °C (100 °F). Flash points may be determined by procedures and apparatus set forth in ASTM D56, D92, D93, D1310, or D3278.

NFPA 11 defined flammable liquids as any liquid having flash point below 37.8 °C (100 °F) and having a vapor pressure not exceeding 276 kPa (40 psi) (absolute) at 37.8 °C (100 °F).

Flammable liquids can be divided into classes (which are further divided into sub-classes), based on their flash points as summarizes in Table B.6-1. Class I - Liquids have a flash point below 38 °C (100 °F) and subdivided as follows:

Table B.6-1. Flammable Liquid Classifications
(NFPA 30, 2000 Edition)

Classification	**Flash Point (°F)**	**Boiling Point (°F)**	**Example(s)**
Class IA Flammable	< 73	< 100	Ethyl ether Acetic aldehyde, Dimethyl sulfide, Furan
Class IB Flammable	< 73	≥ 100	Ethyl alcohol, gasoline-92 octane, Cyclohexane
Class IC Flammable	≥73 and < 100	N/A	Butyl ether

B.6.2 Combustible Liquid

A combustible liquid is defined as any liquid that has a closed-cup flash point above 37.8 °C (100 °F). Combustible liquids can be divided into classes (which are further divided into sub-classes), based on their flash points as summarizes in Table B.6-2.

Class II Combustible liquids with flash points at or above 38 °C (100 °F), but below 60 °C (140 °F).

Class III Combustible liquids with flash points at or above 60 °C (140 °F).

Table B.6-2. Combustible Liquid Classifications
(NFPA 30, 2000 Edition)

Classification	**Flash Point (°F)**	**Boiling Point (°F)**	**Examples**
Class II Combustible	≥ 100	N/A	Fuel oil # 1 (kerosene), diesel fuel oil # 1-D/2-D/4-D, glacial acetic acid, and jet fuel (A & A-1)
Class III A Combustible	≥ 140 and < 200	N/A	Fuel oil # 6, creosote oil, and butyl carbitol
Class III B Combustible	≥ 200	N/A	Fuel oil # 4, mineral oil, olive oil, and lubricating oil (motor oil)

Assume that a liquid spill occurs on a summer day when the ground has been heated by the sun to 35 °C (95 °F). Clearly, a spill of Class I (flammable) liquid is extremely hazardous with regard to fire; however, a spill of a Class II liquid is dangerous from a fire viewpoint only if a heat source exists that is capable of moderately raising the temperature of the liquid and a spill of Class III liquid is safe from ignition unless a heat source exists that can substantially raise its temperature.

Table B.6-3 lists the flash points of some common flammable and combustible liquids. Notice the wide range, from -43 °C to +243 °C (-45 °F to +469 °F). These values are meaningful only for bulk liquids. If a liquid with a high flash point is in the form of a spray, a froth, or a foam, with air present, and comes into contact with even a very small ignition flame, the tiny amount of liquid in contact will be immediately heated to above its flash point and will begin to burn. The combustion energy released will vaporize the surrounding spray or foam, and the fire will propagate (spread).

Table B.6-3. Flash Points of Flammable and Combustible Liquids
(Benedetti, 1997)

Liquid Fuel	**Flash Point °C (°F)**
Class I (Flammable) Liquids	
Gasoline	-43 (-45)
n-Hexane	-26 (-15)
JP-4 (jet aviation fuel)	-18 (0)
Acetone	-16 (3)
Toluene	9 (48)
Methanol	11 (52)
Ethanol	12 (54)
Turpentine	35 (95)
Class II (Combustible) Liquids	
No.2 fuel oil (domestic)	>38 (>100)
Diesel fuel	40–50 (104–131)
Jet A (jet aviation fuel)	47 (117)
Kerosene	52 (126)
No. 5 fuel oil	>54 (>130)
Class III (Combustible) Liquids	
JP-5 (jet aviation fuel)	66 (151)
SAE No. 10 lube oil	171 (340)
Triresyl phosphate	243 (469)

B.6.3 Storage of Flammable and Combustible Liquids

Flammable and combustible liquids are packed, shipped, and stored in bottle, drums, and other containers ranging in size up to 60 gal (225 L). Additionally, liquids are shipped and stored in intermediate bulk containers up to 793 gal (3,000 L) and in portable intermodal tanks up to 5,500 gal (20,818 L). Storage requirements for each these containers are covered in the NFPA 30 chapters entitled, “Containers and Portable Tank Storage,” with the exception of those portable tanks larger than 793 gal (3,000 L) that are required to meet the applicable requirements covered in the NFPA 30 chapter entitled, “Tank Storage.”

Examples of containers types used for the storage of liquids include glass, metal, polyethylene (plastic), and fiberboard. The maximum allowable size for the different types of containers is governed by the class of flammable or combustible liquid to be stored in it. Table B.6-4 lists the maximum allowable size (capacity) of a container or metal tank used to store flammable and combustible liquids.

Table B.6-4. Maximum Allowable Size of Containers and Portable Tanks for Flammable and Combustible Liquids (NFPA 30, 2000 Edition)

Liquid Container Type	**Flammable Liquid**			**Combustible Liquid**	
	Class IA	**Class IB**	**Class IC**	**Class II**	**Class III**
Glass	1 pt	1 qt	1 gal	1 gal	5 gal
Metal (other than DOT drum) or approved plastic	1gal	5 gal	5 gal	5 gal	5 gal
Safety cans	2 gal	5 gal	5 gal	5 gal	5 gal
Metal drum (DOT specification)	60 gal	60 gal	60 gal	60 gal	60 gal
Approved metal portable tank and IBC	793 gal	793 gal	793 gal	793 gal	793 gal
Rigid plastic IBC (UN 31H1 or 31H2) or composite IBC (UN 31HZ1)	NP	NP	NP	793 gal	793 gal
Polyethylene (DOT specification 34, UN 1H1, or as authorized by DOT exemption)	1 gal	5 gal	5 gal	60 gal	60 gal
Fiber drum (NMFC or UFC Type 2A; Types 3A, 3B-H, or 3B-L; or Type 4A)	NP	NP	NP	60 gal	60 gal

SI Units - 1pt = 0.473 L; 1 qt = 0.95 L; 1 gal = 3.8 L
NP = Not Permitted
IBC = Intermediate Bulk Container
DOT = U.S. Department of Transportation

B.6.4 Flammable Combustible Storage Cabinets

Most commercially available and approved storage cabinets are built to hold 60 gallons (227 liters) or less of flammable and/or combustible liquids.

Not more than 120 gal (454 L) of Class I, Class II, and Class IIIA liquids shall be stored in a storage cabinet. Of this 120 gal total, not more than 60 gal (227 L) shall comprise Class and Class II liquids.

B.6.5 Definitions

Flash Point
The minimum temperature to which a liquid must be heated in a standardized apparatus, so that a transient flame moves over the liquid when a small pilot flame is applied.
Alternately, the flash point of a liquid may be defined as the temperature at which the vapor and air mixture lying just above its vaporizing surface is capable of just supporting a momentary flashing propagation of a flame prompted by a quick sweep of small gas pilot flame near its surface (hence the term flash point). The flash point is mainly applied to liquids. The flash point of liquid is one of its characteristics that normally determines the amount of fire safety features required for its handling, storage, and transport.

Fire Point
The minimum temperature to which a liquid must be heated in a standardized apparatus, so that sustained combustion results when a small pilot flame is applied, as long as the liquid is at normal atmospheric pressure.

Boiling Point
The temperature at which the transition from the liquid to the gaseous phase occurs in a pure substance at fixed pressure. Alternatively, the boiling point may be defined as the temperature at which the vapor pressure of a liquid equals the surrounding atmospheric pressure. For purposes of defining the boiling point, atmospheric pressure shall be considered to be 14.7 psia (760 mm Hg). For mixtures that do not have a constant boiling point, the 20-percent evaporated point of a distillation performed in accordance with ASTM D86, “Standard Method of Test for Distillation of Petroleum Products,” shall be considered to be the boiling point.

Autoignition
Initiation of fire or combustion by heat but without the application of a spark or flame.

Autoignition Temperature
The lowest temperature at which a mixture of fuel and oxidizer can propagate a flame without the aid of an initiating energy source (pilot, spark, or flame).

High-Risk Fuel
Class IA, IB, IC, or II liquids as defined by NFPA 30, “Flammable and Combustible Liquids Code,” or Class IIIA, or III B liquids heated to within 10 °C (50 °F) of their flash point, or pressurized to 174.4 kPa (25.3 psi) or more.

B.6.6 Hazardous Materials

A substance (solid, liquid, or gas) capable of creating harm to people, property, and the environment. The general category of hazard assigned to a hazardous material under the U.S. Department of Transportation (DOT) regulation. Table B.6-5 lists the hazardous material classification.

Table B.6-5. Hazardous Material Classification

Hazard Class	**Description**
Class 1 - Explosives	
Division 1.1	Explosive with a mass explosion hazard
Division 1.2	Explosives with a projection hazard
Division 1.3	Explosives with predominantly a fire hazard
Division 1.4	Explosives with no significant blast hazard
Division 1.5	Very insensitive explosives
Division 1.6	Extremely insensitive explosive articles
Class 2	
Division 2.1	Flammable gas
Division 2.2	Nonflammable, non-poisonous compressed gas
Division 2.3	Poison gas
Division 2.4	Corrosive gas
Class 3 - Flammable Liquid	
Division 3.1	Flammable liquids, flash point < 0 °F
Division 3.2	Flammable liquids, flash point 0 °F and above but < 73 °F
Division 3.3	Flammable liquids, flash point 73 °F and up to < 141 °F combustible liquid
Class 4	
Division 4.1	Flammable solid
Division 4.2	Spontaneously combustible material
Division 4.3	Dangerous when wet material
Class 5	
Division 5.1	Oxidizer
Division 5.2	Organic peroxide
Class 6	
Division 6.1	Poisonous material
Division 6.2	Infectious material
Class 7	Radioactive material
Class 8	Corrosive material
Class 9	Miscellaneous hazardous material, ORM-D material

B.6.7 References

Benedetti, R.P., Editor, “Flammable and Combustible Liquids Code Handbook,” 6th Edition, National Fire Protection Association, Quincy, Massachusetts, 1997.

NFPA 11, “Standard for Low-Expansion Foam,” 2002 Edition, National Fire Protection Association, Quincy, Massachusetts.

NFPA 30, “Flammable and Combustible Liquids Code,” 2000 Edition, National Fire Protection Association, Quincy, Massachusetts.

B.7 Classification of Flammable Gases

B.7.1 Classification

Flammable gases are classified according to the maximum experimental safe gap (MESG), which prevents flame passage. MESG is determined by test IEC 79-1A, "Electrical Apparatus for Explosive Gas Atmospheres," International Electrotechnical Commission (IEC), 1975 (Senecal, 1997).

Class I	Group A - acetylene Group B - hydrogen Group C - ethylene Group D - propane
Division 1	Flammable gases or combustible dust may be present at ignitable concentrations, under normal operating conditions.
Division 2	Where hazardous materials may be handled, processed, or used; ignitable atmospheres not normally present due to containment or ventilation of hazardous materials; areas adjacent to Division 1 locations.

B.7.2 Definitions

Flammable Limits
The minimum and maximum concentration of combustible material in a homogeneous mixture with a gaseous oxidizer that will propagate a flame.

Upper and Lower Flammability Limits
Concentration of fuel in air in which a premixed flame can propagate.

Lower Flammability Limit
The lowest concentration of fuel in air at normal temperature and pressure that can support flame propagation is known as the lower flammability limit (LFL) or lower explosive limit (LEL).

Upper Flammability Limit
The highest concentration of fuel in air at normal temperature and pressure that can support flame propagation is known as the upper flammability limit (UFL) or upper explosive limit (UEL).

B.7.3 Reference

Senecal, J.A., "Explosion Prevention and Protection," Section 4, Chapter 14, *NFPA Fire Protection Handbook*, 18th Edition, A.E. Cote, Editor-in-Chief, National Fire Protection Association, Quincy, Massachusetts, 1997.

B.8 Flammability Hazards of Gases

B.8.1 Flammability Potential of Gases

Flammability hazards in a tank or vessel dependent upon the potential for developing a flammable fuel/oxidant/inert gas mixture in the tank or vessel head space. Mixtures of fuel and air are only flammable for limited fuel-to-air ratio. The most flammable mixture is a stoichiometric mixture, in which the fuel and air (oxygen) are present in exactly the right proportions for oxidation, as dictated by the stoichiometry of the fuel/oxygen combustion reaction. Mixtures with some excess oxygen or excess fuel are also flammable, the lowest concentration of fuel in air that can support flame propagation at normal temperature and pressure is known as the lower explosive limit (LEL). Similarly, the highest concentration of fuel in air that can support flame propagation at normal temperature and pressure is known as the upper explosive limit (UEL). Mixtures of fuel in air with intermediate fuel concentrations will support flame propagation.

The flammability of gas mixtures is determined by one of two widely utilized laboratory methods. The first method uses a 5-foot-long tube that is filled with the test mixture, and a spark is used to ignite the mixture at one end to observe whether ignition occurs and whether the flame can propagate to the other end of the tube. The second method uses a spherical tank or vessel that is filled with the test mixture, and a spark is used to ignite the mixture at the center of the tank or vessel to measure the pressure increase to determine whether flame propagation occurred throughout the tank or vessel (Beyler, 1995). The spherical vessel test method is more representative of an actual tank or vessel than is the tube method.

The terms “explosive limits” and “flammable limits” are used interchangeably in the technical literature. Explosive limits simply refer to compositions, which define when flame propagation is possible. The flame propagation is known as a deflagration and results in a pressure increase as the flame passes through a vessel. This resulting overpressure is the origin of the term explosive limit, where an explosion is any event, that results in a sudden overpressure in the vessel.

When the LEL mixture has excess oxygen and insufficient fuel for complete burning, the mixture is known as “fuel lean.” The potential heat output, which defines how hot the products of combustion can be is limited not by oxygen, but by fuel concentration. The ideal “no heat loss” post-combustion temperature is known as the “adiabatic flame temperature” (AFT). For most flammable gases, the AFT at atmospheric pressure is about 2,300 K (3,680 °F) for stoichiometric mixtures of fuel in air, and is reduced to about 1,600 K (2,420 °F) for LEL mixtures. The AFT can be calculated using any of a number of chemical equilibrium computer programs, like STANJAN (Reynolds, 1986). The use of such a computer program allows the analysis to be performed for a tank-specific mixture, so that the results are representative of the actual tank environment.

B.8.2 Flammability Potential of Hydrogen

Hydrogen is a highly flammable gas with novel flammability properties and unusually broad explosive limits. Based on upward propagation in the standard flammability tube, the LEL is 4-percent hydrogen in air and the UEL is 75-percent (Zabetaskis, 1965). For most gases, the LELs for upward and downward propagation do no differ greatly. However, for hydrogen, the LEL for downward propagation is 8-percent (Furno et al., 1971). The significance of this difference is that in order for the flame to propagate throughout a tank or a vessel, it must propagate in all directions. As such, overpressures associated with hydrogen explosions are not observed at hydrogen concentrations below 8-percent. This behavior was observed by Furno et al., 1971, in 12-foot spherical vessel experiments using lean hydrogen/air mixtures. Overpressures were only measured above 8-percent hydrogen, and the pressures did not match the theoretical overpressures until about 10-percent hydrogen. Thus, while the LEL of hydrogen is widely quoted as 4-percent, explosion hazards will not occur below 8-percent.

The novel behavior of hydrogen is not reflected in documents like NFPA 69, “Standard on Explosion Prevention Systems.” As such, standards of care like NFPA 69, provide an implicit additional safety factor for hydrogen that should be understood in assessing hazards.

B.8.3 Flammable Limits, Detonable Limits, and Potential for Deflagration-to-Detonation Transitions

The formation of flammable fuel/oxidant mixtures within a tank can lead to premixed flame propagation in the form of deflagration or a detonation. The formation of a flammable mixture can result from steady-state generation and transport of flammable gases and oxidizers from an aqueous solution or waste containing radioactive isotopes, from episodic releases of such gases trapped within the waste, or from the formation of large gas bubbles within the waste which contain flammable mixtures of fuels and oxidizers.

Before assessing the potential flammable gas generation rates and resulting flammable gas mixture, it is useful to assess the relevant limits. In mixtures with fuel gas concentrations above the LEL indefinite propagation of a deflagration is possible. Above the detonable limit, indefinite propagation of a detonation is possible given a source that is capable of directly detonating the mixture. While LELs are a property of the mixture alone, the detonable limits are also impacted by the environment. The ability for a deflagration-to-detonation transition (DDT) is contingent upon both the mixture and the environment. The primary flammable gas is hydrogen.

B.8.4 Flammable Gas Generation

Flammable gases are generated with the aqueous solution or waste by several processes within a tank or a vessel. Specifically, these processes may include (1) radiolysis of the water and waste to produce hydrogen and ammonia, (2) corrosion of the steel liner to produce hydrogen, and (3) chemical decomposition of the waste. These processes generate hydrogen, methane, ammonia, and nitrous oxide, the first three of which are flammable gases, while the fourth is an oxidizer.

B.8.5 Explosion Prevention Methods

The flammability of a tank or vessel can be managed by controlling either the flammable gas concentration or oxygen concentration. Where the oxygen concentration is to be controlled, it needs to be maintained below the limiting oxidant concentration (LOC) (NFPA 69). (LOC is defined as the concentration of oxidant below which deflagration cannot occur is a specified mixture). Safety margins require maintaining the oxygen at 60-percent of the LOC if the LOC is above 5-percent, or 4-percent of the LOC if the LOC is below 5-percent. Where flammability is measured by controlling the flammable gas concentration, it needs to be maintained below 25 percent of the LEL.

Control of the oxygen concentration is achieved through the use of an inert purge gas. By contrast, control of flammable gas concentration is normally achieved through air dilution or by controlling of flammable gas evolution or regeneration or by catalytic oxidation of flammable gases.

While NFPA 69, provides standards for inerting the tanks, such inerting is not required by codes and standards for flammable liquid storage containers, such as the Uniform Fire Code Article 79; 1997, NFPA 30, 1996 Edition; 49 CFR; FM Data Sheet 7-88, "Storage Tanks for Flammable and Combustible Liquids," 1999; and FM Data Sheet 7-29, "Flammable Liquid Storage," 1999. These codes and standards recognize that ignition sources will not be present in passive containers, so that it is not necessary to control the composition of gases in the tank. By contrast, FM Data Sheet 7-32, "Flammable Liquids Operation," 1993, recommends that processing equipment with the potential for an explosion should have at least one of the following characteristics:

- equipped with explosion venting
- designed to withstand the explosion overpressure
- fitted with an inerting system
- fitted with an explosion suppression system

Tank inerting is recognized as a means of preventing explosions in processing vessels, which are inherently dynamic systems where ignition sources can be limited but not excluded.

B.8.6 References

Beyler, C.L., “Flammability Limits of Premixed and Diffusion Flames,” Section 2, Chapter 2-9, *SFPE Handbook of Fire Protection Engineering*, 2nd Edition, P.J. DiNenno, Editor-in-Chief, National Fire Protection Association, Quincy, Massachusetts, 1995.

FM Data Sheet 7-29, “Flammable Liquid Storage,” Factory Mutual Engineering Corporation, Norwood, Massachusetts.

FM Data Sheet 7-32, “Flammable Liquid Operations,” Factory Mutual Engineering Corporation, Norwood, Massachusetts.

FM Data Sheet 7-88, “Storage Tanks for Flammable and Combustible Liquids,” Factory Mutual Engineering Corporation, Norwood, Massachusetts.

Furno, A., E. Cook, J. Kuchta, and D. Burgess, “Some Observations on Near-Limit Flames,” Thirteenth Symposium (International) on Combustion, The Combustion Institute, Pittsburgh, Pennsylvania, pp. 593–599, 1971.

NFPA 30, “Flammable and Combustible Liquids Code,” 2000 Edition National Fire Protection Association, Quincy, Massachusetts.

NFPA 69, “Standard on Explosion Prevention Systems,” 1997 Edition, National Fire Protection Association, Quincy, Massachusetts.

Reynolds, W.C., “The Element Potential Method for Chemical Equilibrium Analysis: Implementation in the Interactive Program STANJAN, Version 3, Department of Mechanical Engineering, Stanford University, 1986.

Uniform Fire Code (UFC), Article 79, “Flammable and Combustible Liquids,” International Fire Code Institute, 1997.

Code of Federal Regulations, Title 49, Part 100–177, “Hazardous Materials Transportation,” U.S. Government Printing Office, Washington DC.

Zabetakis, M.G., “Flammability Characteristics of Combustible Gases and Vapors,” Bulletin 627, U.S. Bureau of Mines, Washington, DC, 1965.

B.9 Combustion Properties of Pure Metals in Solid Form

Nearly all metals will burn in air under certain conditions. Some oxidize rapidly in the presence of air or moisture, generating sufficient heat to reach their ignition temperatures. Others oxidize so slowly that heat generated during oxidation dissipates before the metal becomes hot enough to ignite. Certain metals (notably magnesium, titanium, sodium, potassium, lithium, zirconium, hafnium, calcium, zinc, plutonium, uranium, and thorium) are referred to as "combustible metals" because of the ease of ignition when they reach a high specific area ratio (thin sections, fine particles, or molten states). However, the same metals are comparatively difficult to ignite in massive solid form. Some metals (such as aluminum, iron, and steel) that are not normally thought of as combustible, may ignite and burn when in finely divided form. Clean fine steel wool, for example, may ignite. Particle size, shape, quantity, and alloy are important factors to be considered when evaluating metal combustibility. Combustibility of metallic alloys may differ and vary widely from the combustibility characteristics of the alloys' constituent elements. Metals tend to be most reactive when in finely divided form and may require shipment and storage under inert gas or liquid to reduce fire risks.

Hot or burning metals may react violently upon contact with other materials, such as oxidizing agents and extinguishing agents used on fires involving ordinary combustibles or flammable liquids. Temperatures produced by burning metals can be higher than temperatures generated by burning flammable liquids. Some metals can continue to burn in carbon dioxide, nitrogen, water, or steam atmospheres in which ordinary combustibles or flammable liquids would be incapable of burning.

Properties of burning metal cover a wide range. Burning titanium, for example, produces little smoke, while burning lithium exudes dense and profuse smoke. Some water-moistened metal powders (such as zirconium) burn with near-explosive violence, while the same powder wet with oil burns quiescently. Sodium melts and flows while burning; calcium does not. Some metals (such as uranium) acquire an increased tendency to burn after prolonged exposure to moist air, while prolonged exposure to dry air makes it more difficult to ignite.

The toxicity of certain metals is also an important factor in fire suppression. Some metals (especially heavy metals) can be toxic or fatal if they enter the bloodstream or their smoke fumes are inhaled. ***Metal fires should never be approached without proper protective equipment (clothing and respirators)***.

A few metals (such as thorium, uranium, and plutonium) emit ionizing radiation that can complicate fire fighting and introduce a radioactive contamination problem. Where possible, radioactive materials should not be processed or stored with other pyrophoric materials because of the likelihood of widespread radioactive contamination during a fire. Where such combinations are essential to operations, appropriate engineering controls and emergency procedures should be in place to prevent or quickly suppress fires in the event that the controls fail.

Because extinguishing fires in combustible metals involves techniques not commonly encountered in conventional fire fighting operations, it is necessary for those responsible for controlling combustible metal fires to be thoroughly trained before an actual fire emergency arises. Table B.9-1 lists the melting, boiling, and ignition temperatures of pure metals in solid form.

Table B.9-1. Melting, Boiling, and Ignition Temperatures of Pure Metals in Solid Form
(Tapscott, 1997, © NFPA. With permission.)

Pure Metal	**Melting Point**		**Boiling Point**		**Solid Metal Ignition Temperature**	
	°C	**°F**	**°C**	**°F**	**°C**	**°F**
Aluminum	660	1,220	2,452	4,445	555[b, c]	1,832[b, c]
Barium	725	1,337	1,140	2,084	175[b]	347[b]
Calcium	824	1,548	1,440	2,625	704	1,300
Hafnium	2,223	4,023	5,399	9,750	-	-
Iron	1,535	2,795	3,000	5,432	930[b]	1,706[b]
Lithium	186	367	1,336	2,437	180	356
Magnesium	650	1,202	1,110	2,030	623	1,153
Plutonium	640	1,184	3,315	6,000	600	1,112
Potassium	62	144	760	1,400	69b	156[b]
Sodium	98	208	880	1,616	115[d]	239[d]
Strontium	774	1,845	1,150	2,102	720[b]	1,328[b]
Thorium	1,845	3,353	4,500	8,132	500[b]	932b
Titanium	1,727	3,140	3,260	5,900	1,593	2,900
Uranium	1,132	2,070	3,815	6,900	3,815[b, e]	6,900[b, e]
Zinc	419	786	907	1,665	900[b]	1,652[b]
Zirconium	1,830	3,326	3,577	6,470	1,400[b]	2,552[b]

Notes:
(a) Variation of test conditions may produce different results
(b) Ignition in oxygen
(c) Spontaneous ignition on moist air
(d) Above indicated temperature
(e) Below indicated temperature

B.9.1 Reference

Tapscott, R.E. "Metals," Section 4, Chapter 16, *NFPA Fire Protection Handbook*, 18th Edition, A.E. Cote, Editor-in-Chief, National Fire Protection Association, Quincy, Massachusetts. 1997.

B.10 Extinguishing Agents for Metal Fires

Water is not usually recommended for fires involving metals since a number of metals can react exothermically with water to form hydrogen, which, of course, burns rapidly. Furthermore, violent steam explosions can result if water enters molten metal. As an exception, fires have been successfully extinguished when large quantities of water were applied to small quantities of burning magnesium in the absence of pools of molten magnesium.

Table B.10-1 lists extinguishing agents used for various metal fires. In general, metal fires are difficult to extinguish because of the very high temperatures involved and the correspondingly long cooling times required. Note that certain metals react exothermically with nitrogen or carbon dioxide, so the only acceptable inert gases for these metals are helium and argon. Halons should not be used on metal fires.

Table B.10-1. Extinguishing Agents for Metal Fires
(Tapscott, 1997, © NFPA. With permission.)

Extinguishing Agent	**Main Ingredient**	**Used On**
Powders		
Metal Guard®	Graphite	Al, Ca, Hf, K, Li, Mg, Na, Pu, Th, Ti, U, Zr
Met-L-X®	NaCl	Al, K, Mg, Na, Ti, U, Zr
TEC® powder	KCl, NaCl, $BaCl_2$	K, Mg, Na, Pu, U
Lith-X®	Graphite	Li, Mg, Na, Zr
Na-X®	Sodium carbonate	Na
Copper powder	Cu	Al, Li, Mg
Salt	NaCl	K, Mg, Na
Soda ash	Sodium carbonate	K, Na
Gases		
Argon	Ar	Any metal
Helium	He	Any metal
Nitrogen	N_2	K, Na
Boron trifluoride	BF_3	Mg
Al-Aluminum, Ca-Calcium, Hf-Hafnium, K-Potassium, Li-Lithium, Mg-Magnesium, Na-Sodium, Pu-Plutonium, Th-Thorium, Ti-Titanium, U-Uranium, Zr-Zirconium		

B.10.1 References

Friedman, R., *Principles of Fire Protection Chemistry and Physics*, “Fire-Fighting Procedures,” Chapter 14, 3rd Edition, National Fire Protection Association, Quincy, Massachusetts, 1998.

Tapscott, R.E., “Combustible Metal Extinguishing Agents and Application Techniques,” Section 6, Chapter 26, *NFPA Fire Protection Handbook*, 18th Edition, A.E. Cote, Editor-in-Chief, National Fire Protection Association, Quincy, Massachusetts, 1997.

B.11 Occupancy Classification and Use Groups

National Fire Code (NFC) requirements are occasionally tied to specific type of occupancy. While NPPs are fundamentally industrial occupancy, it is important to have a basic understanding of other occupancy classifications in order to be able to recognize this connection.

The use group classification of a building is probably the most significant design factor that affects the safety of the occupants and fire suppression forces that are called upon in the event of fire. The building’s height and size, type of construction, type and capacity of exit facilities, and fixed fire suppression systems are all dependent on this classification. The use group classification system as the foundation for the building and fire prevention codes.

B.11.1 Occupancy Classification

The model building codes[1] and NFPA 101 (Life Safety Code®) separate buildings into about 10 general uses:

- Assembly
- Business
- Educational
- Factory or Industrial
- High Hazard or Hazardous
- Institutional
- Mercantile
- Residential
- Storage
- Utility, Miscellaneous, or Special

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[1] Model Building Codes; National Fire Protection Association, NFPA 5000; International Code Council, Inc., International Building Code (IBC).

The uses are further separated into use groups based on specific characteristics. A church, a nightclub, and a family restaurant are all assemblies, but the specific characteristics of their occupants and functions differ drastically, requiring different built-in levels of protection. The occupants of a church are probably very familiar with the building that they occupy. They have been there before and they know the locations of alternative exits. The occupants of a nightclub may not be so familiar with the building. Dim lighting, loud music, and impairment by alcohol are all common features that may further compromise the ability of the occupants to identify a fire emergency and take appropriate measures to escape:

- Assembly (A) occupancies are subdivided by function, as well as the number of occupants they hold. Assemblies that hold fewer than 50 persons are generally considered to be less-restrictive business uses. The International Building Code (IBC) further subdivides assemblies that hold many people. Such assemblies include churches, restaurants with occupant loads that exceed 50 persons, auditoriums, armories, bowling alleys, courtrooms, dance halls, museums, theaters, and college classrooms that hold more than 50 persons.
- Business (B) areas include college classrooms with occupant loads up to 50, doctor's and other professional offices, fire stations, banks, barber shops, and post offices. Dry cleaners who use noncombustible solvents (Types IV and V) also qualify as Business uses.
- Educational (E) areas include facilities that are *not* used for business or vocational training (shop areas) for students up to and including the twelfth grade. Colleges and universities are Business or Assembly areas (depending on the number of occupants). Day care facilities may be classified as Educational or Institutional depending on the model code.
- Factory or Industrial (F) areas include industrial and manufacturing facilities and are subdivided into moderate and low-hazard facilities. High-hazard factory and industrial areas are bumped up from the F Use Group to the H Use Group. Dry cleaners employing combustible solvents (types II and III) are moderate-hazard factory and industrial uses.
- High Hazard or Hazardous (H) areas are those in which more than the exempt amount of a hazardous material or substance is used or stored. Exempt amounts of hazardous materials are not exempt from the provisions of the code. They are threshold amounts by material, above which the occupancy must comply with the stringent requirements of the H Use Group.
- Institutional (I) areas may include halfway houses and group homes, hospitals and nursing homes, and penal institutions. The model codes differ in their breakdown. Care must be taken when considering homes for adults and day care centers as to whether the occupants are ambulatory or capable of self-preservation. The model codes all contain significantly more stringent requirements for institutional occupancies where a "defend-in-place" strategy is necessary because of the inability of the occupants to flee the structure without assistance.
- Mercantile (M) uses include retail shops and stores and areas that display and sell stocks of retail goods. Automotive service stations that do minor repairs are considered Mercantile uses.
- Residential (R) areas include hotels and motels, dormitories, boarding houses, apartments, townhouses, and one- and two-family dwellings.

- Storage (S) areas are used for to store goods and include warehouses, storehouses, and freight depots. Storage uses are separated into low- and moderate-hazard storage uses. Auto repair facilities that perform major repairs, including engine overhauls and body work or painting, are considered Moderate-Hazard Storage Occupancies by the International Building Code (IBC). Occupancies that store more than the exempt amounts of hazardous materials or substances are considered H Use Group Occupancies.
- Utility (U), Miscellaneous, or Special Structures, depending on the model code, include those that are not classified under any other specific use. Such structures may include tall fences cooling towers, retaining walls, and tanks.
- Mixed-use buildings often contain multiple occupancies with different uses. For example, a three-story building might have a restaurant (assembly) and computer store (mercantile) on the first floor and professional offices throughout the rest of the building. The model code provides for such situations either by requiring that the whole building be constructed to all requirements of the most restrictive use group or by separating the areas with fire-rated assemblies, or by separating the building with fire walls, thereby creates separate buildings. By far the least expensive and most attractive method of separating mixed uses is by using fire separating assemblies, but this method is sometimes impossible because of building height and area requirements.

B.11.2 Special Use and Occupancy Requirements

For most buildings and structures, assigning a use group and then specifying building requirements for all buildings within that use group works relatively well. Most mercantile occupancies share common hazards. Most business occupancies have similar occupants and processes. But what if a given business happens to be on the twenty-sixth floor of a high-rise building? Or what if the men’s clothing store is in the middle of a giant shopping mall? The relative hazards suddenly change, and we begin comparing apples to oranges.

Building codes provide an enhanced level of protection for certain occupancies to compensate for special hazards over and above those posed by the use of the building. The inherent hazards posed by being located 26 stories above the ground or in a large open area with high fire loading such as a shopping mall are addressed as special use requirements.

B.11.3 Code Advances/Changes

It is important to recognize that NPPs have their design basis rotted in 1970's era code requirements. In some cases, fire science advances revise, or establish new code requirements. A good example is carpeting found in the MCR. The original NPPs required ASTM E84, “Standard Test for Surface Characteristics of Building Materials,” Class A flame spread requirements. Fire science advances have developed more specialized test methods for carpeting, ASTM E648, “Standard Test Method for Critical Radiant Flux of Floor-Covering Systems Using a Radiant Heat Energy Source.” As a result of this, manufacturers do not test the material to 1970's vintage test method. When NPPs perform a plant modification (e.g., replace the carpet in the MCR, since ASTM E84 rated carpet is no longer manufactured), the licensee will either have to perform their own ASTM E84 testing on the proper carpet or prepare an engineering analysis on the commercially available carpeting that is tested to newer test methods recognized by NFPA 101, “Life Safety Code®.”

Another area of change is cable flame spread testing. Since no new NPPs are being built there is little incentive for cable vendors to qualify electrical cables to IEEE 383 requirements. In parallel, the building code groups are recognizing by grouped electrical cables and testing organizations prepared specialized test methods and rating systems based on application of the cable: UL 910, "Test Method for Fire and Smoke Characteristics of Electrical and Optical-Fiber Cables Used in Air Handling Spaces"; UL 1581, "Reference Standard for Electrical Wires, Cables, and Flexible Cords"; UL 1666, "Standard Test for Flame Propagation Height of Electrical and Optical-Fiber Cable installed Vertically in Shafts"; and UL 1685, "Fire Test of Limited-Smoke Cables."

B.11.4 References

ASTM Fire Test Standard, Fifth Edition, American Society of Testing and Materials, West Conshohocken, Pennsylvania, pp. 765-780, 1999.

ASTM E 648-98$^{\epsilon 1}$, "Standard Test Method for Critical Radiant Flux of Floor-Covering Systems Using a Radiant Heat Energy Source," ASTM Fire Test Standard, Fifth Edition, American Society of Testing and Materials, West Conshohocken, Pennsylvania, pp. 894-907, 1998.

International Building Code, Sixth Edition, International Code Council, Inc., Falls Church, Virginia.

NFPA 101®, "Life Safety Code®," 2003 Edition, National Fire Protection Association, Quincy, Massachusetts.

NFPA 5000, "Building Construction and Safety Code," 2003 Edition, National Fire Protection Association, Quincy, Massachusetts.

UL 910, "Test Method for Fire and Smoke Characteristics of Electrical and Optical-Fiber Cables used in Air Handling Spaces."

UL 1581, "Reference Standard for Electrical Wires, Cables, and Flexible Cords."

UL 1666, "Standard Test for Flame Propagation Height of Electrical and Optical-Fiber Cable Installed Vertically in Shafts."

UL 1685, "Fire Test of Limited-Smoke Cables."

B.12 Building Limitations and Types of Construction

Two of the most effective methods used over the years to limit potential fire spread and prevent conflagration have been limiting the size of buildings and regulating the materials used in their construction. One of the primary purposes of a building code is to prescribe standards that will keep buildings from falling down. Besides gravity, there are many forces that act against a building. Snow loads, wind loads, and potential earthquake loads are provided for in the building code for design and construction of buildings. It can be considered that the potential force that requires the most extensive code provisions is fire. Large portions of the model building codes address fire protection issues, fire safety, emergency egress, and structural stability.

The key to understanding building code provisions for structural protection from fire is the concept of fire resistance. In broad terms, fire resistance (also called fire endurance) it is the ability of a building to resist collapse or total involvement in fire. Fire resistance is measured by the length of time typical structural members and assemblies resist specified temperatures. The building codes define fire resistance as that property of materials or their assemblies which prevents or retards the passage of excessive heat, hot gases, or flames under conditions of use.

B.12.1 Types of Construction

There are three key points to remember when dealing with building construction types:

- All construction is either combustible (it will burn) or noncombustible (it won’t).
- When applied to construction materials, “protected” refers to measures to reduce or eliminate the effects of fire encasement. Concrete, gypsum, and spray-on coatings are all used to protect construction elements. When the code means “protected with a sprinkler system,” it will say just that.
- Having the ability to determine the construction type by eyeballing a building is not a requirement.

B.12.2 Five Construction Types

The model building codes and NFPA 220, “Standard on Types of Building Construction,” recognize five construction types. The Standard Building Code subdivides noncombustible construction and uses six types. The terms vary a little between the different codes, but the concept is the same, based on the classifications from NFPA 220.

Type I Fire Resistive

In Type I construction, the structural elements are noncombustible and protected. Type I is divided into two or three subtypes, depending on the model code. The difference between them is the level of protection for the structural elements (expressed in hours). Only noncombustible materials are permitted, and structural steel must not be exposed. A high-rise building with an encased steel structure is an example of a Type I building.

Type II Noncombustible

In Type II construction, the structural elements are either noncombustible or limited combustible. Type II is subdivided into subtypes, dependent upon the level of protection (in hours) for the structural elements. The buildings are noncombustible, but afford limited or no fire resistance to the structural elements. A strip shopping center, with block walls, steel bar joists, unprotected steel columns, and a steel roof deck is an example of a Type II building.

Type III

Limited Combustible (Ordinary) In Type III construction, the exterior walls are noncombustible (masonry) and may be rated based on the horizontal distance to exposure. The interior structural elements may be combustible or a combination of combustible and noncombustible. Type III is divided into two subtypes (protected and unprotected). The brick, wood joisted buildings that line city streets are of Type III (ordinary) construction. Buildings with a masonry veneer over combustible framing are not Type III.

Type IV

Heavy Timber In type IV construction, the exterior walls are noncombustible (masonry) and the interior structural elements are unprotected wood of large cross-sectional dimensions. Columns must be at least 8 inches if they support a floor load, joists, and beams must be a minimum of 6 inches in width and 10 inches in depth. Type IV is not subdivided. The inherent fire-resistant nature of large-diameter wood members is taken into account. Concealed spaces are not permitted.

Type V

Wood Frame In Type V construction, the interior structure may be constructed of wood or any other approved material. Brick veneer may be applied, but the structural elements are wood frame. Type V is divided into two subtypes (protected and unprotected), again depending on the protection provided for the various structural elements.

B.12.3 Fire Resistance Ratings

The various model codes and NFPA 220 each have a table containing the rating (in hours) of the various structural elements. Table B.12-1 summarizes the required ratings by building component type, depending upon the construction classification of the building. The construction type classifications used by the International Building Code (IBC) and NFPA 220 do not exactly match, type for type. The National Fire Protection Association is consistent, however, within its different standards; therefore, the construction type classifications in NFPA 5000 and NFPA 220 are identical. Table B.12-1 provides an approximate comparison. A notational system was developed to identify the fire resistance required for the three basic elements of the building. These elements are (1) the exterior wall, (2) the primary structural frame, and (3) the floor construction. A three-digit notation was developed, as follows:

(1) First digit: Hourly fire resistance requirement for exterior bearing wall fronting on a street or lot line.

(2) Second digit: Hourly fire-resistance requirement for a structural frame or columns and girders supporting loads from more than one floor.

(3) Third digit: Hourly fire resistance requirement for floor construction.

Thus, for example, a "332" building would have 3-hour fire-resistant exterior bearing walls, a 3-hour fire resistant structural frame, and 2-hour fire-resistant floor construction, and would correspond to the NFPA 220 Type I (332) building and the International Building Code (IBC) Type IA building.

Table B.12-1. Construction Classifications of the Model Codes and NFPA 220

NFPA 220 & NFPA 5000	I 443	I 332	II 222	II 111	II 000	III 211	III 200	IV 2HH	V 111	V 000
IBC Table 601	-	IA	IB	IIA	IIB	IIIA	IIIB	IV	VA	VB

B.12.4 Reference

NFPA 220, "Standard on Types of Building Construction," National Fire Protection Association, Quincy, Massachusetts, 1999 Edition.

International Building Code, Sixth Edition, International Code Council, Inc., Falls Church, Virginia.

NFPA 5000, "Building Construction and Safety Code," 2003 Edition, National Fire Protection Association, Quincy, Massachusetts.

B.13 Deep-Seated Fires in Class A Solid Materials

B.13.1 General Information

Two types of fires can occur in Class A (ordinary) combustibles materials (e.g., wood, cloth, paper, rubber, and many plastics including cable insulation). In the first type, commonly known as flaming combustion, the source of combustion is volatile gases resulting from heating or decomposition of the fuel surface. In the second type, commonly called smoldering or glowing combustion oxidation occurs at the surface of, or within, the mass of fuel. These two types of fires frequently occur concurrently, although one type of burning may precede the other. For example, a wood fire may start as flaming combustion and become smoldering as burning progresses. Conversely, spontaneous ignition in a pile of oily rags may begin as a smoldering fire and break into flames at some later time (Friedman, 1997).

Smoldering combustion cannot be immediately extinguished like flaming combustion. This type of combustion is characterized by a slow rate of heat loss from the reaction zone. Thus, the fuel remains hot enough to react with oxygen, even though the rate of reaction, which is controlled by diffusion processes, is extremely slow. Smoldering fires can continue to burn for many weeks, for example in bales of cotton and jute and within heaps of sawdust or mulch. A smoldering fire ceases to burn only when all of the available oxygen or fuel has been consumed, or when the temperature of the fuel surface becomes too low to react. These fires are usually extinguished by reducing the fuel temperature, either directly by applying a heat absorbing medium (such as water), or indirectly by blanketing the fuel with an inert gas. In the latter case, the inert gas slows the rate of reaction to the point at which heat generated by oxidation is less than the heat lost to the surroundings. This causes the temperature to fall below the level necessary for spontaneous ignition following removal of the inert gas atmosphere.

Smoldering fires are divided into two classes, in which the fire is either deep-seated or not. Basically, “deep-seated” implies the presence of sub-surface smoldering combustion that may continue for some time after surface flaming is suppressed. Deep-seated fires may become established beneath the surface of fibrous or particulate material. This condition may result from flaming combustion at the surface or from the ignition within the mass of fuel. Smoldering combustion then progresses slowly through the mass. Whether a fire will become deep-seated depends, in part, on the length of time it has been burning before the extinguishing agent is applied. This time is usually called the “pre-burn” time (Nolan, 2001).

As described above, a deep-seated fire is embedded in the material being consumed by combustion. To extinguish deep-seated fires, an individual must investigate the interior of the material once the surface fire has been extinguished to determine whether interior smoldering has also been extinguished by a gaseous agent. It should be noted, however, that the concentration of the extinguishing agent must be adequate—and must be applied for an adequate duration—to ensure that the smoldering has been effectively suppressed.

B.13.2 Deep-Seated Cable Fires

A deep-seated fire occurs in cables when the burning involves pyrolysing beneath the surface, in addition to a surface phenomenon. This is postulated to occur when the cable fire reaches the stage of a fully developed fire. Extinguishing a cable surface fire does not guarantee that a deep-seated fire is also eliminated. A deep-seated fire is very difficult to suppress since fire suppressing agent cannot easily get to the seat of the fire, and it is also difficult to detect since combustion is primarily under the cooler surface.

Electrical cable fire tests have been conducted at the Sandia Fire Research Facility (Schmidt and Krause, 1982) in order to evaluate cable tray fire safety criteria. A burn mode concept was developed in order to describe and classify the thermodynamic phenomena which occur in the presence of smoke and to compare the fire growth and recession of different cable types under otherwise unchanged fire test conditions. The importance of deep-seated fires in cables trays from the standpoint of propagation, detection, and suppression is emphasized. The cable tray fire tests demonstrate that fire recession and deep-seated fires can result from a decreasing smoke layer and that reignition and secondary fire growth is possible by readmission of fresh air.

B.13.3 Deep-Seated Charcoal Fires

The use of activated charcoal in NPPs presents a potential for deep-seated fires. Simply, that if it says that it is combustible, that it may be ignited, and that if it does become ignited, it is likely to become a deep-seated fire. It does not predict the frequency of those fires, nor form of ignition (Holmes, 1987). On July 17, 1977, a fire occurred at the Browns Ferry Nuclear Power Plant (BFNP) in Unit 3 off-gas system charcoal adsorber bed (Crisler, 1977). The elevation in adsorber bed temperature caused temperature rises of sufficient magnitude to cause carbon ignition.

B.13.4 References

Crisler, H.E. Jr., “July 17, 1977, Off-Gas System Charcoal Adsorber Bed Fire at Browns Ferry Nuclear Plant,” Proceedings of the CSNI Specialist Meeting on Interaction of Fire and Explosion with Ventilation Systems in Nuclear Facilities, Volume II, Report Number: LA-9911-C, Vol.2; CSNI-83, pp. 309-316, October 1983.

Friedman, R., “Theory of Fire Extinguishment,” Section 1, Chapter 8, NFPA Fire Protection Handbook, 18th Edition, A.E. Cote, Editor-in-Chief, National Fire Protection Association, Quincy, Massachusetts, 1997.

Holmes, W., “Adsorber Fires,” Proceedings of the 19th DOE/NRC Nuclear Air Cleaning Conference, NUREG/CP-0086-Vol. 2; CONF-860820-Vol.2, pp. 797-798, May 1987.

Nolan, D.P., *Encyclopedia of Fire Protection*, Delmar Publishers, Albany, New York, 2001.

Schmidt, W.H., and F.R. Krause, “Burn Mode Analysis of Horizontal Cable Tray Fires,” NUREG/CR-2431, U.S. Nuclear Regulatory Commission, Washington, DC, February 1982.

B.14 Special Hazard Gaseous Fire Extinguishing Agents

B.14.1 Introduction

A gaseous (or gas phase) fire suppression agent remains in the gaseous state at normal room temperature and pressure. It has low viscosity, can expand or contract with changes in pressure and temperature, and has the ability to diffuse readily and distribute itself uniformly throughout an enclosure. Gaseous fire extinguishing agents are categorized into two distinct classes, including halocarbon and inert gases (such as nitrogen and mixtures containing argon). Halocarbon agents (e.g., Halon 1301) act largely by absorbing although they also have some chemical effect on flame combustion reactions. Inert agents contain unreactive gases that act primarily by oxygen depleting. One important advantage of gaseous agents is that no cleaning is required if the agent is released in the absence of a fire; a couple of minutes of venting is all that is required. However, gaseous agents with the exception of Halon require a rather large storage area; this is particularly for nitrogen and argon, which are usually stored as compressed gases.

Halogenated extinguishing agents are hydrocarbons in which one or more hydrogen atoms in an organic compound (carbon) have been replaced by atoms from halogens (the chemicals in group 7 of the periodic table of the elements) chlorine (Cl), fluorine (F), bromine (Br), or iodine (I). This substitution confers flame extinguishing properties to many of the resulting compounds that make them useable for certain fire protection applications. The three halogen elements commonly found in Halon extinguishing agents used for fire protection are fluorine, chlorine, and bromine. Compounds containing combinations of fluorine, chlorine, and bromine can possess varying degrees of extinguishing effectiveness, chemical and thermal stability, toxicity, and volatility. These agents appear to extinguish fire by inhibiting the chemical chain reaction that promotes the combustion process.

Carbon dioxide (CO_2) has a long history as an extinguishing agent, which is primarily used for flammable liquid fires and electrical equipment fires. CO_2 is noncombustible and does not react with most substances. It is a gas, but it can be easily liquified under pressure and is normally stored as a pressure-condensed gas. CO_2 provides its own pressure for release and blankets the fire area when released in sufficient amounts. CO_2 is extremely toxic since it replaces the oxygen in the air; humans become unconscious at a 10-percent volume concentration followed by loss of life. Therefore, CO_2 cannot be released while people are present.

B.14.2 Halogenated Agent Extinguishing Systems

Halogenated extinguishing agents are currently known simply as Halons, and are described by a nomenclature that indicate the chemical composition of the materials without the use of chemical names. In this nomenclature the first digit of the number definition represents the number of carbon atoms in the compound molecule; the second digit is the number of fluorine atoms; the third digit is the number of chlorine atoms; the fourth digit is the number of bromine atoms; and the fifth digit is if any, the number of iodine atoms.

For example, the number definition for the chemical composition of Halon 1301, perhaps the most widely recognized halogenated extinguishing agent, is 1 (carbon), 3 (fluorine), 0 (chlorine), 1 (bromine), and 0 (iodine). This simplified system, proposed in 1950 by James Malcolm of the U.S. Army Corps of Engineers Laboratory, avoids the use of possibly confusing names. By contrast, the United Kingdom and parts of Europe still use the initial capital alphabet system [i.e., bromotrifluoromethane (Halon 1301) is BTM and bromochlorodifuoro-methane (Halon 1211) is BFC].

Due to the many chemical combinations available, the characteristics of halogenated fire extinguishing agents differ widely. It is generally agreed, however, that the agents most widely used for fire protection applications are Halon 1011, Halon 1211, Halon 1301, Halon 2402, and (to a lesser degree) Halon 122, which has been used as a test gas because of its economic advantages. However, because of its widespread use as a test agent, many individuals have wrongly assumed that Halon 122 is an effective fire extinguishing agent. Table B.14-1 illustrates the halogenated hydrocarbons most likely to be used today. Of all of these types, however, the most popular halogenated agent is Halon 1301, which offers superior fire extinguishing characteristics and low toxicity. Because Halon 1301 inhibits the chain reaction that promotes the combustion process, it chemically suppresses the fire very quickly, unlike other extinguishing agents that work by removing the fire's heat or oxygen. Stored as a liquid under pressure and released as a vapor at normal room temperature, Halon 1301 readily spreads into blocked and baffled spaces and leaves no corrosive or abrasive residue after use. A high liquid density permits compact storage containers, which on a comparative weight basis, makes Halon 1301 approximately 2.5 times more effective as an extinguishing agent than CO_2 (Grand, 1995).

Table B.14-1. Halogenated Hydrocarbons Commonly Used for Fire Protection

Common Name	**Chemical Name**	**Formula**
Halon 1001	Methyl Bromide	CH_3Br
Halon 10001	Methyl Iodide	CH_3I
Halon1011	Bromochloromethane	CH_2BrCl
Halon 1202	Dibromodifluoromethane	CF_2Br_2
Halon 1211	Bromochlorodifluoromethane	CF_2BrCl
Halon 122	Dichlorodifluoromethane*	CF_2Cl_2
Halon 1301	Bromotrifluoromethane	CF_3Br
Halon 104	Carbon Tetrachloride	CCl_4
Halon 2402	Dibromotetrafluoroethane	$C_2F_4Br_2$
* A popular test gas without substantial fire extinguishing properties.		

Although halogenated agents may be applied using a variety of methods, the most common is the total flooding system. According to the NFPA 12A, 1997 Edition, Section 2-3.1.1, a Halon 1301 total flooding system shall be automatically actuated for fires involving Class A ordinary combustible materials (e.g., wood, cloth, paper rubber, and many plastics including cables), with the exception that manual actuation shall be permitted if acceptable to the authority having jurisdiction (AHJ). NFPA 12A, 1997 Edition, Section 3-7.1.2, also indicate that the agent discharge shall be substantially completed in a nominal 10 seconds or as otherwise required by the AHJ. The rapid discharge is specified to prevent the fire from becoming deep-seated, minimize unwanted decomposition products, and achieve complete dispersal of the agent throughout the enclosure so that the Halon quickly knocks down the flames and extinguishes the fire. When exposed to deep-seated fires for long period of times, Halon 1301 decomposes into decomposition products, that are toxic to personnel and corrosive to electronic components (See Section B.18 for further discussion). Therefore, to extinguish fire effectively, while limiting the formation of hazardous decomposition products, it is important to disperse the agent during the incipient stage of the fire.

A significant problem in using of Halon 1301 is that, in the normal firefighting concentrations of 5-percent to 6-percent, it may fail to completely extinguish fires which originate in Class A solid materials (e.g., wood, cloth, paper, rubber, and many plastics). External and visible flame is instantly extinguished by Halon 1301, but internal and unseen flameless (but glowing) combustion may continue. As defined by the NFPA, if a 5-percent concentration of Halon 1301 will not extinguish a fire within 10 minutes of application, it is considered to be deep-seated, as described above. Such deep-seated fires usually require concentrations much higher than 10-percent and soaking times much higher than 10 minutes (NFPA 12A, 1971 Edition). The technical literature does not provide any satisfactory explanation for the ineffectiveness of Halon 1301 in deep-seated fires (Fielding and Woods, 1975).

Sandia National Laboratories (SNL) investigation of the effectiveness of the Halon 1301 fire suppression agent on electrical cables fires in 1981 and again in 1986 at the behest NRC. These full-scale fire suppression tests were performed to determine the concentration and minimum soaking time necessary to suppress electrical cable tray fires and prevent reignition of those fires. Halon 1301 was very effective in suppressing surface fires, but took much longer to suppress deep-seated cable tray fires. The results of Test 60 depicted on Figure B.14-1 indicated that even after Halon 1301 is discharged, the interior temperature of the cable bundle continues to rise, probably as a resulting of continued combustion of the cable insulation. Moreover, a second increase in temperature occurs, air is readmitted during ventilation, thereby causing reignition of the cable insulation (Klamerus, 1981).

As illustrated in Figure B.14-1 the Halon 1301 concentration applied to the fire has a direct relationship to the time required to completely extinguish the fire. When the agent is first applied to the cable trays, the flames are immediately extinguished, but the deep-seated combustion (or glow), continues and the fire will reignite if the enclosure is then ventilated.

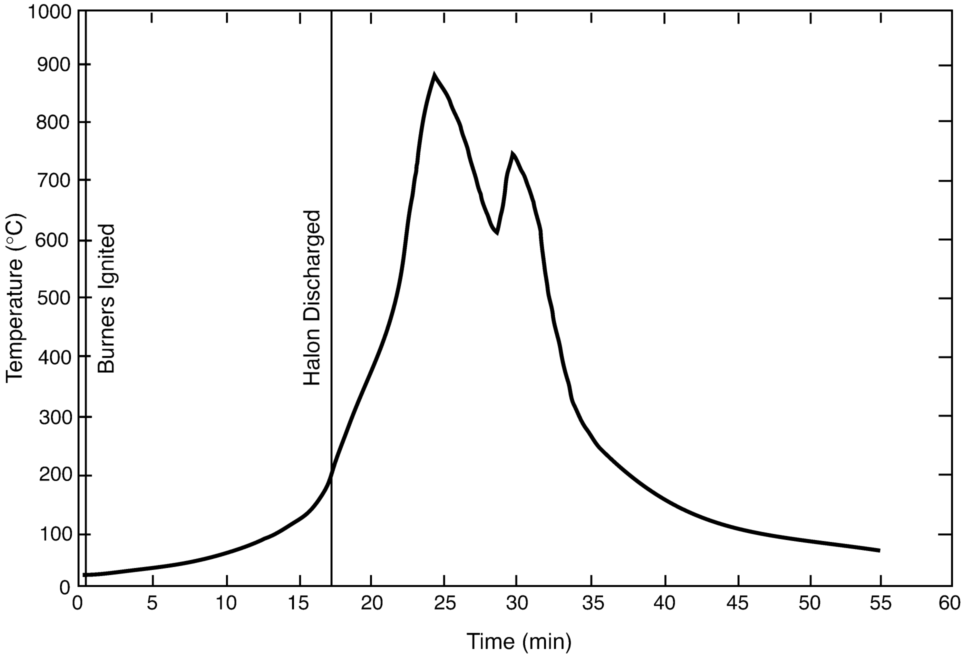

Figure B.14-1 Indication of Deep-Seated Fire and Reignition of Cables, Test # 60, IEEE-383-Qualified Cables, Horizontal Trays, 4-Minute Halon Soak Acceptor Tray Center Temperature (Klamerus, 1981)

B.14.2.1 Halon Concentration and Soaking Time

Soaking time is an important requirement for a Halon 1301 total flooding system. This is especially true for Class A fires that may reflash. A minimum soaking period of 10-minutes is typically required for fires in these applications, based on the full-scale total flooding fire suppression tests for electrical cable tray fires conducted by Klamerus (1981), and Chavez and Lambert (1986). A 6-percent Halon 1301 concentration with a 10-minute soak time successfully extinguished all cable fires in horizontally and vertically oriented trays filled with IEEE-383 unqualified cables, while IEEE-383 qualified cables required a 15-minute soaking time. The measure concentrations in these tests were based on a completely air-tight enclosure during discharge (see Figure B.14-2 for Halon 1301 concentration requirements) with 15-minute soak time successfully extinguished all cable fires in horizontal and vertical oriented tray filled. The measured concentrations in this testing are based on completely tight enclosure during discharge and soaking time of Halon 1301 (see Figure B.14-2 for Halon 1301 concentration requirements).

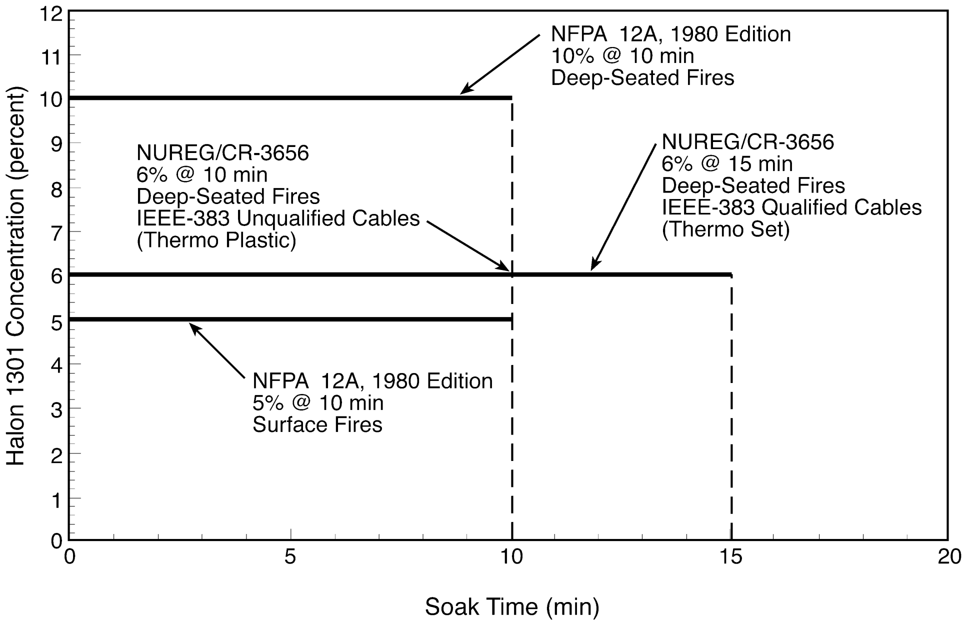

Figure B.14-2 Soaking Time vs. Halon 1301 Concentration
for Deep-Seated and Surface Fires

B.14.2.2 Agent Leakage

Because Halon 1301 is approximately five times heavier than air (with molecular weight 148.93 g/mol compared to 29 g/mol for air), there is a risk of Halon leakage from the protected space if the space is not completely airtight. Therefore, it is important to know the Halon percent and soak time at the highest combustible in the protected enclosure. NFPA 12A requires that the leakage rate should be low enough so that the design concentration is held in the hazard area long enough to ensure that the fire is completely extinguished. Reignition of the fire is a potential concern if the effective concentration is not maintained. In case of leakage during and after discharge, a greater amount of the agent is required to develop a given concentration. To maintain the agent concentration at a given level requires continuous agent discharge for the duration of the soaking period. The leakage rate from an enclosure could be predicted from the detailed knowledge of the size, location, and geometry of any leaks. However, these details are rarely known, as leakage may occur around doors and door seals; wall; ceiling; and floor cracks, duct, conduit, and cable tray penetrations; and fire and isolation dampers. Appendix B to NFPA 12A presents methods of estimating leakage area.

Discharging Halon 1301 into an enclosure to achieve total flooding results in an air/agent mixture with a higher specific gravity than the air surrounding the enclosure. Therefore, any openings in the lower portions of the enclosure will allow the heavier air/agent mixture to flow out and the lighter outside air to flow in. Fresh air entering the enclosure will collect toward the top, forming an interface between the air/agent mixture and fresh air. As the leakage proceeds, the interface will descend toward the bottom of the enclosure. The space above the interface will be completely unprotected, while the lower space will essentially contain the original extinguishing concentration. Grant (1995) presented methods of adjusting the Halon 1301 concentration to unprotected openings (leakage).

Rapid detection of a fire and prompt application of the extinguishing agent without outside assistance can help to prevent a Class A fire from becoming deep-seated. If a fire becomes deep-seated or (begins as a deep-seated fire), it will not likely be extinguished by Halon 1301 concentrations below 10-percent, and some deep-seated fires require concentrations above 18–30-percent to ensure that the glow is completely extinguished (Grant, 1995).

It is important to remember that in most cases, halogenated agent extinguishing systems have only a single chance to extinguish a fire. Such systems should be tested and Halon concentrations measured at various heights within the protected space (at least at the point of the highest combustible) to demonstrate the design concentrations. Timely and automatic actuation of Halon systems would also provide reasonable assurance that a fire would be extinguished before spreading through the combustible material and becoming deep-seated.

B.14.3 Carbon Dioxide Fire Extinguishing Systems

Carbon Dioxide (CO_2) is a colorless, odorless, inert, and electrically nonconductive agent that extinguishes a fire by displacing the normal atmosphere, thereby reducing the oxygen content below the 15-percent required for diffusion flame production. The CO_2 from either low-pressure or high-pressure extinguishing systems is stored and transported as a liquid through the piping system to the nozzles. With the release of pressure at the nozzles, the liquid CO_2 converts to a gas, with some minute solid particles, making it approximately 50-percent heavier than air.

Flame extinguishment by CO_2 is predominantly by a thermophysical mechanism in which reacting gases are prevented from achieving a temperature high enough to maintain the free radical population necessary for sustaining the flame chemistry. For inert gases presently used as fire suppression agent (argon, nitrogen, carbon, carbon, and mixture of these), the extinguishing concentration (as measured by the cup burner method, NFPA 2001) is observed to be linearly related to the heat capacity of the agent-air mixture. Although of minor importance in accomplishing fire suppression, CO_2 also dilutes the concentration of the reacting species in the flame, thereby reducing collision frequency of the reacting molecular species and slowing the rate of heat release.

CO_2 fire extinguishing systems are useful in protecting against fire hazards when an inert, electrically nonconductive, three-dimensional gas is essential or desirable and where clean up from the agent must be minimal. According to the NFPA, some of the types of hazards and equipment that carbon dioxide systems protect are “flammable liquid materials; electrical hazards, such as transformers, switches, circuit breakers, rotating equipment, and electronic equipment; engines utilizing gasoline and other flammable liquid fuels; ordinary combustibles such as paper, wood, and textiles; and hazardous solids” (NFPA 12).

Over the years, two methods of applying CO_2 have been developed. The first technique is the total flooding application, which involves filling an enclosure with CO_2 vapor to a prescribed concentration. In this technique, the CO_2 vapor flows through nozzles that are designed and located to develop a uniform concentration of the agent in all parts of the enclosure. The quantity of CO_2 required to achieve an extinguishing atmosphere is calculated on the basis of the volume of the enclosure and the concentration of the agent required for the combustibles material in the enclosure. This technique is applicable for both surface-type fires and potentially deep-seated fires.

For surface-type fires, as would be expected with liquid fuels, the minimum concentration is 34-percent of CO_2 by volume. Considerable testing has been done with using CO_2 on liquid fuels and appropriate minimum design concentrations have been derived at for a large number of common liquid fire hazards.

For deep-seated hazards, the minimum concentration is 50-percent of CO_2 by volume. This 50-percent design concentration is used for hazards involving electrical gear, wiring insulation, motors, and the like. Hazards involving record storage, such as bulk paper, require a 65-percent concentration of CO_2, while substances such as fur and bag-type house dust collectors require a 75-percent concentration. It should be noted that most surface burning and open flaming will stop when the concentration of CO_2 in the air reaches about 20-percent or less by volume. Thus, it should be apparent that a considerable margin of safety is built into these minimum CO_2 concentrations required by the standard. This is because those who developed the CO_2 standard never considered it sufficient to extinguish the flame. By contrast, the guidelines given in some of the standards for other gaseous extinguishing agents merely mandate concentrations that are sufficient to extinguish open flame but will not produce a truly inert atmosphere.

The other method of applying CO_2 is local application. This method is appropriate only for extinguishing surface fires in flammable liquids, gases, and very shallow solids where the hazard is not enclosed or where the enclosure of the hazard is not sufficient to permit total flooding. Hazards spray booths, printing presses, rolling mills, and the like can be successfully protected by a local application system designed to discharge CO_2 and direct the flow at the localized fire hazard. The entire fire hazard area is then blanketed in CO_2 without actually filling the enclosure to a predetermined concentration.

The integrity of the enclosure is a very important part of total flooding, particularly if the hazard has a potential for deep-seated fire. If the enclosure is air tight, especially on the sides and bottom, the CO_2 extinguishing atmosphere can be retained for a long time to ensure complete extinguishment of the fire. If there are openings on the sides and bottom, however, the heavier mixture of CO_2 and air may rapidly leak out of the enclosure. If the extinguishing atmosphere is lost too rapidly, glowing embers may remain and cause reignition when air reaches the fire zone. Therefore, it is important to close all openings to minimize leakage or to compensate for the openings by discharging additional CO_2.

An extended discharge of CO_2 is used when an enclosure is not sufficiently air tight to retain an extinguishing concentration as long as needed. The extended discharge is normally at a reduced rate, following a high initial rate to develop the extinguishing concentration in a reasonably short time. The reduced rate of discharge should be a function of the leakage rate, which can be calculated on the basis of leakage area, or of the flow rate through ventilating ducts that cannot be shut.

Extended discharge is particularly applicable to enclosed rotating electrical equipment, such as generators, where it is difficult to prevent leakage until rotation stops. Extended discharge can be applied to ordinary total flooding systems, as well to the local application systems where a small hot spot may require prolonged cooling.

B.14.3.1 Carbon Dioxide Requirements for Deep-Seated Fires (NFPA 12)

NFPA 12 recognizes two types of CO_2 extinguishing systems. The first type is the high-pressure CO_2 system, and the second is a low-pressure CO_2 system. The basic difference between the two types lies in the method of storing the CO_2.

The high-pressure system utilizes the U.S. Department of Transformation (DOT) spun steel storage cylinders, which are usually kept at room temperature. At an ambient temperature of 21 °C (70 °F), the internal pressure in such a unit reaches 850 psi. These cylinders are available in capacities of 50, 75, or 100 pounds.

By contrast, the low-pressure storage unit maintains the CO_2 in a refrigerated pressure vessel with a typical storage temperature of -18 °C (0 °F) with a corresponding CO_2 vapor pressure of 300 psi. The refrigerated storage concept uses an American Society of Mechanical Engineers (ASME) coded pressure vessel with a working pressure of 2,413 kPa (350 psi). Such units are available in standard capacities from 1.25–60 tons. Larger units have also been made for special applications.

This basic difference in storage configuration inspired different application and control methods for the two types of systems. Since the maximum capacity of a high-pressure cylinder is 100 pounds of CO_2, most systems consist of multiple cylinders manifolded together to provide the required quantity of agent. Each cylinder has its own individual discharge valve and, once opened, the cylinder contents will completely discharge.

NFPA 12 requires that the quantity of CO_2 for deep-seated fires must be based on fairly air tight enclosures. After the design concentration is reached, it shall be maintained for a substantial period of time, but not less than 20-minutes. Any possible leakage shall receive special consideration, because the basic flooding factor does not include any leakage allowance.

For deep-seated fires the design concentration shall be achieved within 7-minutes from the start of discharge, but the rate shall be not less than that required to develop a concentration of 30-percent within 2 minutes. For surface fires, the design concentration shall be achieved within 1-minute from the start of discharge.

B.14.3.2 Personnel Protection from Carbon Dioxide

The CO_2 that is used to extinguish the diffusion combustion may pose a threat to human life, and NPP personnel must recognize and plan to cope with this threat

Human subjects exposed to low concentrations (less than 4-percent) of CO_2 for up to 30-minutes, dilation of cerebral blood vessels, increased pulmonary ventilation, and increased oxygen delivery to the tissues were observed (Gibbs et al., 1943, Patterson et al., 1955). These results were used by the United Kingdom regulatory community to differentiate between inert gas systems for fire suppression that contain CO_2 and those that do not (HAG, 1995). During similar low-concentration exposure scenarios in humans, however, other researchers have recorded slight increases in blood pressure, hearing loss, sweating, headache, and dyspnea (Gellhorn and Speisman, 1934, 1935; Schneider and Schulte, 1964). 6–7-percent CO_2 is considered the threshold level at which harmful effects become noticeable in human beings. At concentration above 9-percent, most people lose consciousness within a short time. Since the minimum concentrations of CO_2 in air used to extinguish fire exceed 9-percent, adequate safety precautions must be designed into every CO_2 fire extinguishing system.

B.14.3.3 Harmful Effects of Carbon Dioxide Fire Suppression Systems

As described above CO_2 is lethal to humans at the minimum concentrations required to suppress fires. Accidents involving the discharge of CO_2 fire suppression systems have resulted in numerous deaths and injuries. Given its inherent hazard, CO_2 should not be used in areas that are subject to occupancy, except when the risk of fire is documented to be greater than the risk to personnel and no viable suppression alternatives exist.

In land-based workplace environments, the Occupational Safety and Health Administration (OSHA) regulates the use of CO_2. These regulations are provided in 29 CFR Parts 1910.160 and 1910.162, which outline the requirements for general and gaseous fixed extinguishing systems, respectively. Despite the fact that the concentration of CO_2 needed to extinguish fires is above the lethal level, OSHA does not prevent the use of CO_2 in normally occupied areas. (However, OSHA does explicitly limit the use of chlorobromomethane and carbon tetrachloride as extinguishing agents where employees may be exposed [29 CFR Part 1910.160 (b) (11)]. For CO_2 systems, OSHA requires a predischarge alarm for alerting employees of the impending release of CO_2 when the design concentration is greater than 4-percent (which is essentially true for all CO_2 systems). This predischarge alarm must allow sufficient time delay for personnel to safely exit the area prior to discharge. Although it is speculative, it is likely that these regulations would confer adequate protection only in the event of planned discharge, not accidental discharge. Accidental discharges have occurred, however, in which adherence to regulations has provided personnel protection, whereas some planned discharges have resulted in injury to personnel.

The U.S. Environmental Protection Agency (EPA) has published a report to provide information on the use and effectiveness of CO_2 in fire protection systems and describe incidents involving inadvertent exposure of personnel to the gas (EPA430-R-00-02, 2000). The results of this comprehensive review identify that from 1975 to the present, a total of 51 CO_2 incident records were located that reported a total of 72 deaths and 145 injuries resulting from accidents involving the discharge of CO_2 fire extinguishing systems. All the deaths that were attributed to CO_2 were the result of asphyxiation. Details about the injuries were generally not provided in the incident reports, although some OSHA inspections listed asphyxia as the nature of the injury. Prior to 1975, a total of 11 incident records were located that reported a total of 47 deaths and 7 injuries involving CO_2. Twenty of the 47 deaths occurred in England prior to 1963; however, the cause of these deaths is unknown. The remainder of this section presents representative examples of the hazards of CO_2 fire suppression systems:

- On July 28, 2000, a bank employee accidentally suffocated in a New York City bank vault after pulling a fire alarm that flooded the space with CO_2. The bank employee was putting stock receipts in the bank's basement vault when she accidentally became locked inside. Apparently thinking she could get help by pulling a fire alarm, she instead activated a CO_2 fire extinguishing system that sucked air from the vault. She was taken to a local hospital in extremely critical condition and was pronounced dead.

- On January 15, 1999, at 5:49 p.m., with the plant at full power, an inadvertent discharge of the CO_2 fire suppression system occurred in the Millstone Unit 3 cable spreading room (CSR), which is located in the control building directly below the control room. The actuation occurred when a non-licensed plant equipment operator trainee in the service building blew dust off a printed circuit board located in the CSR CO_2 control panel, which is located in the service building, rather than the control building. There were no plant personnel in the CSR at the time of the discharge. Shortly after the discharge, CO_2 was found to have migrated down into the switchgear rooms located directly below the CSR. Approximately 37-minutes after initiation, the licensee used a portable instrument to measure the concentration of CO_2 in one of the control building stairwells, which allows access to the control room, the CSR, and the switchgear rooms. The reading was off-scale high indicating that the CO_2 concentration was in excess of 50,000 parts per million (ppm). NRC Regulatory Guide 1.78 currently recommends a CO_2 toxicity limit of 10,000 ppm. On the basis of this indication, the licensee declared the area uninhabitable.

  Approximately 2 hours after the CO_2 discharge, operators aligned the control building purge system to remove CO_2 from the switchgear rooms. The switchgear rooms were selected for purging first because they contained important plant equipment, such as the auxiliary shutdown panel. The purge system is a non-safety-related system designed to remove CO_2 and smoke from various control building areas. Placing the purge system in service diverted air from the control room to the switchgear rooms, which reduced the pressure in the control room relative to the CSR. This pressure reduction in the control room may have allowed CO_2 from the CSR room to migrate up through penetrations into the control room. When the concentration of CO_2 reached 5,000 ppm in the control room, the operators donned self-contained breathing apparatus (SCBA), as required by the plant procedures. The concentration of CO_2 in the control room reached a peak level in excess of 17,000 ppm before it began to decrease. The operators wore SCBA for approximately 6 hours until the CO_2 was successfully purged from the control room.

- On July 29, 1998, a high-pressure, total flooding CO_2 extinguishing system discharged without warning during routine maintenance of electrical equipment, resulting in one fatality and several serious injuries in Building 648 of the Idaho National Engineering and Environmental Laboratory (INEEL) (EH2PUB/09-98/01A1). At the time of the accident, the newly installed CO_2 system releasing panel was electronically disabled and considered to be out of service. The work crew began opening circuit breakers in preparation for the preventive maintenance work. Shortly after the last breaker was opened, the CO_2 system discharge, creating near zero visibility. While the evacuation alarms may have briefly sounded for less than one second, they did not continuously sound in conjunction with CO_2 release. After the CO_2 discharge, the worker ran toward the exits, which were visible since they were held open by cables running into the building from portable generators. Eight of the workers were able to exit on their own; however, five remained inside of the building and were rendered unconscious by the CO_2. Three were later rescued by the workers who had earlier escaped, which left two people remaining in the building. One of the remaining workers was later revived, and the other perished.

- At Duane Arnold Unit 1 on March 22, 1992 (LER 331/92-004), the licensee performed a special test of the CO_2 fire suppression system in the CSR. This test was conducted to check corrective actions taken following a CO_2 discharge in 1990. At the time of this test, the reactor had been shut down and defueled. As a result of this test, CO_2 intruded into the control room, and this intrusion led to an unacceptable reduction in the oxygen level in the area within a few minutes. The operator recorded oxygen levels of 17-percent (at chest level) and 15-percent (at floor level), both of which were below the plant's acceptance criterion of 19.5-percent. Essential control room personnel donned SCBA and were able to remain in the control room. The reduced oxygen levels resulted from increased pressure in the CSR, which is directly beneath the control room. Sealed penetrations between the two rooms leaked under the high differential pressure.

  In this incident, the migration of CO_2 into various fire zones may have adversely affected the operators' ability to shut down the plant during a fire in the CSR. Consequently, one can conclude that a severe fire in the CSR may adversely affect the operators' ability to safely shut down the plant from the control room. In the event that the operators are required to evacuate the control room, plant procedures require operators to shut down the plant from the auxiliary shutdown panel and other panels, which are located in the switchgear rooms. During this event, the CO_2 concentration at the auxiliary shutdown panel would prohibit access without SCBA.

- At Surry Nuclear Power Station on December 9, 1986, an accidental discharge of both the CO_2 and Halon extinguishing systems was caused by water damage to the extinguishing system control panels. The water came from a pipe break in the feedwater system. Four died and four were injured in a fire associated with the accident. However, it is not clear if the release of the gases from fire extinguishing systems were responsible for these injuries and deaths (Warnick, 1986).

- At Hope Creek Generating Station, on September 4, 1984, a 10-ton CO_2 system was inadvertently discharged into a diesel generator fuel storage area. The warning bell and beacon light did not operate and workers who were cleaning the corridor walls outside of the fuel storage room with air/water guns under pressure were not alerted. The cause of the discharge was determined to be moisture (that entered the CO_2 control panel through openings at the top of an inadequately installed protective panel) that shorted the CO_2 control panel circuitry. The moisture was believed to have originated from the workers cleaning the corridor walls (PNO-I-85-64a).

B.14.4 References

Chavez, J.M., and L.D. Lambert, “Evaluation of Suppression Methods for Electrical Cables Fires,” NUREG/CR-3656, U.S. Nuclear Regulatory Commission, Washington, DC, October 1986.

EPA430-R-00-02, “Carbon Dioxide as a Fire Suppressant: Examining the Risk,” U.S. Environmental Protection Agency, Office of Air and Radiation, Stratospheric protection Division, Washington DC, February 2000.

Fielding, G.H., and F.J. Woods, “Halon 1301: Mechanism of Failure to Extinguish Deep-Seated Fires,” *Journal of Fire & Flammability*, Volume 6, pp. 37–43, January 1975.

Gellhorn, E., and I. Spiesman, “Influence of Variations of O_2- and Carbon Dioxide Tension in the Inspired Air Upon Hearing,” Proceedings of Society of Exp. Biol. Med., Volume 32, pp. 46–44, 1934.

Gellhorn, E., and I. Spiesman, “Influence of Hyperpnea and Variations of O2- and CO2-Tension in the Inspired Air Upon Hearing,” *American Journal of Physiol*ogy, Volume 112, pp. 519–528, 1935.

Gibbs, F.A., E.L Gibbs, E.G. Lennox, and L.F. Nims, “The Value of Carbon Dioxide in Counteracting the Effects of Low Oxygen,” *Journal of Aviat. Med.*, Volume 14, pp, 250–261, 1943.

Grand, C.C., “Halon Design Calculations,” Section 4, Chapter 6, *SFPE Handbook of Fire Protection Engineering*, 2nd Edition, P.J. DiNenno, Editor-in-Chief, National Fire Protection Association, Quincy, Massachusetts, 1995.

HAG, “A Review of the Toxic and Asphyxiating Hazards of Clean Agent Replacements for Halon 1301,” Prepared by the Halon Alternatives Group (HAG) in the UK, February 1995. As Cited in a Letter dated May 9, 1995 from J.S. Nicholas, Ansul Inc., to Karen Metchis, EPA.

Klamerus, L.J., “Electrical Cable Fire Suppression Tests with Halon 1301,” SAND 81-1785, Sandia National Laboratories (SNL), Albuquerque, New Mexico, August 1981.

NFPA 12, “Carbon Dioxide Extinguishing Systems,” National Fire Protection Association, Quincy, Massachusetts.

NFPA 12A, “Standard on Halon 1301 Fire Extinguishing Systems,” 1992 Edition, National Fire Protection Association, Quincy, Massachusetts.

NFPA 12A, “Standard on Halon 1301 Fire Extinguishing Systems,” 1971 Edition, National Fire Protection Association, Quincy, Massachusetts, pp. 59–69.

NFPA 2001, “Standard on Clean Agent Fire Extinguishing Systems,” 2000 Edition, National Fire Protection Association, Quincy, Massachusetts.

NRC Information Notice: 99-05, “Inadvertent Discharge of Carbon Dioxide Fire Protection System and Gas Migration, March 8, 1999.

Patterson, J.L., H. Heyman, L.L Battery, and R.W. Ferguson, “Threshold of Response of the Cerebral Vessels of Man to Increases in Blood Carbon Dioxide,” *Journal of Clin. Invest,* Volume 34, pp. 1857–1864, 1955.

Preliminary Notification of Event or Unusual Occurrence PNO-I-99-004: Carbon Dioxide Discharge into Cable Spreading Room, Millstone Unit 3. January 20, 1999.

Preliminary Notification of Event or Unusual Occurrence - PNO-I-85-64a, U.S. Nuclear Regulatory Commission Region I, September 5, 1985.

Schult, J.H., “Sealed Environments in Relation to Health and Disease,” Arch. Environment Health, Volume 8, pp. 438–452, 1964.

Sinclair, R.D., J.M. Clark, and B.E. Welch, “Comparison of Physiological Responses of Normal man to Exercise in Air and in Acute and Chronic Hypercapnia,” Underwater Physiology, C.J. Lambertsen, Editor, Academic Press, New York, New York, pp. 409–417, 1971.

“Type A Accident Investigation Board Report of the July 28, 1998, Fatality and Multiple Injuries Resulting from the Release of Carbon Dioxide at Building 648, Test Reactor Area,” Idaho National Engineering and Environmental Laboratory, U.S. Department of Energy, EH2PUB/09-98/01A1, September 1998.

Warnick, L., “Inadvertent Actuation of Fire Suppression Systems, Surry Nuclear Power Station, Feedwater Pipe Failure,” Virginia Power, Richmond, Virginia, 1986.

B.15 Dry Chemical Extinguishing Agents

Dry chemicals or powders, or solid phase agents provide an alternative to water or gaseous agents for extinguishing fire. Table B.15-1 lists the chemical names, formulae, and (commercial) names of the various dry chemical agents. In each case, the particles of powder (10–76 m in size) are coated with an agent (such as zinc stearate or a silicone) to prevent caking and promote flowing, and are projected by an inert gas. The effectiveness of any of these agents depends on the particle size. The smaller the particles, the less agent is needed as long as particles are larger than a critical size. The reason for this fact is believed to be that the agent must vaporize rapidly in the flame to be effective. However, if an extremely fine agent were used, it would be difficult to disperse and apply to the fire.

Table B.15-1. Dry Chemical Agents

Chemical Name	**Formula**	**Popular Name(s)**
Sodium bicarbonate	$NaHCO_3$	Baking soda
Sodium chloride	$NaCl$	Common salt
Potassium bicarbonate	$KHCO_3$	Purple K
Potassium chloride	KCl	Super K
Potassium sulfate	K_2SO_4	Karate Massive
Monoammonium phosphate	$(NH_4)H_2PO_4$	ABC or multipurpose
Urea and Potassium bicarbonate	$NH_2CONH_2 + KHCO_3$	Monnex

It is difficult to draw a precise comparison of effectiveness of one dry chemical with another because a comparison based on chemical differences would require each agent to have identical particle size. Furthermore, gaseous agents can be compared by studying the flammability limits of uniform mixtures at rest; however, if particles were present, they would settle out unless the mixture is agitated, thus modifying the combustion behavior. Nonetheless, some general comparisons of various powders have been made:

- Sodium bicarbonate (standard dry chemical) and sodium chloride have comparable effectiveness and are several times as effective (on a weight basis) as powders such as limestone or talc, which are supposedly chemically inert in a flame. Sodium bicarbonate (standard dry chemical) primarily consists of sodium bicarbonate (over 90-percent) with additives to improve fluidity, non-caking, and water-repellent characteristics.
- Potassium bicarbonate or potassium chloride is up to twice as effective (on a weight basis) as the corresponding sodium compounds.

- Under some conditions, monoammonium phosphate is more effective than potassium bicarbonate, however, it can be less effective under other conditions.
- Monnex is twice as effective as potassium bicarbonate because of the rapid thermal decomposition of the complex formed between urea and potassium bicarbonate, which cause a breakup of the particles in the flame to form very fine fragments, which then rapidly gasify.

Dry chemical formulations may be ranked with regard to their effectiveness in extinguishing fires according to their performance in tests. As previously described, this performance is a function of both the chemical composition and the particle size. It seems clear that the effective powders act on a flame through some chemical mechanism, presumably forming volatile species that react with hydrogen atoms or hydroxyl radicals. However, science has not yet firmly established the precise reactions. Although the primary action is probably removal of active species, the powders also discourage combustion by absorbing heat, blocking radiative energy transfer, and in the case of monoammonium phosphate, forming a surface coating.

Of the seven types of dry chemicals commonly in use, only monoammonium phosphate is considered effective against deep-seated fires because of a glassy phosphoric acid coating that forms over the combustible surface. All seven types of dry chemical extinguishing agents act to suppress the flame of a fire (Friedman, 1998), but require significant cleaning after use. As a result their use is limited almost exclusively to environments where this is not a serious concern. Dry chemicals are very common in manual extinguishers and to some extent for local applications. The most common application of these agents is for relatively small flammable liquid fires. Dry chemical total flooding suppression systems are designed to reach the design concentration within the entire protected volume in less than 30 seconds (NFPA 17, “Standard for Dry Chemical Extinguishing System”). Additional dry chemical is required to compensate for losses attributable to openings and ventilation in a compartment.

One reason for the popularity of dry chemical extinguishing agents other than monoammonium phosphate has to do with corrosion. Any chemical powder can produce some degree of corrosion or other damage, but monoammonium phosphate is notably acidic and corrodes more readily than other dry chemicals, which are neutral or mildly alkaline. Furthermore, corrosion by the other dry chemicals is stopped by a moderately dry atmosphere, while phosphoric acid has such a strong affinity for water that an exceedingly dry atmosphere would be needed to stop corrosion. Monoammonium phosphate is also not recommended for kitchen fires involving hot fat because of its acidic nature; an alkaline dry chemical (such as potassium bicarbonate) is preferred.

Application of a dry chemical extinguishing agent on an electrical fire is safe (from the viewpoint of electric shock) for fire fighters. However, these agents (especially monoammonium phosphate) can damage delicate electrical equipment.

B.15.1 Hazards Associated with Dry Chemicals

One hazard associated with the use of dry chemical extinguishing agents is attributable to the sudden release of the agent. Another hazard is unexpected reignition. The main toxic hazards following the use of dry chemical agents will generally be those attributable to the combustion processes, since dry chemicals themselves are non-toxic. According to Hague (1997), the ingredients used in dry chemical agents are nontoxic but can cause temporary breathing difficulty and can interfere with visibility.

B.15.2 References

Friedman, R., *Principles of Fire Protection Chemistry and Physics*, 3rd Edition, Chapter 14, "Fire-Fighting Procedures," National Fire Protection Association, Quincy, Massachusetts, pp. 229–230, 1998.

Hague, D.R., "Dry Chemical Agents and Applications Systems," Section 6, *NFPA Fire Protection Handbook*, 18th Edition, National Fire Protection Association, Quincy, Massachusetts, 1997.

NFPA 17, "Standard for Dry Chemical Extinguishing Systems," 2002 Edition, National Fire Protection Association, Quincy, Massachusetts.

B.16 Fire Protection Using Foam

Extinguishing foams provide a primary alternative to water, particularly for large fires. Foams are widely used to control and extinguish fires involving flammable and combustible Class B liquids (e.g., solvents, oil-based paints, petroleum greases, paraffin or heavy lubricants, tars, lacquers, hydrocarbons, alcohols, LPG, LNG, and cooking fats). Foams are also suitable for Class A fires involving ordinary combustible materials (e.g., wood, cloth, paper, rubber, and many plastics).

If a flammable liquid is lighter than water and is insoluble in water, application of water to extinguish a fire would simply cause the liquid to float on the water and continue to burn. Moreover, if the burning liquid is an oil or fat, the temperature of which is substantially above the boiling point of water, the water will penetrate the hot oil, turn into steam below the surface, and cause an eruption of oil (boilover) that will accelerate the burning rate and possibly spread the fire. By contrast, if the flammable liquid is water soluble (such as alcohols), addition of sufficient water will dilute the liquid to the point where it is no longer flammable. However, if the fire involves a deep pool of alcohol (rather than a shallow spill), the time required to obtained sufficient dilution might be so great that an aqueous foam would be a better choice of extinguishing agent. If the nature of a liquid is unknown, an aqueous foam might still be chosen over direct application of water. Another important application of foam is on liquids or solids that are burning in spaces that are difficult to assess (such as a room in a basement or the hold of a ship). In such instances, the foam is used to flood the compartment completely.

Fire-fighting foam is a mass of bubbles formed by various methods from aqueous solutions of specially formulated foaming agents. Some foams are thick and viscous, forming tough heat-resistant blankets over burning liquid surfaces and vertical areas. Other foams are thinner and spread more rapidly. Some are capable of producing a vapor-sealing film of surface-active water solution on a liquid surface, and others are meant to be used as large volumes of wet gas cells to inundate surfaces and fill cavities. The foam initially acts as a blanketing agent and then as a cooling agent as the water drains from the foam, as a cooling agent.

The effectiveness of foam is attributable to the following factors:

- prevents air from reaching fire
- generates steam, which dilutes the air as well as absorbed heat
- penetrates crevices because of low surface tension
- provides protection of exposed material that not yet burning

Nonetheless, foam is an unstable air-water emulsion, which can easily be broken down by physical or mechanical forces, and certain chemical vapors or fluids can quickly destroy foam. Consequently, when certain other extinguishing agents are used in conjunction with foam, severe breakdown of the foam can occur. In addition, turbulent air or violently uprising combustion gases can divert light foam from the burning area.

Foam breaks down and vaporizes its water content under attack by heat and flames. Therefore, it must be applied to a burning surface in sufficient volume and at a sufficient rate to compensate for this loss and guarantee a residual foam layer over the extinguished portion of the burning liquid. The process of foam spread over a burning liquid fuel is similar to the spread of a less dense liquid (such as oil) on a more dense liquid (such as water).

B.16.1 Properties of Foam

Foams used for fire fighting should possess certain general properties, including (1) expansion, (2) cohesion, (3) stability, (4) fluidity, (5) fuel resistance, and (6) resistance. Clearly, foam extinguishing agents must have an appreciable expansion ratio, the bubbles must adhere together to form a blanket, and the foam must retain its water and remain stable, flowing while freely over the liquid surface and around any obstacles. In addition, foam agents must not pick up so much fuel that the foam would be liable to burn, and the agent must resist the heat of flames on the liquid. Foams for use on alcohol fires must also be alcohol resistant.

Three quantitative criteria for foam are (1) the expansion (2) the fluidity and (3) the drainage time. Expansion is quantitatively measured by the expansion ratio. While fluidity is measured in terms of shear stress. A shear stress in the range 150–200 dyn/cm^2, measured on a torsional viscometer, is typical of a good foam extinguishing agent. The drainage of liquid out of the foam is usually expressed as the 25-percent drainage rate, which is the time in minutes for 25-percent of the total liquid content to drain away under standard conditions. For a good foam, this drainage time is typically 2–5 minutes.

Foam extinguishing agents can also be affected by the quality of the water used. A study by Dimaio and Lange (1984) detected deleterious effects from contaminants (such as corrosion inhibitors, anti-fouling agents, etc.). In general, however, such effects were found to be much weaker if high application rates were used.

B.16.2 Hazards Associated with Foam

Foam is water-based; consequently, hazards associated with water also apply to foam. These hazards include increased vaporization of low-boiling flammable combustible liquids, reaction with incompatible materials and electric shock from live electrical equipment. Another hazard is rupture of the foam blanket and burn back, which may put fire fighters at risk. Hazards can also arise from the use of a foam on a liquid at a temperature of 100 °C (212 °F) or above, because the formation of steam can cause a four-fold expansion of the foam with boilover of the burning liquid. In the case of the medium- and high-expansion foams used to fill spaces, there is the additional hazard of asphyxiation of personnel or visibility and spacial limitations resulting in injury.

Another hazard of foam is ignition of hydrocarbons in a storage tank roof by static electricity from foam injection, as described by Howells (1993). This author describes several incidents in which ignition of volatile refined products in a floating roof storage tank appears to have been caused by foam injection. He suggests two possible modes of charge generation, including (1) the setting of water droplets through the hydrocarbon liquid and (2) the streaming current of the foam mixture leaving the nozzle.

B.16.3 Delivery Systems for Foam

Foam is delivered to a fire by means similar to those used for water, which primarily include fixed systems such as foam-water spray systems and fixed foam-water monitors, and mobile foam-water systems such as fire hoses. For low-expansion foam, one type of fixed-foam system used for low-expansion foam is the foam-water deluge system. Fixed-foam systems are used for fire prevention, extinguishment, and control in bunds or on spills. Subsurface application of low-expansion foam to hydrocarbon storage tanks was developed in the 1960s and is now an NFPA-recognized design procedure. Relevant codes are NFPA 11, “Standard for Low-Expansion Foam”; NFPA 11A, “Standard for Medium-and High-Expansion Foam Systems”; and NFPA 16, “Standard for the Installation of Foam-Water Sprinkler and Foam-Water Spray Systems.” There is limited use of foam in portable devices except in wildland fire situations involving Class A fuels. The Class A foams are generally mixed in 0.1% to 1.0% concentration ratios in water and are utilized in compressed air/foam systems which discharge through hose lines equipped with air aspirating foam nozzles or conventional fog nozzles.

The delivery of foam involves three stages, including (1) proportioning the foam concentrate, (2) generating foam, and (3) distributing foam. There are a number of methods for proportioning the foam concentrate. The devices for generating the foam are incorporated in the devices used for its distribution, as previously described. The basic generation method is aspiration of air into the foam.

B.16.4 Application of Foam

Fire extinction by blanketing may be achieved using foam. Foam can be used for all modern fire protection in warehouses, high storage areas, and process plants of all types for commodities such as rubber tires, rolled paper, and plastics; in bulk storage areas and conveyor tunnels, coal mines, coal handling equipment tunnels, and diked areas; in electric power plants aircraft hangars, and aboard ships. An example of application in a BWR is the use of a foam water sprinkler system (NFPA 16) to protect the large oil hazard of the recirculation pumps motor generator (MG) set.

Low expansion foam is mainly used to prevent, extinguish, or control fires in storage tank tops and bunds and on spills. Medium- and high-expansion foams are used to prevent, extinguish, or control fire in spaces such as fires below grades (e.g., basement).

Foam should be used only if compatible with the hazardous liquid. In particular, foam is essentially expanded water and, apart from its density, has the general characteristics of water. Consequently, it is just as unsuitable as water for fighting fires involving electrical equipment or substances that have undesirable reactions with water. Other prerequisites for the use of foam are that the liquid surface must be horizontal and the temperature of the liquid must be below the boiling point. In addition, the liquid temperature is below the boiling point of the given hazardous liquid, but above 100 °C (212 °F), water in the foam will turn to steam, which can result in very large expansion of the foam.

There are optimum rates of foam application. For low-expansion foam with an expansion ratio of 8:1, an application rate of 0.1 US gal/ft^2-min will give 0.8 US gal/ft^2-min of foam. Application systems for medium- and high-expansion foams comprise both (1) total flooding systems and (2) local application systems. Fighting a major fire requires a very large quantity of foam. An example quoted by Nash (1966) is a requirement of 300 x 5 UK gal drums for a 30-minute foam attack on a single 150-ft diameter oil storage tank. The supply and disposal of such a large number of drums in an area congested with appliances and hoses constitute a major problem. Consequently, Nash describes the alternative of providing a piped supply of foam concentrate.

A particularly important application of foam is the protection of storage tanks. For fixed roof tanks, some principle arrangements are foam chambers, internal tank distributors, and subsurface foam injection. Foam chambers are installed at intervals on the outside near the top of the tank wall, providing an over-the-top foam generation. An alternative is internal distributors fitted inside the tank. Application of foam at the top of the tank poses several problems. If the fire is initiated by an explosion, the explosion itself may also disable the foam system. The upward flow of air caused by the fire may also interfere with the distribution of the foam and the foam may not reach the center of a large tank. Subsurface foam injection is designed to counter these difficulties. Such systems inject under pressure up through the liquid in the tank. Injection may be through the product pipe or a dedicated line. Mobile foam trucks may be used to provide the foam supply.

Floating roof tanks may be open topped or closed. Both have a good fire record, so foam systems are generally not required. The one exception to this rule is the need to allow for rim fires, which can occur on either type of tank. An open-topped floating roof tank may be protected by a fixed foam system, which pours foam into the annulus formed by the tank wall and a foam dam. A closed floating roof tank may be protected using a top injection system similar to those used in fixed roof tanks. Subsurface foam injection is not generally used for floating roof tanks, since a tilted or sunken roof can cause poor foam distribution.

Foam trucks are the principal means of mobile foam of delivery. The trucks are typically purpose-built twin-agent trucks with the capability to deliver dry chemicals in addition to aqueous film forming foam (AFFF). Foam trucks carry a supply of foam concentrate and delivery hoses and can be equipped with telescoping booms or articulated towers. They also have low clearances to allow passage under pipe bridges. Monitor capacities are on the order of 500–1000 US gal-min.

A variety of mobile devices can be used to apply foam to the top of a storage tank that is on fire. These include mobile foam monitors and foam towers. However, using a foam monitor for this purpose poses numerous problems, such as crosswinds and fire updrafts, which can waste a significant proportion of the foam.

Use of foam extinguishing agents is not limited to fire control and extinguishment. Another important application is the suppression of vaporization from toxic liquid spills. This use of foam is treated in ASTM F1129-88, “Standard Guide for Using Aqueous Foams to Control the Vapor Hazard from Immiscible Volatile Liquids.” A 500 to 1 foam ratio can be used to control fires and reduce vaporization from liquefied natural gas (LNG) spills.

B.16.5 Types of Foam

A large family of foams of different types and applications are currently available. Water-based foams are available in the following forms:

- chemical foam
- protein-based mechanical foam
  - standard low-expansion foam
  - high-expansion foam
  - medium-expansion foam
- special foam
  - fluorochemical for light-water foam
  - fluoroprotein foam
- synthetic detergent foam
  - aqueous film-forming foam (AFFF)
  - film-forming fluoroprotein (FFFP) foam
  - alcohol-resistant foam
  - low-temperature foam

One broad distinction is the viscosity of the foam. The blanket formed by the more viscous type is resistant to rupture by flame, but the less viscous type flows more readily over a liquid surface.

- *Chemical Foam*

  Chemical foam is produced by reacting an aqueous solution of sodium bicarbonate and aluminum sulphate in the presence of a foam stabilizer. The reaction generates CO_2, which both forms foam and ejects the mixture from the apparatus. This type of foam may be generally regarded as obsolete, given that its use has long been almost entirely confined to chemical foam portable extinguishers which are no longer listed by Underwriters Laboratories.

- *Protein-Based Mechanical Foam*
  - Mechanical foam is generated by mechanical aeration of aqueous solutions of certain chemicals, which usually have a protein base. For example, one type is based on protein rich slaughter house byproducts for the foam stabilizing agent. Standard foam is made by introducing the foam compound into the water in the hose to give a 3–6-percent aqueous solution and then mixing the solution with air in an ejector nozzle to give an expansion of approximately 10:1. This type of foam is the most widely used for both fixed and mobile apparatus. Such standard low-expansion foam is often very economical.
  - High-expansion foam is generally similar to standard foam, with the exception that it has a much higher expansion of approximately 1,000:1. Because this type of foam contains little water, it acts almost entirely by blanketing rather than cooling. In addition, it is very light and become easily blown away, it is more suitable for fires in contained spaces than for those in open situations (such as bunds).
  - Medium-expansion foam is also generally similar to standard foam, with the exception that has an expansion of approximately 100–150:1. This type of foam is also light, but is not so easily blown away as high-expansion foam. Both medium- and high-expansion foams have a good three-dimensional extinction capability and can be used against fires on piles of materials (such as rubber).

    A disadvantage of protein foams is that if the foam blanket is broken, the liquid may reignite and burn back the blanket. Low-expansion foam, however, has an advantage in this regard, given that it has reasonably good heat and burnback resistance.

- *Special Foam*
  - Fluorochemical or Light-Water Foam

    Fluorochemical foam is one agent that has been developed to overcome the problem of reignition and burnback. One type is fluorochemical foam. This light-water foam contains a straight-chain fluorocarbon surface active agent. This has the effect that as the water drains from the foam, it spreads in a thin film over the liquid and seals it. Even if the film is disturbed by agitation, it reforms rapidly. Light-water foam behaves differently, however, on different liquids, and it is expensive and not universally effective.

  - *Fluoroprotein Foam*
    Another agent that works in a manner similar to fluorochemical light-water foam is fluoroprotein foam, which contains a branched-chain fluorocarbon. Where good burnback resistance is needed, this alternative is less expansive and appears (in many cases) to be more effective than light-water foam. In particular, fluoroprotein foam is less prone to pick up oil particles when passed through oil. This fuel-shedding property is useful in subsurface foam injection on storage tanks. This type of foam also tends to have good compatibility with dry chemicals.

- *Synthetic Detergent Foam*
  Synthetic detergent foam is generated by mechanical aeration of an aqueous solution containing 2–3 -percent detergent. This foam is less stable than protein-based foam, but it appears to be useful in massive application in a knockout attack. Despite its limitations, detergent foam has enjoyed some popularity, because it is even less expensive than protein foam.
  - *Aqueous Film-Forming Foam (AFFF)*
    AFFF has low viscosity and spreads easily over a liquid surface so it can be an effective agent against deep-seated fires. Another useful property of AFFF is that it does not need elaborate foaming devices and can be used in many water sprinkler and water spray systems.
  - Film-Forming Fluoroprotein (FFFP) Foam
    FFFP foam is another type of foam that has low viscosity and good spreading properties and can be used in many water spray systems. FFFP foam tends to drain rapidly and, therefore, is less reliable in maintaining a foam blanket.
  - *Alcohol-Resistant Foam*
    Regular air foams do not perform well on liquids that are of the polar solvent type (notably alcohol). Alcohol-resistant foams have been developed to solve that problem. The first generation of alcohol-resistant foams were not entirely satisfactory, but effective foams have since been developed. One type of alcohol-resistant foam is polymeric-alcohol resistant AFFF.
  - *Low-Temperature Foam*
    Foams have been developed for use at low ambient temperatures; one quoted temperature for such foams is -29 °C (-20 °F). These foams come in both protein and AFFF types.

B.16.6 References

Dimaio, L.R., and R.F. Lange, "Effect of Water Quality on Fire Fighting Foams," *Plant/Operations Progress*, Volume, 3, 1984.

Friedman, R., *Principles of Fire Protection Chemistry and Physics*, 3rd Edition, National Fire Protection Association, Quincy, Massachusetts, 1998.

Howells, P., "Electrostatic Hazards of Foam Blanketing Operations," *Health, Safety and Loss Prevention*, p. 312, 1983.

Nash, G., "New Concept in the Supply of Foam Compound to Oil Fires," *Fire International*, Volume 1, No. 12, p. 40, 1966.

NFPA 11, "Standard for Low-Expansion Foam," 2002 Edition, National Fire Protection Association, Quincy, Massachusetts.

NFPA 11A, "Standard for Medium-and High-Expansion Foam Systems," 1999 Edition, National Fire Protection Association, Quincy, Massachusetts.

NFPA 16, "Standard for the Installation of Foam-Water Sprinkler and Foam-Water Spray Systems," 1999 Edition, National Fire Protection Association, Quincy, Massachusetts.

NFPA 1150, "Fire Fighting Chemicals for Class A Fuels in Rural, Suburban, and Vegetated Areas," 1999 Edition, National Fire Protection Association, Quincy, Massachusetts.

B.16.7 Additional Reading

Woodworth, S.P., and J.A. Frank, *Fighting Fire with Foam*, Van Nostrand Reinhold, New York, 1994.

B.17 Harmful Properties of Toxic Gases Found in Fires

B.17.1 Introduction

Historically, more people are injured or killed by fire combustion products than by direct exposure to heat and flame. Evaluations have shown that personnel at a distance from the source of a fire are particularly at risk from fire effluent in post-flashover fire scenarios (Beitel et al., 1998). Toxic gases are lethal largely because they cause people to become disoriented and suffer respiratory distress, often losing consciousness and physical mobility. Following a period of hyperventilation, resulting from inhaling irritant gases the final cause of death is often carbon monoxide (CO) poisoning or scorching of the lungs by hot fire gases, rather than thermal exposure or flame impact.

The most significant effluent toxicants in ordinary fires are CO, hydrogen cyanide (HCN), carbon dioxide (CO_2), hydrogen chloride (HCl), and nitrogen dioxide (NO_2). Speaking very generally, CO alone accounts for half of the fire toxicity problem, although it is far less toxic than many of the other gases found in fires. Nonetheless, CO is considered to be the primary toxicant because of its copious generation by all fires. The importance of any toxic gas species to a particular fire must reflect both its toxicity and its actual concentration in that particular fire. The time of exposure is also important for determining the effects from toxic gases. In general, a higher concentration allows the same biological effect to be reached in a shorter time. For toxicity data, the exposure period normally used is 30 minutes.

The following definitions of toxicity related terms are commonly used in fire and combustion toxicology, as defined by ASTM Standard E176-98:

- ***Toxic hazard*** is the potential for physiological harm from the toxic products of combustion. Toxic hazard reflects both the quantity and quality of toxic products (quality is typically expressed as toxic potency. Toxic hazard is not the only hazard associated with fire, and is not an intrinsic characteristic of a material or product. Rather, toxic hazard depends upon the fire scenario, the condition of use of the material or product, and possibly other factors.
- ***Toxic potency*** is a quantitative expression that relates concentration and exposure time to a particular degree of adverse physiological effects (for example, death) on exposure of humans or animals. The toxic potency of the smoke from any material, product, or assembly is related to the composition of that smoke, which, in turn, depends upon the conditions under which the smoke is generated. Toxic potency of the smoke from a specimen or product is determined on a per-unit-specimen-mass basis. At present, for fire research, the dominant biological end point adopted is death and the measured quantity is the LC_{50}, which is the concentration (g/m^3) of smoke which is lethal to 50-percent of the exposed specified test animals in a specified time period. (The meaning of this variable is the amount of mass that needs to be dispersed into a volume of 1 m^3 in order to cause a 50-percent probability of lethality.) For substances where the composition is known (e.g., purge gases), the LC_{50} is usually expressed in units of ppmv. The definition here is that 1 ppmv of gas means that there is one part of gas per million parts of air. The “v” denotes parts by volume rather than weight. The LC_{50} notation must include the exposure time, generally 30 minutes (along with a 14-day post-exposure observation period) (Babrauskas et al., 1991). The toxic potency is not an intrinsic characteristic of a material.

B.17.2 Smoke and Toxic Gases

Many studies have been undertaken on toxic combustion products of organic materials, with the objective of realistically assessing the associated hazard. Toxicities of CO, CO_2, HCN, HCl, and low O_2 have been examined in depth by Babrauskas (1991), who determined that narcosis is caused by fire gases, such as CO and HCN, as well as low O_2 concentrations and high CO_2 concentrations. Narcotic gases cause incapacitation mainly by acting on the central nervous system and, to some extent, the cardiovascular system. Most narcotic fire gases produce their effects by causing brain tissue hypoxia. Since the body possesses powerful adaptive mechanisms designed to maximize oxygen delivery to the brain, it is usually possible to maintain normal body functions up to a certain concentration of a narcotic, and be unaware of the impending intoxication. However, once the threshold is reached where normal functioning can no longer be maintained, deterioration is rapid and severe, beginning with signs similar to the effects of alcohol intoxication, including lethargy or euphoria with poor physical coordination, followed rapidly by unconsciousness and death if exposure continues (Tamura, 1994).

The manual of the American Conference of Governmental Industrial Hygienists, Inc., gives the threshold limit values (TLVs) and a description of various toxic gases. The TLV is defined as the time-weighted average concentration for a normal 8-hour workday and a 40-hour workweek to which nearly all workers may be repeatedly exposed, day after day without adverse effect. The TLVs and biological effects of concentrations above the TLV for toxic gases are discussed in the following subsections (Tamura, 1994).

B.17.2.1 Carbon Monoxide (CO)

CO is a common product of combustion generated in a fire environment. This highly toxic, non-irritating gas has long been recognized as a primary cause of fatalities related to combustion sources including fire. In fact, the majority of all fire fatalities are attributed to CO inhalation. CO is produced as a result of incomplete combustion of materials containing carbon and is present in large quantities in most fires. Invisible, odorless, tasteless, and slightly lighter than air, CO is the most significant toxicant as it can cause occupants to become incapacitated if the concentration is high enough and the exposure is long enough. CO acts by combining with hemoglobin in the blood to form carboxyhemoglobin (COHb). This is important because hemoglobin carries oxygen throughout the body, and it cannot do this if it is tied up as COHb and, therefore, unavailable for oxygen transport. In the absence of other contributing factors, a COHb concentration of 50-percent or greater is generally considered lethal in the blood of fire victims.

The highest concentration of CO to which people can be exposed day after day without adverse effect is 50 ppm. This concentration keeps the COHb level below 10-percent. Concentrations of 400 to 500 ppm can be inhaled for 1 hour without appreciable effect. Concentrations of 1,000 to 1,200 ppm cause unpleasant symptoms after 1 hour of exposure. Concentrations of 1,500 to 2,000 ppm for 1 hour of exposure are dangerous, and concentrations above 4,000 ppm are fatal in exposure of less than 1 hour (Sumi and Tsuchiya, 1971).

B.17.2.2 Hydrogen Cyanide (HCN)

HCN is one of the most rapidly acting toxicants, being approximately 20 times more toxic than CO. HCN is produced when materials involved in a fire contain nitrogen [for example, polyacrylonitrile (Orlon®), polyamide (nylon), wool, polyurethane, urea-formaldehyde, and acrylonitrile-butadiene-styrene (ABS)]. Inhalation of HCN may cause severe toxic effects and death within a few minutes up to several hours, depending upon the concentration inhaled. The action of HCN is attributable to the cyanide ion, which is formed by hydrolysis in the blood. Unlike CO, which remains primarily in the blood, the cyanide ion is distributed throughout the body fluids, bringing it into contact with the cells of vital tissues and organs.

The TLV for HCN is 10 ppm, and it can be inhaled for several hours without appreciable effect at concentrations of 20–40 ppm. The maximum amount that can be inhaled for 1 hour without serious reaction is 50–60 ppm. Concentrations of 120–150 ppm are dangerous in 30–60 minutes, and concentrations of 3,000 ppm or more are rapidly fatal (Sumi and Tsuchiya, 1971).

B.17.2.3 Carbon Dioxide (CO_2)

CO_2 usually evolves in large quantities from fires. While not particularly toxic at observer levels, moderate concentrations of CO_2 (on the order of 2-percent) increase both the rate and depth of breathing by about 50-percent, thereby increasing the respiratory minute volume (RMV). This condition contributes to the overall hazard of a fire gas environment by causing accelerated inhalation of toxicants and irritants. If 4-percent CO_2 is breathed, the RMV is approximately doubled, but the individual may scarcely notice the effect. Given any further increase in CO_2 from 4 percent up to 10-percent, the RMV may be 8 to 10 times the resting level (Hartzell, 1989).

The TLV of CO_2 is 5,000 ppm. Stimulation of respiration is pronounced at a concentration of 5-percent (50,000 ppm), and a 30-minute exposure produces signs of intoxication. Above 70,000 ppm, unconsciousness results in a few minutes (Sumi and Tsuchiya, 1971).

B.17.2.4 Hydrogen Chloride (HCl)

HCl is formed from the combustion of materials containing chlorine, the most notable of which is polyvinyl chloride (PVC) as used in common thermoplastic electrical cables. HCL is both a potent sensory irritant and potent pulmonary irritant. It is a strong acid, being corrosive to sensitive tissue, such as the eyes. If inhaled, HCl will irritate and damage the upper respiratory tract and lead to asphyxiation or death.

The TLV for HCl is 5 ppm. Concentrations as low as 75 ppm are extremely irritating to the eyes and upper respiratory tract, and behavioral impairment has been suggested. The maximum concentration allowable for short exposures of 30–60 minutes is 50 ppm. Concentrations of 1,000–2,000 ppm are dangerous even for short exposures (Sumi and Tsuchiya, 1971).

B.17.2.5 Nitrogen Dioxides

Nitrogen dioxides (NO_2 and N_2O_4) are the common oxides of nitrogen (N) that are produced in a fire. (The other is nitric oxide, or NO.) Nitrogen dioxide, which is very toxic, can be produced from the combustion of N-containing material. Nitric oxide has a short life in atmospheric air because it is converted into dioxide in the presence of oxygen. These compounds are strong irritants, particularly to mucous membranes. When inhaled, they damage tissues in the respiratory tract by reacting with moisture to produce nitrous and nitric acids. The TLV for nitrogen dioxide is 5 ppm. Immediate throat irritation can begin at 62 ppm. Short-exposure concentrations of 117–154 ppm are dangerous, and rapidly fatal at 140–775 ppm (Sumi and Tsuchiya, 1971).

B.17.3 Toxicity Data

Toxicity or toxic data usually reflect the results of animal testing. The table of relative acute toxicity criteria given below was published by the National Institute for Occupational Safety and Health (NIOSH) in the Registry of the Toxic Effects of Chemical Substances (RTECS) in 1967. It is widely used to interpret animal toxicity data; the lower the dose number, the greater the toxicity. The measures of toxicity used in the Table B.17-1, LD_{50} and LC_{50} are explained in the discussion following the table (Spero, Devito, and Theodore, 2000).

Table B.17-1. Toxicity Data

Rating	Keywords	LD_{50} Single Oral Dose* (mg/kg)	LC_{50} Inhalation Vapor Exposure* (ppm)	LD_{50} Skin** (mg/kg)
4	Extremely hazardous	#1	#10	#5
3	Highly hazardous	50	100	43
2	Moderately hazardous	500	1000	340
1	Slightly hazardous	5,000	10,000	2,800
0	No significant hazard	>5,000	>10,000	>2,800

* Rats
**Rabbits

Data on animal toxicity usually identify the route of entry into the body (oral ingestion, inhalation, adsorption through the skin, etc.) first, followed by the test animal (mouse, rat, human, etc.), followed by the measure of toxicity. The most common measures of toxicity are as follows:

- Lethal Dose 50-percent (LD_{50}) is the dose required to kill 50-percent of the test animals when administered by a route of entry other than inhalation. The dose of the chemical (usually solids or liquids) is given as mg/kg, which represents milligrams of chemical per kilogram of body weight of the test animal. The LD_{50} is expressed in this manner because more chemical is needed to kill a larger animal. For example, the oral rat LD_{50} for the HAP calcium cyanamide is 159 mg/kg.
- Lethal Concentration 50-percent (LC_{50}) is similar to LD_{50} except that the route of entry is inhalation. The concentrations of the inhaled chemicals (usually gases) are expressed as parts per million (ppm) or milligrams per cubic meter (mg/m^3).
- Lethal Dose Low (LDL_o) is the lowest dose required to kill any of the animals in the study when administered by a route of entry other than inhalation.
- Lethal Concentration Low (LCL_o) is the same as LDL_o except that the route of entry is inhalation.
- Toxic Dose Low (TDL_o) is the lowest dose used in the study that caused any toxic effect (not just death) when administered by a route of entry other than inhalation.
- Toxic Concentration Low (TCL_o) is the same as TDL_o except that the route of entry is inhalation.
- EC_{50} is the concentration required to cause a 50-percent reduction in growth.
- Acute Risks are the risks associated with brief exposures to high concentrations.
- Chronic Risks are the risks associated with long-term exposures to low concentrations.

B.17.4 References

ASTM E176-98, “Standard Terminology of Fire Standards,” ASTM Fire Test Standard, 5th Edition, American Society of Testing and Materials, West Conshohocken, Pennsylvania, pp. 834–842, 1999.

Babrauskas, V., “Effective Measurement Techniques for Heat, Smoke, and Toxic Fire Gases,” *Fire Safety Journal*, Volume 17, No. 1, pp. 13–26, 1991.

Babrauskas, V., B.C. Levin, R.G. Gann, M. Paabo, R.H. Harris, R.D. Peacock, and S. Yusa, “Toxic Potency Measurement for Fire Hazard Analysis,” NIST Special Publication 827, U.S. Department of Commerce, National Institute of Standards and Technology (NIST), Building and Fire Research Laboratory (BFRL), Gaithersburg, Maryland, 1991.

Beitel, J.J., C.L. Beyler, L.A. McKenna, and F.W. Williams, “Overview of Smoke Toxicity Testing and Regulations,” NRL/MR/6180-98-8128, Naval Research Laboratory, Naval Technology Center for Safety and Survivability Branch, Chemistry Division, Washington, DC, April 15, 1998.

Clarke, Frederick B. “Toxicity of Combustion Products: Current Knowledge,” Fire Journal, 77, 5 (September 1983), 84-97, 101, 108.

Hartzell, G.E., “Understanding of Hazards to Humans,” Chapter 3, *Advances in Combustion Toxicology*, Volume One, Gordon, E. Hartzell, Editor, Technomic Publishing, Inc., 1989.

Spero, J.M., B. Devito, and L. Theodore, *Regulatory Chemicals Handbook*, Marcel Dekker, Inc., New York, 2000.

Sumi, K., and Y. Tsuchiya, “Toxic Gases and Vapors Produced at Fires,” *Canadian Building Digest*, National Research Council of Canada, CBD 144, December 1971.

Tamura, G.T., *Smoke Movement & Control*, National Fire Protection Association, Quincy, Massachusetts, December 1994.

B.18 Effects of Decomposition Products of Halogenated Fire Extinguishing Agents

B.18.1 Introduction

When an ineffective Halon fire extinguishing system that is incapable of extinguishing its design-basis fire is installed in a compartment, the system discharge will actually degrade environmental conditions by introducing additional toxic gases.

The 18th Edition of the National Fire Protection Association (NFPA) Fire Protection Handbook (Taylor, 1997) identifies the effects of the decomposition products of Halon 1301 and 1211 fire extinguishing agents, as follows:

> *Consideration of life safety during the use of halogenated agents must also include the effects of decomposition (or breakdown) products, which are relatively more toxic to humans. Decomposition of halogenated agents takes place on exposure to flame or surface temperatures above approximately 482 °C (900 °F). In the presence of available hydrogen (from water vapor or the combustion process itself), the main decomposition products of Halon 1301 are hydrogen fluoride (HF), hydrogen bromide (HBr), and free bromine (Br_2). Although small amounts of carbonyl halides (COF_2, $COBr_2$) were reported in the early tests, more recent studies have failed to confirm the presence of these compounds.*

Table B.18.1-1 summarizes the major decomposition products of Halon 1301 and 1211. The approximate lethal concentrations (ALCs) for a 15-minute exposure to some of these compounds are given in Column 2 of Table B.18-1. Column 3 gives the concentrations of these materials that have been quoted as “dangerous” for short exposure.

Even in minute concentrations of only a few parts per millions (ppm), the decomposition products of the halogenated agents have a characteristically sharp, acrid odor. This characteristic provides a built-in warning system for the agent, but also creates a noxious, irritating atmosphere for those who must enter the hazard area following a fire. It also serves as a warning that other potentially toxic products of combustion (such as CO) will be present.

B.18.2 Toxicity of Decomposition Products of Halogenated Fire Suppression Agents

Hill (1977) summarizes the effects of hydrogen fluoride (HF) on humans at various concentrations. At concentrations as low as 32 ppm, irritation of eyes and nose occurs. At 60 ppm, irritation of the respiratory tract occurs after 60 seconds. At concentrations of 120 ppm, irritation of the conjunctival and respiratory tracts is tolerable for only 60 seconds. Concentrations between 50 and 100 ppm are considered dangerous to life after several minutes of exposure. Generally, the HF containing atmospheres are so irritating that personnel will be forced to evacuate before serious health risk is incurred. Decomposition product data clearly indicate that life-threatening concentrations of HF likely. HF concentrations of 300 ppm are typically measured in full-scale tests.

Table B.18-1. Approximate Lethal Concentrations (ALCs)
for Predominant Halon 1301 and Halon 1211 Decomposition Products

Compound	**ALC for 15-minute Exposure (ppm by Volume in Air)**	**Dangerous Concentrations (ppm by Volume in Air)**
Hydrogen fluoride, HF	2,500	50–250
Hydrogen bromide, HBr	4,752	-
Hydrogen chloride, HCl	-	-
Bromine, Br_2	550	-
Chlorine, Cl_2	-	50
Carbonyl fluoride, COF_2	1,500	-
Carbonyl chloride, $COCl_2$	100–150	-
Carbonyl bromide, $COBr_2$	-	-

DeMonburn and McCormick (1973) have reported on the design and testing of Halon 1301 in extinguishing a wool bag filter fire in an industrial baghouse situation. The baghouse studied has an area of approximately 13.3 m^2 (144 ft^2). These studies indicate that using rate-of-rise thermal detectors and the complete shutdown of the air flow through the baghouse, a 4-percent concentration of Halon 1301 would extinguish a fully developed fire. However, it should be noted that following extinguishment and 20 minutes soaking time, toxic levels of hydrogen fluoride, hydrogen cyanide, and hydrogen sulfide were detected in the unoccupied baghouse as shown in Table B.18-2.

Table B.18-2. Concentration of Hazardous Gases Attributable to Decomposition of Halon 1301 in Industrial Baghouse Fire Situation

Time (minutes)	**Decomposition Product Concentration (ppm)**		
	Hydrogen Fluoride (HF)	**Hydrogen Cyanide (HCN)**	**Hydrogen Sulfide (H_2S)**
0–4	55	1,643	2,452
20–24	10	194	112

The National Research Council Advisory Center reviewed the toxicity of Halon 1301 for consideration by NASA. In a letter to Dr. G.J. Stopps of the Haskell Laboratory, dated September 22, 1967, R.C. Wands, Director of the Toxicology Center, stated:

> *Personnel can be exposed without significant hazard for a maximum of 5 minutes to normal air at 1 atmosphere and mixed with up to 6-percent mean concentration by volume of bromotrifluoromethane [CF_3Br (Halon 1301)] as a fire extinguishing agent. This assumes appropriate engineering design to sense the fire and deliver the agent so as to extinguish the fire promptly in order to minimize that pyrolysis products* (Atomic Energy Commission, 1970).

Ford (1975) has evaluated the issue of the decomposition of Halon 1301, and believes caution and limitations should be applied to the utilization of extinguishing systems containing that agent:

- Although safe at a design concentration of 5–7-percent, the Halon 1301 agent will not extinguish deep-seated Class A fires with these concentrations. Thus, water systems should be provided and higher concentrations of Halon 1301 should be used for extinguishment in these situations. If higher concentrations of Halon 1301 are provided, the design of the system should incorporate all of the requirements of the NFPA Standard 12A, and the operation of the system in relation to the personnel hazard should be identical to that of a CO_2 extinguishing system.
- Halon 1301 may decompose to untenable concentrations of hydrogen fluoride and hydrogen bromide when the vapor is in contact with a heated surface above 482 °C (900 °F), or when the agent is applied to a large fire in a small enclosure. Table B.18-3 summarizes the relationship between the flame shield exposure and room size. Note in Situation One that the ratio of flame dimension to room size is 0.60, while in Situation Two, the ratio of flame dimension to room size is 6.0. The concentrations of the hydrogen fluoride and hydrogen bromide acid gases in situation two are beyond tolerable limits for human exposure. However, it must be remembered in this situation and the previous industrial baghouse situation presented by DeMonburn and McMormick, that the toxic products of combustion from the fire would in all probability also create an intolerable atmosphere for human exposure. The primary life hazard involves the entry of personnel into the area immediately following extinguishment. These characteristics of the Halon agent under intense thermal or flame exposure make the installation of these systems for an oven or furnace chamber unsuitable where the temperature is above 260 °C (500 °F).

B.18.3 Physical Properties of Halon 1301

Under normal conditions, Halon 1301 is a colorless, odorless gas with a density approximately 5 times that of air. It can be liquefied upon compression for convenient shipping and storage. Unlike CO_2, Halon 1301 cannot be solidified at temperatures above -167.8 °C (-270 °F). The molecular weight of Halon 1301 is 148.93 (see Table B.18-4).

B.18.4 Physical Properties of Halon 1211

Under normal conditions, Halon 1211 is a colorless gas with a faintly sweet smell and a density about 5 times that of air. It can be readily liquefied by compression for storage in closed vessels. The molecular weight of Halon 1211 is 165.38 (see Table B.18-4 for properties of Halon).

Table B.18-3. Halon 1301 Decomposition Produced by n-Heptane Fires

Situation One: 1,695-foot Enclosure Volume; 4-Percent Halon 1301 by Volume					
Fire pan size (ft^2)	**Fuel area to volume $ft^2/1000\ ft^2$**	**Discharge time (sec)**	**Extinguishment time (sec)**	**Decomposition products (ppm volume in air)**	
				Hydrogen Fluoride (HF)	**Hydrogen Bromide (HBr)**
0.1	0.06	23.0	11.5	1.8	3.5
0.1	0.06	13.5	7.1	1.8	2.1
0.1	0.06	5.7	4.8	1.4	2.8

Situation Two: 1,695-foot Enclosure Volume; 4-Percent Halon 1301 by Volume					
Fire pan size (ft^2)	**Fuel area to volume $ft^2/1000\ ft^2$**	**Discharge time (sec)**	**Extinguishment time (sec)**	**Decomposition products (ppm volume in air)**	
				Hydrogen Fluoride (HF)	**Hydrogen Bromide (HBr)**
10.0	6.0	25.0	20.0	1,907	397
10.0	6.0	15.0	16.3	1,206	382
10.0	6.0	6.0	10.0	666	112
10.0	6.0	6.0	5.2	320	38

Table B.18-4. Selected Properties of Halon 1301, 1211, and 2402

Extinguishing Agent	**Halon 1301 (CF_3Br)**	**Halon 1211 (CF_2ClBr)**	**Halon 2402 ($C_2F_4Br_2$)**
Boiling point °C (°F)	-58 (-72.5 °F)	-4 (25 °F)	47 (117 °F)
Liquid density at 20 °C (g/cc)	1.57	1.83	2.17
Latent heat of vaporization (J/g)	117	134	105
Vapor pressure at 20 °C (atm)	14.5	2.5	0.46

B.18.5 References

Atomic Energy Commission, “Prepackaged Halon 1301 Fire Suppression System Tests,” Number 294, Atomic Energy Commission, Health and Safety Information, Washington, DC, 1970.

DeMonburn, J.R., and J.W. McCormick, “Extinguishment of Wool Bag Filter Fires Using Halon 1301,” Y-JA-94, Union Carbide Corporation, 1973.

Ford, C.B., “Why Not Halon1301?” *Fire Journal*, Volume 69, pp. 80–81, 1975.

Hill, R., “Evaluation of Halon 1301 System for Aircraft Internal Protection from a Postcrash External Fuel Fire,” National Aviation Facilities Experimental Center, Atlantic City, New Jersey, March 1977.

Taylor, G.M., Halogenated Agent and Systems, Chapter 18, Section 6, *NFPA Fire Protection Handbook*, 18th Edition, Edition, A.E. Cote, Editors-in-Chief, National Fire Protection Association, Quincy, Massachusetts, 1997.