

CHAPTER 19
CHEMICAL STORAGE AND USE

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Chapter 19

CHEMICAL STORAGE AND USE

I. Introduction

All operators producing or using a hazardous chemical must comply with the Hazard Communication Standard 30 CFR Part 47.

One very important compliance function of an inspector is the determination of proper usage and storage of chemicals at a mine site. Certain chemicals and combinations of chemicals pose significant health and safety risks to miners working near them. For example, some chemicals, if accidentally spilled, can result in an explosion, a fire, or the release of toxic vapors. Even empty chemical storage tanks may have residual vapors or be oxygen deficient so that working in them may lead to injury or illness, unless appropriate precautions are taken.

In addition to process and laboratory chemicals, the use of alternative fuel sources is increasing in the mining industry, especially at operations with kilns, dryers, or other industrial furnaces (*e.g.*, cement plants). Alternative fuels range from the burning of whole or shredded vehicle tires, or shredded oil filters, to mixtures of liquid or solid hazardous waste. MSHA classifies operations using alternative fuels that contain hazardous waste as hazardous waste fuel (HWF) burning facilities. MSHA has jurisdiction for the health and safety of the miners at these facilities. The Environmental Protection Agency (EPA) has jurisdiction to regulate the burning of hazardous wastes as supplemental fuels. The EPA issues operating permits that specify system designs and operating procedures to ensure protection of the environment (*i.e.*, air, soil, and water). The mine operator's operating permits should be available at the mine site and at the local EPA office.

II. Definitions

Alternative Fuel - any substitute or supplemental fuel other than fuel oil, pulverized coal, or natural gas used to fire a kiln, dryer, or other industrial furnace. Examples of alternative fuels include: used or off-specification oils, organic solvents, pesticides, herbicides, poly-chlorinated biphenyls (PCBs), paints, pigments, sludges, metals, resins, shredded or whole tires and agricultural products. Some alternative fuels may be classified by EPA as Hazardous Waste Fuels (HWF).

Department of Transportation (DOT) - the Federal agency that regulates transportation of materials to protect the public as well as fire, law enforcement, and other emergency response personnel. DOT classifications specify the use of appropriate warnings, such as "Oxidizing Agent" or "Flammable Liquid."

DOT Identification Number - four-digit number (e.g., 1203, gasoline) used on placards or labels to identify particular materials for regulation of their transportation (49 CFR §172.101). These numbers are called product identification numbers (PINs) in Canada. Those numbers used internationally may carry a UN prefix (e.g., UN 1170, ethyl alcohol), and those used only in North America may have an NA prefix (e.g., NA 9163, zirconium sulfate).

Environmental Protection Agency (EPA) - the Federal agency with environmental protection regulatory and enforcement authority. EPA administers the Clean Air Act (CAA), Clean Water Act (CWA), Resource Conservation and Recovery Act (RCRA), Toxic Substances Control Act (TSCA), and other Federal environmental laws.

Flash Point means the minimum temperature at which sufficient vapor is released by a liquid or solid to form a flammable vapor-air mixture at atmospheric pressure. (30 CFR §§56/57.2)

HazCom - Acronym for Hazard Communication Standard, an MSHA standard that requires mine operators to provide miners with information about the hazards of chemicals miners are exposed to in their work areas (30 CFR Part 47).

Hazardous Waste – chemicals regulated by EPA under the Solid Waste Disposal Act as amended by the Resource Conservation and Recovery Act. (30 CFR §§47.11, Table 47.11). EPA defines solid or liquid waste as materials exhibiting any of the following characteristics: ignitability, corrosiveness, reactivity, or toxicity. Resource Conservation and Recovery Act (RCRA), 40 CFR §261.

Hazardous Waste Number - a four-digit alpha numeric identification code (e.g., D003, F001, U169) assigned by the EPA per RCRA (40 CFR §261, 40 CFR §302) to identify and track wastes for recordkeeping and reporting purposes.

Hazardous Materials (HAZMAT) - any substance or mixture of substances capable of producing adverse effects on the health and safety of humans.

HAZWOPER - acronym for Hazardous Waste Operations and Emergency Response, an OSHA standard for protection of workers in hazardous waste operations.

Label - any written, printed, or graphic material displayed on or affixed to a container to identify its contents and convey other relevant information. (30 CFR §47.11, Table 47.11). MSHA's HazCom Standard requires a label to identify a hazardous material, give appropriate hazard warnings, and have a chemical identifier that permits cross-referencing between a list of hazardous materials, the chemical and its MSDS.

Laboratory - a facility that is equipped to perform scientific experiments, research, or qualitative and quantitative testing. Relatively small quantities of hazardous chemicals may be used on a non-production basis.

Material Safety Data Sheet (MSDS) – written or printed material concerning a hazardous chemical which – (1) An operator prepares in accordance with Table 47.52 – Contents of MSDS: or (2) An employer prepares in accordance with 29 CFR 1910.1200, 1915.1200, 1917.28, 1918.90, 1926.59, or 1928.21 (OSHA Hazard Communication regulations): or (3) An independent source prepares which contains equivalent information, such as International Chemical Safety Cards (ICSC) and Workplace Hazardous Materials Information Sheets (WHIMS). (30 CFR § 47.11, Table 47.11.) MSDSs provide information about material identification; hazardous ingredients; health, physical and fire hazards, first aid, chemical reactivities and incompatibilities; spill, leak and disposal procedures, and protective measures for safe handling and storage.

National Fire Protection Association (NFPA) - an international voluntary membership organization formed to promote and improve fire protection and prevention and develop consensus standards to safeguard against loss of life and property by fire. The National Fire Codes, a sixteen volume set of standards and recommended practices, were developed by NFPA committees and are periodically updated.

pH - a value that represents the acidity or alkalinity of a water solution. Pure water has a pH of 7. A pH below 7 indicates an acid solution (a pH of 1 is extremely acidic). A pH above 7 indicates an alkaline solution (a pH of 14 is extremely alkaline).

Polymerization - a chemical reaction in which one or more small molecules combine to form larger molecules. Some polymerization reactions take place at rates that release large amounts of energy that can cause fires or explosions or burst containers.

III. Applicable Metal/Nonmetal Standards

The Metal/Nonmetal standards commonly associated with chemical storage and use are as follows:

30 CFR Part 47	Hazard Communication
30 CFR §§56/57.5001	Exposure limits for airborne contaminants
30 CFR §§56/57.5002	Exposure monitoring
30 CFR §§56/57.5005	Control of exposure to airborne contaminants
30 CFR §§56/57.5006	Restricted use of chemicals
30 CFR §§56/57.15001	First-aid materials
30 CFR §§56/57.15004	Eye protection

30 CFR §§56/57.15006	Protective equipment and clothing for hazards and irritants
30 CFR §§56/57.16001	Stacking and storage of materials
30 CFR §§56/57.16002	Bins, hoppers, silos, tanks, and surge piles
30 CFR §§56/57.16003	Storage of hazardous materials
30 CFR §§56/57.16004	Containers for hazardous materials
30 CFR §§56/57.16005	Securing gas cylinders
30 CFR §§56/57.16006	Protection of gas cylinder valves
30 CFR §§56/57.16012	Storage of incompatible substances
30 CFR §§56/57.18002	Examination of working places
30 CFR §§56/57.18006	New employees
30 CFR §§56/57.18012	Emergency telephone numbers
30 CFR §§56/57.18013	Emergency communications system
30 CFR §§56/57.18014	Emergency medical assistance and transportation
30 CFR §56.18020	Working alone
30 CFR §57.18020	Working alone [Surface only]
30 CFR §57.18025	Working alone [Underground only]
30 CFR §§56/57.20011	Barricades and warning signs
30 CFR §§56/57.20014	Prohibited areas for food and beverages

For chemicals that are flammable or combustible, many of the standards in 30 CFR §§ 56/57, Subpart C - Fire Protection and Control are also applicable, especially those in the sections pertaining to firefighting procedures/alarms/drills, and flammable and combustible liquids and gases.

IV. Identifying the Hazard

Mine operators must identify chemical hazards under §47.21. Whenever chemicals are used or stored on mine property, the inspector should carefully review the Material Safety Data Sheets (MSDSs) and any other available reference information. Labels on containers may also provide important information. Chapter 3 of this Handbook and the *NIOSH Pocket Guide to Chemical Hazards* provide similar information. For more information or questions concerning identifying chemical hazards, contact your District Office.

It is a violation of HazCom if the mine has hazardous chemicals and has no MSDS available. At certain mine sites, the absence of MSDSs may be a violation of EPA regulations that require facilities to have MSDSs and to provide copies or lists of them to the Local Emergency Planning Committee (LEPC - see Section VII. below). If you suspect a violation of EPA regulations, inform the district manager so that the district can notify the appropriate EPA office.

Review the operator's HazCom Program, solid waste inventory and profile sheets (shipping manifests), process flow charts, and any other process information related to chemical storage and use. A complete inventory would include raw materials, additives, catalysts, products, wastes, and their final destination (*i.e.*, used in processing the ore; burned as fuel; liberated to water, air, or soil; or shipped from mine property as waste). Any of these may pose a risk to miners if not properly controlled. The inventory should also specify locations, use, and type of storage. Attempt to visualize a "worst case" scenario, such as the failure of valves, sensors, alarms, pressure vessels (bulk tanks, rail cars, or tank trucks), or backup systems. Do any of the chemicals, if released, have the potential to cause a catastrophic incident? Contact the district office if you need help in evaluating the hazard.

V. Evaluating the Work Environment

Once the hazard information is carefully reviewed, evaluate areas where the chemicals are stored and used. MSHA regulations require that the operator:

- Store hazardous materials in approved containers (§§ 56/57.16004)
- Store materials that can create a hazard if accidentally liberated in a manner that minimizes the danger (§§ 56/57.16003)
- Provide water or neutralizing agents wherever corrosive chemicals or other harmful substances are stored, handled, or used (this may also be used to require immediate access to automatic spray devices such as eyewash stations and deluge showers) (§§ 56/57.15001)
- Provide personal protective equipment (including appropriate respirators, gloves, eye protection, etc.) (§§ 56/57.5005, §§ 56/57.15004, and §§ 56/57.15006) and
- Provide container labels and other forms of warning for hazardous chemicals (§ 47 Subpart E).

MSDSs are a good source of information on the hazards the chemical may present, appropriate personal protective equipment, and the proper spill and emergency procedures.

A. Incompatibility

The accidental mixing of incompatible chemicals may result in explosions, fires, or toxic releases. For this reason, §§56/57.16012 prohibits mine operators from storing incompatible chemicals and materials together. If a chemical can be spilled and reach an incompatible chemical or material, they are both improperly stored. This includes the shelving material itself, as well as any berm material used. Chemicals are classified into compatibility groups according to the unique reactivity and corresponding storage criteria of each group. Consider the following chemical compatibility groups when inspecting work areas where chemicals are present:

1. **Corrosives** - chemicals that cause visible destruction of or irreversible alterations in living tissue by chemical action at the site of contact, or that destroy metallic materials.

a. **Acid** - inorganic or organic compound that has a pH of less than 7.0. It also:

- may be corrosive and must be handled with extra care (corrosive acids have a pH less than or equal to 2);
- neutralizes bases (alkalis) to form salts;
- dissociates in water yielding hydrogen or hydronium ions;
- may react with metals to yield hydrogen; and
- turns blue litmus paper to red.

Examples

Inorganic: boric acid, hydrobromic acid, hydrochloric acid, sulfuric acid, phosphoric acid

Organic: acetic acid, citric acid

b. **Base (also called alkali or caustic)** - inorganic or organic compound that has a pH of greater than 7.0. It also:

- may be corrosive and must be handled with extra care (corrosive bases have a pH greater than or equal to 12);
- neutralizes acids to form salts;
- dissociates in water yielding hydroxide ions; and
- turns red litmus paper to blue.

Examples

Common commercial alkalis are sodium carbonate (soda ash), caustic soda and caustic potash, lime, lye, aqueous ammonia, and ammonium hydroxide. Oxides and hydroxides of certain metals (lithium, sodium, potassium, rubidium, cesium, and francium) are also bases.

c. Additional Recommendations for Safe Storage and Use of Corrosive Chemicals:

- Segregate acids from alkalis.
- Isolate from toxic materials, organic materials, flammable substances, and substances that may release corrosive, toxic, or flammable vapors on reaction.
- Store in cool, dry, well-ventilated areas that are not subject to rapid temperature changes, and that are protected from direct sunlight.
- If storage cabinets are used, store liquid containers in trays with compatible absorbent material of sufficient volume to contain and prevent leakage onto materials stored below.
- Structural materials should be non-corroding or should be metal covered with acid-fume resistant paint.
- Have fire-fighting equipment readily available.

2. Reactive Materials - chemicals or mixtures that vigorously polymerize, decompose, condense, or become self-reactive due to shock, pressure, and/or temperature.

- a. Oxidizers**
- chemicals or chemical combinations (usually gases or liquids) that spontaneously release oxygen at room temperature or with slight heating, which accelerate combustion, and that on contact with combustible material may cause a fire or explosion.

Examples

Bromic acid, bromine, chlorine, chromic acid, fluorine, hypochlorite solutions (i.e., bleach), nitric acid, many perchlorates, perchloric acid, permanganates, and silver nitrate.

- b. Water Reactives** - a substance or mixture that reacts with water releasing heat, or flammable or toxic gas.

Examples

Aluminum chloride-anhydrous, calcium carbide, acetyl chloride, chlorosulfonic acid, phosphorous pentachloride, sodium, potassium, calcium, aluminum tribromide, calcium oxide, acid anhydrides, and metal hydrides.

- c. Pyrophoric Materials** - materials that ignite spontaneously in air below 54° C (130° F).

Examples

Boron, diborane, dichloroborane, diethyl aluminum chloride, 2-furaldehyde, lithium, white or yellow phosphorus, trimethyl aluminum.

- d. Additional Recommendations for Safe Storage and Use of Reactive Materials:**

Oxidizers -

- Isolate from organic materials, flammable solvents, corrosives, toxic materials.
- Store in cool, dry, well-ventilated areas out of direct sunlight.
- Protect from temperature extremes.
- Do not store containers directly on wooden shelves or on paper shelf liners (spills may react with the organic portion of the shelf or paper and ignite spontaneously).
- Storage building should be fireproof and provided with an automatic sprinkler system.

Water Reactive and Pyrophoric Materials -

- Isolate from water and water solutions, moist air, aqueous acids and alkalis, flammable storage areas, and other reactive chemicals.
- Store in cool, dry, well-ventilated areas.
- Store pyrophors under nonflammable, inert solvents.
- Locate storage building on high ground and remote from other storage areas. It should be fireproof, waterproof, and without an automatic sprinkler system.

- If materials are handled or soil clothing, do not use water to clean off. Consult the MSDS or NIOSH Pocket Guide for alternative to water (specific for each chemical).

3. Flammable and Combustible Materials

a. Flammable means capable of being easily ignited and of burning rapidly. (30 CFR §§56/57.2)

- **Flammable liquid.** A liquid that has a flash point below 100 °F (37.8 °C), a vapor pressure not exceeding 40 pounds per square inch (absolute) at 100 °F (37.8 °C), and is known as a Class I liquid. (30 CFR §§56/57.4000)
- **Flammable gas.** A gas that will burn in the normal concentrations of oxygen in the air. (30 CFR §§56/57.4000)

b. Combustible liquids. See definition under § 47.11, “physical hazard” heading.

Liquids having a flash point at or above 100 °F (37.8 °C). They are divided into the following classes:

Class II liquids--those having flash points at or above 100 °F (37.8 °C) and below 140 °F (60°C).

Class IIIA liquids--those having flash points at or above 140 °F (60 °C) and below 200 °F (93.4°C).

Class IIIB liquids--those having flash points at or above 200 °F (93.4 °C). (30 CFR §§56/57.4000)

c. Combustible material. A material that, in the form in which it is used and under the conditions anticipated, will ignite, burn, support combustion, or release flammable vapors when subjected to fire or heat. Wood, paper, rubber, and plastics are examples of combustible materials. (30 CFR §§56/57.4000)

- d. Safety can.** A container of not over five gallons capacity that is designed to safely relieve internal pressure when exposed to heat and has a spring-closing lid and spout cover.
(30 CFR §§56/57.4000)
- e. Storage tank.** A container exceeding 60 gallons in capacity used for the storage of flammable or combustible liquids.
(30 CFR §§56/57.4000)

Many of the storage and use criteria for flammable and combustible materials are contained in 30 CFR §§ 56/57, Subpart C - Fire Protection and Control (§§ 56.4000 - 56.4604 and §§ 57.4000 - 57.4761). In addition, see 30 CFR §§ 56/57.16005 Securing gas cylinders, 30 CFR §§ 56/57.16006 Protection of gas cylinder valves, and 30 CFR §§ 56/57.20011 Barricades and Warning Signs.

- 4. Toxic Materials** - any chemical or material that can poison or otherwise injure the organs or tissues of the body. The **dose**, or the amount of the chemical exposure (usually a combination of exposure concentration and time), will elicit the degree of **response** of the miner. The dose-response relationship is an important variable in assessing a miner's health risk.

Examples

Cyanide, mercury, isocyanates, beryllium and ... are examples of toxic materials that may be encountered in a mining environment.

Additional Recommendations for Safe Storage and Use of Toxic Materials:

- Secure in locked area and minimize access.
- Minimize stored quantities.
- Store in cool areas with constant humidity.
- Operate independent and filtered ventilation system.
- Isolate from areas where workers gather.
- Post poison control, first aid, and other safety information.
- In addition to container labels, post warning signs where appropriate, for example, "Danger-Poison" or "Caution-Chemical Carcinogen."

The National Fire Protection Association (NFPA) has many useful pamphlets on chemical storage including:

- NFPA 43A - Storage of Liquid and Solid Oxidizing Materials
- NFPA 43C - Storage of Gaseous Oxidizing Materials.

For more information, contact your district office.

B. Laboratory

All HazCom requirements apply to laboratories. Because most laboratories use hazardous chemicals, the facilities should be specifically designed and engineered for such work. Inspectors should check that fume hoods and other appropriate methods of containment are used properly, safe work practices are followed, and that laboratory and support personnel use the appropriate personal protective equipment. If deficiencies are observed during an inspection, health sampling should be conducted. Mine operators are required to conduct monitoring of air quality and noise exposures in laboratories the same as in other areas of the work environment. Inspectors should be aware that, in addition to chemical hazards, there may be electrical, fire, and other safety hazards due to the equipment used in the laboratory. For general information on best practices for laboratory safety, NIOSH provides a page of links to other websites on laboratory safety at <http://www.cdc.gov/niosh/labsafe.html>. One of the links, for example, is to the University of Virginia's Office of Environmental Health and Safety website for their basic, user-friendly guide, "Laboratory Survival Manual," at <http://keats.admin.virginia.edu/lsm/home.html> (accessed 3/19/2001, Internet).

C. Bulk Storage

The requirements previously discussed for the safe storage and use of chemicals apply to bulk (storage tanks) as well as to small quantities of chemicals. The risk of hazardous spills and vapor releases can be minimized by the proper design and construction of bulk storage tanks provided with suitable diking systems for containment of spills. Chemical filters may be needed to prevent escape of vapors from tank head spaces due to "tank breathing" during use, particularly during filling operations. These requirements are addressed in general by the application of §§56/57.16003--Storage of hazardous materials and §§56/57.16004--Containers for hazardous materials. For facilities storing flammable or combustible materials, additional requirements are included in 30 CFR Parts 56/57, Subpart C--Fire Prevention and Control. Consult the Program Policy Manual, Volume IV, for policy on enforcement of: §§56/57.16004--Containers for Hazardous Materials; §56.4531--Flammable or combustible liquid

storage buildings or rooms; §57.4531--Surface flammable or combustible liquid storage buildings or rooms; §57.4533--Mine openings; and §§56/57.16003--Storage of Hazardous Materials.

VI. Non-hazardous Alternative Fuel Operations

Some mining operations with kilns or dryers may use non-hazardous alternative fuels as a substitute or supplement to standard fuels. Although the EPA may not classify such fuels as hazardous, they will likely still be regulated or permitted by federal or state environmental agencies. Alternative fuels are either combustible or flammable, and may be explosive, so there are safety issues with which MSHA is concerned. At operations where fuels are burned, inspectors should ask if alternative fuels are being used and, if so, what they are. If alternative fuels are burned, inspect the storage, handling, conveying, pulverizing, firing and dust collection systems in addition to those of the more traditional fuel systems. (Note: Fuels that are not pulverized may still generate explosive dust.) Determine what fire and explosion prevention and protection systems and equipment are provided, if they are properly maintained and what practices are used to prevent injury to miners.

VII. Hazardous Waste Fuel Operations

Hazardous waste fuels are, in general, various types of used fuels or combustible chemicals which may contain one or more hazardous waste as listed by the EPA. The EPA regulations pertaining to burning used fuel oils and hazardous wastes are found in 40 CFR Part 266, Subparts D and E.

HazCom covers hazardous waste. Three categories of waste fuels defined by EPA are as follows:

1. Used Oil Fuel - any oil that has been refined from crude oil, used, and thereby contaminated by physical or chemical impurities. Used oil fuel includes any fuel produced from oil by processing, blending, or other treatment which is burned for energy recovery.

The supplier of used oil fuel is required to document analytical results demonstrating that the oil meets EPA specifications. The used oil fuel may also be tested at the mine site for other chemical and physical properties such as PCBs, pesticides, sulfur, heavy metals, BTU output, and specific gravity.

2. Off-Specification Used Oil Fuel - used oil fuel that exceeds EPA specifications. It can be burned for energy recovery only in EPA-

approved industrial furnaces and boilers and is handled in the same manner as hazardous waste fuel.

3. Hazardous Waste Fuel (HWF) - contains an assorted mixture of chemical compounds from industrial waste processes and exhibits any of the following characteristics: ignitability, corrosiveness, reactivity, or toxicity. Not all hazardous waste can be used as fuel. By EPA regulations, waste products can be burned as fuel if the incineration process is 99.99 % efficient.

A. **Health and Safety Hazards**

Mining personnel who work in and around HWF storage facilities and related operations are at risk from exposures associated with the handling, storage, processing, and burning of large amounts of flammable and combustible materials. The most prevalent hazards are fire, various forms of chemical reactivity, and toxicological effects from exposure to contaminants.

1. **Fire Hazard** - The threat of fire is a real and ever present hazard. Operating personnel must be constantly on guard against conditions which could result in a fire or explosion. Fire hazard conditions may occur during operations involving receiving and off-loading fuel shipments, maintaining and repairing storage tanks, fuel lines, pumps, and other equipment and transferring and burning of HWF. During burning operations, the hazard also exists for rupture of pressurized fuel lines located near sources of ignition.
 - a. **HWF Fires** - HWF fires are NFPA Class B fires, or fires that occur in the vapor-air mixture formed above the surface of flammable or combustible liquids. These fires produce intense heat and noxious, debilitating smoke, fumes, and gases. Such fires are extremely difficult to control and may do extensive damage to the facility and the environment. As with any fire, sampling for air contaminants should be performed to ensure that potentially exposed miners are not overexposed to the vapors and gases generated by the fire.

- b. **HWF Fire Response** - HWF fires may be controlled and extinguished by equipment, methods, and materials which deprive them of oxygen and additional fuel and/or inhibit the combustible effects of the fuel. Some general classes of fire extinguishing agents found to be effective in controlling this type of fire are dry chemicals foam, inert gases such as carbon dioxide, and halogenated hydrocarbons such as halon gas.

Water is not effective in fighting HWF fires because HWF will float on water and spread fire to other locations. However, water can be used for cooling supplies of stored fuels which are threatened. EPA permits and MSDSs specify the appropriate fire response for permitted-HWF.

- 2. **Chemical Reactivity** - The following types of chemical reactivity have been identified as being of greatest concern for mine operators and miners working at HWF sites. Fortunately, these hazards can be minimized through the implementation of safe handling and storage procedures (as discussed above in Section V.). Pre-screening of fuel streams prior to on-site acceptance could serve to aid in the selection of equipment and personal protective equipment that will not react excessively with the HWF.
 - a. **Reactivity with Strong Oxidizers** - HWF may react violently with oxidizing agents such as peroxides, nitric acid, and bottled oxygen, causing a fire or explosion. HWF facilities should be kept free and clear of oxidizing agents.
 - b. **Reactivity with Polymer Materials** - HWF may erode a variety of polymer materials such as seals, gaskets, linings, and personal protective equipment (PPE). Inspection of these items and prompt replacement when needed is required by §§56/57.18002 during the examination of working places.
 - c. **Reactivity with Metals, Water, and Alcohols** - HWF may contain organic compounds which can react with these materials. Organic acids such as acetic acid will erode metals. Some organic chlorides such as benzyl chloride and methyltrichlorosilane will decompose and form hydrochloric acid on contact with metals, water, or alcohols.

- d. Potential Polymerization of Hazardous Waste Fuels -**
Depending on content and conditions, certain mixtures of HWF may polymerize in storage. That is, chemical reactions within the mixture may cause complex, heavier, and more viscous or solid substances to form within the storage vessel. Some examples of liquid organic compounds which can undergo polymerization are methyl acrylate, methyl methacrylate, methylene diisocyanate (MDI), and toluene-2,4-diisocyanate (TDI).

Under normal circumstances, most shipments of HWF materials received at storage facilities operating under EPA permits are not expected to chemically react with each other.

- 3. Toxicological Hazards -** Potential health hazards due to HWF use depend on the chemistry of the fuel, how miners are exposed, the duration of the exposures, and the toxic mechanisms of the fuel components.

- a. Potential Hazard -** The potential hazard of HWF is based on the toxicities of the liquid organic constituents in the mixture. Combinations of different organic compounds in the fuel mixture will often enhance the hazard of the mixture as a whole.
- b. Routes of Entry –** There are three common type of exposure to HWF materials: skin absorption through direct contact, inhalation and ingestion.

The skin can be penetrated by certain chemicals, allowing the bloodstream to carry the chemical to other organs. Some areas of the skin are more susceptible to absorption than others, and moisture, heat, and damaged skin can enhance skin absorption. Some chemicals injure the skin directly, while others can sensitize the skin, causing an allergic-type response.

The eyes are particularly vulnerable to direct contact with chemicals. Irritation and absorption are much more pronounced on the surface of the eye than on most exposed skin surfaces.

Inhalation as a route of entry increases with importance as the temperature or pressure of the fuel increases and as the ventilation effectiveness diminishes. Inhaled vapors may affect the respiratory system directly or may be transferred to the bloodstream and carried to other organs. Some chemicals may be

odorless and invisible to the miners or may not induce detectable health effects immediately.

Ingestion of HWF may occur due to mishandling, unsafe work practices or poor housekeeping. Ingestion can affect the gastrointestinal tract directly or, after absorption, can affect other organs throughout the body. Food should never be stored or consumed near HWF. Miners should be provided with facilities and supplies so they can practice good personal hygiene.

B. Assessing the Health Hazard

Exposure to HWF is usually limited to a few points in the waste fuel operation. Normally, a waste fuel circuit is a closed-circuit to the point of the flame. Miners may be at risk as a result of either routine or accidental exposure. Ensure that the PPE in use is appropriate for the chemicals being handled.

- 1. Routine Exposures (fuel handlers)** - usually occur only when the circuit is open for quality control sampling, during transfer from a delivery vehicle, or during cleaning and disposal of normal spillage.
 - a. Quality Control Sampling** - Sampling exposures occur during the collection of core samples from delivery vehicles or collection of mixed samples through valves or storage tanks. Lab personnel also risk exposure during handling and storage of raw fuel samples.
 - b. Off-Loading From Tank Trucks** - Exposures may occur while opening the delivery vehicle, attaching or disconnecting hoses, cleaning and discharging in-line fuel filters or emptying the sump. Of particular concern is the truck driver who may not be regularly involved with the delivery and transfer of toxic or flammable materials and who may not be aware of the hazards. Delivery vehicle hatches should not be left open because vapors may evolve out of the liquids and adversely affect miners near or far.
 - c. Maintenance Activities** - Exposures may occur during the regular maintenance of waste fuel circuit equipment. These procedures include disassembling, cleaning, or other servicing of storage vessels, piping, valves, pumps, agitators, filters, and tanks.

Depending on burning conditions, especially temperature, HWF may deposit toxic chemical residue in the kiln and which could be encountered during the removal of an old refractory lining in preparation for re-bricking. Toxic elements such as heavy metals may be deposited in the storage and processing equipment, and they or hazardous vapors may be encountered during maintenance and/or cleaning activities. Cutting and welding operations on metals contaminated with HWF in confined spaces present a significant potential for exposure to hazardous contaminants.

2. **Accidental Spills (exposure to maintenance or production workers)** – A mine having significant quantities of hazardous substances is required by other agencies to have an Emergency Response Plan (ERP) and possibly a Spill Prevention, Containment and Countermeasures Plan (SPCC) too. Spillage, leakage or vapors vented from unloading operations, ruptured or improperly vented tanks, disconnected or ruptured lines, or defective seals or valves could result in large-scale exposures. Proper facility design and maintenance, and adherence to safe operating and repair procedures can minimize accidental exposures. Determine miners' knowledge of spill response procedures and proper PPE.

VIII. Personal Exposure Sampling

Even with substantial control measures in place and the wearing of personal protective equipment, when handling or using chemicals in the laboratory, maintenance shop, or other areas of the mine (including hazardous waste fuel sites), miners may be exposed to airborne concentrations of chemicals above the TLVs[®]. Mine operators are required to monitor employee exposures in accordance with §§56/57.5002. Inspectors should conduct sampling where there is a potential for overexposure. Refer to Chapter 3 of this manual for individual contaminants and the chapters pertaining to specific sampling equipment and methods for additional guidance. When in doubt, call the district office for advice concerning suspected exposures and sampling for chemical contaminants.

IX. Other Regulatory Agencies

Inspectors should be aware there are chemical environmental, health and safety laws enforced by other governmental agencies; however, inspectors are not expected to be well versed in each agency's regulations. If, during an inspection, it appears that there is an unsafe chemical-related situation, advise the field office supervisor or district office as soon as possible, in order to coordinate intervention by other agencies as appropriate. Table 19-1 lists the relevant regulations of the two Federal agencies which are most likely to become involved in activities on a mine site in an emergency situation because

of overlapping jurisdiction. In most cases, there are also state and local entities, including state emergency response commissions. A mine having significant quantities of hazardous substances usually reports to the EPA-appointed Community Emergency Coordinator and Local Emergency Planning Committees (LEPC). LEPCs consist of representatives of government, police, fire department, hospitals, the media, community groups, and industry. They are also responsible for maintaining emergency plans covering hazardous substance facilities, and must be notified immediately in the event of release of certain amounts of hazardous chemicals. **In all situations, however, MSHA standards must be followed.**

Table 19-1. DOT and EPA Hazardous Material and Emergency Regulations That May Apply at Mine Sites		
Agency	Recommended Regulations	Regulated Activity
Department of Transportation (DOT)	<ol style="list-style-type: none"> 1. Hazardous Materials Transportation Act 2. Natural Gas Pipeline Safety Act 3. Hazard Liquid Pipeline Safety Act 4. Hazardous Materials Regulations and Procedures, Title 49 CFR Parts 100-185 	Shipping of hazardous materials: packing, handling, labeling, marking, placarding, level of training, safety assurance during shipment, hazard classes, UN ID numbers, and quantity restrictions. 49 CFR 172 lists the hazardous materials subject to these laws.
Environmental Protection Agency (EPA)	<ol style="list-style-type: none"> 1. Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) - (Superfund Act) (42 U.S.C. 9620) 2. Title III, Superfund Amendments and Reauthorization Act (SARA) - Community Right to Know (42 U.S.C. 11001) 3. Resource Conservation and Recovery Act (RCRA) (42 U.S.C. 6901) 4. Clean Water Act (40 CFR §§100 - 140, §§400 - 470) (33 U.S.C. 1251) 5. Clean Air Act, “National Emission Standard for Hazardous Air Pollutants” (40 CFR 61 Subpart M) 6. Risk Management Program, (40 CFR 68.130) 7. Toxic Substances Control Act (TSCA) (regulations 40 CFR 761 Subpart B) (15 U.S.C. 2601) 8. Solid Waste Disposal Act (42 U.S.C. 6901) 	Chemical Entering the Environment: Reportable Quantities List [of Chemicals stored at a site]; Emergency planning, reporting & training requirements; Hazardous Waste treatment disposal and storage; Accidental Release Prevention Requirements (including a facility risk management plan & list of regulated substances); Accidental Release Reporting; and Permit Requirements (approval and issuance).