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Working Safely with Corrosive Chemicals

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Working Safely with Corrosive Chemicals

1.0 Introduction

This document describes the common hazards associated with corrosive chemicals and provides guidance on how to handle these chemicals. Corrosive chemicals are any solids, liquids, or gases capable of irreparably harming living tissues or material damage on contact. Representative corrosive chemicals are grouped by their classes:

- Acids.
- Bases ("caustics" or "alkalis").
- Dehydrating agents such as phosphorous pentoxide and calcium oxide.
- Halogens and halogen salts such as bromine, iodine, zinc chloride, sodium hypochlorite.
- Organic halides and organic acid halides such as acetyl chloride and benzyl chloroformate.
- Acid anhydrides.
- Some organic materials such as phenol ("carbolic acid").

This document also addresses the procurement and use of corrosives. The disposal of corrosives wastes is not addressed by this document, but requirements can be found in Document 14.1, "LLNL Chemical Safety Management Program," in the *Environment, Safety, and Health (ES&H) Manual* and in Document 36.1, "Hazardous, Radioactive, and Biological Waste Management Requirements," in the *ES&H Manual*.

2.0 Hazards

Corrosive chemicals pose a hazard by

- Directly attacking tissue: Injuries to the eyes are a special concern. Hydrofluoric acid and caustics are particularly dangerous to the eyes. Hydrofluoric acid is also a serious skin hazard.
- Attacking materials: Care is required when selecting materials to use with corrosive chemicals so that the equipment, including storage containers, will not be damaged by the chemicals.

- Contributing to fire hazards:
 - Many acids are oxidizers that support combustion. Perchloric acid and its salts are especially reactive and may cause explosions.
 - Some corrosives are flammable, e.g., glacial acetic acid and phenol.
- Generating hydrogen gas. Acids are particularly hazardous when they react with metals. Caustics can also participate in reactions that evolve hydrogen, for example when sodium hydroxide contacts aluminum, zinc, or tin.
- Creating heat when they contact water, which can cause splatter. Mechanical damage to equipment aggravated by heating is also a possibility.
- Creating heat when acids and caustics mix.
- Possessing inherent toxicity. Inhalation exposures to high concentrations of corrosives can cause serious lung injuries or even death if the exposure is not terminated. Acid-forming materials that are modestly soluble in water, such as nitrogen dioxide and phosgene, are particularly hazardous because they cause delayed lung injuries that become evident a few hours to a day after the exposure occurs.
- Generating incompatible or toxic or reactive products upon mixing. The classic examples are mixing cyanide or sulfide salts with strong acids, which generate potentially lethal hydrogen cyanide or hydrogen sulfide.

Corrosive hazards can be identified by:

- Manufacturers' literature and product descriptions.
- Material Safety Data Sheets, (MSDSs) available from ChemTrack
<http://ctmsds.llnl.gov>
- Product labels. Document 10.2, "LLNL Health Hazard Communication Program," in the *ES&H Manual* requires personnel in non-laboratory settings to read and understand the labels for all new products.

3.0 Controls for Corrosive Chemicals

This section specifies controls for dealing with corrosive chemicals, which are implemented in accordance with the following documents:

- Document 10.2.
- Document 14.1.

- Document 14.2, "LLNL Chemical Hygiene Plan for Laboratories," in the *ES&H Manual*.

All workers required to handle corrosive chemicals or likely to come into contact with these chemicals shall be informed of the hazards involved and trained accordingly. Controls tailored to types and severity of the hazards are developed to

- Protect personnel from the toxic or other hazards associated with the materials, such as flammability, reactivity, etc.
- Prevent exposures to air contamination above Occupational Exposure Limits and Action Limits specified by Hazards Control.
- Assure waste disposal meets the requirements established by the Environmental Protection Department.
- Ensure materials are properly packaged so they can be safely transported on- or off-site.

3.1 Material Selection

Whenever practical, experimenters or persons developing work procedures and process planning shall substitute non-corrosive or less hazardous materials for corrosive materials, especially hydrofluoric acid and its precursors and perchloric acid. If this is not practical, then they shall modify or develop a process or procedure that eliminates or reduces the use of corrosive materials. If the above options are not feasible, the following controls (engineered, administrative, personal protective equipment (PPE), or combinations of these) shall be used.

3.2 Engineered Controls

Engineered controls shall be used whenever practical. Engineered controls to be used with corrosive chemicals include:

- Using less dispersible forms such as coarse dusts in lieu of fine dusts, solids instead of liquids or gases, or liquids instead of gases.
- Avoiding or minimizing operations that create dispersible forms such as producing dusts, mists, or vapors, and minimizing pour heights.
- Minimizing or eliminating potential leak points such as:
 - Connections in lines, container openings, and gaps in equipment housings, or providing spill catching pans and splash shields, etc., when such gaps can not be avoided for liquids.
 - Providing exhaust ventilation at potential leak points for gases and vapors.

- Using hoses or, preferably in the case of non-laboratory workplaces, durable rigid pipes or tubes to transfer materials.
- Enclosing the operation.
- Conducting operations involving potential exposures to airborne corrosives in a ventilated enclosure or with an engineered close-capture exhaust system (see Document 12.2, "Ventilation," in the *ES&H Manual* and its supporting documents).
- Scrupulously selecting compatible materials for all equipment that will come into contact with the corrosive.
- Selecting commercially available equipment recommended for use with the corrosive substances of interest.
- Minimizing operating pressures for corrosive liquids and gases.
- Providing a safety eyewash and shower where the potential for eye or skin exposure exists, particularly if pH values are less than 2 or greater than 12. Requirements for training the users of eyewashes/safety showers are found in Section 3.1.3 of Document 10.2 (for non-laboratory situations) and Section 3.2.6 of Document 14.2 (for laboratory situations). Requirements for the testing of safety showers/eyewashes are specified in Appendix B of Document 14.1. Engineering specifications are found in LLNL Facility Standard PEL-M-11610, "Emergency Eyewash & Shower Units."

3.3 Administrative Controls for Corrosives

3.3.1 Work Plans

Before beginning any LLNL operation involving the use of corrosive chemicals, the Responsible Individual (RI) shall

- Assess the hazards associated with the particular operation using the Integration Work Sheet (IWS) and implement the necessary controls, including the proper emergency response in case of an accident. See Document 2.1, "Laboratory and ES&H Policies, General Worker Responsibilities, and Integrated Safety Management," and Document 2.2, "Managing ES&H for LLNL Work," in the *ES&H Manual* to determine whether a safety plan is needed for the corrosive chemicals involved in specific operations. A Hazard Assessment Control form (HAC) will be needed if the IWS shows that a corrosive material exposure hazard exists and to guide and document the selection of personal protective equipment (PPE)

in accordance with Document 11.1, "Personal Protective Equipment," in the *ES&H Manual*.

- Determine if the current training of the workers is adequate for the activity. See Document 10.2 and Document 14.3, "Toxic, Corrosive, or Reactive Gases," in the *ES&H Manual* for additional details about ES&H training requirements for non-laboratories and laboratories, respectively.
- Contact the ES&H Team for assistance when planning work involving hydrofluoric acid, hydrogen fluoride, hydrofluoric acid precursors, perchloric acid, perchlorate compounds, or nitric acid at concentrations >98%. Contact the ES&H Team for assistance as necessary when planning operations involving other corrosives. The ES&H Team will
 - Provide guidance on the selection of controls.
 - Assist with job-specific training.
 - Evaluate the operation to determine if air permits are required or the appropriate National Environmental Policy Act (NEPA) documentation has been prepared and approved.
 - Help determine if additional documentation, such as a Safety Plan (SP), is necessary for operations that involve heating or the use of corrosive materials such as hydrofluoric acid and perchloric acids.

3.3.2 Signs and Labels

Warning devices such as signs and labels shall be posted at entrances to non-laboratory areas where corrosive chemicals are used.

Signs can warn against more than one hazard, especially if the same response(s) to the sign protect against all of the hazards. Please note that signs are more effective when combined with barriers and, where there is a high probability of serious injury, interlocks (see Document 12.1, "Access Control, Safety Signs, Safety Interlocks, and Alarm Systems," in the *ES&H Manual*).

Signs shall direct visitors to the nearest visitors' safety spectacle dispenser.

Access to laboratories shall be controlled while corrosives and other splash-hazardous chemicals are being used. The Health Hazard Communication (HHC) door poster shall be labeled to show that corrosives are present. A WARNING sign can be posted at the entrance to a laboratory space directing visitors to the nearest visitors' safety spectacle dispenser. The workers in the laboratory shall ensure that

- Unauthorized people are kept out unless splash hazards can be controlled by lowering hood sashes, turning down temperatures of the hot plates, etc.
- People entering the area are wearing suitable PPE (see Section 3.4).

3.3.3 Acquisition and Purchasing Procedures

Procedures for acquiring toxic and corrosive gases have been established and are specified in Document 14.3. There are no special procurement procedures for corrosives. Uses of hydrofluoric acid, hydrogen fluoride, hydrofluoric acid precursors, perchloric acid, perchlorate compounds, or nitric acid at concentrations >98% shall be addressed in work planning as specified in Section 3.3.1 of this document.

3.3.4 Receipt Procedures

Most hazardous materials, including chemicals, are received at the Livermore site by the Industrial Gases Section of the Materials Distribution Division (MDD), Procurement and Materiel Department, except when MDD and the ES&H Team leader have reviewed and authorized a specific, direct delivery area. Once the chemical arrives at LLNL, the Industrial Gases Section logs the container into the ChemTrack system and delivers the chemical to the designated delivery point. Appendix 8-B of Document 21.1, "Acquisition, Receipt, Transportation, and Tracking of Hazardous Material," in the *ES&H Manual* contains detailed information about establishing a direct delivery area.

Materials shipped to Site 300 shall enter through MDD's Shipping and Receiving Group.

3.3.5 Corrosive Chemicals' Labeling

The manufacturer's original label on incoming corrosive chemical containers will include a corrosive hazard warning. The manufacturer's label shall not be defaced until the container has been emptied. Secondary containers shall have such warnings whenever feasible, as required by Document 14.2 or Document 10.2.

3.3.6 Packaging

Corrosive chemicals shall be packaged to prevent splash to the person carrying them and contamination of the area if they are particularly eye or skin hazardous and they are being hand-carried over distances longer than within a room or laboratory. Examples of materials which should be so packaged are hydrofluoric acid and concentrated corrosives. When they are to be transported on-site by bicycle or motor vehicle, corrosive chemicals shall be packaged to withstand shocks, pressure changes, or any other condition that may cause leakage of contents during transport.

Corrosives being shipped off-site shall be packaged in DOT-approved packaging and be shipped via the Shipping Section of MDD.

3.3.7 Storage

Corrosive chemicals shall be stored in designated areas, cabinets, or refrigerators within the primary work or storage area.

- Use corrosion-resistant cabinets for storage. Cabinets used to store corrosive chemicals and containers of corrosive chemicals shall be well ventilated and labeled to indicate the nature of their contents. For flammable corrosives use a flammable storage cabinet.
- Oxidizers shall be packed in material that will not burn on contact. Glass and other breakable containers of corrosives shall be stored on shelves with restraints to prevent migration and falling to the ground in earthquakes. Larger bottles shall be stored on lower shelves.
- Acid anhydrides shall be protected from contact with water during storage. For example, containers should be stored off of floors or the ground, in places protected from the weather, and be covered with plastic sheet if exposure to water from above is possible.

For storage purposes, the container labeling requirements for laboratories and non-laboratories are different. These requirements are outlined in Appendix 21-C of Document 14.1. Users shall evaluate hazards, identify proper containers and controls before transferring or dispensing chemicals from manufacturer-supplied chemical containers to secondary containers. The secondary container shall be labeled appropriately. Appendix 21-A of Document 14.1 provides an overview of several labeling formats commonly used. Labels for common chemicals are available from the ES&H Team. The ES&H Team can also assist in obtaining labels for unique chemicals.

3.3.8 Safe Work Practices

The following safe work practices shall be implemented:

- Store incompatible materials separately. For example, do not store acids together with bases or oxidizing acids with organic materials.
- Follow the facility emergency procedures.
- Only trained personnel can clean up large spills of corrosive materials or spills involving hydrofluoric acid or perchloric acid. See "Special Precautions for Use of Hydrofluoric Acid, Hydrogen Fluoride, and Precursors of Hydrogen Fluoride" and "Special Precautions for Use of Perchloric Acid" (Appendices B and C) for additional information.

- Package and dispose of corrosive wastes as specified in the *ES&H Manual* and the Environmental Protection Division (EPD) Waste Generation and Certification Course (EP0006). Contact your area environmental analyst or hazardous waste technician for guidance.
- Do not mix acid waste with organic waste because fire, or other undesirable reactions, may occur.
- Do not add water to acid. Always add acid to water, while slowly stirring.
- Transport liquid corrosive materials in rubberized bottle carriers or suitable secondary containers.
- Use a pump system whenever possible to remove the contents of carboys or drums. Be sure the pump is compatible with the corrosives.
- Avoid pressurizing containers of corrosives.
- Store personal protective equipment in a location and manner that protects it from contamination or other damage. Do not reuse damaged equipment.
- Dispose of the contaminated equipment as hazardous waste. Save rinsate (rinse water) for possible disposal as hazardous waste.
- Do not pour corrosive solutions into the sanitary sewer or allow them to enter any drain.

3.3.9 Emergency Procedures

If accidental contact with a corrosive chemical occurs, follow these emergency procedures:

- First actions:
 - Leave the area if a hazardous condition exists.
 - Flush off the eye/skin area splashed as soon as it is safe to do so.
 - Limit access to the area affected by the spill.
 - Report large spills and spills of hot or otherwise particularly hazardous acids or bases to the Fire Dispatcher (dial 911).
- Do not attempt to clean up spills involving perchloric acid or hydrofluoric acid unless you have been trained to do so (see Appendices B and C).
- In the event of eye exposure to a corrosive chemical:
 - Immediately flush the eyes with the eyewash system. (For eyewash engineering specifications, see LLNL Facility Standard PEL-M-11610, "Emergency Eyewash & Shower Units.")

- Have another person summon the paramedics for help (Dial 911 from a Laboratory phone or 925-447-6880 [from a cellular phone on- or offsite] for both the Livermore site and Site 300 to obtain help if an emergency arises).
- Continue to flush the eyes (including lifting the eyelids and rolling the eyes around in their sockets while flushing) for at least 15 minutes or until the paramedics direct otherwise.
- In the event of skin exposure:
 - Wash the affected area with water.
 - Use the emergency shower if the exposure covers the face or a significant portion of the body. (For safety shower engineering specifications, see LLNL Facility Standard PEL-M-11610, "Emergency Eyewash & Shower Units.")
 - If necessary, remove *all* contaminated clothing and drench the body with water until the paramedics arrive. Have a coworker keep people away if modesty is an issue. Serious skin burns have occurred when people continued to wear splash-contaminated clothing, even though they washed the splashed clothing.
 - See Appendix B for additional procedures following contact with hydrofluoric acid.
- If inhalation of potentially harmful airborne levels of corrosive chemicals occurs, move the victim to an area where fresh air is available. Summon the paramedics for help (Dial 911 from a Laboratory phone or 925-447-6880 [from a cellular phone on- or offsite] for both the Livermore site and Site 300 to obtain help if an emergency arises).

3.4 Personal Protective Equipment

When workers cannot be fully protected with engineered and administrative controls, PPE is utilized. PPE is selected based on the contaminant and the anticipated severity of the exposure. The selection of PPE should and the selection of RPE shall be documented using a HAC form.

Face and eye protection shall be provided where chemical splashes present a hazard. The minimum protection is safety glasses with full sideshields for use with small quantities of chemicals that are not highly corrosive. Goggles shall be used for eye protection when handling corrosive materials under the following conditions:

- Caustics and hydrofluoric acid—eye injuries are more serious than with other acids.

- High concentrations.
- At elevated working temperatures. Heat can either be added from easily identified external energy sources, such as electrical or steam heaters, or hazardous quantities of heat can be created by chemical reactions. Heat-releasing chemical reactions include acid-base, fuel-oxidizer/reducing chemical, and solution reactions. These reactions can be hazardous in labs or shops. MSDSs provide advice about these types of hazards in industrial settings.
- Performing work that generates splash, dust, mists, or aerosols. Some electroplating and chemical processes create airborne mists. Other processes that may require the use of goggles include air agitation, pouring either large quantities of liquids or powders or pouring from greater heights, vigorous mixing or sparging, or any operation that creates corrosive splash or mists.

Use chemical goggles, a face shield, a rubber or neoprene body apron, and enclosed shoes when splashing may occur to protect other parts of the body.

Use portless chemical goggles or full facepiece respirators with the appropriate cartridges or canisters when corrosive mists or gases are present in the air.

Gloves are required when handling corrosives. Check gloves before each use for:

- Cracks
- Tears
- Discoloration or fading
- Bubbling
- Peeling
- Brittle spots

Gloves should either be filled with water or inflated (if clean) by mouth before use to check for pin hole leaks which will become apparent when the glove is pressurized. Manual inflation shall be done in a manner that prevents skin contact with potentially contaminated glove material, such as turning the glove inside out so the mouth contacts the clean inside of the glove after checking the glove to ensure that contaminant has not reached the inside. Use a new pair of gloves for each operation, especially if it cannot be determined that the inside of the gloves is clean.

Respiratory protection or a fully encapsulating suit is used to protect against airborne corrosives and/or severe whole body contact with high concentrations of airborne corrosive mists. Refer to the LLNL Respiratory Protection Program (see Document 11.1 for requirements).

4.0 Responsibilities

This section describes the responsibilities of personnel who work in areas where exposure to corrosive chemicals is possible. General responsibilities for all workers are described in Document 2.1.

4.1 Workers

- Conduct work in accordance with applicable controls and requirements (e.g., FSPs, , IWSs, safety plans, and HAC forms).
- Complete required training.
- Participate in medical surveillance when required.
- Use PPE as required.

4.2 Responsible Individual

- Ensure that all workers understand the hazards involved and follow the required work procedures.
- Properly select PPE and ensure that it is properly used. Contact the ES&H Team industrial hygienist when
 - There is uncertainty regarding the selection and use of PPE or any other safety issue.
 - Considering use of a new corrosive chemical that is not covered by existing safety documentation.
 - Scaling up the operation.
 - Reducing the use of extant engineered or administrative controls.
- Ensure corrosive materials are appropriately labeled, handled, used, and stored.
- Ensure that first aid and spill-response supplies are readily available and advise personnel about first aid procedures annually.
- Ensure that corrosive materials are disposed in accordance with Environmental Protection Department requirements.
- Ensure that the controls specified in Section 3.0 of this document are implemented in the planning stages in accordance with Document 2.1 and Document 2.2.
- Ensure that ventilation systems are designed by appropriately trained engineers in accordance with Document 12.2.

- Ensure safety eyewash and shower testing is documented.

4.3 Facility Point of Contact

- Help ensure that facility-provided safety equipment is maintained in satisfactory operating condition.
- Coordinate with the ES&H Team to develop a roof-access classification for any new corrosive chemical operation involving a ventilation system. See Document 15.1, "Roof Access," in the *ES&H Manual* for requirements.

4.4 Hazards Control

- Review the procurement for some corrosive chemicals such as concentrated nitric acid (>98%).
- Ensure that the Fire Department is equipped to handle large-scale corrosive material fires onsite at all times.
- Provide respiratory protective equipment.

4.4.1 ES&H Teams

- Assist the RI in ensuring the proper design of safety-related systems and preparing safety plans, if necessary.
- Evaluate roof-access classifications arising from new uses of corrosive materials.
- Respond to spills, fires, exposures, or other emergencies involving corrosive materials.

4.4.2 Hazards Control Education and Training Division

Provide the following classes:

- HS4200, "Hydrofluoric Acid"
- HS4240-W, "Chemical Safety—Web"
- HS4246-W, "Laboratory Safety—Web"

4.5 Environmental Protection Department

Provide guidance to the RI on waste generation, characterization, storage, and disposal.

4.6 Health Service Department

- Provides medical treatment services or medical referral for chemical injuries.
- Maintains antidotes and salves, as requested, for emergency response.
- Provides work areas with 2.5 % calcium gluconate skin cream and eye rinse for use by employees who could be exposed to hydrogen fluoride or hydrofluoric acid.
- Ensures that local hospitals can provide specialized care for personnel seriously exposed to corrosive materials, particularly hydrofluoric acid or hydrogen fluoride. This care includes the capability of administering subcutaneous and intravenous calcium gluconate, and providing nebulized calcium gluconate for inhalation exposures.

More details can be found in Document 10.1, "Occupational Medical Program," in the *ES&H Manual*.

4.7 Plant Engineering

Provides engineered controls that meet applicable LLNL, local, State, and Federal ES&H requirements, including ventilation systems.

4.8 Mechanical Engineering Department

Assists the RI to prepare Engineering Safety Notes (ESNs) pertaining to the design of corrosive material-handling systems.

5.0 Work Smart Standards

22 CCR §§ 66261.1-66261.126 and appendices, "Identification and Listing of Hazardous Waste."

29 CFR 1910.119, "Process Safety Management of Highly Hazardous Chemicals." This regulation applies to the use of greater than specified quantities ("threshold quantities") of hazardous materials, January 1999.

29 CFR 1910.120, "Hazardous Waste Operations and Emergency Response," January 1999. This regulation applies whenever hazardous waste is handled or treated, or where remediation work is performed.

29 CFR 1910.1000, "Air Contaminants," January 1999. This regulation establishes permissible exposure limits for a number of corrosive materials.

29 CFR 1910.1200, "Health Hazard Communication," January 1999. This regulation sets requirements for labeling, training, storing, and maintaining MSDSs for non-laboratories. (See Document 10.2 for details.)

29 CFR 1910.1450, "Occupational Exposure to Hazardous Chemicals in Laboratories," January 1999. This regulation covers the laboratory use of chemicals. (See Document 14.2 for further details.)

29 CFR 1910, Subpart K, "Medical and First Aid," (1910.151 to 1910.152) January 1999.

29 CFR 1926.50, "Medical Services and First Aid," January 1999.

40 CFR 261, "Identification and Listing of Hazardous Waste."

49 CFR 100-199, Research and Special Programs Administration, DOT (Off-site).

ANSI Z88.2-1992, "American National Standard for Respiratory Protection."

ANSI Z358.1-1990, "Emergency Eyewash and Shower Equipment." Testing frequency for emergency showers is to be monthly rather than weekly as required by the standards

NFPA 45, Chapter 6 "Laboratory Ventilation Systems and Hood Requirements," is mandatory. This section covers perchloric acid fume exhaust systems.

6.0 Resources for Information

6.1 Contacts

Contact the area ES&H Team for more information about working safely with corrosive chemicals.

6.2 Applicable Lessons Learned

For lessons learned applicable to working in confined spaces, refer to the following Internet address:

http://www-r.llnl.gov/es_and_h/lessons/lessons.shtml

6.3 Other Sources

A. A. Schilt, "Perchloric Acid and Perchlorates," G. Frederick Smith Chemical Company, Columbus, OH (1979).

Waste Acceptance Criteria, UCRL-MA-115877 rev 2, November 2003. This document is available at:

| http://www.llnl.gov/es_and_h/wac_rev2/wac_contents.html

Appendix A

Terms and Definitions

Action level	An airborne concentration of hazardous material that triggers implementation of health and safety controls such as workplace surveillance, monitoring, training, and medical examinations. The action level is often set at 50% of the OSHA permissible exposure limit.
Compatible	Able to withstand contact with a chemical without corrosion, degradation, or the formation of significant heat or undesirable reaction products.
Corrosive	<ol style="list-style-type: none">1. A substance that chemically attacks tissue and/or materials on contact.2. According to OSHA: "A chemical that causes visible destruction of, or irreversible alterations in, living tissue by chemical action at the site of contact. A chemical is considered to be corrosive if, when tested on the intact skin of albino rabbits by the method described in Appendix A of 49 CFR 173, it destroys or changes irreversibly the structure of the tissue at the site of contact following an exposure period of four hours. This term shall not refer to action on inanimate surfaces."

According to DOT, 49 CFR 173.137 c(2): "A liquid or solid that causes full thickness destruction of human skin at the site of contact within a specified period of time. A liquid that has a severe corrosion rate. Materials that do not cause full thickness destruction of intact skin tissue but exhibit a corrosion rate on steel or aluminum surfaces exceeding 6.25 mm (0.25 inch) a year at a test temperature of 55°C (130°F). For the purpose of testing steel P3 (ISO 9328-1) or a similar type, and for testing aluminum, non-clad types 7075-T6 or AZ5GU-T6 should be used. An acceptable test is described in ASTM G 31-72."

DOT lists corrosive materials in the Hazardous Material Table, 49 CFR Table 172.101. Corrosivity is a characteristic that is described in 22 CCR 66261.22 and 40 CFR 261.22 as an aqueous waste that has the pH less than or equal to 2, or greater than or equal to 12.5; a liquid waste that corrodes steel at a rate greater than 6.35 mm (0.250 inch) per year at a test temperature of 55 degrees C (130 Degrees F); or a solid that exhibits the characteristics of corrosivity. Aluminum is also a corrosive material.

Engineered	Designed by a competent engineer in accordance with good practice as specified in Document 12.2 and then installed as designed.
Hazard	<p>A substance or agent that can be harmful or create a nuisance to personnel.</p> <p>A chemical or physical property of a substance or agent that can be harmful or create a nuisance.</p>
Laboratory	<p>For the purpose of OSHA regulations, 29 CFR 1910.1450, laboratories are places where all of the following occur:</p> <ul style="list-style-type: none"> • Chemical manipulations are carried out on a laboratory scale. • Multiple chemical procedures or chemicals are used. • The procedures involved are neither part of a production process nor simulate one. • Protective laboratory practices are commonly used and equipment is available to minimize the potential for employee exposure to hazardous chemicals.
Medical surveillance	A regulatory or institutionally prescribed examination protocol for specified occupational hazards.
Non-laboratory	A place other than a laboratory as specified in a preceding definition. Generally a place where chemistry and biochemistry work is not done. This includes shops, maintenance facilities, physics and engineering laboratories, and biological experiment facilities where animals are handled.

Occupational Exposure Limit (OEL)	The OSHA permissible exposure limit (PEL) for an airborne concentration of a hazardous chemical in the workplace or the equivalent limit from another source. Most OSHA OELs were developed before 1970 so other, more up-to-date, limits from other sources are used, such as the American Conference of Governmental Industrial Hygienists (ACGIH) threshold limit values (TLVs).
Permissible Exposure Limit (PEL)	The OSHA permissible exposure limit for an airborne concentration of a hazardous chemical in the workplace. Permissible exposure limits are listed in 29 CFR 1910, Subpart Z.
Precursor (of hydrogen fluoride)	A substance that produces hydrogen fluoride on contact with air or water. Includes BF_3 , WF_6 , SiF_4 , AsF_5 , PF_5 , or UF_6 .
Sensitive (materials)	Unstable compounds that explode spontaneously or if disturbed.
Threshold Limit Values (TLVs)	Time-weighted average concentrations of materials for a normal eight-hour workday to which nearly all workers may be repeatedly exposed without adverse effect. These values are developed and published annually by the American Conference of Governmental Industrial Hygienists (ACGIH).

Appendix B

Special Precautions for Use of Hydrofluoric Acid, Hydrogen Fluoride, and Precursors of Hydrogen Fluoride

B.1 Hazards

Hydrofluoric acid (HF) is the most hazardous of the halide acids. In addition to exhibiting all the hazards typical of strong inorganic acids, hydrofluoric acid and hydrogen fluoride pose several unique hazards:

- Hydrofluoric acid is highly corrosive to many materials, including iron, concrete, carbonaceous natural materials (e.g., woody materials), animal products (e.g., leather), other natural materials used in the laboratory (e.g., rubber), and notably, glass containers. Thus, unlike other acids, hydrofluoric acid cannot be stored in glass containers or used in standard chemistry glassware.
- Chemical burns by strong (above 50%) hydrofluoric acid solutions cause severe immediate pain. Weaker solutions may cause delayed pain. Burns from 25% solutions may be felt within minutes, and burns from 1 to 20% solutions may not be immediately painful or visible or felt for several hours. The first symptom is a delayed throbbing pain, followed by damage that may penetrate deep down to the bone. Workers may not realize they have been injured until they return home after finishing work and the burns became painful. Burns to more than 2% of the body (an area the size of a hand) with 70% or stronger hydrofluoric acid can be fatal. Fluoride ions readily penetrate skin and tissue, and, in extreme cases, may result in necrosis of the subcutaneous tissue, which eventually may become gangrenous. If the penetration is sufficiently deep, decalcification (systemic hypocalcemia) of the bones may result. Extensive skin exposure can be life threatening.
- Hydrofluoric acid is corrosive to the nose, throat, and lungs. At more than three parts per million (ppm) in the air, hydrogen fluoride has a sharp, irritating odor. It is dangerous when heated or concentrated (above 50% solution) as it gives off highly corrosive and poisonous vapor. Severe exposure causes rapid inflammation and congestion of the lungs. Breathing difficulties may not occur until some hours after exposure has ceased. Death may occur from breathing this chemical.
- Hydrofluoric acid liquid or vapor causes severe irritation and deep-seated burns of the eye and eyelids if it comes in contact with the eyes. If the chemical is not removed immediately, permanent visual damage (e.g., blindness) may result.

- If swallowed, hydrofluoric acid will immediately cause severe damage to the throat and stomach.

The precautions given here also apply to hydrogen fluoride progenitors, as defined in Appendix A.

B.2 Engineered Controls

B.2.1 Hydrogen Fluoride Gas

Observe the following precautions when handling anhydrous hydrogen fluoride:

- Ship and store anhydrous HF in low-pressure steel cylinders that have been approved by the Department of Transportation (DOT). At room temperature, these cylinders are under slight positive pressure. Hydrogen fluoride is often removed from the cylinder by heating it.
- Remove gaseous hydrogen fluoride in a ventilated enclosure. The preferred system is a gas storage cabinet; however, small lecture bottles may be set up in a laboratory hood if the ES&H Team industrial hygienist concurs. The average velocity of air entering a gas storage cabinet shall be 200 fpm or higher and shall never fall below 150 fpm at any point in the face of the opening. See Document 14.3 for more information about gas storage cabinets.
- Conduct operations involving gaseous hydrogen fluoride in stainless steel or other compatible lines. Seamless, all welded construction is preferred. Non-welded joints should be in exhaust vented enclosures. The outer line of double tubing should be exhaust ventilated.
- Do not use incompatible materials in systems that conduct or distribute gaseous hydrogen fluoride. Stainless steel is probably the best choice for tubing and plumbing. Teflon and polyethylene are good materials for gaskets and other fittings.
- Place hydrogen fluoride detectors with local alarms at the cylinder or any other places deemed necessary by the ES&H Team industrial hygienist. If large quantities of hydrogen fluoride are in use, it may be necessary to connect the alarm system to the Emergency Command Center.

B.2.2 Hydrofluoric Acid (Hydrogen Fluoride Solutions)

All uses of unheated hydrofluoric acid at concentrations above 5% and any use of heated hydrofluoric acid should be in ventilated enclosures, such as a laboratory fume hood. If hydrofluoric acid is used extensively, the sash should be made of a shatter-

resistant non-glass material (e.g., polymethylmethacrylate) because hydrofluoric acid vapor will etch and weaken the glass.

B.3 Administrative Controls

Observe the following precautions when using hydrogen fluoride or hydrofluoric acid:

- Describe all operations involving the use of hydrofluoric acid in an IWS. During review of the IWS, a determination will be made if additional controls need to be identified beyond those in the *ES&H Manual*, (which requires a Safety Plan) or if a HAC will be needed to specify monitoring requirements or PPE that must be used.
- Assure that skin contact with hydrofluoric acid or hydrogen fluoride is avoided. Minimize the need for PPE as much as possible through the use of engineered controls.
- Employees who work with hydrogen fluoride gas at concentrations that could be above twice the OEL or with hydrofluoric acid solutions stronger than 5% shall take course HS4200, "Hydrofluoric Acid" or receive a hydrofluoric acid safety briefing from the area industrial hygienist.
- Hydrofluoric acid waste solutions shall be stored in polyethylene or other compatible containers. Lead, platinum, wax, polyethylene, polypropylene, polymethylpentene (PMP), and Teflon will resist the corrosive action of hydrofluoric acid. Glass bottles shall not be used.
- Evaluate building discharges in accordance with procedures specified by Hazards Control.
- Dial 911 if hydrogen fluoride or hydrofluoric acid exposure occurs. Any worker contaminated with hydrofluoric acid shall have immediate first aid, followed by treatment at a hospital as soon as possible. In the event of skin contact with the acid, immediately wash off the acid with plenty of cool water in an emergency shower. Remove contaminated clothing, shoes, watch, rings and any other items as quickly as possible while under running water. Make sure that the acid does not spread to other parts of the body or contaminate other workers. Scrub the acid from crevices such as under fingernails to minimize pain and tissue necrosis that may result in amputation of the finger. The removed articles of clothing will need to be disposed of.
- Apply 2.5% calcium gluconate ointment liberally to the exposed/contaminated area. Gently massage the ointment into the contaminated areas using rubber gloves. White specks appearing around the contaminated area indicate the antidote reaction is occurring. Continue to apply fresh gel for at least 15 minutes

after the pain has stopped. Calcium gluconate should not be applied to the eyes. The full extent of hydrofluoric acid injuries may not be obvious for several hours, even from minor accidents. Repeat the process if pain recurs. Calcium gluconate shall be refrigerated and inspected at least annually to ensure that mold does not develop.

- Hydrofluoric acid spill kits shall be available wherever hydrofluoric acid is used. Only those specifically trained for hydrofluoric acid spill response shall attempt to clean up such spills.

B.4 Personal Protective Equipment

A HAC shall be prepared to specify PPE (see Document 11.1). Use chemical goggles with covered ventilation ports when handling hydrofluoric acid solutions and a face shield when there is reason to believe that there is a risk of splash. The HAC shall be used to specify the appropriate gloves, apron, sleeve coverings, shoe coverings, or coveralls, as needed, to keep splash off of skin and personal clothing.

Under normal working conditions, respirators should not be necessary, but may be needed when working with gaseous hydrogen fluoride. Nasal/eye irritation is a clear sign that engineered controls are needed. Consult with your ES&H Team industrial hygienist for guidance about respirators. In responding to hydrogen fluoride emergencies, where vapors or mists are irritating, the Fire Department shall use self-contained breathing apparatus.

B.5 Environmental Controls

HF wastes are considered to be extremely hazardous waste. As such, the generator is limited to accumulating a maximum of one quart of HF waste stream in a satellite accumulation area (SAA). However, HF is no longer considered extremely hazardous if the concentration in the waste is less than 5.5%.

All empty HF containers shall be managed as hazardous waste since HF, like HCl, is an extremely hazardous chemical. Even after rinsing, don't discard empty corrosive containers in the trash or glass bins.

Appendix C

Special Precautions for Use of Perchloric Acid

C.1 Hazards

Perchloric acid is the strongest acid. In addition to having all the hazards typical of strong inorganic acids, this material has several additional hazardous properties:

- Concentrated perchloric acid (>75%) can explode spontaneously.
- Hot perchloric acid reacts with many organic materials, including paper and wood, and can detonate.
- Perchloric acid can react with many metals and organic materials to form unstable compounds that explode spontaneously, or if disturbed.
- The following are known to be sensitive perchlorate compounds/mixtures: fluorine perchlorate, inorganic nitrogenous perchlorates, heavy metal perchlorates, organic perchlorates (unless specific testing discloses this is not so), perchlorate esters, hydrazine perchlorate/hydrazinium diperchlorate, and the mixtures of perchlorates with sulfur, finely divided metals, and organic compounds.

C.2 Controls

- The following materials are *not* recommended for use with 72% perchloric acid: Nylon/polyamides, Dynel/modacrylic ester, Dacron/polyester, Bakelite, Lucite, vegetable-based Micarta, cellulose-based lacquers, copper/brass/bronze (which form shock sensitive salts), aluminum (dissolves), high nickel alloys (dissolve), cotton, wool, wood, and letharge (glycerin and lead oxide).
- The following *are* suitable for use with 72% perchloric acid: Viton, tantalum, chemically pure titanium, zirconium, niobium, Hastelloy C (slight corrosion rate), PVC, teflon, polyethylene, polypropylene, Kel-F, vinylidene fluoride, Saran, epoxy resins, glass, glass-lined steel, alumina, and Fluorolube.
- The hazards if an apparatus cracks or breaks due to thermal or mechanical shock are sufficient to make it desirable to consider using quartz apparatus since it is necessary in many experiments to chill rapidly from the boiling point. Glass-to-glass unions, lubricated with 72% perchloric acid, seal well and prevent joint freezing arising from the use of silicon lubricants. Rubber stoppers, tubes, or stopcocks are incompatible with perchloric acid.

- Pneumatically-driven stirrers are recommended rather than the electric motor type. Repeated exposure of the motor windings to perchloric acid vapor could result in a fire, unless the motor is an explosion-proof type, which is unlikely.
- An IWS is required.
- The following activities require a Safety Plan (SP):
 - Operations where perchloric acid is heated or boiled.
 - Any operation that involves forming perchloric acid at concentrations greater than 75% on a weight basis.
 - Projects involving the disassembly of a perchloric acid ventilation system.
 - Maintenance of perchloric acid ventilation system components. Facility personnel should assume that maintenance would be needed.

C.3 Ventilation Systems

Hoods in which perchloric acid is used shall be specially constructed. When perchloric acid is heated, the entire ventilation system shall be specifically designed and constructed for that service. The following design and use requirements apply to hoods where perchloric acid is heated on any repeating frequency to minimize the perchlorate salt buildup on the inside of the hood, its ductwork, or fan.

- Construct hood interiors using materials that will not corrode or react with perchloric acid such as type 316 stainless steel and ceramic. Polyvinyl chloride may be used for light-duty systems or as a liner for a stainless steel hood.
- Provide 1/2 inch "dished" liquid-tight hood floors. An integral trough should be placed at the back to collect wash water runoff and shall be provided for new perchloric acid hoods. Minimize joints wherever possible. Use non-reactive sealants or gasket materials if joints are present (Teflon and fluorocarbon greases and caulking are usually acceptable.) The collected water runoff shall be processed and handled in a manner specified by the area ES&H Team.
- Construct the exhaust ducting using non-reactive and perchloric acid resistant materials. Type 316 stainless steel or PVC is acceptable. Never manifold the ductwork to any other ventilation system. Use the steepest, straightest, and shortest route for ductwork. Avoid sharp turns. Slope horizontal runs of ductwork at least 1 inch per foot back toward the hood and, where possible, avoid horizontal runs where condensed perchloric acid can accumulate. Never use flexible connections. Seal ductwork to prevent liquid from escaping. Preferred methods are welded stainless steel or welded

PVC. Use screws of 316 stainless steel or equivalent corrosion-resistant and non-reactive material to connect sections of ductwork. Use only gaskets or sealants that are non-reactive and resistant to perchloric acid.

- Install fan blades that are non-reactive, spark- and corrosion-resistant. Teflon or PVC coated blades can be used. The exhaust fan motor shall not be installed in the ductwork and the pulley shall be conductive as specified by NFPA 45.
- Equip the ventilation system with a built-in water spray nozzle wash-down system. Ensure that the system will adequately spray all interior surfaces of the ducting, stack, fan, plenum, baffles, and hood. The hood shall be washed down at least each day after use or more frequently if specified in a safety plan. The water shall be drained to an appropriate holding tank pending removal for treatment and disposal.
- Thoroughly flush the interior of a perchloric acid hood just prior to maintenance or removal of the hood, wash joints, the fan motor, and its housing. Check the various surfaces and joints using the methylene blue or diphenylamine tests. If perchlorates are detected, further washing is required. Collect the rinse water for evaluation to determine if it is hazardous waste.
- Inspect new systems for the presence of inappropriate gaskets, caulking, or other materials that may be potentially explosive as part of acceptance procedure. Require vendors and contractors to furnish blueprints and specifications describing the materials of construction.
- The baffles of new hoods shall be easily removable to allow for inspecting and cleaning of accumulations of explosive perchlorate residues.
- Design and construct perchloric acid ventilation systems to allow for the easiest possible visual inspection. Include easily removed hood baffles for routine inspection of perchlorate buildup.
- Assure that hoods in which perchloric acid is heated are designated as perchloric acid hoods, dedicated to perchloric acid work, and are labeled:

"WARNING: Perchloric acid work is done in this hood."

Specify shatterproof hood sashes.

- Test hoods and exhaust systems for perchlorate residues before doing any inspection, maintenance, or cleaning if the perchloric acid was heated above ambient temperature. Also test perchloric acid hoods being put into use for any other purpose after water washing them to remove perchlorate residues.

C.4 Storage

Perchloric acid shall be kept in its original shipping container in a pan and stored in metal cabinets. The pan should be made of compatible materials capable of containing the volume of the bottle.

C.5 Precautions for Use

Observe the following precautions when using perchloric acid:

- Use established procedures, whenever possible. New procedures shall be:
 - Pre-approved as specified in Document 14.2, if the work is performed in a laboratory, or
 - Addressed in a Safety Plan for a non-laboratory workplace.
- Always use impact-resistant chemical goggles, a face shield, neoprene gloves, and a rubber apron when handling perchloric acid. Use the hood sash as a blast shield to the extent possible.
- Inspect bottles of acid before use. If the acid is discolored or has formed a precipitate, do not use it. Contact the area ES&H Team who will determine what special handling may be needed and help to arrange for disposing of it as a hazardous waste.
- Be sure you understand the reaction(s) that can occur when using perchloric acid. Perchloric acid may react violently with many chemicals, including acetic anhydride, alcohol, reducing agents, and many metals.
- Always transfer acid over a sink in a designated perchloric acid hood with wash down system designated for perchloric acid use in order to catch any spills and afford a ready means of disposal.
- Heat perchloric acid in a designated perchloric acid hood with the sash down or using a safety shield to provide splatter/splinter protection.
- Never heat perchloric acid in an oil bath or with an open flame. Electric hot plates, electrically or steam-heated sand baths, heating mantles, or steam baths are preferred.
- In wet digestions with perchloric acid, treat the sample first with nitric acid to destroy easily oxidizable matter.
- Use great care when heating perchloric acid, perchloric acid salts, high-boiling acids, or dehydrating agents. The unstable anhydride may be formed and an explosion may result.

- Do not distill perchloric acid in a vacuum, because the unstable anhydride may be formed and cause a spontaneous explosion.
- Avoid allowing hot perchloric acid to come into unplanned or uncontrolled contact with any organic materials, including paper or wood, because a fire or explosion can occur.
- Avoid storing organic materials in perchloric acid work hoods.
- Keep dilute perchloric acid solutions from contacting strong dehydrating agents (concentrated sulfuric acid, anhydrous phosphorous pentoxide, etc.).
- Avoid using incompatible greases or hoses on glass fittings.
- Wash down perchloric acid hoods equipped with wash down systems until the rinse water has a pH of 7, or for at least 20 minutes.
- In the event of a spill in the hood, wash the hood down with water as described in Section C.3 of this appendix. In the event of a spill of any quantity outside the hood, call the building health and safety technician.
- Protect vacuum sources from perchloric acid/ perchlorate contamination. Vacuum pumps should be thoroughly flushed and refilled with Kel-F or Fluorolube.

Handling Perchloric Acid Solutions Stronger than 85%

- Allow only experienced research workers to handle anhydrous perchloric acid. These workers shall be thoroughly familiar with the literature on the acid.
- Use a safety shield to protect against a possible explosion, and use the acid in a designated perchloric acid hood with a minimum of equipment present. No extraneous chemicals should be present in the hood.
- Assure that a second worker is informed of the intended use of the anhydrous perchloric acid. This second worker should be in the same room with the worker using this extremely strong oxidizer.
- Wear safety goggles, face shield, thick gauntlets, and a rubber apron.
- Use only freshly prepared acid.
- Do not make any more anhydrous perchloric acid than is required for a day/shift.
- Dispose of any unused anhydrous perchloric acid at the end of each day by dilution and neutralization.
- Remember that contact of the anhydrous acid with organic materials will usually result in an explosion.

- Do not handle discolored anhydrous perchloric acid. Immediately contact the area ES&H Team who will determine what special handling will be needed and arrange for disposing of it as a hazardous waste.

Spills of Perchloric Acid

Do not use combustible materials to mop up or absorb perchloric acid spilled on the floor or bench top. Neutralize the corrosive chemical and then soak it up with rags or paper towel. Keep the contaminated rags and paper towels wet to prevent combustion upon drying. When the spill cleanup is completed, place the contaminated rags and paper towels in a plastic bag, seal it, and then place in a compatible waste container for proper disposal. Contact your Radioactive and Hazardous Waste Management (RHWM) Technician for container and labeling support.

Collect and dispose of rinse water, then neutralization of the wetted area is recommended followed by additional rinsing. Cover the spill with a dilute solution of sodium thiosulfate. Transfer the slurry into a large container of water, where it should be neutralized with soda ash.

Disposal of unused acid

Contact RHWM for disposal of both unused and waste acid.

Surface Contamination Tests:

- Diphenylamine Test: Use a medicine dropper to apply a solution of diphenylamine sulfate which is one gram dissolved in 10 ml of "1 to 1" (18 normal) H_2SO_4 . The liquid turns *black* upon contact with perchlorate. The solution also reacts with nitrates, but turns blue.
- Methylene Blue Test: Use 0.4% solution of methylene blue in water. Add a few drops of indicator solution to about 25 ml of trial solution, such as water used to test rinse from a length of potentially contaminated duct. Perchlorates will produce a violet precipitate.

C.6 Environmental Control

Unlike HF, perchloric acid is not considered to be an extremely hazardous waste; however, according to 22 CCR and 40 CFR, it is considered to be corrosive, reactive, ignitable, and toxic. Manage perchloric acid waste in accordance with the guidelines provided for corrosive waste management in EPD's Hazardous Waste Generation and Certification Course (EP0006).