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Compilation of Requirements for Safe Handling of Fluorine and Fluorine-Containing Products of Uranium Hexafluoride Conversion

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MANAGED AND OPERATED BY
LOCKHEED MARTIN ENERGY RESEARCH CORPORATION
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Chemical Technology Division

COMPILATION OF REQUIREMENTS FOR SAFE HANDLING OF FLUORINE AND FLUORINE-CONTAINING PRODUCTS OF URANIUM HEXAFLUORIDE CONVERSION

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1. INTRODUCTION

Public Law (PL) 105–204 requires the U.S. Department of Energy to develop a plan for inclusion in the fiscal year 2000 budget for conversion of the Department's stockpile of depleted uranium hexafluoride (DUF_6) to a more stable form over an extended period. The conversion process into a more stable form will produce fluorine compounds (e.g., elemental fluorine or hydrofluoric acid) that need to be handled safely. This document compiles the requirements necessary to handle these materials within health and safety standards, which may apply in order to ensure protection of the environment and the safety and health of workers and the public.

Fluorine is a pale-yellow gas with a pungent, irritating odor. It is the most reactive nonmetal and will react vigorously with most oxidizable substances at room temperature, frequently with ignition. Fluorine is a severe irritant of the eyes, mucous membranes, skin, and lungs. In humans, the inhalation of high concentrations causes laryngeal spasm and broncospasms, followed by the delayed onset of pulmonary edema. At sublethal levels, severe local irritation and laryngeal spasm will preclude voluntary exposure to high concentrations, unless the individual is trapped or incapacitated. A blast of fluorine gas on the shaved skin of a rabbit causes a second degree burn. Lower concentrations cause severe burns of insidious onset, resulting in ulceration, similar to the effects produced by hydrogen fluoride.

Hydrofluoric acid is a colorless, fuming liquid or gas with a pungent odor. It is soluble in water with release of heat. Ingestion of an estimated 1.5 grams produced sudden death without gross pathological damage. Repeated ingestion of small amounts resulted in moderately advanced hardening of the bones. Contact of skin with anhydrous liquid produces severe burns. Inhalation of AHA or aqueous hydrofluoric acid mist or vapors can cause severe respiratory tract irritation that may be fatal.

Based on the extreme chemical properties of these chemicals as noted above, fluorine or fluorine compounds must be handled appropriately within the boundaries of many safety requirements for the protection of the environment and the public. This report analyzes the safety requirements that regulatory agencies have issued to handle fluorine or fluorine compounds and lists them in Table 1. Table 1 lists the source of the requirements, the specific section of the source document, and a brief description of the requirements.

Table 1. Listing of requirement sources and applicable sections

Requirement Sources	Applicable sections	Description
Title 49—Transportation	172.101	Purpose and use of hazardous materials table. Fluorine and fluorine compounds are included in this table.
	173.34(d)(4)	Qualification, maintenance, and use of cylinders with fluorine.
	173.302(d)	Specification of containers for shipping fluorine.
	178.36	Specification 3A and 3AX seamless steel cylinders to ship fluorine.
	178.37	Specification 3AA and 3AAX seamless steel cylinders to ship fluorine.
	178.38	Specification 3B seamless steel cylinders to ship fluorine.
Title 10—Energy	Appendix F to Part 110	Fluorination systems [molecular laser isotope separation (MLIS)].
	Appendix J to Part 110	Illustrative list of uranium conversion plant equipment. Under NRC Export Licensing Authority.
Title 29—Labor	1910.252.(c).(1).(C)	Specification of requirements on fire prevention and protection, protection of personnel, and health protection and ventilation.
	1910.252.(c).(5).(i).	In confined spaces, welding or cutting involving fluxes, coverings, or other materials which contain fluorine compounds.
	1910.252.(c).5.(ii).	Maximum allowable concentration.
	Appendix A to Sect. 1910.119	Listing of toxic and reactive highly hazardous chemicals which present a potential for a catastrophic event at or above the threshold quantity.
	1910.1000	Air contaminants for employee’s exposure.
	1910.306(h)	Specific-purpose equipment and installations.
	1915.1000	Air contaminants for shipyard employment
	1926.55	Safety and health regulations for construction: gases, vapors, fumes, dusts, and mists.
	Appendix A to Sect. 1926.64.	Listing of toxic chemicals that present a potential for a catastrophic event at or above the threshold quantity.
Title 40—Protection Of Environment	68.22	Sets forth the list of regulated substances and thresholds: Offsite consequence analysis parameters
	68.130	The list of regulated toxic substances and TQ for accidental release prevention.
	266.206	Standards applicable to the treatment and disposal of waste military munitions.
	Part 302	Designation, reportable quantities, and notification of hazardous substances.
	Part 355	Emergency planning and notification.

Table 1 (continued)

Requirement Sources	Applicable sections	Description
	Part 372	Toxic chemical release reporting: community right-to-know.
DOE Order 6430.1A DIV 1-7: General Design Criteria	1322-43	Uranium recovery facilities.
	1530-99.12.1	Gaseous diffusion and centrifuge facilities. Storage areas for UF_6 and process areas handling UF_6.
	1530-99.16	Uranium conversion and recovery facilities. Fire-resistant, physical isolation barriers design.
	1574-1	Coverage in cryogenic systems.
OSHA	Table of regulated substances	Provides industrial exposure data and control technologies for fluorine and 649 other substances that are currently regulated or candidates for regulation.
Doe National Laboratory Plant Safety Standards	Oak Ridge Gaseous Diffusion Plant Safety Standards	Safety standards for its operations that included the handling of fluorine.
	LLNL's Health & Safety Manual, Supplement Document 21.12	This is a supplement to the Health &Safety Manual. Describes the common hazards associated with fluorine and details engineering and procedural controls required for its safe use.
Industrial Practices	Handling Hydrofluoric Acid: Anhydrous and Aqueous	Industrial practices of how to handle fluorine and fluorine compounds are given by Pennsalt Chemicals in one of their industrial documents.
Compressed-Gas Association	Manual for handling fluorine	Safe handling of fluorine including storage, shipping, and manipulation.
National Fire Protection Association	Guide On Hazardous Materials	Describes fire and explosion hazards.
Emergency Planning And Community Right-To-Know Act (EPCRA)	SARA Title III, CERCLA, EPCRA Section 302, EPCRA Section 313, RCRA	Chemicals are listed in a consolidated list if they are known to cause or can reasonably be anticipated to cause significant adverse acute effects on health at concentrations likely beyond facility boundaries.

2. BACKGROUND

Approximately 700,000 metric tons (MT) of DUF_6 is stored, or will be produced under a current agreement with the United States Enrichment Corporation (USEC), at the Paducah site in Kentucky, Portsmouth site in Ohio, and East Tennessee Technology Park (ETTP) site in Tennessee that are subject to PL 105–204,[1] which directs DOE to prepare and submit a plan to Congress that ensures that all funds accrued on the books of USEC for the disposition of DUF_6 will be used for the construction and operation of plants to treat and recycle the DUF_6 consistent with the National Environmental Policy Act (NEPA). The Final Plan for the Conversion of DUF_6,[2] issued by DOE in March 1999 is based on an aggressive schedule to begin construction of conversion facilities in FY 2002.

To begin construction of conversion facilities by FY 2002, the DOE DUF_6 Management Program is currently planning for conversion facilities to convert DUF_6 to compounds that are chemically stable. These conversion processes will generate anhydrous hydrogen fluoride or other fluorine-containing compounds, including elemental fluorine. To support program decisions and communications regarding conversion plant deployment, this study was conducted to provide an analysis of the pertinent regulatory framework for handling fluorine and fluorine compounds, such as anhydrous or aqueous hydrofluoric acid. This study includes an analysis of the existing regulations related to fluorine compounds in the DOE Orders, Title 49, Title 40, Title 29, and Title 10 and industrial practices about how to handle fluorine or fluorine compounds.

3. OBJECTIVE

The objective of this report is to compile a listing of the requirements—the safety fundamentals, safety requirements, safety guides, and safety reports—which apply to the fluorine-containing compounds produced as a result of the UF_6 conversion project. The review focuses on applicable government laws, regulations, DOE orders, policies, technical standards and guidance, and industry standards and practices related to the safe handling, storage, transportation, and disposal of fluorine and fluorine compounds.

The safety requirements and the associated safety fundamentals documents, the safety guidance documents, and the safety reports documents are listed in the body of the document. Details of some of these requirements are listed in Appendixes A–D.

4. REQUIREMENTS DOCUMENTS

The approach taken in this report is to state first the requirements that appear in the pertinent Code of Federal Regulations (CFR). The review begins by analyzing the sections describing the requirements for the transportation of elemental fluorine or fluorine compounds in CFR 49, which was issued by the U.S. Department of Transportation (DOT). The review continues with CFR 10, which was issued by the U.S. Nuclear Regulatory Commission, concerning what pertains to the importing and exporting of nuclear materials and operational details of uranium conversion plants. It follows the analysis of CFR 29, which was issued by the U.S. Department of Labor, concerning what pertains to occupational safety and health standards for handling fluorine and fluorine compounds. The review continues with CFR 40, which was issued by the U.S. Environmental Protection Agency, concerning what pertains to chemical accident prevention provisions and management of hazardous waste, including fluorine and fluorine compounds.

This report also (1) analyzes the requirement documents that appear in the respective DOE orders and that mainly relate to general design criteria involving fluorine and fluorine compounds; (2) reviews two volumes of information issued by the Occupational Safety and Health Act (OSHA) concerning technical, health, and safety requirements for handling fluorine and fluorine compounds; (3) analyzes requirements for handling fluorine that have been issued at DOE national laboratories, in particular, the Oak Ridge Gaseous Diffusion Plant (now the East Tennessee Technology Park) and the Lawrence Livermore National Laboratory; (4) reviews the technical requirements involving industrial practices of how to transfer anhydrous and aqueous hydrofluoric acid from one tank to another; (5) transcribes the requirements that the Compressed Gas Association has issued in a manual that describes its requirements for safe handling and storage of fluorine; and (6) reviews some of the requirements for handling fluorine and fluorine compounds that are considered important by the National Fire Protection Association.

4.1 TITLE 49—TRANSPORTATION

Chapter I of Title 49 Part 172, "Research and special programs administration, Department of Transportation," provides hazardous materials table, special provisions, hazardous materials communications, emergency response information, and training requirements. This part applies to (1) each person who offers a hazardous material for transportation, and (2) each carrier by air, highway, rail, or water who transports a hazardous material.

4.1.1 Part 172: Hazardous Materials Table, Special Provisions, Hazardous Materials Communications, Emergency Response Information, and Training Requirements

This part of Title 49 lists and classifies those materials which the DOT has designated as hazardous materials for transportation and prescribes the requirements for shipping papers, package marking, labeling, and transport-vehicle placarding applicable to the shipment and transportation of those hazardous materials.

Sect. 172.101: Purpose and use of hazardous materials table. This section of the regulations provides the Hazardous Materials Table (HMT) that designates the materials listed as hazardous materials for the purpose of transportation of those materials. The HMT includes information about (1) the descriptions and proper shipping names of the hazardous materials, (2) the hazard class or division corresponding to each proper shipping name, (3) the identification number assigned to each proper shipping name, (4) the packing groups assigned to a material corresponding to the proper shipping name and hazard class for that material, (5) the hazard warning labels, (6) the special provisions applicable to hazardous materials, (7) the packaging authorizations, (8) the maximum quantities that may be offered for transportation in one package, and (9) the authorized stowage locations on board cargo and passenger vessels. Fluorine appears on the HTM with the characteristics as shown in Appendix A.

Table 1 of Appendix A—Hazardous Substances Other than Radionuclides. This section of the regulation illustrates the reportable quantities of substances that are transported. Quantities above the figures shown in this table should be reported. Fluorine is indicated on this table with a value of 10 lb as reportable quantity and shown in Appendix A of this report.

4.1.2 Part 173: Shippers—General Requirements for Shipments and Packagings

This part includes (1) definitions of hazardous materials for transportation; (2) requirements to be observed in preparing hazardous materials for shipment by air, highway, rail, or water, or any combination thereof; and (3) inspection, testing, and retesting responsibilities for persons who retest, recondition, maintain, or repair and rebuild containers used or intended for use in the transportation of hazardous materials.

Sect. 173.34: Qualification, maintenance and use of cylinders. This section specifies the general qualification for use of cylinders, date of use, marking, and pressure-relief-device systems.

Sect. 173.34(d)(4). A pressure-relief device is prohibited on a cylinder charged with fluorine.

Sect. 173.302: Charging of cylinders with nonliquefied compressed gases. This section provides charging specifications for detailed requirements, filling limits, special filling limits for cylinders, special gases, verification of container pressure, carbon monoxide, diborane and diborane mixtures, and poisonous mixtures.

Sect. 173.302(d): Fluorine. Fluorine must be shipped in Specification 3A1000, 3AA1000, or 3BN400 (Sect. 178.36, Sect. 178.37, or Sect. 178.39 of this subsection) cylinders without safety-relief devices and equipped with a valve-protection cap. Such containers must not be charged to over 400 psig at 70^{o}F and must not contain over 6 lb of gas.

4.1.3 Part 178: Specifications for Packagings

This part prescribes the manufacturing and testing specifications for packaging and containers used for the transportation of hazardous materials in commerce.

Sect. 178.36: Specification 3A and 3AX seamless steel cylinders. This section specifies the type, size, and service pressure of the 3A and 3AX cylinders; steel; and the material, manufacture, etc.; in addition, it provides equations to calculate the maximum longitudinal tensile stress resulting from bending and the maximum longitudinal tensile stress resulting from hydrostatic test pressure (shown in Appendix B).

Sect. 178.37: Specification 3AA and 3AAX seamless steel cylinders. This section specifies the type, size, and service pressure of the 3AA and 3AAX cylinders; steel; and the material, manufacture, etc.; in addition, it provides equations to calculate the maximum longitudinal tensile stress resulting from bending and the maximum longitudinal tensile stress resulting from hydrostatic test pressure (shown in Appendix B).

Sect. 178.38: Specification 3B seamless steel cylinders. This section specifies the type, size, and service pressure of the 3B seamless steel cylinders and identifies material, manufacture, etc.; in addition, it provides equations to calculate the wall thickness of the cylinder (shown in Appendix B).

4.2 TITLE 10—ENERGY

These regulations are issued by the U.S. Nuclear Regulatory Commission (NRC) which has, among its duties, the authority to issue rules of practice for domestic licensing proceedings and issuance of orders. Import and export licensing proceedings are also described in these regulations. Proceedings include (a) granting, suspending, revoking, amending, or taking other action with respect to any license, construction permit, or application to transfer a license; (b) issuing orders and demands for information to persons subject to the Commission's jurisdiction, including licensees and persons not licensed by the Commission; and (c) imposing civil penalties under Sect. 234 of the Act.

4.2.1 Part 110: Export and Import of Nuclear Equipment and Material

This part of the regulations prescribes licensing, enforcement, and rulemaking procedures and criteria, under the Atomic Energy Act (AEA), for the export and import of nuclear equipment and material. This part also gives notice to all persons who knowingly provide to any licensee, applicant, contractor, or subcontractor, components, equipment, materials, or other goods or services, that relate to a licensee's or applicant's activities subject to this part, that they may be individually subject to NRC enforcement action for violation of Sect. 110.7b.

Sect. 110.135: Notice of rulemaking. This section includes the following rulemaking mechanisms: (a) Upon approval of an amendment, the Commission will publish in the *Federal Register* a notice of rule making which includes a statement of its basis and purpose, effective date, and, where appropriate, any significant variations from the amendment as proposed in any notice of proposed rulemaking and (b) the effective date of an amendment will normally be no earlier than 30 d after publication of the notice of rulemaking, unless the Commission for good cause provides otherwise in the notice.

This section also has several appendixes, of which Appendix F to Part 110—Illustrative List of Laser-Based Enrichment Plant Equipment and Components Under NRC Export Licensing Authority—includes item 9, which is related to fluorine.

Appendix F to Part 110 (9): Fluorination systems [molecular laser isotope separation (MLIS)]. Especially designed or prepared systems for fluorinating UF_5 (solid) to UF_6 (gas). These systems are designed to fluorinate the collected UF_5 powder to UF_6 for subsequent collection in product containers or for transfer as feed to MLIS units for additional enrichment. In one approach, the fluorination reaction may be accomplished within the isotope separation system to react and recover directly off the product collectors. In another approach, the UF_5 powder may be removed or transferred from the product collectors into a suitable reaction vessel (e.g., fluidized-bed reactor, screw reactor, or flame tower) for fluorination. In both approaches, equipment is used for storage and transfer of fluorine (or other suitable fluorinating agents) and for collection and transfer of UF_6.

Appendix J to Part 110: Illustrative list of uranium conversion plant equipment under NRC export licensing authority. (2) Especially designed or prepared systems for the conversion of UO_3 to UF_6. Conversion of UO_3 to UF_6 can be performed directly by fluorination. The process requires a source of fluorine gas or chlorine trifluoride. (5) Especially designed or prepared systems for the conversion of UF_4 to UF_6. Conversion of UF_4 to UF_6 is performed by exothermic reaction with fluorine in a tower reactor. UF_6 is condensed from the hot effluent gases by passing the effluent stream through a cold trap cooled to -10^oC. The process requires a source of fluorine gas.

4.2.2 Part 30: Rules of General Applicability to Domestic Licensing of By-Product Material

This part prescribes rules (applicable to all persons in the United States) governing domestic licensing of by-product material under the AEA of 1954, as amended (68 Stat. 919), and under Title II of the Energy Reorganization Act (ERA) of 1974 (88 Stat. 1242), and exemptions from the domestic licensing requirements permitted by Sect. 81 of the Act. This part also gives notice to all persons who knowingly provide to any licensee, applicant, certificate of registration holder, contractor, or subcontractor, components, equipment, materials, or other goods or services, that relate to a licensee's, applicant's, or certificate of registration holder's activities subject to this part, that they may be individually subject to NRC enforcement action for violation of Sect. 30.10.

Sect. 30.70, Schedule A: Exempt concentrations. This section refers to ^{18}F. The requirements analyzed in this report are related to nonisotopic fluorine. Consequently, this information will not be described herein.

4.3 TITLE 29—LABOR

The U.S. Department of Labor is the organization in charge of issuing these regulations. Parts of these regulations that include fluorine are the (1) Occupational Safety and Health Standards, (2) Occupational Safety and Health Standards For Shipyard Employment, and (3) Safety and Health Regulations for Construction.

4.3.1 Part 1910: Occupational Safety and Health Standards

Sect. 1910.252: General requirements. This part specifies requirements on fire prevention and protection, protection of personnel, and health protection and ventilation.

Sect. 1910.252.(c).(1).(C). Brazing and gas-welding fluxes containing fluorine compounds shall have a cautionary wording to indicate that they contain fluorine compounds. One such cautionary wording recommended by the American Welding Society for brazing and gas-welding fluxes reads as follows:

CAUTION
CONTAINS FLUORIDES

This flux, when heated, gives off fumes that may irritate eyes, noses, and throats.

1. Avoid fumes—use only in well-ventilated spaces.
2. Avoid contact of flux with eyes or skin.
3. Do not take internally.

Sect. 1910.252.(c).(5).(i). In confined spaces, welding or cutting involving fluxes, coverings, or other materials which contain fluorine compounds shall be done in accordance with paragraph (c)(4) of this section. A fluorine compound is one that contains fluorine, as an element in chemical combination, not as a free gas.

Sect. 1910.252.(c).5.(ii) Maximum allowable concentration. The need for local exhaust ventilation or airline respirators for welding or cutting in other than confined spaces will depend upon the individual circumstances. However, experience has shown such protection to be desirable for fixed-location production welding and for all production welding on stainless steels. Where air samples taken at the welding location indicate that the fluorides liberated are below the maximum allowable concentration, such protection is not necessary.

Sect. 1910.119: Process safety management of highly hazardous chemicals. This section contains requirements for preventing or minimizing the consequences of catastrophic releases of toxic, reactive, flammable, or explosive chemicals. These releases may result in toxic, fire, or explosion hazards.

Appendix A to Sect. 1910.119—list of highly hazardous chemicals, toxics, and reactives (mandatory). This appendix contains a listing of toxic and reactive highly hazardous chemicals which present a potential for a catastrophic event at or above the threshold quantity. The list includes chemical name, Chemical Abstracts Service (CAS) number, and the threshold quantity given in pounds.

Chemical name	CAS No.	Threshold quantity (TQ), lbs.
Fluorine	7782-41-4	1000
Hydrogen fluoride	7664-39-3	1000

Sect. 1910.1000: Air contaminants. An employee's exposure to any substance listed in Tables Z-1 of this regulation shall be limited in accordance with the requirements of the paragraphs of this section.

Substance	CAS No.	ppm	mg/m^3	Skin designation
Fluorides (as F)		---	2.5	----
Fluorine	7782-41-4	0.1	0.2	----
Hydrogen fluoride (as F)	7664-39-3			

Sect. 1910.306(h): Specific-purpose equipment and installations. Electrolytic cells. (1) Scope. These provisions for electrolytic cells apply to the installation of the electrical components and accessory equipment of electrolytic cells, electrolytic cell lines, and process power supply for the production of aluminum, cadmium, chlorine, copper, fluorine, hydrogen peroxide, magnesium, sodium, sodium chlorate, and zinc. Cells used as a source of electric energy and for electroplating processes and cells used for production of hydrogen are not covered by these provisions.

4.3.2 Part 1915: Occupational Safety and Health Standards for Shipyard Employment

This part applies to all ship repairing, shipbuilding, and shipbreaking employments and related employments.

Sect. 1915.1000: Air contaminants. Wherever this section applies, an employees's exposure to any substance listed in Table Z—Shipyards of this section shall be limited in accordance with the requirements provided in this section of the regulations.

Substance	CAS No.	ppm	mg/m^3	Skin Designation
Fluorides (as F)	Varies with compound	---	2.5	----
Fluorine	7782-41-4	0.1	0.2	----
Hydrogen fluoride (as F)	7664-39-3	3	2	----

4.3.3 Part 1926: Safety and Health Regulations for Construction

This part sets forth the safety and health standards promulgated by the Secretary of Labor under Sect. 107 of the Contract Work Hours and Safety Standards Act. It also contains statements of general policy and interpretations of Sect. 107 of this act having general applicability.

Sect. 1926.55: Gases, vapors, fumes, dusts, and mists. This section of the regulations establishes that the exposure of employees to inhalation, ingestion, or skin absorption or contact with any material or substance at a concentration above those specified in the "Threshold Limit Values of Airborne Contaminants for 1970" of the American Conference of Governmental Industrial Hygienists shall be avoided (as shown in Appendix A of Part 1926.55).

Substance	CAS No.	ppm	mg/m^3	Skin Designation
Fluorine	7782-41-4	0.1	0.2	--
Hydrogen fluoride (as F)	7664-39-3	3	2	--

Sect. 1926.64: Process safety management of highly hazardous chemicals. This section contains requirements for preventing or minimizing the consequences of catastrophic releases of toxic, reactive, flammable, or explosive chemicals. These releases may result in toxic, fire or explosion hazards.

Appendix A to Sect. 1926.64—list of highly hazardous chemicals, toxics and reactives (mandatory). This appendix contains a listing of toxic and reactive highly hazardous chemicals which present a potential for a catastrophic event at or above the threshold quantity.

Chemical name	CAS	TQ, lb.
Hydrogen fluoride	7664-39-3	1000
Fluorine	7782-41-4	1000

4.4 TITLE 40—PROTECTION OF ENVIRONMENT

These regulations are issued by the U.S. Environmental Protection Agency. Fluorine and fluorine compounds regulations are included in parts about (1) chemical accident prevention provisions and (2) standards for the management of specific hazardous wastes and specific types of hazardous waste management facilities

4.4.1 Part 68: Chemical Accident Prevention Provisions

This part sets forth the list of regulated substances and thresholds, the petition process for adding or deleting substances to the list of regulated substances, the requirements for owners or operators of stationary sources concerning the prevention of accidental releases, and the state accidental release prevention programs approved under Sect. 112(r). The list of substances, threshold quantities, and accident prevention regulations promulgated under this part do not limit in any way the general duty provisions under Sect. 112(r)(1).

Sect. 68.22: Offsite consequence analysis parameters. The Table of Toxic Endpoints (as defined in Sect. 68.22 of this part) is as follows:

CAS No.	Chemical name	Toxic endpoint (mg/L)
7782-41-4	Fluorine	0.0039

Sect. 68.130: List of substances. The section lists regulated toxic and flammable substances under Sect. 112(r) of the Clean Air Act. Threshold quantities for listed toxic and flammable substances are specified in the tables. The following table from this section of the regulations has the list of regulated toxic substances and TQ for accidental release prevention.

Chemical name	CAS No.	TQ (lb)	Basis for listing
Fluorine	7782-41-4	1,000	On EHS list, vapor pressure 10 mm Hg or greater.
Hydrogen Fluoride/Hydrofluoric acid (concentration 50% or greater) Hydrofluoric acid	7664-39-3	1,000	Mandated for listing by Congress. On EHS list, vapor pressure 10 mm Hg or greater.

Regulated toxic substances and TQ for accidental release prevention are listed in Sect. 68.130.

CAS No.	Chemical name	TQ (lb)	Basis for listing
7782-41-4	Fluorine	1,000	On EHS list, vapor pressure 10 mm Hg or greater
7664-39-3	Hydrogen fluoride/hydrofluoric acid (concentration 50% or greater) Hydrofluoric acid	1,000	Mandated for listing by Congress. On EHS list, vapor pressure 10 mm Hg or greater.

4.4.2 Part 266: Standards for the Management of Specific Hazardous Wastes and Specific Types of Hazardous Waste Management Facilities

Sect. 266.206: Standards applicable to the treatment and disposal of waste military munitions. The treatment and disposal of hazardous waste military munitions are subject to the applicable permitting, procedural, and technical standards in 40 CFR Parts 260 through 270. Appendix IV to this part of the regulations lists the reference air concentrations of some substances.

Constituent	CAS No.	Reference air concentration ($\mu g/m^3$)
Fluorine	7782-41-4	50

Appendix VII to this part of the regulations lists the health-based limits for exclusion of waste-derived residues of some nonmetals.

Constituent	CAS No.	Concentration limits for residues (mg/kg)
Fluorine	7782-41-4	4.0

4.4.3 Part 302: Designation, Reportable Quantities, and Notification

This regulation designates under section 102(a) of the Comprehensive Environmental Response, Compensation, and Liability Act of 1980 ("the Act") those substances in the statutes referred to in section 101(14) of the Act, identifies reportable quantities for these substances, and sets forth the notification requirements for releases of these substances. This regulation also sets forth reportable quantities for hazardous substances designated under section 311(b)(2)(A) of the Clean Water Act.

4.4.4 Part 355: Emergency Planning and Notification

This regulation establishes the list of extremely hazardous substances, threshold planning quantities, and facility notification responsibilities necessary for the development and implementation of state and local emergency response plans. The requirements of this section apply to any facility at which there is present an amount of any extremely hazardous substance equal to or in excess of its threshold planning quantity, or designated, after public notice and opportunity for comment, by the Commission or the Governor for the state in which the facility is located. For purposes of this section, an amount of any extremely hazardous substance means the total amount of an extremely hazardous substance is present at any one time at a facility at concentrations greater than 1 wt %, regardless of location, number of containers, or method of storage.

4.4.5 Part 372: Toxic Chemical Release Reporting: Community Right-To-Know

This part sets forth requirements for the submission of information relating to the release of toxic chemicals under section 313 of Title III of the Superfund Amendments and Reauthorization Act of 1986. The information collected under this part is intended to inform the general public and the communities surrounding covered facilities about releases of toxic chemicals, to assist research, to aid in the development of regulations, guidelines, and standards, and to serve other purposes. This part also sets forth requirements for suppliers to notify persons to whom they distribute mixtures or trade name products containing toxic chemicals that they contain such chemicals.

4.5 DOE ORDERS

4.5.1 DOE Order 6430.1A DIV 1-7: General Design Criteria (GDC)

This order provides GDC to use in the acquisition of the DOE's facilities and to establish responsibilities and authorities for the development and maintenance of these criteria.

Sect. 1322-4.3: Uranium recovery facilities. In addition to provisions for handling uranium and other radioactive materials such as trace quantities of fission products and transuranics, the design shall provide for the safe handling of other hazardous materials (e.g., acids, bases, organic solvents, fluorine, hydrogen, hydrogen fluoride, and magnesium) used or generated during recovery operations.

Sect. 1530-99.12.1: Gaseous diffusion and centrifuge facilities. Storage areas for UF_6 and process areas handling UF_6 shall be physically isolated from other areas by fire-resistant barriers. In addition, UF_6 storage areas shall be protected by water sprinklers designed to keep the UF_6 area cool in case of fire. Fire-resistant physical-isolation barriers shall be designed for both the fluorine gas storage area and process areas that use fluorine. All off-gas that can contain fluorine (or hydrogen fluoride) shall be scrubbed with a caustic (or equivalent) solution in a scrubber to reduce hydrogen fluoride, fluorine, and ozone (minor product resulting from reaction between fluorine and moisture) in the off-gas to less than the allowable EPA emission limits.

Jet exhausters and caustic or soda-lime traps shall be provided to purge manifold pigtail connections.

Nitrogen shall be used as a fluorine system purge.

Fluorine and hydrogen fluoride monitors shall be provided at strategic points to detect and to cut off fluorine flow at the source (by self-activation of the monitor and positive shutoff valves).

Sect. 1530-99.16: Uranium conversion and recovery facilities. Fire-resistant, physical isolation barriers shall be designed for both the fluorine gas storage area and process areas that use fluorine. All off-gas that can contain fluorine (or hydrogen fluoride) shall be scrubbed with a caustic (or equivalent) solution in a scrubber to reduce hydrogen fluoride, fluorine, and ozone (minor product resulting from reaction between fluorine and moisture) in the off-gas to less than the allowable EPA emission limits.

Jet exhausters and caustic or soda-lime traps shall be provided to purge manifold pigtail connections.

Nitrogen shall be used as a fluorine system purge.

Sect. 1574: Cryogenic systems

Sect. 1574-1: Coverage. These criteria shall apply to cryogenics as defined by the National Bureau of Standards (NBS), that is, involving temperatures below 120 K (−124ºF). Systems involving hydrogen and methane are not covered by these criteria. Systems involving oxygen and fluorine (because of their reactivity) may require special design and cleanliness requirements in addition to these basic criteria.

4.6 OSHA

The OSHA establishes the federal regulatory framework for the control of workplace safety. OSHA's goal is to make sure employers provide their workers a place of employment that is free from recognized hazards to safety and health, including exposure to toxic chemicals. OSHA establishes permissible exposure limits (PELs) to regulate workplace exposure to air contaminants. The universe of substances covered by OSHA PELs has largely been determined by whether a substance has a Threshold Limit Value (TLV), a voluntary exposure standard developed by the American Conference of Governmental Industrial Hygienists (ACGIH).

Two volumes of information provide industrial exposure data and control technologies for fluorine and 649 other substances that are currently regulated, or are candidates for regulation, by the OSHA.[3] The health, toxicity, economic, and technological data provided are intended to serve as a reference for those who are potentially exposed to one or more of these substances in their workplace.

4.6.1 Description of Substance

Fluorine is a pale, yellow gas with a pungent, irritating odor. It is the most reactive nonmetal and will react vigorously with most oxidizable substances at room temperature, frequently with ignition.

4.6.2 Health Effects

Fluorine is a severe irritant of the eyes, mucous membranes, skin, and lungs. In humans, the inhalation of high concentrations causes laryngeal spasm and broncospasms, followed by the delayed onset of pulmonary edema. At sublethal levels, severe local irritation and laryngeal spasm will preclude voluntary exposure to high concentrations, unless the individual is trapped or incapacitated. A blast of fluorine gas on the shaved skin of a rabbit causes a second degree burn. Lower concentrations cause severe burns of insidious onset, resulting in ulceration, similar to the effects produced by hydrogen fluoride.

Chronic absorption can cause osteosclerosis and calcification of ligaments. Inhalation of fluorine causes coughing, choking, and chills lasting 1–2 h after exposure. After an asymptomatic period of 1–2 d, fever, cough, tightness in chest, rales, and cyanosis indicate pulmonary edema. Symptoms progress for 1–2 d and then regress slowly over a period of 10–30 d.

Small amounts of gas in the air have been reported to be strongly irritating to exposed portions of bulbar conjunctiva, to cornea, and to eyelids. Exposure of volunteers to fluorine in air showed it caused very little irritation up to 25 ppm, caused much irritation of eyes and nose at 100 ppm. There were no after effects from exposure of eyes to 100 ppm for 0.5 min. Contact with high concentrations of fluorine gas or liquid fluorine would be extremely dangerous. In animals, liver and kidney damage has been observed.

4.6.3 Toxicity Hazard Rating

Acute local: irritant 3. Acute systemic: irritant 3. Chronic systemic: ingestion 3; inhalation 3. (A rating of 3 is considered high and may cause death or permanent injury after very short exposure to small quantities).

Immediately dangerous to life or health : 25 ppm

OSHA Permissible Exposure Limit (PEL): 1.00 ppm, 2.00 mg/m^3; time-weighted average (TWA)
ADOPTED ACGIH/threshold limit value (TLV): 1.00 ppm, 2.00 mg/m^3; TWA and 2.00 ppm, 4.00 mg/m^3; STEL.

4.6.4 Industry-Use Data

- Manufacture of fluorochemicals, plastics, and rocket propellant
- Chemical intermediate for sulfur hexafluoride, chlorine trifluoride, bromine trifluoride, uranium hexafluoride, molybdenum hexafluoride, perchloryl fluoride, and oxygen difluoride
- Uranium fluorochemicals
- Trace amounts in animal feed

4.6.5 Engineering Data Controls

General ventilation, local exhaust ventilation, hood, and enclosure of process worker.

4.6.6 Personal Protective Equipment

People should wear positive pressure breathing apparatus and special protective clothing. Workers handling dangerous substances should be supplied with eye and face protection, respiratory protective equipment, protective clothing, and foot and leg protection. Personal safety precaution include full gas-tight protective clothing. Respiratory protection should be as follows: up to 1 ppm—any supplied-air respirator or self-contained breathing apparatus. Up to 2.5 ppm—any supplied air respirator operated in a continuous flow mode. Substances reported to cause eye irritation or damages—may require eye protection. Up to 5 ppm—any supplied air respirator with a full face-piece. Up to 25 ppm—any supplied air-respirator with a half mask and operated in a pressure-demand or other positive pressure mode.

Substance reported to cause eye irritation or damage may require eye protection.

For emergency or planned entry in areas containing unknown concentrations, the following equipment should be used: any self-contained breathing apparatus with a full face piece and operated in the pressure demand mode or other positive pressure mode or any supplied-air respirator with a full face-piece and operated in the pressure mode or any supplied-air respirator with a full face-piece and operated in the pressure-demand or any other positive pressure mode or any appropriate self-contained breathing apparatus.

4.6.7 Storage

Protect against physical damage. Isolate from other items being stored, especially materials with which fluorine is known to react. Keep away from sources of heat and ignition.

4.7 DOE PLANT SAFETY STANDARDS

Several DOE sites have safety standards for handling fluorine, including Oak Ridge Gaseous Diffusion Plant (ORGDP) [now known as the East Tennessee Technology (ETTP)] and the Lawrence Livermore National Laboratory (LLNL).

4.7.1 ORGDP Safety Standards

The ORGDP had safety standards for its operations that included the handling of fluorine. The information is contained in reference document number K-SS-1.1.[4] What follows is a transcription of this document.

Safety Standard Oak Ridge Gaseous Diffusion Plant, K-SS-1.1 App.: Compressed Cylinder Gas-Safety Guide

D. Fluorine [Oxidizer Gas (OG)] F_2

1. Double valving shall be employed near the source of high-pressure fluorine to facilitate a safe reduction of pressure. Regulators and double valving are required where large quantities of fluorine are being handled, such as when handling manifolded pigs.
2. Any equipment to be used for fluorine service shall first be thoroughly cleaned, degreased, and dried, and then treated with increasing concentrations of fluorine gas so that any impurities may be burned out without the simultaneous ignition of the equipment.
3. Clean neoprene gloves should be worn when directly handling equipment which contains fluorine or has recently contained fluorine. This precaution not only affords protection against fluorine, but also against films of hydrofluoric acid which may be formed by escaping fluorine reacting with moisture in the air. Neoprene coats and boots may be required to afford overall body protection for short intervals of contact with low-pressure fluorine. All such protective clothing should be designed and used, however, in such a manner that it can be shed easily and quickly. Protective clothing shall be maintained clear of any foreign matter that would result in a fire hazard.
4. Chemical goggles and face shields should be worn at all times. Face shields made of transparent, highly fluorinated polymers like Genetron Plastic VK™ should be worn whenever operators must approach equipment containing fluorine under pressure. All face shields afford limited (though valuable) protection against air-diluted blasts of fluorine.
5. Avoid repeated bending or excessive vibration of piping or equipment. Such mechanical action can result in a flaking of the protective fluoride film, resulting in a rupture of the metal with or without the occurrence of a fluorine-metal flame. Flaking, furthermore, can be accompanied by dusting with the resultant fouling of valves.
6. Any equipment that has contained fluorine must be thoroughly purged with a dry nitrogen or inert gas and evacuated prior to opening or refilling. If the quantity of fluorine to be purged is large, the purge system should include a fluorine-hydrocarbon-air burner, scrubber, and stack to prevent any undue exit hazards. A soda-lime tower followed by a drier should be included in the vacuum line to pick up trace amounts of fluorine in order to protect the vacuum pump.
7. All areas containing fluorine under pressure should be inspected for leaks at suitable intervals. All leaks should be repaired at once, but not while the system contains fluoride. It is recommended that all headers from the fluorine supply be measured for wall thickness (containing ammonium

hydroxide) at suspected points may be used to a very sensitive means of detecting fluorine (down to about 25 ppm). The potassium iodine paper should be held with the aid of 18–24 in. long metal tongs or forceps. The odor of fluorine is sufficiently strong such that it can be detected in very low concentrations. Fluorine will also fume readily in air.

8. Adequate ventilation is essential. There should be a minimum of ten air changes per hour for enclosed spaces. Portable floor-level 36-in. fans are desirable for auxiliary ventilation at outdoor installations or semiopen installation.
9. Positive instant-acting types of safety showers and eye-washing fountains shall be strategically located near the area where fluorine is being used. These should be tested at least weekly.
10. Air-line hose masks shall be located in strategic positions for use in emergencies.
11. It is recommended that personnel work in pairs and within sight and sound of each other, but not in the same immediate working area. Only trained and competent personnel should be permitted to handle fluorine. Frequent checks should be made of the operation.
12. An alarm system should be provided so that the area may be alerted and cleared, if needed.
13. Do not store with fuel gases (FGs).

4.7.2 LLNL's Health & Safety Manual, Supplement Document 21.12: Safe Handling of Fluorine

This supplement to the Health &Safety Manual describes the common hazards associated with fluorine and details engineering and procedural controls required for its safe use. This supplement is organized according to the process anyone must go through to safely handle fluorine at LLNL: (1) education on the chemical and physical hazards of fluorine, (2) design the fluorine system with appropriate engineering controls, and (3) understanding of the procedure for purchasing fluorine and the administrative controls for the safe use of fluorine and the maintenance of fluorine systems. Appendix D expands this document.

The section of this document on hazards of fluorine refers to the reactivity and toxicity of the fluorine. The section on health hazards talks about the health effects on the worker exposed to fluorine contamination. The section on precautions for the safe use of fluorine describes (a) the appropriate engineering controls, (b) administrative controls, (c) procedural controls, (d) personal protective equipment, (e) fluorine emergency procedures, (f) accepted materials for fluorine system components, (g) fluorine system cleaning and passivation procedures.

4.8 INDUSTRIAL HANDLING OF FLUORINE COMPOUNDS

Industrial practices on how to handle fluorine and fluorine compounds are given by some chemical companies. One of these companies is Pennsalt Chemicals, and the handling requirements that Pennsalt deems necessary are as follows:[5]

4.8.1 Handling Hydrofluoric Acid

Hydrofluoric acid can be handled safely if proper provision is made for its physical and corrosive characteristics and for the hazards it presents to personnel. Despite careful design and construction practice, the possibility of human or mechanical failure remains, and additional precautions must be taken to provide protection for employees in the event of accidental release of hydrofluoric acid (HF) liquid or vapor. Some of the items that may be required for a possible exposure to HF include:

- Coveralls or other clothing that will protect all skin areas and that fit tightly at wrists and neck
- Gauntlet-type gloves of a resistant material such as neoprene or polyvinylidene chloride
- Full face mask and chemical goggles with plastic lenses
- Protective head covering
- Rubber shoes or boots with neoprene or some equally resistant materials for soles
- Complete rubber suit, which provides maximum protection against liquid
- Self-contained breathing apparatus for those who must enter tanks
- Positive pressure hose masks, air line masks, or self-contained breathing equipment that is readily available for use when vapor concentrations in the air are high.

Personnel handling HF should be educated to its hazards, and a continuing safety training program should be in effect wherever hydrofluoric acid is handled or used.

Materials and equipment for use with hydrofluoric acid. The choice of a material to be used with hydrofluoric acid will be governed by the conditions of a particular application. Four factors require consideration—concentration, temperature, velocity of movement of the acid, and the presence of other chemicals in the solution. As the acid increases in strength from dilute solutions of 5–10 wt % to the anhydrous materials, marked changes take place in the nature of its corrosive action. For example, below 60–65 wt % it attacks lead very slowly, whereas at higher concentrations, lead is practically nonresistant. Below 60–65 wt %, mild steel is attacked rapidly; at concentrations above this range, very little attack is evident on steel of the proper composition.

Rubber, neoprene, and many plastics show a similar concentration dependence in their resistance to hydrofluoric acid. Their resistance to weak solutions is generally good, but they are increasingly attacked as concentration rises. The exception to this are the fluorine-containing polymers, which show good HF resistance both to acid solutions and anhydrous hydrofluoric acid (AHA).

Elevated temperatures tend to accelerate the rate of attack on structural materials by hydrofluoric acid. Carbon steels are generally used below 150^{o}F. Above this temperature, it is usually necessary to use Monel or other special alloy metals. Initial contact with hydrofluoric acid will cause some attack even on highly resistant metals. The reaction forms a metal fluoride layer on the surface. This layer prevents further attack as long as the film remains unbroken. Some metals are "velocity sensitive" (i.e., flow of acid erodes the film, exposing the surface and allowing further attack by the acid). Velocity sensitive materials are generally avoided in valves, piping, and other equipment where they come into contact with moving acid.

Rubber, leather, most organic materials, and those containing silica are readily attacked by AHA and by its solutions. This susceptibility to attack precludes the storage and handling of HF in glass, concrete, cast iron, and many organic container materials.

4.8.2 Handling Anhydrous Hydrofluoric Acid

Materials of construction. Mild steel, Monel, and some of the plastics including, Teflon™ and Kel-F™ will handle AHA satisfactorily at temperatures below 150^{o}F. When temperatures above 150^{o}F are encountered, Monel is usually recommended. Copper has been used for some applications at high temperatures, although it is velocity sensitive and is attacked readily in the presence of H_2S or SO_2. Magnesium, some of the Dow metals, and copper-nickel alloys have been reported as satisfactory for high-temperature AHA service, but experience with these materials has been limited.

Storage tanks. AHA tanks must be corrosion resistant and strong enough to withstand the pressures normally applied when unloading tank cars and transferring acid from storage to process. Storage tanks should be made of mild-flange steel and designated to conform with the American Society of Mechanical Engineers (ASME) code for unfired vessels. AHA tanks must be provided with inside support to prevent collapse in the event of internal pressure drops below atmospheric pressure. Design pressure requirements will determine the thickness of the steel plate, but the minimum for any tank should be 3/8 in. As an additional precaution, it is recommended that the plate be specified 1/8 in. thicker than that required by the ASME code to allow for initial corrosion before the surface becomes pacified. The tank should be shielded-arc, butt-welded inside and out, and the welds should be free from slag and other nonmetallic inclusions. A bolted steel-plate manhole for access and nipples and flange-type nozzles for transferring acid should also be specified, as required. The acid is usually withdrawn through an eduction pipe and nozzle at the top of the tank by means of compressed air or a positive displacement pump. Bottom outlets should be avoided, but, if necessary, they should be double valved with inside drop-plug valves. Tank content can be gaged most satisfactorily by mounting the tank on load cells or strain gauges.

Valves, pumps, and piping. Schedule 80 (extra heavy) seamless or welded steel pipe is recommended as the minimum for AHA service. If welded pipe is used, the welds must be free from slag and other nonmetallic inclusions. Welded connections which conform to Sect. 8 of the ASME code should be used whenever possible. Glove, gate, and plug-type valves are all satisfactory for use with AHA. The valves should be all-Monel, forged steel. Parts in all-steel valves tend to freeze due to the formation of fluorides and are no longer recommended. In larger sizes, OS and Y flanged types are used. Smaller sizes, such as those used for vents, may be block valves. Teflon and Kel-F packings are recommended for all AHA valves.

The preferred procedure for transferring AHA is by means of dry compressed air and moving the material by differential pressure. Hydrofluoric acid may be transferred with air having a dew point as high as -10^{o}F; however, -40^{o}F is considered optimum. In the presence of damp air, AHA will form aqueous HF which may become entrapped in sections of equipment, thus, causing corrosion damage. AHA may be pumped if necessary, using all-bronze or Monel centrifugal or gear pump.

Unloading AHA tanks cars. AHA may be transferred from tank cars to storage by means of differential pressure or by pumping. The use of compressed air is recommended, however. Procedures for both methods are given as follows for the benefit of those whose facilities may not include a compressor or other source of pressure. Figures C.1 and C.2 (Appendix C) are schematic drawings showing suggested equipment layouts for unloading AHA tank cars. The accompanying schedules give detailed instructions for the layouts shown. The figures and their accompanying schedules are provided as guides. Other arrangements are possible provided they are designed with proper consideration for safety.

Preliminary operation. Whether the car is to be unloaded by pressure or by pump, the same preliminary schedule applies. Spot the car accurately at the unloading line. Set brakes, block wheels, and properly place derails and caution signs at each end of the car. Lift the dome cover and make certain that all service valves on the car are closed tightly before making any connections to the car. If there is any sign of leakage when removing the plugs from valves, retighten the valve immediately and use the alternate valve.

Unloading with compressed air. Compressed air used for unloading AHA must be dry and oil free. To ensure this, the air line is equipped with a separator, and the air supply is taken from the top of the reservoir. Always blow out the air line before connecting it to the tank car. Although 180 psi is the maximum safe unloading pressure, 150 psi is normally sufficient and is recommended as a maximum. High pressures will rupture safety devices on hydrofluoric acid tank cars and storage tanks. Unloading any AHA tank car requires the following operation:

- Connect the unloading line and air pressure line to the tank car
- Equalize the pressures in the tank car and the storage tank if necessary
- Set the air pressure to provide proper padding
- Apply air to the car and transfer the acid to the storage tank
- Vent and drain liquid and air lines
- Disconnect lines, close that car, and prepare it for return shipment

Unloading by pump. The preliminary operations mentioned previously apply to pump unloading as well as to differential pressure transfer. In Fig. C.2 of Appendix C, an air line is provided in case the pump has to be primed. The following general schedule of operations is usually followed when using a pump for unloading hydrofluoric acid:

- Connect the unloading and pressure equalizing lines to the tank car
- Equalize pressures in car and storage tank, if necessary, and provide for maintaining equal pressures during unloading
- Transfer acid to storage
- Clear and drain lines
- Disconnect lines, close the car, and prepare it for return shipment

4.8.3 Handling 70% Aqueous Hydrofluoric Acid

Materials of construction. Low carbon steel has been found to be the most satisfactory material for general use with 70% aqueous hydrofluoric acid. Note, however, that mild steel is not sufficiently resistant for aqueous HF in concentrations of less than about 65%. Monel resists 70% hydrofluoric acid and is often used for valve trim. Among the plastics, Teflon, Kel-F, polyethylene, polyvinyl chloride (PVC), and polyvinylidene chloride are satisfactory for aqueous HF service.

Storage tanks. The requirements for a 70% hydrofluoric acid tank are generally the same as those for anhydrous acid tanks. The tank should be made of mild steel and constructed to conform with the Unfired Pressure Vessel Code of the ASME. Plate thickness will be determined by capacity; 3/8 in. is considered minimum for small tanks. For safety, specify 1/8 in. over the required minimum to allow for corrosion before the tank becomes specified. The tank should be shielded-arc, butt-welded inside and out. All welds must be slag free. Acid from the top of the tank is withdrawn through an eduction pipe. If bottom outlets are necessary, they should be double valved and provided with inside drop plug valves.

Valves, pumps, and piping. Seamless or welded steel pipe and welded construction are recommended for 70% HF service. Forged-steel welding fittings should be used throughout. Whenever a flanged connection has to be used, it should be sealed with a Teflon or Kel-F envelope gasket. All Monel, steel with Monel trim, or bronze with Monel trim, and globe or gate valves are used with 70% hydrofluoric acid. Outside screw and yoke types are preferred for larger-sized valves. Vents and other small valves can be block valves. Other suitable aqueous HF valves include plug valves with Teflon, Kel-F, or polyvinylidene chloride sleeves and diaphram valves with polyethylene, PVC, polyvinylidene chloride, Kel-F or Teflon-lined bodies and polyethylene, and Teflon or Kel-F diaphrams.

Seventy percent hydrofluoric acid can be moved with dry compressed air or with a pump. If there is a choice between the two, the pressure method is preferred. All-bronze or all-Monel positive displacement pumps are satisfactory for aqueous acid service.

Unloading aqueous hydrofluoric acid tank cars. Both pumping and pressure unloading are acceptable means for transferring aqueous HF, although the pressure method is preferred. Procedures for both methods are outlined below. Figures C.3 and C.4 of Appendix C illustrate typical equipment layouts schematically. The accompanying detailed schedules apply to the layouts shown. Variations can be made in the detailed procedures—provided they are made according to recognized safety practices.

Preliminary operations. Before connecting transfer lines to the tank car, make certain the car is accurately spotted at the unloading station. Make sure, too, that all car valves are tightly closed. Set the brakes and block wheels and properly place derails and caution signs at each end of the car.

Unloading with compressed air. Only dry, oil-free air should be used for aqueous hydrofluoric acid transfer. Install an air dryer in the line and take the air from the top of the reservoir. Always blow out the line before connecting it to the tank. The safety-relief device on the tank car limits the amount of pressure that can be applied to the car during unloading. If 30 psi is not enough to transfer the acid, a booster pump will have to be provided. The schedule for unloading aqueous hydrofluoric acid tank cars with compressed air involves the following operations:

Connect the unloading line and air pressure lines to the tank car; equalize pressures if necessary
Apply pressure to the car
Transfer acid to storage
Clear and drain lines
Disconnect lines, close the car, and prepare it for return shipment

Unloading by pump. If a source of pressure is not available or if more than 30 psi would be needed to transfer acid, aqueous HF should be pumped to storage. The same preliminary schedule applies to both pump unloading and air-pressure transfer. The following operations constitute a pump-unloading schedule:

Connect the unloading and air pressure lines to the tank car, equalize pressures if necessary
Pump the acid to storage
Clear and drain the lines
Disconnect lines and close the car and prepare it for return shipment

Handling AHA in drums. Seventy percent aqueous hydrofluoric acid is available in drums as well as in tank cars. Table 1 shows the available drums, approximate net contents, and ICC specifications.

Table 1. Seventy percent hydrofluoric acid drums

	ICC specification	Approximate net content (lb)
Steel drum	5A	900
Steel drum—polyethylene insert	6J-2S	450
Steel drum	5A	450
Steel drum—polyethylene insert	6J-2S	260
Steel drum	5A	165

Steel drums. Steel drums for hydrofluoric acid are passivated before being put into service to minimize corrosion; however, despite passivation, hydrogen may be generated in steel drums during shipment or storage. To relieve any excess pressure, the drums must be vented on arrival and at least once a week during storage. Loosening the plug carefully with a long-handle wrench will reduce the pressure in the container. Employees should wear adequate protective clothing when venting hydrofluoric acid drums.

Always check to be sure that the closures are tight before moving HF drums. If the closures are tight, steel drums may be moved by rolling them on their hoops. Heavier drums may be lifted by means of a hoist with a chain and drum hook attachment, engaging the drum at the chimes. A double sling can also be used, provided that the sling circles the drum outside its rolling hoops.

Store steel drums on their sides, bung up. Avoid exposing the drums to dampness, heat, and sunlight by storing them in cool, dry locations away from heat, flames, sparks, and combustible material. Drums, stored outside or in buildings without floors, should be raised so that they are not in contact with the ground. Store the drums on a first-in, first-out schedule to avoid prolonged storage.

Polyethylene drums. Polyethylene drums are inserted in a steel drum, which provides protection. Polyethylene-insert drums are moved by hand truck or by rolling them on the bottom chime. Hydrofluoric acid will not attack the polyethylene drums to form hydrogen, thereby eliminating the need for periodic venting.

Stand polyethylene-insert drums upright during storage. Store the drums in cool, dry areas where they are sheltered from dampness, heat, and direct sunlight. Avoid storing HF drums near combustible materials. Drums that are stored outside or in buildings without floors should be raised so that they are not in contact with the ground. Storage should be arranged on a first-in, first-out basis.

Emptying. Drums containing hydrofluoric acid should be emptied by gravity. Never use air pressure to empty an HF drum. Aqueous HF can also be removed from drums by means of a pump or a siphon made of an HF-resistant material.

Never add water or other foreign material to the contents of a steel drum containing hydrofluoric acid. Introduction of water or other materials will change the concentration of the acid, thus allowing serious internal corrosion in steel drums. The introduction of foreign materials can also lead to the generation of dangerous internal pressure.

4.9 FLUORINE: A COMPRESSED GAS MANUAL FROM THE COMPRESSED- GAS ASSOCIATION

The information contained in this section is taken from the *Handbook of Compressed Gases*, issued by the Compressed Gas Association.[6]

4.9.1 Description

Fluorine is a highly toxic, pale-yellow gas about 1.7 times heavier than air at atmospheric temperature and pressure. Heats of reaction with fluorine are always high, and most reactions take place with ignition. Fluorine at low pressures and concentrations reacts slowly with many metals at room temperatures, however, and the reaction often results in formation of a metal fluoride film on the metal's surface; in the case of some metals, this film retards further action.

Fluorine gas is a powerful caustic irritant and is highly toxic. Contact between the skin and high concentration of fluorine gas under pressure will produce burns comparable with thermal burns; contact with lower concentrations results in a chemical type of burn resembling that caused by hydrofluoric acid.

4.9.2 Safe Handling and Storage

Materials suitable for containers and storage. Nickel, iron, aluminum, magnesium, copper, and certain alloys are quite satisfactory for handling fluorine at room temperature, for these are among the metals which form a surface fluoride film that retards further action. Listed in Table 2 are various materials that have been used with satisfactory results in gaseous fluorine service at normal temperatures and liquid service at low temperatures.

Nickel and Monel are generally considered to be by far the best materials for fluorine service at high temperatures and pressures, but selection of suitable materials for service at elevated temperatures and pressures must be based on the conditions of the specific application.

Table 2. Materials to handle gaseous and liquid hydrofluoric acid

Type of equipment	Gaseous service, normal temperature	Liquid service, low temperature
Storage tanks	Stainless steel type 304L	Monel
	Aluminum 6061	Stainless steel type 304L
	Mild steel (low pressure)	Aluminum 6061
Lines and fittings	Nickel	Monel
	Monel	Stainless steel type 304L
	Copper	Copper
	Brass	Aluminum 1100
	Stainless steel type 304L	
	Aluminum 2017, 2024, 5052, 6061	
	Mild steel (Low Pressure)	
Valve bodies	Stainless steel type 304	Monel
	Bronze	Stainless steel type 304
	Brass	Bronze
Valve seats	Copper	Copper
	Aluminum 1100	Aluminum 1100
	Stainless steel type 303	Monel
	Brass	Bronze
Valve plugs	Stainless steel type 304	Stainless steel type 304
	Monel	Monel
Valve packing	Tetrafluoroethylene polymer	Tetrafluoroethylene polymer
Valve bellows	Stainless steel 300 series	Stainless steel 300 series
	Monel	Monel
	Bronze	Bronze
Gaskets	Aluminum 1100	Aluminum 1100
	Lead	Copper
	Copper	
	Tin	
	Tetrafluoroethylene polymer	
	Red rubber (5 psig)	
	Neoprene (5 psig)	

Storage and handling in normal use. All precautions necessary for the safe handling of any flammable gas must be observed with fluorine, in addition to the precautions outlined below. Fluorine fires that break out may be most simply extinguished by first cutting off the fluorine supply at a primary point and using then conventional fire-fighting methods. The dry types of extinguishers are recommended. Only trained and competent personnel should be permitted to handle fluorine. Supervisory personnel should make frequent checks of the operations.

Personal protective equipment. Clean neoprene gloves must be worn when handling equipment which contains (or has recently contained fluorine). This precaution affords not only limited protection against fluorine contact but also protection against contact with possible films of hydrofluoric acid that are formed by escaping fluorine and air moisture that collect on valve handles and other surfaces. Neoprene coats and boots afford overall body protection for short intervals of contact with low-pressure fluorine. All protective clothing must be designed and used so that it can be shed easily and quickly. Safety glasses must be worn at all times.

Face shields (made preferably of transparent, highly fluorinated polymers like Aclar™) should be worn whenever operators must approach equipment containing fluorine under pressure. Face shields made of any conventional materials afford limited, though valuable, protection against air-diluted blasts of fluorine.

Leak detection. All areas containing fluorine under pressure should be inspected for leaks at suitable intervals, and any leaks discovered should be repaired at once after fluorine has been removed from the system. Ammonia vapor expelled from the squeeze bottle of ammonium hydroxide at suspected points of leakage may be used to detect leaks. Filter paper moistened with potassium iodide provides a very sensitive means of detecting fluorine; when using it, hold the paper with metal tongs or forceps about 18–24 in. long.

Equipment preparation and decontaminating. Equipment to be used for fluorine service should first be thoroughly cleaned, degreased and dried, and then treated with increasing concentrations of fluorine gas so that any impurities will be burned out without the simultaneous ignition of the equipment. The passive metal fluoride film thus formed will inhibit further corrosion by fluorine.

Before opening or refilling equipment that has contained fluorine, thoroughly purge it with a dry inert gas (such as nitrogen) and evacuate it if possible. Minor quantities of fluorine to be vented and purged can be converted to harmless carbon fluoride gases by passage through a lump-charcoal-packed column. Large quantities to be purged require a purge system with a fluorine-hydrocarbon-air burner, scrubber, and stack to prevent any undue exit hazards. Should a purged fluorine system require evacuation, a soda-lime tower followed by a drier should be included in the vacuum system to pick up trace amounts of fluorine in order to protect the vacuum pump.

Liquid-fluorine spills. In the event of a large spillage of liquid fluorine, the contaminated area can be neutralized with sodium carbonate. The dry powder can be sprayed on the spill area from a fluidized system similar in principle to that of dry-chemical fire extinguishers. If major spillage occurs in areas where the formation of hydrofluoric acid liquid and vapor pose no undue danger, water in the form of a fine mist or fog is recommended. The major portion of the fluorine will be converted to hot, light gaseous products which rise vertically and diffuse quickly into the atmosphere.

4.9.3 Methods of Shipment: Regulations

Under the appropriate regulations and tariffs, fluorine is authorized for shipment as follows:

By rail	In cylinders (via freight and express rates to a maximum quantity of 6 lb in one outside container).
By highway	In cylinders on trucks, and, under special DOT permit, in trailer-mounted tank transports.
By water	In cylinders on cargo vessels only. On barges of U.S. Coast Guard Classes A, CA and CB only.
By air:	Not acceptable for shipment.

Containers. Fluorine is authorized for shipment in cylinders as a compressed gas under DOT regulations and as a liquefied, low-temperature gas in liquid-nitrogen refrigerated tanks mounted on truck trailers—by special permit of the DOT.

Filling limits. The maximum filling density authorized for fluorine in cylinders is 400 psig at 70^{o}F (3000 kPa gage at 21^{o}C), and cylinders must not contain over 6 lb of fluorine gas.

Cylinders. Cylinders that meet DOT specifications 3A1000, 3AA1000, and 3BN400 are authorized for fluorine service. The cylinders must not be equipped with safety-relief devices and must be fitted with valve-protection caps. Commonly available sizes of cylinders are 0.5, 4.9, and 6 lb net weight, respectively. All cylinders authorized for fluorine must be requalified by hydrostatic retest every 5 years under current regulations.

Valve-outlet connections. Standard connection, United States and Canada, No. 670.

Safe handling and storage of cylinders. Personnel working with fluorine cylinders must be protected by use of a cylinder enclosure or barricade and remote-control valves, preferably ones operated by manual extension handles passing through the barricade. The main function of a barricade is to dissipate and prevent the breakthrough of any flame or flow of molten metal, which, in case of equipment failure, could issue from any part of a system containing fluorine under pressure. Barricades of ¼-in. steel plate, brick, or concrete provide satisfactory protection for fluorine in cylinder quantities. Adequate ventilation of enclosed working spaces is essential. Installation of a fume hood is recommended for laboratory use of fluorine cylinders.

Fluorine cylinders should be securely supported while in use to prevent movement or straining of connections. Store full or empty cylinders in a well-ventilated area, making sure that they are protected from excessive heat, located away from organic or flammable materials, and chained in place to prevent falling. Valve-protection caps and valve-outlet caps must be securely attached to cylinders not in use.

4.10 FIRE PROTECTION GUIDE ON HAZARDOUS MATERIALS

The National Fire Protection Association has specifications for fluorine[7] that involve the following items:

- Description: Pale-yellow gas with pungent odor
- Fire and Explosion Hazards: Dangerously reactive gas. Reacts vigorously with most oxidizable substances at room temperature, frequently with ignition. Reacts with water to form hydrogen fluoride and oxygen. Reacts with nitric acid to form explosive gas, fluorine nitrate.
- Life Hazard: Toxic gas. Causes severe irritation or burns to eyes, skin, and respiratory tract.
- Personal Protection: Wear special protective clothing.
- Fire-Fighting Phases: Fight fires from an explosion-resistant location. Use water from unmanned monitors or hoseholders to keep fire-exposed containers cool. Do not direct water onto fluorine leaks because the fire may be intensified.
- Usual Shipping Containers: Special steel cylinders

- Storage: Protect against physical damage. Isolate from other storage, especially materials with which fluorine is known to react. Keep away from sources of heat and ignition.

4.11 EMERGENCY PLANNING AND COMMUNITY RIGHT-TO-KNOW ACT (EPCRA)

The federal Emergency Planning and Community Right-to-Know Act (EPCRA) of 1986 established the Toxic Release Inventory (TRI). This program requires manufacturing companies in certain industrial sectors (SIC codes 20–39) to publicly report environmental releases and transfers of chemicals on a list established by Sect. 313. The Environmental Protection Agency (EPA) recently expanded the TRI to include seven additional industries beyond manufacturing: metal mining, coal mining, electric utilities, commercial hazardous-waste treatment, petroleum bulk terminals, chemical wholesalers, and solvent recovery services. EPCRA is also known as SARA Title III, because the right-to-know program was created as part of the Superfund Amendments and Reauthorization Act (SARA) of 1986.

Chemicals are listed if they are known to cause or can reasonably be anticipated to cause significant adverse acute effects on health at concentrations likely beyond facility boundaries, including cancer, teratogenic effects, reproductive effects, neurological effects, heritable genetic mutations, or other chronic effects on health or significant damage to the environment. The current TRI chemical list contains 579 individually listed chemicals and 28 chemical categories (including 2 delimited categories containing 39 chemicals).

Fluorine is listed in a consolidated list of chemicals subject to reporting requirements under Title III of the SARA of 1986 with references to their reporting status under the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA or Superfund), the Resource Conservation and Recovery Act (RCRA), and Sections 302 and 313 of EPCRA. This consolidated list has been prepared to help firms handling chemicals determine whether they will be subject to accident prevention regulations under CAA section 112(r). These lists should be used as a reference tool, not as a definitive source of compliance information. Compliance information for EPCRA is published in the 40 CFR 302, 355, and 372. Compliance information for CAA section 112(r) is published in 40 CFR 68.

The chemicals on the consolidated list are ordered by CAS registry number. Column 1 of the list is EPCRA Section 302 Extremely Hazardous Substance (EHS). The presence of EHSs in quantities in excess of Threshold Planning Quantity (TPQ) requires certain emergency planning activities to be conducted. The extremely hazardous substances and their TPQs are listed in 40 CFR 355, Appendices A and B. TPQs are given in pounds. Column 2 of the list is about EHSs Reportable Quantities (RQ). Releases of RQ of EHSs are subject to state and local reporting under Sect. 304 of SARA Title III (EPCRA). RQ are given in pounds. Column 3 is about CERCLA Hazardous Substances. Releases of CERCLA hazardous substances in quantities equal to or greater than their RQ are also subject to state and local reporting under Sect. 304 of SARA Title III (EPCRA). CERCLA hazardous substances, and their reportable quantities, are listed in 40 CFR 302, Table 302.4. RQ are given in pounds. Column 4 is about Section 112(r). EPA developed a list of toxic substances and flammable substances. Threshold Quantities (TQ) were established for these substances. The list of substances and TQs and the requirements for risk management programs for accidental release prevention are found in 40 CFR 68. Column 5 is about EPCRA Sect. 313 Toxic Chemicals. Emissions, transfers, and waste data for chemicals listed under Sect. 313 must be reported annually as part of the community right-to-know provisions of SARA Title III (40 CFR 372). The notation 313 indicates that the chemical is subject to reporting under Sect. 313 and Sect. 6607 of the Pollution Prevention Act under the name listed. An “X” in this column may indicate that the same chemical with the same CAS number appears on another list with a different chemical name. Column 6 is about RCRA Hazardous Wastes. The list includes chemicals from RCRA only (40 CFR 261.33). Fluorine and hydrofluoric acid appear in the consolidated list as follows:

CAS number	Chemical name	Sect. 302 (EHS) TPQ	EHS RQ	CERCLA RQ	CAA 12(r) TQ	Sect. 313	RCRA CODE
7782-41-4	Fluorine	500	100	10	1000	313	P056
7664-39-3	Hydrofluoric acid	100	100	100	-	X	U134
7664-39-3	Hydrofluoric acid (conc. 50% or greater)	100	100	100	1000	X	U134
7664-39-3	Hydrogen fluoride	100	100	100		313	U134
7664-39-3	Hydrogen fluoride (anhydrous)	100	100	100	1000	313	U134

4.12 URANIUM CONCENTRATION SPECIFICATIONS FOR INDUSTRIAL USE OF HYDROFLUORIC ACID

A search for commercial specifications on allowable uranium (naturally occurring) concentrations was made to establish any limits that industries that consume HF may have. Little information in the open literature was found, but discussions with Allied Signal (a major producer of hydrofluoric acid) provided the information described as follows.[8]

The HF industry is segmented into several markets (fluorocarbon, 70%; chemical derivatives, 14%; alkylation, 4%; nuclear, 3%; and aqueous, 9%). Consequently, it is difficult to establish an overall uranium specification for the entire hydrofluoric acid markets.

Current production of anhydrous hydrofluoric acid produces a nondetectable level at <0.4 ppm uranium made from naturally occurring fluorspar. Several industries are very sensitive to any kind of metal (i.e., quartz manufacturing, electronic materials, and chemical derivatives) contained in hydrofluoric acid supplied by the producers. There is no exact specification limit for uranium in the producer's literature. However, a quarterly analysis is performed for all metals for all customers. Customers' main concern is when those levels change from quarter to quarter.

It is the opinion of the hydrofluoric industry that the specification determined by customers is more of a political concern rather than one based on process needs and capabilities. Normally there is a strong resistance to change, and suppliers of the anhydrous hydrofluoric acid co-product in the nuclear fuel cycle come from within the nuclear system, which is not as sensitive to uranium.

The pilot program performed for DOE by Allied Signal has set a maximum level of 3 ppm uranium, with a target level of 1 ppm. This is a comfortable level of uranium in HF to be used within the nuclear fuel cycle, according to the company.

4.13 DRAFT DOE HANDBOOK FOR CONTROLLING RELEASE FOR REUSE OR RECYCLE OF NON-REAL PROPERTY CONTAINING RESIDUAL RADIOACTIVE MATERIAL

DOE offers a draft handbook for controlling release for reuse or recycle material potentially containing radioactive substances.[9] This document will assist in insuring radiological doses to the public from reuse or recycle of release non-real property containing residual radioactive material meets applicable regulatory standards, meets ALARA principles, and meets DOE requirements for release of such materials. These requirements are currently found in Order DOE 5400.5, "Radiation Protection of the Public and the Environment" and will be promulgated in 10 CFR Part 834 to codify and clarify the requirements of DOE 5400.5.

Steps 1 through 10 of this handbook define a logic diagram for satisfying both Order 5400.5 and future 10 CFR Part 834 property release restrictions when a DOE facility plans to release non-real property containing residual radioactive materials for reuse or recycle. The steps of the release process for non-real property include the following:

- Characterize property and prepare a description.
- Determine whether applicable authorized or supplemental limits exist.
- Define authorized or supplemental limits needed.
- Develop authorized or supplemental limits.
- Compile and submit applications for DOE Operations Office approval.
- Document approved limits in the public record.
- Implement approved limits.
- Conduct survey/measurements.
- Verify that applicable authorized or supplemental limits have been met.
- Release property.

These steps can be applied to fluorine or fluorine compounds produced from depleted UF_6. This handbook suggested that if contamination cannot be detected, the products can be released without further concern for the safety of the public.

5. DESCRIPTION OF APPENDIX MATERIAL

This report contains four appendixes, which are described in the following list:

Appendix A. This appendix contains the portion of the Hazardous Materials Table from Sect. 172.101 that pertains to fluorine. Following this table is an extended description (from the same source), including explanations of the columns and definitions. Appendix A to Sect. 172.101—List of Hazardous Substances and Reportable Quantities—is also included, as well as the portion of Table 1 of this appendix pertaining to reportable quantities of fluoride.

Appendix B. This appendix directly quotes material from Sects. 178.36, 178.37, and 178.38. Section 178.36—Specification 3A and 3AX seamless steel cylinders—describes the mechanical specifications of the type 3A and 3AX tanks used to store fluorine. Section 178.37—Specification 3AA and 3AAX seamless steel cylinders—addresses mechanical specifications of the type 3AA and 3AAX tanks used to store fluorine. Section 178.38—Specification 3B seamless steel cylinders—describes the mechanical specifications of the type 3B tanks used to store fluorine.

Appendix C. This appendix describes the requirements for (1) unloading anhydrous hydrofluoric acid with compressed air, (2) unloading anhydrous hydrofluoric acid by pump, (3) unloading aqueous hydrofluoric acid with compressed air, and (4) unloading aqueous hydrofluoric acid by pump. Each of the process descriptions is followed by an illustration.

Appendix D. This appendix contains material from the *LLNL Health and Safety Manual* that addresses the safe handling of fluorine.

6. REFERENCES

1. Public Law 105-204 [Page 112, STAT. 681], 105 Congress, Approved July 21, 1998.

2. U.S. Department of Energy, Final Plan for the Conversion of Depleted Uranium Hexafluoride As Required by Public Law 105-204, July 1999.

3. OSHA, *OSHA Regulated Hazardous Substances, Health, Toxicity, Economic and Technological Data*, Volume 1, A-I, Noyes Data Corporation, New Jersey, 1990.

4. Oak Ridge Gaseous Diffusion Plant Safety Standard, "Compressed Cylinder Gas—Safety Guide," K-SS-2.1, App., Oak Ridge, Tennessee, February 1987.

5. Pennsalt Chemicals Corporation, "Hydrofluoric Acid Handling and Engineering Data," Philadelphia, Pennsylvania, 1958.

6. Compressed Gas Association, *Handbook of Compressed Gases,* 2nd ed., Van Nostrand Reinhold Company, New York.

7. National Fire Protection Association, *Fire Protection Guide on Hazardous Materials,* 9th ed., NFPA, Quincy, Massachusetts.

8. Don Taylor, Allied Signal, personal communication with Juan J. Ferrada, November 1999.

9. U.S. Department of Energy, Draft Handbook of Controlling Release for Reuse or Recycle of Non-real Property Containing Residual Radioactive Material (in preparation by the Department of Energy).

APPENDIX A

SECT. 172.101 PURPOSE AND USE OF HAZARDOUS MATERIALS TABLE

This appendix refers to the table for transportation of hazardous materials. This document only refers to fluorine compounds, and the table will only include these chemicals. The table will be fully described, although not all the table elements may correspond to the fluorine compounds.

(a) The Hazardous Materials Table (Table) in this section designates the materials listed therein as hazardous materials for the purpose of transportation of those materials. For each listed material, the Table identifies the hazard class or specifies that the material is forbidden in transportation and gives the proper shipping name or directs the user to the preferred proper shipping name. In addition, the Table specifies or references requirements in this subchapter pertaining to labeling, packaging, quantity limits aboard aircraft, and stowage of hazardous materials aboard vessels.

(b) Column 1: Symbols. Column 1 of the Table contains five symbols (“+”, “A”, “D”, “I”, and “W”), as follows:

(1) The plus (+) fixes the proper shipping name, hazard class, and packing group for that entry without regard to whether the material meets the definition of that class or packing group or meets any other hazard class definition. An appropriate alternate proper shipping name and hazard class may be authorized by the Associate Administrator for Hazardous Materials Safety.
(2) The letter “A” restricts the application of requirements of this subchapter to materials offered or intended for transportation by aircraft, unless the material is a hazardous substance or a hazardous waste.
(3) The letter “D” identifies proper shipping names which are appropriate for describing materials for domestic transportation but may be inappropriate for international transportation under the provisions of international regulations (e.g., IMO, ICAO). An alternate proper shipping name may be selected when either domestic or international transportation is involved.
(4) The letter “I” identifies proper shipping names which are appropriate for describing materials in international transportation. An alternate proper shipping name may be selected when only domestic transportation is involved
(5) The letter "W" restricts the application of requirements of this subchapter to materials offered or intended for transportation by vessel, unless the material is a hazardous substance or a hazardous waste.

(c) Column 2: Hazardous materials descriptions and proper shipping names. Column 2 lists the hazardous materials descriptions and proper shipping names of materials designated as hazardous materials. Modification of a proper shipping name may otherwise be required or authorized by this section. Proper shipping names are limited to those shown in Roman type (not italics).

(1) Proper shipping names may be used in the singular or plural and in either capital or lowercase letters. Words may be alternatively spelled in the same manner as they appear in the ICAO Technical Instructions or the IMDG Code. For example “aluminum” may be spelled “aluminium” and “sulfur” may be spelled “sulphur.” However, the word “inflammable” may not be used in place of the word “flammable.”
(2) Punctuation marks and words in italics are not part of the proper shipping name but may be used in addition to the proper shipping name. The word “or” in italics indicates that terms in the sequence may be used as the proper shipping name, as appropriate.

Title 49, Sect. 172.101, Hazardous Materials Table													
Symbols	Hazardous materials description and proper shipping names	Hazard class or division	Identification number	PG	Label codes	Special provisions	(8) Packaging (Sect. 73.***)			(9) Quantity limitations		(10) Vessel stowage	
							Exceptions	Non-bulk	Bulk	Passenger aircraft/rail	Cargo Aircraft only	Location	Other
	Fluorine, compressed	2.3	UN1045		2.3, 5.1, 8	1	None	302	None	Forbidden	Forbidden	D	40, 89, 90
	Hydrogen fluoride, anhydrous	8	UN1052	I	8, 6.1	3, B7, B46, B71, B77,T24, T27	None	163	243	Forbidden	Forbidden	D	12, 40
	Hydrofluoric acid, with more than 60% strength	8	UN1790	I	8, 6.1	A6, A7, B4, B15, B23, N5, N34, T18, T27	None	201	243	0.5 L	2.5 L	D	12, 40
	Hydrofluoric acid, with no more than 60% strength	8	UN1790	II	8, 6.1	A6, A7, B15, B110, N5, N34, T18, T27	None	202	243	1 L	30 L	D	12, 40

(3) The word “poison” or “poisonous” may be used interchangeably with the word “toxic” when only domestic transportation is involved. The abbreviation “n.o.i.” (no otherwise indicated) or “n.o.i.b.n.” may be used interchangeably with “n.o.s.” (no otherwise specified).

(4) Except for hazardous wastes, when qualifying words are used as part of the proper shipping name, their sequence in the package markings and shipping paper description is optional. However, the entry in the Table reflects the preferred sequence.

(5) When one entry references another entry by use of the word “see,” if both names are in Roman type, either name may be used as the proper shipping name (e.g., Ethyl alcohol, see Ethanol).

(6) When a proper shipping name includes a concentration range as part of the shipping description, the actual concentration, if it is within the range stated, may be used in place of the concentration range. For example, an aqueous solution of hydrogen peroxide containing 30 percent peroxide may be described as “Hydrogen peroxide, aqueous solution with not less than 20 percent but not more than 40 percent hydrogen peroxide” or “Hydrogen peroxide, aqueous solution with 30 percent hydrogen peroxide.”

(7) Use of the prefix “mono” is optional in any shipping name, when appropriate. Thus, Iodine monochloride may be used interchangeably with Iodine chloride. In “Glycerol alpha-monochlorohydrin” the term “mono” is considered a prefix to the term “chlorohydrin” and may be deleted.

(8) Hazardous substances. Appendix A to this section lists materials which are listed or designated as hazardous substances under Sect. 101(14) of the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA). Proper shipping names for hazardous substances (see appendix A to this section and Sect. 171.8 of this subchapter) shall be determined as follows:

   (i) If the hazardous substance appears in the Table by technical name, then the technical name is the proper shipping name.

   (ii) If the hazardous substance does not appear in the Table and is not a forbidden material, then an appropriate generic, or “n.o.s.”, shipping name shall be selected corresponding to the hazard class (and packing group, if any) of the material as determined by the defining criteria of this subchapter (see Sects. 173.2 and 173.2a of this subchapter). For example, a hazardous substance which is listed in appendix A but not in the Table and which meets the definition of flammable liquid might be described as “Flammable liquid, n.o.s.” or other appropriate shipping name corresponding to the flammable liquid hazard class.

(9) Hazardous wastes. If the word “waste” is not included in the hazardous material description in Column 2 of the Table, the proper shipping name for a hazardous waste (as defined in Sect. 171.8 of this subchapter) shall include the word “Waste” preceding the proper shipping name of the material. For example: Waste acetone.

(10) Mixtures and solutions.

   (i) A mixture or solution not identified specifically by name, comprised of a hazardous material identified in the Table by technical name and nonhazardous material, shall be described using the proper shipping name of the hazardous material and the qualifying word “mixture” or “solution,” as appropriate, unless—

      (A) Except as provided in Sect. 172.101(i)(4) the packaging specified in Column 8 is inappropriate to the physical state of the material;

      (B) The shipping description indicates that the proper shipping name applies only to the pure or technically pure hazardous material;

(C) The hazard class, packing group, or subsidiary hazard of the mixture or solution is different from that specified for the entry;
(D) There is a significant change in the measures to be taken in emergencies;
(E) The material is identified by special provision in Column 7 of the Sect. 172.101 Table as a material poisonous by inhalation; however, it no longer meets the definition of poisonous by inhalation or it falls within a different hazard zone than that specified in the special provision; or
(F) The material can be appropriately described by a shipping name that describes its intended application, such as "Coating solution," 'Extracts, flavoring," or "Compound, cleaning liquid."

(i) If one or more of the conditions specified in paragraph (c)(10)(i) of this section is satisfied, then a proper shipping name shall be selected as prescribed in paragraph (c)(12)(ii) of this section.
(ii) A mixture or solution not identified in the Table specifically by name, comprised of two or more hazardous materials in the same hazard class, shall be described using an appropriate shipping description (e.g., "Flammable liquid, n.o.s."). The name that most appropriately describes the material shall be used; e.g., an alcohol not listed by its technical name in the Table shall be described as "Alcohol, n.o.s." rather than "flammable liquid, n.o.s." Some mixtures may be more appropriately described according to their application, such as "Coating solution" or "Extracts, flavoring liquid" rather than by an n.o.s. entry. Under the provisions of subparts C and D of this part, the technical names of at least two components most predominately contributing to the hazards of the mixture or solution may be required in association with the proper shipping name.

(11) Except for a material subject to or prohibited by Sects. 173.21, 173.54, 173.56(d), 173.56(e)(1), 173.124(a)(2)(iii) or 173.128(c) of this subchapter, a material for which the hazard class is uncertain and must be determined by testing or a material that is a hazardous waste may be assigned a tentative shipping name, hazard class, identification number, and packing group, based on the shipper's tentative determination according to—

(i) defining criteria in this subchapter;
(ii) the hazard precedence prescribed in Sect. 173.2a of this subchapter; and
(iii) the shipper's knowledge of the material.

(12) Except when the proper shipping name in the Table is preceded by a plus (+)—

(i) If it is specifically determined that a material meets the definition of a hazard class, packing group or hazard zone, other than the class, packing group or hazard zone shown in association with the proper shipping name, or does not meet the defining criteria for a subsidiary hazard shown in Column 6 of the Table, the material shall be described by an appropriate proper shipping name listed in association with the correct hazard class, packing group, hazard zone, or subsidiary hazard for the material.
(ii) Generic or n.o.s. descriptions. If an appropriate technical name is not shown in the Table, selection of a proper shipping name shall be made from the generic or n.o.s. descriptions corresponding to the specific hazard class, packing group, hazard zone, or subsidiary hazard, if any, for the material. The name that most appropriately describes the material shall be used; e.g., an alcohol not listed by its technical name in the Table shall be described as "Alcohol, n.o.s." rather than "Flammable liquid, n.o.s." Some mixtures may be more appropriately described according to their application, such as

"Coating solution" or "Extracts, flavoring, liquid," rather than by an n.o.s. entry, such as "Flammable liquid, n.o.s." It should be noted, however, that an n.o.s. description as a proper shipping name may not provide sufficient information for shipping papers and package markings. Under the provisions of subparts C and D of this part, the technical name of one or more constituents which makes the product a hazardous material may be required in association with the proper shipping name.

(iii) Multiple hazard materials. If a material meets the definition of more than one hazard class and is not identified in the Table specifically by name (e.g., acetyl chloride), the hazard class of the material shall be determined by using the precedence specified in Sec. 173.2a of this subchapter, and an appropriate shipping description (e.g., "Flammable liquid, corrosive n.o.s.") shall be selected as described in paragraph (c)(12)(ii) of this section.

(iv) If it is specifically determined that a material is not a forbidden material and does not meet the definition of any hazard class, the material is not a hazardous material.

(13) Self-reactive materials and organic peroxides. A generic proper shipping name for a self-reactive material or an organic peroxide, as listed in Column 2 of the Table, must be selected based on the material's technical name and concentration, in accordance with the provisions of Sects. 173.224 or 173.225 of this subchapter, respectively.

(14) A proper shipping name that describes all isomers of a material may be used to identify any isomer of that material if the isomer meets criteria for the same hazard class or division, subsidiary risk(s), and packing group, unless the isomer is specifically identified in the Table.

(15) Hydrates of inorganic substances may be identified using the proper shipping name for the equivalent anhydrous substance if the hydrate meets the same hazard class or division, subsidiary risk(s), and packing group, unless the hydrate is specifically identified in the Table.

(d) Column 3: Hazard class or Division. Column 3 contains a designation of the hazard class or division corresponding to each proper shipping name, or the word "Forbidden".

(1) A material for which the entry in this column is "Forbidden" may not be offered for transportation or transported. This prohibition does not apply if the material is diluted, stabilized, or incorporated in a device and it is classed in accordance with the definitions of hazardous materials contained in part 173 of this subchapter.

(2) When a reevaluation of test data or new data indicates a need to modify the "Forbidden" designation or the hazard class or packing group specified for a material specifically identified in the Table, this data should be submitted to the Associate Administrator for Hazardous Materials Safety.

(3) A basic description of each hazard class and the section reference for class definitions appear in Sect. 173.2 of this subchapter.

(4) Each reference to a Class 3 material is modified to read "combustible liquid" when that material is reclassified in accordance with Sect. 173.150 (e) or (f) of this subchapter or has a flash point above 60.5°C (141°F) but below 93°C (200°F).

(e) Column 4: Identification number. Column 4 lists the identification number assigned to each proper shipping name. Those preceded by the letters "UN" are associated with proper shipping names considered appropriate for international transportation as well as domestic transportation. Those preceded by the letters "NA" are associated with proper shipping names not recognized for international transportation, except to and from Canada. Identification numbers in the "NA9000" series are associated with proper shipping names not appropriately covered by international hazardous materials (dangerous goods) transportation standards, or not appropriately addressed by international transportation standards for emergency response information purposes, except for transportation between the United States and Canada.

(f) Column 5: Packing group. Column 5 specifies one or more packing groups assigned to a material corresponding to the proper shipping name and hazard class for that material. Class 2, Class 7, Division 6.2 (other than regulated medical wastes), and ORM-D materials do not have packing groups. Packing Groups I, II, and III indicate the degree of danger presented by the material is either great, medium, or minor, respectively. If more than one packing group is indicated for an entry, the packing group for the hazardous material is determined using the criteria for assignment of packing groups specified in subpart D of part 173. When a reevaluation of test data or new data indicates a need to modify the specified packing group(s), the data should be submitted to the Associate Administrator for Hazardous Materials Safety. Each reference in this column to a material which is a hazardous waste or a hazardous substance, and whose proper shipping name is preceded in Column 1 of the Table by the letter "A" or "W", is modified to read "III" on those occasions when the material is offered for transportation or transported by a mode in which its transportation is not otherwise subject to requirements of this subchapter.

(g) Column 6: Labels. Column 6 specifies codes which represent the hazard warning labels required for a package filled with a material conforming to the associated hazard class and proper shipping name, unless the package is otherwise excepted from labeling by a provision in subpart E of this part, or part 173 of this subchapter. The first code is indicative of the primary hazard of the material. Additional label codes are indicative of subsidiary hazards. Provisions in Sect. 172.402 may require that a label other than that specified in Column 6 be affixed to the package in addition to that specified in Column 6. No label is required for a material classed as a combustible liquid or for a Class 3 material that is reclassed as a combustible liquid. The codes contained in Column 6 are defined according to the following table:

Label Substitution Table	
Label code	Label name
1	Explosive
1.1[1]	Explosive 1.1[1]
1.2[1]	Explosive 1.2[1]
1.3[1]	Explosive 1.3[1]
1.4[1]	Explosive 1.4[1]
1.5[1]	Explosive 1.5[1]
1.6[1]	Explosive 1.6[1]
2.1	Flammable gas
2.2	Nonflammable gas
2.3	Poison gas
3	Flammable liquid
4.1	Flammable solid
4.2	Spontaneously combustible
4.3	Dangerous when wet
5.1	Oxidizer
5.2	Organic peroxide
6.1 (inhalation hazard, Zone A or B)	Poison inhalation hazard
6.1 (I or II, other than Zone A or B inhalation hazard)[2]	Poison
6.1 (III)[2]	Keep away from food
7	Radioactive
8	Corrosive
9	Class 9

[1]Refers to the appropriate compatibility group letter.
[2]The packing group for a material is indicated in column 5 of the table.

(h) Column 7: Special provisions. Column 7 specifies codes for special provisions applicable to hazardous materials. When Column 7 refers to a special provision for a hazardous material, the meaning and requirements of that special provision are as set forth in Sect. 172.102 of this subpart.

(i) Column 8: Packaging authorizations. Columns 8A, 8B, and 8C specify the applicable sections for exceptions, nonbulk packaging requirements and bulk packaging requirements, respectively, in part 173 of this subchapter. Columns 8A, 8B, and 8C are completed in a manner which indicates that Sect. 173 precedes the designated numerical entry. For example, the entry “202” in Column 8B associated with the proper shipping name “Gasoline” indicates that for this material, conformance to non-bulk packaging requirements prescribed in Sect. 173.202 of this subchapter is required. When packaging requirements are specified, they are in addition to the standard requirements for all packagings prescribed in Sect. 173.24 of this subchapter and any other applicable requirements in subparts A and B of part 173 of this subchapter.

(1) Exceptions. Column 8A contains exceptions from some of the requirements of this subchapter. The referenced exceptions are in addition to those specified in subpart A of part 173 and elsewhere in this subchapter. A “None” in this column means no packaging exceptions are authorized, except as may be provided by special provisions in Column 7.

(2) Non-bulk packaging. Column 8B references the section in part 173 of this subchapter which prescribes packaging requirements for non-bulk packagings. A “None” in this column means non-bulk packagings are not authorized, except as may be provided by special provisions in Column 7. Each reference in this column to a material which is a hazardous waste or a hazardous substance, and whose proper shipping name is preceded in Column 1 of the Table by the letter “A” or “W”, is modified to include “Sect. 173.203” or “Sect. 173.213,” as appropriate for liquids and solids, respectively, on those occasions when the material is offered for transportation or transported by a mode in which its transportation is not otherwise subject to the requirements of this subchapter.

(3) Bulk packaging. Column 8C specifies the section in part 173 of this subchapter which prescribes packaging requirements for bulk packagings, subject to the limitations, requirements and additional authorizations of Column 7. A “None” in this column means bulk packagings are not authorized, except as may be provided by special provisions in Column 7. Additional authorizations and limitations for use of IM portable tanks are set forth in Column 7. For each reference in this column to a material which is a hazardous waste or a hazardous substance, and whose proper shipping name is preceded in Column 1 of the Table by the letter “A” or “W” and which is offered for transportation or transported by a mode in which its transportation is not otherwise subject to the requirements of this subchapter:

(i) The column reference is Sect. 173.240 or Sect. 173.241, as appropriate.

(ii) For a solid material, the exception provided in Special provision B54 is applicable.

(iii) For a Class 9 material which meets the definition of an elevated temperature material, the column reference is Sect. 173.247.

(4) For a hazardous material which is specifically named in the Table and whose packaging sections specify packagings not applicable to the form of the material (e.g., packaging specified is for solid material and the material is being offered for transportation in a liquid form), the following table should be used to determine the appropriate packaging section:

Packaging section reference for solid materials	Corresponding packaging section for liquid materials
Sect. 173.187	Sect. 173.181
Sect. 173.211	Sect. 173.201
Sect. 173.212	Sect. 173.202
Sect. 173.213	Sect. 173.203
Sect. 173.240	Sect. 173.241
Sect. 173.242	Sect. 173.243

(j) Column 9: Quantity limitations. Columns 9A and 9B specify the maximum quantities that may be offered for transportation in one package by passenger-carrying aircraft or passenger-carrying rail car (Column 9A) or by cargo aircraft only (Column 9B), subject to the following:

(1) "Forbidden" means the material may not be offered for transportation or transported in the applicable mode of transport.
(2) The quantity limitation is "net" except where otherwise specified, such as for "Consumer commodity" which specifies "30 kg gross."
(3) When articles or devices are specifically listed by name, the net quantity limitation applies to the entire article or device (less packaging and packaging materials) rather than only to its hazardous components.
(4) A package offered or intended for transportation by aircraft and which is filled with a material forbidden on passenger-carrying aircraft but permitted on cargo aircraft only, or which exceeds the maximum net quantity authorized on passenger-carrying aircraft, shall be labeled with the CARGO AIRCRAFT ONLY label specified in Sect. 172.448 of this part.

(k) Column 10: Vessel stowage requirements. Column 10A [Vessel stowage] specifies the authorized stowage locations on board cargo and passenger vessels. Column 10B [Other provisions] specifies codes for stowage requirements for specific hazardous materials. The meaning of each code in Column 10B is set forth in Sect. 176.84 of this subchapter. Section 176.63 of this subchapter sets forth the physical requirements for each of the authorized locations listed in Column 10A. (For bulk transportation by vessel, see 46 CFR parts 30 to 40, 70, 98, 148, 151, 153 and 154.) The authorized stowage locations specified in Column 10A are defined as follows:

(1) Stowage category "A" means the material may be stowed "on deck" or "under deck" on a cargo vessel and on a passenger vessel.
(2) Stowage category "B" means—
    (i) The material may be stowed "on deck" or "under deck" on a cargo vessel and on a passenger vessel carrying a number of passengers limited to not more than the larger of 25 passengers, or one passenger per each three meters of overall vessel length; and
    (ii) "On deck only" on passenger vessels in which the number of passengers specified in paragraph (k)(2)(i) of this section is exceeded.
(3) Stowage category "C" means the material must be stowed "on deck only" on a cargo vessel and on a passenger vessel.
(4) Stowage category "D" means the material must be stowed "on deck only" on a cargo vessel and on a passenger vessel carrying a number of passengers limited to not more than the larger of 25 passengers or one passenger per each three meters of overall vessel length, but the material is prohibited on passenger vessels in which the limiting number of passengers is exceeded.
(5) Stowage category "E" means the material may be stowed "on deck" or "under deck" on a cargo vessel and on a passenger vessel carrying a number of passengers limited to not more than the

larger of 25 passengers, or one passenger per each three meters of overall vessel length, but is prohibited from carriage on passenger vessels in which the limiting number of passengers is exceeded.

(l) Changes to the Table.

(1) Unless specifically stated otherwise in a rule document published in the Federal Register amending the Table—

(i) Such a change does not apply to the shipment of any package filled prior to the effective date of the amendment; and
(ii) Stocks of preprinted shipping papers and package markings may be continued in use, in the manner previously authorized, until depleted or for a one-year period, subsequent to the effective date of the amendment, whichever is less.

(2) Except as otherwise provided in this section, any alteration of a shipping description or associated entry which is listed in the Sect. 172.101 Table must receive prior written approval from the Associate Administrator for Hazardous Materials Safety.
(3) The proper shipping name of a hazardous material changed in the May 6, 1997, final rule, in effect on October 1, 1997, only by the addition or omission of the word “compressed,” “inhibited,” “liquefied” or “solution” may continue to be used to comply with package marking requirements, until January 1, 2003.

APPENDIX A TO SECT. 172.101—LIST OF HAZARDOUS SUBSTANCES AND REPORTABLE QUANTITIES

1. This appendix lists materials and their corresponding reportable quantities (RQ's) that are listed or designated as "hazardous substances" under section 101(14) of the Comprehensive Environmental Response, Compensation, and Liability Act, 42 U.S.C. 9601(14) (CERCLA; 42 U.S.C. 9601 et seq). This listing fulfills the requirement of CERCLA, 42 U.S.C. 9656(a), that all "hazardous substances," as defined in 42 U.S.C. 9601(14), be listed and regulated as hazardous materials under 49 U.S.C. 5101-5127. That definition includes substances listed under sections 311(b)(2)(A) and 307(a) of the Federal Water Pollution Control Act, 33 U.S.C. 1321(b)(2)(A) and 1317(a), section 3001 of the Solid Waste Disposal Act, 42 U.S.C. 6921, and section 112 of the Clean Air Act, 42 U.S.C. 7412. In addition, this list contains materials that the Administrator of the Environmental Protection Agency has determined to be hazardous substances in accordance with section 102 of CERCLA, 42 U.S.C. 9602. It should be noted that 42 U.S.C. 9656(b) provides that common and contract carriers may be held liable under laws other than CERCLA for the release of a hazardous substance as defined in that Act, during transportation that commenced before the effective date of the listing and regulating of that substance as a hazardous material under 49 U.S.C. 5101-5127.
2. This appendix is divided into two TABLES which are entitled ''TABLE 1--HAZARDOUS SUBSTANCES OTHER THAN RADIONUCLIDES" and "TABLE 2--RADIONUCLIDES." A material listed in this appendix is regulated as a hazardous material and a hazardous substance under this subchapter if it meets the definition of a hazardous substance in Sect. 171.8 of this subchapter.
3. The procedure for selecting a proper shipping name for a hazardous substance is set forth in Sec. 172.101(c)(8).
4. Column 1 of TABLE 1, entitled "Hazardous substance," contains the names of those elements and compounds that are hazardous substances. Following the listing of elements and compounds is a listing of waste streams. These waste streams appear on the list in numerical sequence and are referenced by the appropriate "D", "F", or "K" numbers. Column 2 of TABLE 1, entitled "Reportable quantity (RQ)", contains the reportable quantity (RQ), in pounds and kilograms, for each hazardous substance listed in Column 1 of TABLE 1.
5. A series of notes is used throughout TABLE 1 and TABLE 2 to provide additional information concerning certain hazardous substances. These notes are explained at the end of each TABLE.
6. TABLE 2 lists radionuclides that are hazardous substances and their corresponding RQ's. The RQ's in table 2 for radionuclides are expressed in units of curies and terabecquerels, whereas those in table 1 are expressed in units of pounds and kilograms. If a material is listed in both table 1 and table 2, the lower RQ shall apply. Radionuclides are listed in alphabetical order. The RQ's for radionuclides are given in the radiological unit of measure of curie, abbreviated "Ci", followed, in parentheses, by an equivalent unit measured in terabecquerels, abbreviated "TBq".
7. For mixtures of radionuclides, the following requirements shall be used in determining if a package contains an RQ of a hazardous substance: (i) if the identity and quantity (in curies or terabecquerels) of each radionuclide in a mixture or solution is known, the ratio between the quantity per package (in curies or terabecquerels) and the RQ for the radionuclide must be determined for each radionuclide. A package contains an RQ of a hazardous substance when the sum of the ratios for the radionuclides in the mixture or solution is equal to or greater than one; (ii) if the identity of each radionuclide in a mixture or solution is known but the quantity per package (in curies or terabecquerels) of one or more of the radionuclides is unknown, an RQ of a hazardous substance is present in a package when the total quantity (in curies or terabecquerels) of the mixture or solution is equal to or greater than the lowest RQ of any individual radionuclide in the mixture or solution; and (iii) if the identity of one or more radionuclides in a mixture or solution is unknown (or if the identity of a radionuclide by itself is unknown), an RQ of a hazardous substance is present when the total quantity (in curies or

terabecquerels) in a package is equal to or greater than either one curie or the lowest RQ of any known individual radionuclide in the mixture or solution, whichever is lower.

Table 1 to Appendix A—Hazardous Substances Other Than Radionuclides

Hazardous substance	Reportable quantity (RQ) pounds (kilograms)
Fluorine	10 (4.54)

APPENDIX B

Sect. 178.36 Specification 3A and 3AX seamless steel cylinders

(a) Type, size, and service pressure. In addition to the requirements of Sect. 178.35, cylinders must conform to the following:

(1) A DOT-3A cylinder is a seamless steel cylinder with a water capacity (nominal) not over 1,000 pounds and a service pressure of at least 150 pounds per square inch.
(2) A DOT-3AX is a seamless stainless steel cylinder with a water capacity not less than 1,000 pounds and a service pressure of at least 500 pounds per square inch, conforming to the following requirements:

(i) Assuming the cylinder is to be supported horizontally at its two ends only and to be uniformly loaded over its entire length consisting of the weight per unit of length of the straight cylindrical portion filled with water and compressed to the specified test pressure; the sum of two times the maximum tensile stress in the bottom fibers due to bending, plus that in the same fibers (longitudinal stress), due to hydrostatic test may not exceed 80 percent of the minimum yield strength of the steel at such maximum stress. Wall thickness must be increased when necessary to meet the requirement.
(ii) To calculate the maximum longitudinal tensile stress due to bending, the following formula must be used:

$$\mathbf{S = MC/I}$$

(iii) To calculate the maximum longitudinal tensile stress due to hydrostatic test pressure, the following formula must be used:

$$\mathbf{S = A_1 * P / A_2}$$

Where:

S = tensile stress, pounds per square inch;
M = bending moment, inch pounds ($wl^2/8$);
w = weight per inch of cylinder filled with water;
l = length of cylinder, inches;
C = radius (D)/(2) of cylinder, inches;
I = moment of inertia, 0.04909 (D^4-d^4) inches fourth;
D = outside diameter, inches;
d = inside diameter, inches;
A_1 = internal area in cross section of cylinder, square inches;
A_2 = area of metal in cross section of cylinder, square inches;
P = hydrostatic test pressure, pounds per square inch.

(b) Steel. Open-hearth or electric steel of uniform quality must be used. Content percent may not exceed the following: carbon, 0.55; phosphorous, 0.045; sulphur, 0.050.

(c) Identification of material. Material must be identified by any suitable method, except that plates and billets for hot-drawn cylinders must be marked with the heat number.

(d) Manufacture. Cylinders must be manufactured using equipment and processes adequate to ensure that each cylinder produced conforms to the requirements of this subpart. No fissure or other defect is permitted that is likely to weaken the finished cylinder appreciably. A reasonably smooth and uniform surface finish is required. If not originally free from such defects, the surface may be machined or otherwise treated to eliminate these defects. The thickness of the bottoms of cylinders welded or formed by spinning is, under no condition, to be less than two times the minimum wall thickness of the cylindrical shell; such bottom thickness must be measured within an area bounded by a line representing the points of contact between the cylinder and floor when the cylinder is in a vertical position.

(e) Welding or brazing. Welding or brazing for any purpose whatsoever is prohibited except as follows:

(1) Welding or brazing is authorized for the attachment of neckrings and footrings which are non-pressure parts and only to the tops and bottoms of cylinders having a service pressure of 500 pounds per square inch or less. Cylinders, neckrings, and footrings must be made of weldable steel, the carbon content of which may not exceed 0.25 percent except in the case of 4130X steel which may be used with proper welding procedures.
(2) As permitted in paragraph (d) of this section.
(3) Cylinders used solely in anhydrous ammonia service may have a 1/2-in.-diameter bar welded within their concave bottoms.

(f) Wall thickness. For cylinders with service pressure less than 900 pounds, the wall stress may not exceed 24,000 pounds per square inch. A minimum wall thickness of 0.100 inch is required for any cylinder over 5 inches outside diameter. Wall stress calculation must be made by using the following formula:

$$\mathbf{S = [P(1.3D^2 + 0.4d^2)]/(D^2 - d^2)}$$

Where:

S = wall stress in pounds per square inch;
P = minimum test pressure prescribed for water jacket test or 450 pounds per square inch, whichever is the greater;
D = outside diameter in inches;
d = inside diameter in inches.

(g) Heat treatment. The completed cylinder must be uniformly and properly heat treated prior to tests.
(h) Openings in cylinders and connections (valves, fuse plugs, etc.) for those openings. Threads are required on openings.

(1) Threads must be clean cut, even, without checks, and to gauge.
(2) Taper threads, when used, must be of length not less than as specified for American Standard taper pipe threads.
(3) Straight threads having at least 6 engaged threads are authorized. Straight threads must have a tight fit and calculated shear strength of at least 10 times the test pressure of the cylinder. Gaskets, adequate to prevent leakage, are required.

(i) Hydrostatic test. Each cylinder must successfully withstand a hydrostatic test, as follows:

(1) The test must be by water-jacket, or other suitable methods, operated so as to obtain accurate data. The pressure gauge must permit reading to an accuracy of 1 percent. The expansion gauge must permit reading of total expansion to an accuracy of either 1 percent or 0.1 cubic centimeter.

(2) Pressure must be maintained for at least 30 seconds and sufficiently longer to ensure complete expansion. Any internal pressure applied after heat-treatment and previous to the official test may not exceed 90 percent of the test pressure. If, due to failure of the test apparatus the test pressure cannot be maintained, the test may be repeated at a pressure increased by 10 percent or 100 pounds per square inch, whichever is the lower.

(3) Permanent, volumetric expansion may not exceed 10 percent of the total volumetric expansion at test pressure.

(4) Each cylinder must be tested to at least 5/3 times service pressure.

(j) Flattening test. A flattening test must be performed on one cylinder taken at random out or each lot of 200 or less, by placing the cylinder between wedge-shaped knife edges having a 60^o included angle, rounded to 1/2-inch radius. The longitudinal axis of the cylinder must be at a 90° angle to knife edges during the test. For lots of 30 or less, flattening tests are authorized to be made on a ring at least 8 inches long cut from each cylinder and subjected to the same heat treatment as the finished cylinder.

(k) Physical test. A physical test must be conducted to determine yield strength, tensile strength, elongation, and reduction of area of material as follows:

(1) The test is required on 2 specimens cut from 1 cylinder taken at random out of each lot of 200 or less. For lots of 30 or less, physical tests are authorized to be made on a ring at least 8 inches long cut from each cylinder and subjected to same heat treatment as the finished cylinder.

(2) Specimens must conform to the following:

(i) Gauge length of 8 inches with a width of not over 11/2 inches, a gauge length of 2 inches with a width of not over 11/2 inches, or a gauge length of at least 24 times the thickness with width not over 6 times the thickness is authorized when cylinder wall is not over 3/16 inch thick.

(ii) The specimen, exclusive of grip ends, may not be flattened. Grip ends may be flattened to within 1 inch of each end of the reduced section.

(iii) When the size of the cylinder does not permit securing straight specimens, the specimens may be taken in any location or direction and may be straightened or flattened cold, by pressure only, not by blows. When specimens are so taken and prepared, the inspector's report must show in connection with record of physical tests detailed information in regard to such specimens.

(iv) Heating of a specimen for any purpose is not authorized.

(3) The yield strength in tension must be the stress corresponding to a permanent strain of 0.2 percent of the gauge length. The following conditions apply:

(i) The yield strength must be determined by either the "offset" method or the "extension under load" method as prescribed in ASTM Standard E8.

(ii) In using the "extension under load" method, the total strain (or "extension under load") corresponding to the stress at which the 0.2 percent permanent strain occurs may be determined with sufficient accuracy by calculating the elastic extension of the gauge length under appropriate load and adding thereto 0.2 percent of the gauge length. Elastic extension calculations must be based on an elastic modulus of

30,000,000. In the event of controversy, the entire stress-strain diagram must be plotted and the yield strength determined from the 0.2 percent offset.

(iii) For the purpose of strain measurement, the initial strain must be set while the specimen is under a stress of 12,000 pounds per square inch, and the strain indicator reading must be set at the calculated corresponding strain.

(iv) Cross-head speed of the testing machine may not exceed 1/8 inch per minute during yield strength determination.

(l) Acceptable results for physical and flattening tests. Either of the following is an acceptable result:

(1) An elongation at least 40 percent for a 2-inch gauge length or at least 20 percent in other cases and yield strength not over 73 percent of tensile strength. In this instance, the flattening test is not required.

(2) An elongation at least 20 percent for a 2-inch gauge length or 10 percent in other cases and a yield strength not over 73 percent of tensile strength. In this instance, the flattening test is required, without cracking, to 6 times the wall thickness.

(m) Leakage test. All spun cylinders and plugged cylinders must be tested for leakage by gas or air pressure after the bottom has been cleaned and is free from all moisture subject to the following conditions and limitations:

(1) Pressure, approximately the same as but no less than service pressure, must be applied to one side of the finished bottom over an area of at least 1/16 of the total area of the bottom but not less than ¾ inch in diameter, including the closure, for at least 1 minute, during which time the other side of the bottom exposed to pressure must be covered with water and closely examined for indications of leakage. Except as provided in paragraph (n) of this section, a cylinder that is leaking must be rejected.

(2) A spun cylinder is one in which an end closure in the finished cylinder has been welded by the spinning process.

(3) A plugged cylinder is one in which a permanent closure in the bottom of a finished cylinder has been effected by a plug.

(4) As a safety precaution, if the manufacturer elects to make this test before the hydrostatic test, the manufacturer should design the test apparatus so that the pressure is applied to the smallest area practicable, around the point of closure, and so as to use the smallest possible volume of air or gas.

(n) Rejected cylinders. Reheat treatment is authorized for rejected cylinders. Subsequent thereto, cylinders must pass all prescribed tests to be acceptable. Repair by welding or spinning is not authorized. Spun cylinders rejected under the provisions of paragraph (m) of this section may be removed from the spun cylinder category by drilling to remove defective material, tapping and plugging.

Sect. 178.37 Specification 3AA and 3AAX seamless steel cylinders

(a) Type, size, and service pressure. In addition to the requirements of Sect. 178.35, cylinders must conform to the following:

(1) A DOT-3AA cylinder is a seamless steel cylinder with a water capacity (nominal) of not over 1000 pounds and a service pressure of at least 150 pounds per square inch.
(2) A DOT-3AAX cylinder is a seamless steel cylinder with a water capacity of not less than 1000 pounds and a service pressure of at least 500 pounds per square inch, conforming to the following requirements:

(i) Assuming the cylinder is to be supported horizontally at its two ends only and to be uniformly loaded over its entire length consisting of the weight per unit of length of the straight cylindrical portion filled with water and compressed to the specified test pressure; the sum of two times the maximum tensile stress in the bottom fibers due to bending, plus that in the same fibers (longitudinal stress), due to hydrostatic test pressure may not exceed 80 percent of the minimum yield strength of the steel at such maximum stress. Wall thickness must be increased when necessary to meet the requirement.
(ii) To calculate the maximum tensile stress due to bending, the following formula must be used:

$$\mathbf{S = MC/I}$$

(iii) To calculate the maximum longitudinal tensile stress due to hydrostatic test pressure, the following formula must be used:

$$\mathbf{S = A_1P/A_2}$$

Where:

S = tensile stress, pounds per square inch;
M = bending moment, inch pounds $(wl^2)/8$;
w = weight per inch of cylinder filled with water;
l = length of cylinder, inches;
C = radius (D)/(2) of cylinder, inches;
I = moment of inertia, 0.04909 (D^4-d^4), inches fourth;
D = outside diameter, inches;
d = inside diameter, inches;
A_1 = internal area in cross section of cylinder, square inches;
A_2 = area of metal in cross section of cylinder, square inches;
P = hydrostatic test pressure, pounds per square inch.

(b) Authorized steel. Open-hearth, basic oxygen, or electric steel of uniform quality must be used. A heat of steel made under the specifications in table 1 of this paragraph (b) (check chemical analysis of which is slightly out of the specified range) is acceptable, if satisfactory in all other respects, provided the tolerances shown in table 2 of this paragraph (b) are not exceeded. When a carbon-boron steel is used, a hardenability test must be performed on the first and last ingot of each heat of steel. The results of this test must be recorded on the Record of Chemical Analysis of Material for Cylinders required by Sect. 178.35. This hardness test must be made 5/16 inch from the quenched end of the Jominy quench bar, and the hardness must be at least Rc 33 and no more than Rc 53. The following chemical analyses are authorized:

(c) Identification of material. Material must be identified by any suitable method except that plates and billets for hot-drawn cylinders must be marked with the heat number.

(d) Manufacture. Cylinders must be manufactured using equipment and processes adequate to ensure that each cylinder produced conforms to the requirements of this subpart. No fissure or other defects are permitted that are likely to weaken the finished cylinder appreciably. A reasonably smooth and uniform surface finish is required. If not originally free from such defects, the surface may be machined or otherwise treated to eliminate these defects. The thickness of the bottoms of cylinders welded or formed by spinning is, under no condition, to

Table 1—Authorized Materials

Designation	4130X (percent) (see Note 1)	NE-8630 (percent) (see Note 1)	9115 (percent) (see Note 1)	9125 (percent) (see Note 1)	Carbon-boron (percent)	Intermediate manganese (percent)
Carbon	0.25/0.35	0.28/0.33	0.10/0.20	0.20/0.30	0.27-0.37	0.40 max.
Manganese	0.40/0.90	0.70/0.90	0.50/0.75	0.50/0.75	0.80-1.40	1.35/1.65.
Phosphorus	0.04 max	0.04 max	0.04 max	0.04 max	0.035 max	0.04 max.
Sulfur	0.05 max	0.04 max	0.04 max	0.04 max	0.045 max	0.05 max.
Silicon	0.15/0.35	0.20/0.35	0.60/0.90	0.60/0.90	0.3 max.	0.10/0.30.
Chromium	0.80/1.10	0.40/0.60	0.50/0.65	0.50/0.65.		
Molybdenum	0.15/0.25	0.15/0.25				
Zirconium			0.05/0.15	0.05/0.15		
Nickel		0.40/0.70				
Boron					0.0005/0.003	

Note 1: This designation may not be restrictive, and the commercial steel is limited in analysis as shown in this table.

Table 2—Check Analysis Tolerances

Element	Limit or maximum specified (percent)	Tolerance (percent) over the maximum limit or under the minimum limit	
		Under minimum limit	Over maximum limit
Carbon	To 0.15 incl	0.02	0.03
	Over 0.15 to 0.40 incl	.03	.04
Manganese	To 0.60 incl	.03	.03
	Over 0.60 to 1.15 incl	0.04	0.04
	Over 1.15 to 2.50 incl	0.05	0.05
Phosphorus1	All ranges		.01
ulphur	All ranges		.01
Silicon	To 0.30 incl	.02	.03
	Over 0.30 to 1.00 incl	.05	.05
Nickel	To 1.00 incl	.03	.03
Chromium	To 0.90 incl	.03	.03
	0.90 to 2.90 incl	.05	.05
Molybdenum	To 0.20 incl	.01	
	Over 0.20 to 0.40	.02	.02
Zirconium	All ranges	.01	.05

[1]Rephosphorized steels not subject to check analysis for phosphorus.

be less than two times the minimum wall thickness of the cylindrical shell; such bottom thicknesses must be measured within an area bounded by a line representing the points of contact between the cylinder and floor when the cylinder is in a vertical position.

(e) Welding or brazing. Welding or brazing for any purpose whatsoever is prohibited except as follows:

(1) Welding or brazing is authorized for the attachment of neckrings and footrings which are non-pressure parts, and only to the tops and bottoms of cylinders having a service pressure of 500 pounds per square inch or less. Cylinders, neckrings, and footrings must be made of weldable steel, the carbon content of which may not exceed 0.25 percent except in the case of 4130X steel which may be used with proper welding procedure.
(2) As permitted in paragraph (d) of this section.

(f) Wall thickness. The thickness of each cylinder must conform to the following:

(1) For cylinders with a service pressure of less than 900 pounds, the wall stress may not exceed 24,000 pounds per square inch. A minimum wall thickness of 0.100 inch is required for any cylinder with an outside diameter of over 5 inches.
(2) For cylinders with service pressure of 900 pounds per square inch or more, the minimum wall must be such that the wall stress at the minimum specified test pressure may not exceed 67 percent of the minimum tensile strength of the steel as determined from the physical tests required in paragraphs (k) and (l) of this section and must be not over 70,000 pounds per square inch.
(3) Calculation must be made by the formula:

$$\mathbf{S = [P(1.3D^2 + 0.4d^2)]/(D^2 - d^2)}$$

Where:

S = wall stress in pounds per square inch;
P = minimum test pressure prescribed for water jacket test or 450 pounds per square inch, whichever is the greater;
D = outside diameter in inches;
d = inside diameter in inches.

(g) Heat treatment. The completed cylinders must be uniformly and properly heat treated prior to tests. Heat treatment of cylinders of the authorized analyses must be as follows:

(1) All cylinders must be quenched by oil, or other suitable medium except as provided in paragraph (g)(5) of this section.
(2) The steel temperature on quenching must be that recommended for the steel analysis, but may not exceed 1750 °F.
(3) All steels must be tempered at a temperature most suitable for that steel.
(4) The minimum tempering temperature may not be less than 1000°F, except as noted in paragraph (1)(vi) of this section.
(5) Steel 4130X may be normalized at a temperature of 1650°F instead of being quenched and cylinders so normalized need not be tempered.
(6) Intermediate manganese steels may be tempered at temperatures not less than 1150°F, and after heat treating each cylinder must be submitted to a magnetic test to detect the presence of quenching cracks. Cracked cylinders must be rejected and destroyed.

(7) Except as otherwise provided in paragraph (g)(6) of this section, all cylinders, if water quenched or quenched with a liquid producing a cooling rate in excess of 80 percent of the cooling rate of water, must be inspected by the magnetic particle, dye penetrant or ultrasonic method to detect the presence of quenching cracks. Any cylinder designed to the requirements for specification 3AA and found to have a quenching crack must be rejected and may not be requalified. Cylinders designed to the requirements for specification 3AAX and found to have cracks must have cracks removed to sound metal by mechanical means. Such specification 3AAX cylinders will be acceptable if the repaired area is subsequently examined to ensure no defect, and it is determined that design thickness requirements are met.

(h) Openings in cylinders and connections (valves, fuse plugs, etc.) for those openings. Threads are required on openings.

(1) Threads must be clean cut, even, without checks, and to gauge.
(2) Taper threads, when used, must be of a length not less than as specified for American Standard taper pipe threads.
(3) Straight threads having at least 6 engaged threads are authorized. Straight threads must have a tight fit and a calculated shear strength of at least 10 times the test pressure of the cylinder. Gaskets, adequate to prevent leakage, are required.

(i) Hydrostatic test. Each cylinder must successfully withstand a hydrostatic test as follows:

(1) The test must be by water jacket, or other suitable method, operated so as to obtain accurate data. The pressure gauge must permit reading to an accuracy of 1 percent. The expansion gauge must permit reading of total expansion to an accuracy of either 1 percent or 0.1 cubic centimeter.
(2) Pressure must be maintained for at least 30 seconds and sufficiently longer to ensure complete expansion. Any internal pressure applied after heat-treatment and previous to the official test may not exceed 90 percent of the test pressure. If, due to failure of the test apparatus, the test pressure cannot be maintained, the test may be repeated at a pressure increased by 10 percent or 100 pounds per square inch, whichever is the lower.
(3) Permanent volumetric expansion may not exceed 10 percent of total volumetric expansion at test pressure.
(4) Each cylinder must be tested to at least 5/3times the service pressure.

(j) Flattening test. A flattening test must be performed on one cylinder taken at random out of each lot of 200 or less by placing the cylinder between wedge-shaped knife edges having a 60^{o} included angle, rounded to a 1/2-inch radius. The longitudinal axis of the cylinder must be at a 90° angle to knife edges during the test. For lots of 30 or less, flattening tests are authorized to be made on a ring at least 8 inches long cut from each cylinder and subjected to the same heat treatment as the finished cylinder.

(k) Physical test. A physical test must be conducted to determine yield strength, tensile strength, elongation, and reduction of area of material as follows:

(1) The test is required on 2 specimens cut from 1 cylinder taken at random out of each lot of 200 or less. For lots of 30 or less, physical tests are authorized to be made on a ring at least 8 inches long cut from each cylinder and subjected to the same heat treatment as the finished cylinder.
(2) Specimens must conform to the following:

(i) Gauge length of 8 inches with a width of not over 11/2 inches, a gauge length of 2 inches with a width of not over 11/2 inches, or a gauge length of at least 24 times the thickness with width not over 6 times the thickness when the thickness of the cylinder wall is not over 3/16 inch.
(ii) The specimen, exclusive of grip ends, may not be flattened. Grip ends may be flattened to within 1 inch of each end of the reduced section.
(iii) When the size of the cylinder does not permit securing straight specimens, the specimens may be taken in any location or direction and may be straightened or flattened cold, by pressure only, not by blows. When specimens are so taken and prepared, the inspector's report must show in connection with record of physical tests detailed information in regard to such specimens.
(iv) Heating of a specimen for any purpose is not authorized.

(3) The yield strength in tension must be the stress corresponding to a permanent strain of 0.2 percent of the gauge length. The following conditions apply:

(i) The yield strength must be determined by either the "offset" method or the "extension under load" method as prescribed in ASTM Standard E8.
(ii) In using the “extension under load" method, the total strain (or "extension under load") corresponding to the stress at which the 0.2 percent permanent strain occurs may be determined with sufficient accuracy by calculating the elastic extension of the gauge length under appropriate load and adding thereto 0.2 percent of the gauge length. Elastic extension calculations must be based on an elastic modulus of 30,000,000. In the event of controversy, the entire stress-strain diagram must be plotted and the yield strength determined from the 0.2 percent offset.
(iii) For the purpose of strain measurement, the initial strain must be set while the specimen is under a stress of 12,000 pounds per square inch, the strain indicator reading being set at the calculated corresponding strain.
(iv) Cross-head speed of the testing machine may not exceed 1/8 inch per minute during yield strength determination.

(l) Acceptable results for physical and flattening tests. An acceptable result for physical and flattening tests is elongation at least 20 percent for 2 inches of gauge length or at least 10 percent in other cases. Flattening is required, without cracking, to 6 times the wall thickness of the cylinder.

(m) Leakage test. All spun cylinders and plugged cylinders must be tested for leakage by gas or air pressure after the bottom has been cleaned and is free from all moisture. Pressure, approximately the same as but no less than the service pressure, must be applied to one side of the finished bottom over an area of at least 1/16 of the total area of the bottom but not less than ¾ inch in diameter, including the closure, for at least one minute, during which time the other side of the bottom exposed to pressure must be covered with water and closely examined for indications of leakage. Except as provided in paragraph (n) of this section, a cylinder must be rejected if there is any leaking.

(1) A spun cylinder is one in which an end closure in the finished cylinder has been welded by the spinning process.
(2) A plugged cylinder is one in which a permanent closure in the bottom of a finished cylinder has been effected by a plug.

(3) As a safety precaution, if the manufacturer elects to make this test before the hydrostatic test, the manufacturer should design the test apparatus so that the pressure is applied to the smallest area practicable, around the point of closure, and so as to use the smallest possible volume of air or gas.

(n) Rejected cylinders. Reheat treatment is authorized for rejected cylinders. Subsequent thereto, cylinders must pass all prescribed tests to be acceptable. Repair by welding or spinning is not authorized. Spun cylinders rejected under the provision of paragraph (m) of this section may be removed from the spun cylinder category by drilling to remove defective material, tapping and plugging.

Sect. 178.38 Specification 3B seamless steel cylinders

(a) Type, size, and service pressure. A DOT 3B cylinder is seamless steel cylinder with a water capacity (nominal) of not over 1,000 pounds and a service pressure of at least 150 to not over 500 pounds per square inch.

(b) Steel. Open-hearth or electric steel of uniform quality must be used. Content percent may not exceed the following: carbon, 0.55; phosphorus, 0.045; sulfur, 0.050.

(c) Identification of material. Material must be identified by any suitable method except that plates and billets for hot-drawn cylinders must be marked with the heat number.

(d) Manufacture. Cylinders must be manufactured using equipment and processes adequate to ensure that each cylinder produced conforms to the requirements of this subpart. No fissure or other defect is permitted that is likely to weaken the finished cylinder appreciably. A reasonably smooth and uniform surface finish is required. If not originally free from such defects, the surface may be machined or otherwise treated to eliminate these defects. The thickness of the bottoms of cylinders welded or formed by spinning is, under no condition, to be less than two times the minimum wall thickness of the cylindrical shell; such bottom thickness to be measured within an area bounded by a line representing the points of contact between the cylinder and floor when the cylinder is in a vertical position.

(e) Welding or brazing. Welding or brazing for any purpose whatsoever is prohibited except as follows:

(1) Welding or brazing is authorized for the attachment of neckrings and footrings which are non-pressure parts, and only to the tops and bottoms of cylinders having a service pressure of 500 pounds per square inch or less. Cylinders, neckrings, and footrings must be made of weldable steel, the carbon content of which may not exceed 0.25 percent except in the case of 4130X steel, which may be used with proper welding procedure.

(2) As permitted in paragraph (d) of this section.

(f) Wall thickness. The wall stress may not exceed 24,000 pounds per square inch. The minimum wall thickness is 0.090 inch for any cylinder with an outside diameter of 6 inches. Calculation must be made by the following formula:

$$S = [P(1.3D^2 + 0.4d^2)]/(D^2 - d^2)$$

Where:

S = wall stress in pounds per square inch;
P = at least two times the service pressure or 450 pounds per square inch, whichever is the greater;
D = outside diameter in inches;
d = inside diameter in inches.

(g) Heat treatment. The completed cylinders must be uniformly and properly heat treated prior to tests.

(h) Openings in cylinders and connections (valves, fuse plugs, etc.) for those openings. Threads, conforming to the following, are required on all openings:

(1) Threads must be clean cut, even, without checks, and to gauge.

(2) Taper threads, when used, must be of a length not less than as specified for American Standard taper pipe threads.

(3) Straight threads having at least 4 engaged threads are authorized. Straight threads must have a tight fit and calculated shear strength at least 10 times the test pressure of the cylinder. Gaskets, adequate to prevent leakage, are required.

(i) Hydrostatic test. Cylinders must successfully withstand a hydrostatic test, as follows:

(1) The test must be by water jacket, or other suitable method, operated so as to obtain accurate data. The pressure gauge must permit reading to an accuracy of 1 percent. The expansion gauge must permit reading of total expansion to an accuracy either of 1 percent or 0.1 cubic centimeter.
(2) Pressure must be maintained for at least 30 seconds and sufficiently longer to ensure complete expansion. Any internal pressure applied after heat treatment and previous to the official test may not exceed 90 percent of the test pressure. If, due to failure of the test apparatus, the test pressure cannot be maintained, the test may be repeated at a pressure increased by 10 percent or 100 pounds per square inch, whichever is the lower.
(3) Permanent volumetric expansion may not exceed 10 percent of total volumetric expansion at test pressure.
(4) Cylinders must be tested as follows:

(i) Each cylinder: to at least 2 times service pressure; or
(ii) 1 cylinder out of each lot of 200 or less: to at least 3 times service pressure. Others must be examined under a pressure of 2 times service pressure and show no defect.

(j) Flattening test. A flattening test must be performed on one cylinder taken at random out or each lot of 200 or less, by placing the cylinder between wedge shaped knife edges having a 60^{o} included angle, rounded to a 1/2-inch radius. The longitudinal axis of the cylinder must be at a 90° angle to knife edges during the test. For lots of 30 or less, flattening tests are authorized to be made on a ring at least 8 inches long cut from each cylinder and subjected to the same heat treatment as the finished cylinder.
(k) Physical test. A physical test must be conducted to determine yield strength, tensile strength, elongation, and reduction of area of material, as follows:

(1) The test is required on 2 specimens cut from 1 cylinder taken at random out of each lot of 200 or less. For lots of 30 or less, physical tests are authorized to be made on a ring at least 8 inches long cut from each cylinder and subjected to same heat treatment as the finished cylinder.
(2) Specimens must conform to the following:

(i) Gauge length of 8 inches with a width of not over 11/2 inches; or a gauge length of 2 inches with a width of not over 11/2 inches; or a gauge length at least 24 times the thickness with a width not over 6 times thickness is authorized when a cylinder wall is not over 3/16 inch thick.
(ii) The specimen, exclusive of grip ends, may not be flattened. Grip ends may be flattened to within one inch of each end of the reduced section.
(iii) When size of cylinder does not permit securing straight specimens, the specimens may be taken in any location or direction and may be straightened or flattened cold, by pressure only, not by blows. When specimens are so taken and prepared, the inspector's report must show in connection with record of physical tests detailed information in regard to such specimens.
(iv) Heating of a specimen for any purpose is not authorized.

(3) The yield strength in tension must be the stress corresponding to a permanent strain of 0.2 percent of the gauge length. The following conditions apply:

(i) The yield strength must be determined by either the "offset" method or the "extension under load" method as prescribed in ASTM Standard E8.
(ii) In using the "extension under load" method, the total strain (or "extension under load") corresponding to the stress at which the 0.2 percent permanent strain occurs may be determined with sufficient accuracy by calculating the elastic extension of the gauge length under appropriate load and adding thereto 0.2 percent of the gauge length. Elastic extension calculations must be based on an elastic modulus of 30,000,000. In the event of controversy, the entire stress-strain diagram must be plotted and the yield strength determined from the 0.2 percent offset.
(iii) For the purpose of strain measurement, the initial strain must be set while the specimen is under a stress of 12,000 pounds per square inch, and the strain indicator reading being set at the calculated corresponding strain.
(iv) Cross-head speed of the testing machine may not exceed 1/8 inch per minute during yield strength determination.

(l) Acceptable results for physical and flattening tests. Either of the following is an acceptable result:

(1) An elongation of at least 40 percent for a 2-inch gauge length or at least 20 percent in other cases and yield strength not over 73 percent of tensile strength. In this instance, the flattening test is not required.
(2) An elongation of at least 20 percent for a 2-inch gauge length or 10 percent in other cases and yield strength not over 73 percent of tensile strength. Flattening is required, without cracking, to 6 times the wall thickness.

(m) Leakage test. All spun cylinders and plugged cylinders must be tested for leakage by gas or air pressure after the bottom has been cleaned and is free from all moisture, subject to the following conditions and limitations:

(1) Pressure, approximately the same as but no less than service pressure, must be applied to one side of the finished bottom over an area of at least 1/16 of the total area of the bottom but not less than 3/4 inch in diameter, including the closure, for at least one minute, during which time the other side of the bottom exposed to pressure must be covered with water and closely examined for indications of leakage. Except as provided in paragraph (n) of this section, a cylinder must be rejected if there is any leaking.
(2) A spun cylinder is one in which an end closure in the finished cylinder has been welded by the spinning process.
(3) A plugged cylinder is one in which a permanent closure in the bottom of a finished cylinder has been effected by a plug.
(4) As a safety precaution, if the manufacturer elects to make this test before the hydrostatic test, he should design his apparatus so that the pressure is applied to the smallest area practicable, around the point of closure, and so as to use the smallest possible volume of air or gas.

(n) Rejected cylinders. Reheat treatment of rejected cylinders is authorized. Subsequent thereto, cylinders must pass all prescribed tests to be acceptable. Repair by welding or spinning is not authorized. Spun cylinders rejected under the provisions of paragraph (m) of this section may be removed from the spun cylinder category by drilling to remove defective material, tapping and plugging.

(o) Marking. Markings may be stamped into the sidewalls of cylinders having a service pressure of 150 psi if all of the following conditions are met:

(1) Wall stress at test pressure may not exceed 24,000 pounds per square inch.
(2) Minimum wall thickness must be not less than 0.090 inch.
(3) Depth of stamping must be no greater than 15 percent of the minimum wall thickness, but may not exceed 0.015 inch.
(4) Maximum outside diameter of cylinder may not exceed 5 inches.
(5) Carbon content of cylinder may not exceed 0.25 percent. If the carbon content exceeds 0.25 percent, the complete cylinder must be normalized after stamping.
(6) Stamping must be adjacent to the top head.

APPENDIX C

APPENDIX C

UNLOADING

Unloading Anhydrous Hydrofluoric Acid with Compressed Air

1. Connect Lines – connect air line to A1, liquid to line L1.
2. Equalize Pressure – open A1 and A2 making sure that A3 is closed. Read tank car pressure on G1, storage tank pressure on G3. If tank pressure exceeds tank car pressure open A6, than open A5 until G1 and G3 read the same. Close A5 and A6.
3. Adjust Air Pressure – set the pressure regulator so that G2 reads about 25 pounds higher than G3. This 25 pounds is in addition to any differential to lift the acid to storage tank level. Total pressure must not exceed pressure limits of relief devices on tank car or storage tank. Open A4 until G1 and G2 indicate the same pressure. Close A4.
4. Unload – open L4, L2, L1, making sure that L3 is closed. Open A4. If the pressure on G3 approaches that on G2 open A6 and A7 intermittently as necessary to maintain the proper differential. Adjust A4 to maintain the desired rate of flow.
5. Vent Car and Air Lines – when car is empty close A6 (if open), L4, A4. Open A5 and A7 (if closed) and allow tank car and air lines to vent. After venting close A1 and A2.
6. Drain Liquid Lines – close A5, A7, L1 and L2. Carefully open A3 and L3. (Drain should be located at the lowest point in the line). Close A3 and L3 after lines have drained.
7. Disconnect – disconnect liquid and air lines at car. Replace all pipe caps and plugs on the car, reverse tank car placards.

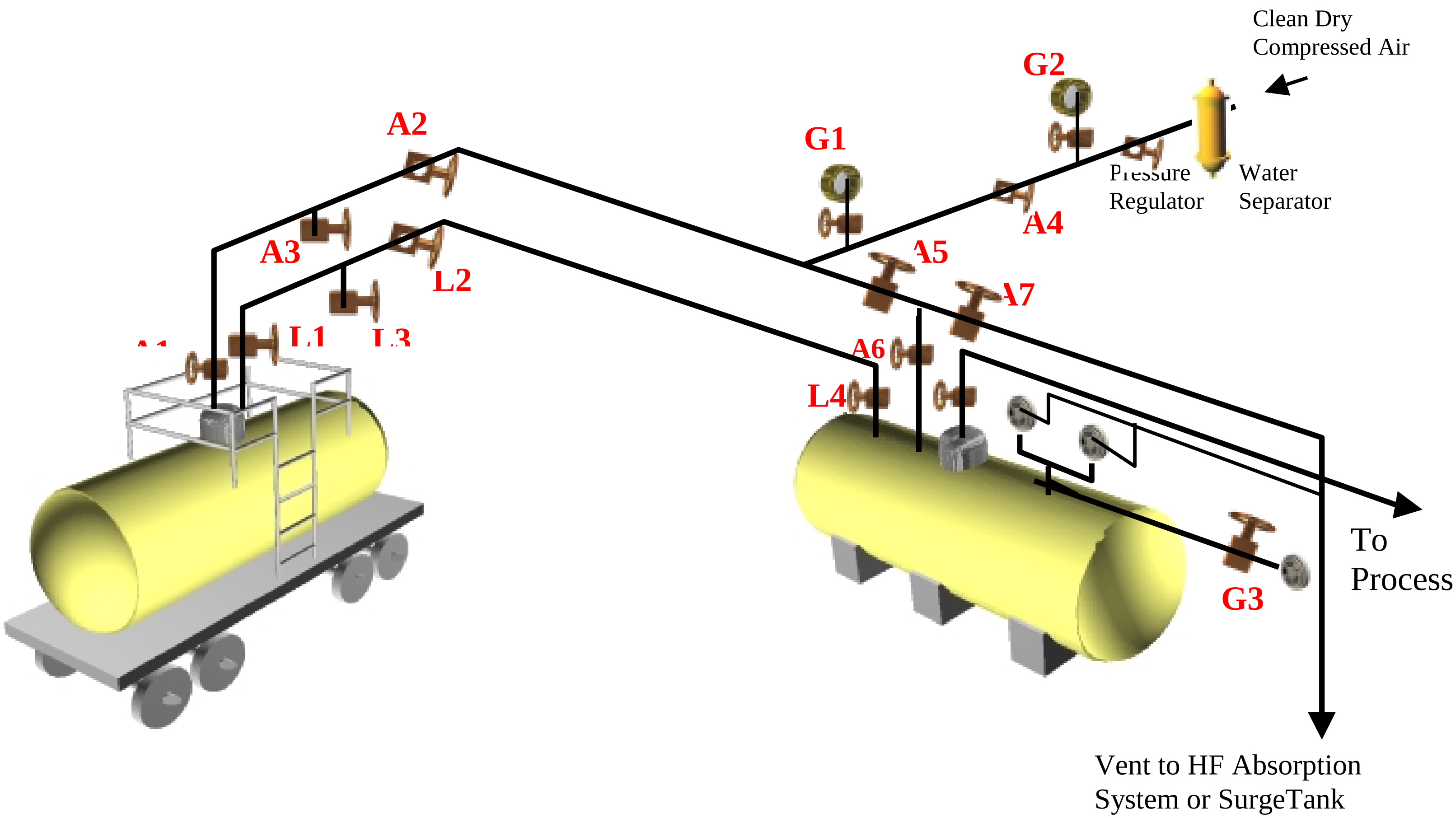

Figure C1. Unloading Anhydrous Hydrofluoric Acid with Compressed Air

Unloading Anhydrous Hydrofluoric Acid by Pump

1. Connect Lines -- connect L1 to the inlet side of pump then open A1. Read tank car pressure on G1, storage tank pressure on G2. Open A2, A5 and A3 to equalize pressures. Leave A1, A2, A3 and A5 open during unloading to maintain equal pressures. Open L1, L2, L4, L5, L7, making sure that all drain valves are closed.
2. Unload – start pump and continue pumping until car is empty as indicated by scale weights on storage tank. (If pump needs priming connect air supply as shown, close A2 and apply only enough pressure to start the pump. When pump starts, close air line and open A2).
3. Clear Lines – allow pump to run until liquid line is clear. Stop pump, close A3, L1, L2, L4, L5, L7 (never close the valves on the discharge side of a positive pump while the pump is running). Open L3, L6, L9. If the pump is equipped with a drain, open it. When lines have drained close drain valves.
4. Disconnect – if the car is under pressure open A4 and vent to absorption system. Close A1, A2, A4, A5. Disconnect the liquid line and pressure equalizing line. Replace plugs and caps on the car, reverse tank car placards.

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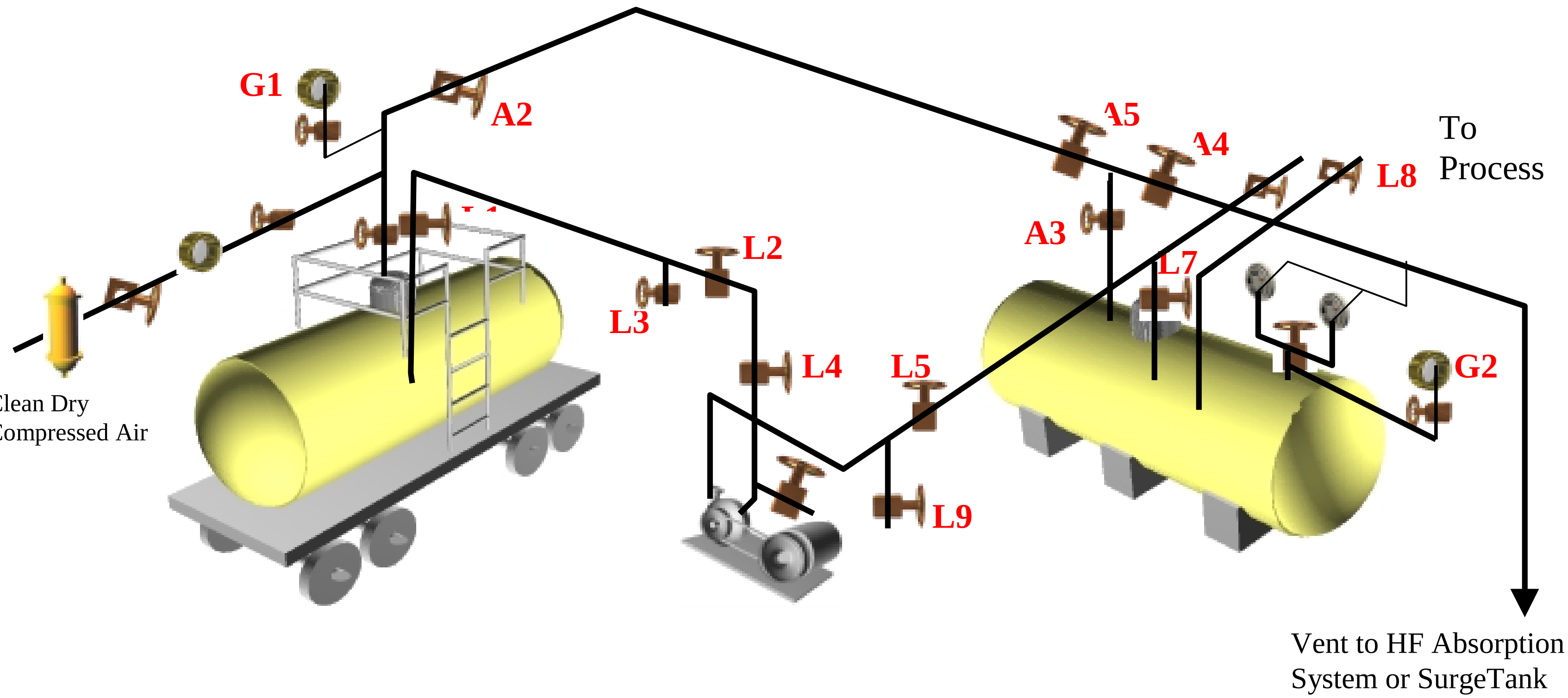

Fig. C2. Unloading Anhydrous Hydrofluoric Acid by Pump

Unloading Aqueous Hydrofluoric Acid with Compressed Air

1. Connect Lines—carefully remove the plug from L1, and connect the liquid line with the valve closed. With A2, A3, and A4 closed, connect the air line to A1.
2. Apply Pressure—open L1, L2 and L4. Make sure L3 is closed. Open A1, A4, then A3. Admit only enough air to provide a reasonable rate of flow—do not exceed 30 pounds per inch. Vent storage tank during unloading, as required.
3. Release Pressure—after unloading close A3, A4, L1, and L4. Open A2 to vent pressure. (Vent HF vapor to an absorption system rather than to the air.) After the pressure has been released, close A1 and disconnect the air line.
4. Close the Car—open L3 to drain the liquid line. Close L3. Disconnect the liquid line from L1. Replace all caps and plugs; reverse tank car placards.

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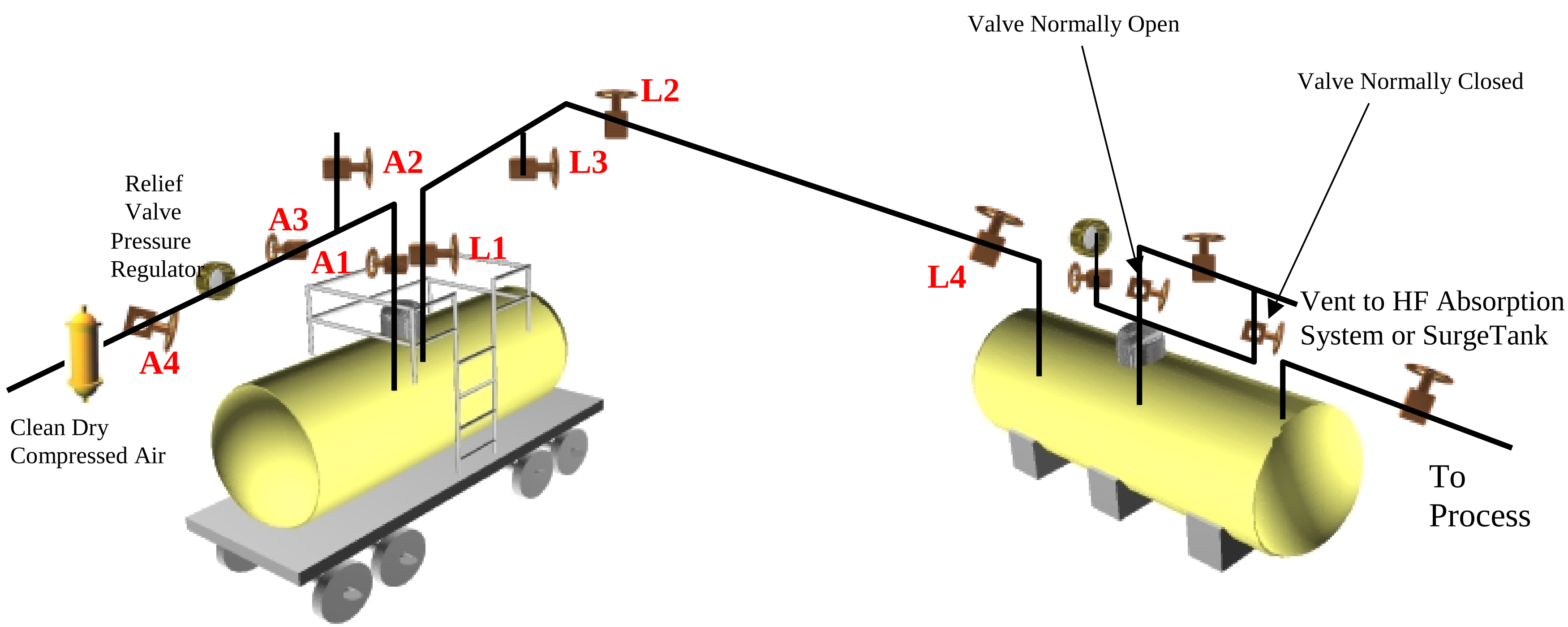

Fig. C3. Unloading Aqueous Hydrofluoric Acid with Compressed Air.

Unloading Aqueous Hydrofluoric Acid by Pump

1. Connect Lines—connect the liquid line to L1. Make sure that A3 and A4 are closed. Connect the air line to A1 (the air line is provided only to prime the pump).
2. Unload— open L1, L2, and L3. Make certain that drain valves L4 and L6 are securely closed. Open L5 and vent on storage tank. Start pump and open A1, A3 and A4. As soon as acid starts to flow close A3 and A4. When the pressure in the tank has dropped, open A2 to admit air during unloading. Pump until the car is empty.
3. Close the Car—stop the pump and close A1, L1, L2, and L5 (never close the valves on the discharge side of a positive pump while is running). Drain the liquid lines through L4 and L6. Close A2, L3, L4, and L6. Disconnect the air line. Disconnect the liquid line. Replace plugs and caps on tank car valves; reverse tank car placards.

ORNL No. 99-06781

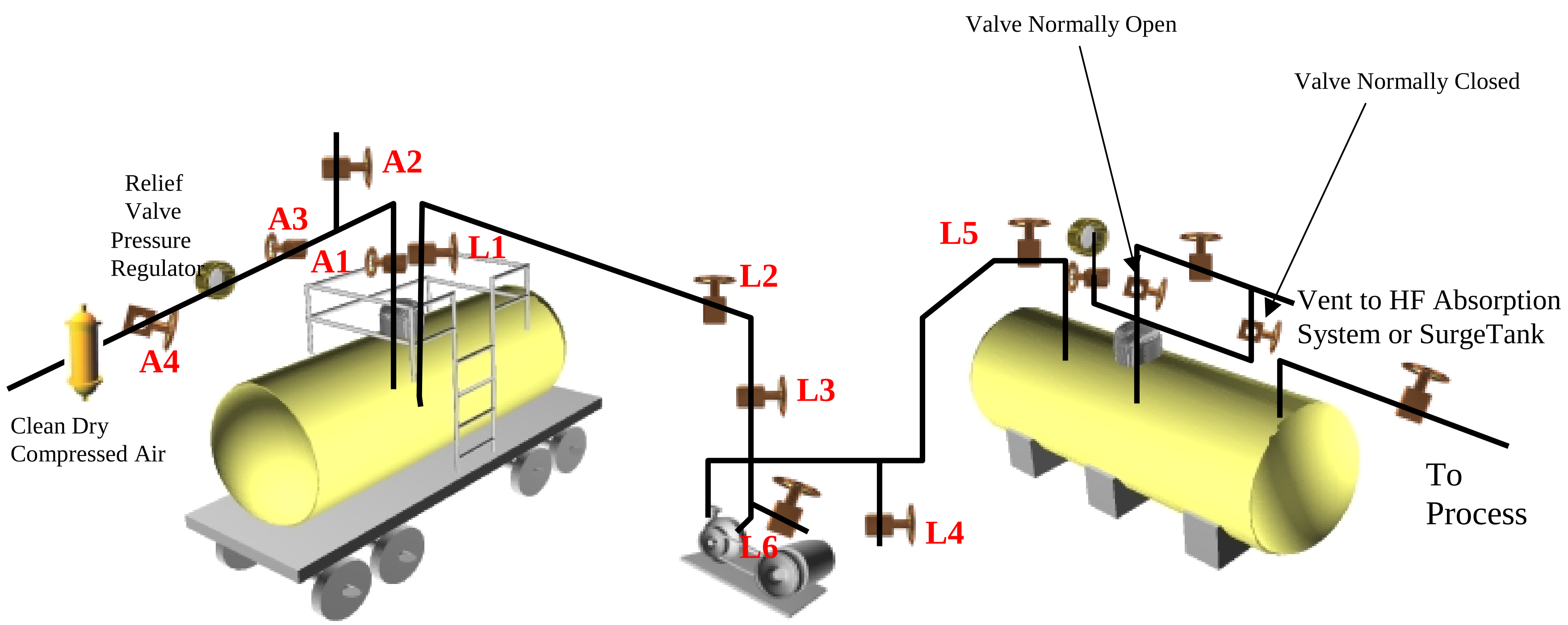

Fig. C4. Unloading Aqueous Hydrofluoric Acid by Pump.

APPENDIX D

The LLNL Health and Safety Manual
Sect. 21.12: Safe Handling of Fluorine

Introduction

This supplement to the Health & Safety Manual describes the common hazards associated with fluorine and details engineering and procedural controls required for its safe use. This supplement is organized according to the process you must go through to safely handle fluorine at LLNL: (1) educate yourself on the chemical and physical hazards of fluorine, (2) design the fluorine system with appropriate engineering controls, (3) understand the procedure for purchasing fluorine, and understand the administrative controls for the safe use of fluorine and the maintenance of fluorine systems.

Because fluorine is a controlled item, you, the requestor, must contact your area Safety Team when operations require its use or the use of its inert gas mixtures. You will be directed to write an Operational Safety Procedure (OSP) and obtain an Engineering Safety Note for each operation. Your Safety Team will review the safety controls outlined in these documents and approve the purchase of fluorine if controls are judged to be adequate.

Treat mixtures of fluorine and inert gases with the same care as pure fluorine unless otherwise noted in this supplement or unless individual exceptions have been approved by your Safety Team. Document any exceptions in the operation's OSP and in an Engineering Safety Note.

Although fluorine is extremely hazardous, it can be handled safely if the proper precautions are taken. Only trained and competent personnel are permitted to handle fluorine; therefore, you should be familiar with the contents of this supplement and with such information as the Material Safety Data Sheet available from the supplier and the OSP and Engineering Safety Note associated with your operation.

This supplement covers pure fluorine, mixtures of fluorine in other gases and oxidizing fluorides such as XeF_6, ClF, ClF_3, ClF_5, and other halogen fluorides unless otherwise specified. Other reactive fluorides which are not vigorous oxidizers (i.e., HF, BF_3, WF_6, and NF_3) are not covered by this supplement.

Hazards of Fluorine

Chemical Hazards. Fluorine is a highly toxic and corrosive pale yellow gas whose sharp, penetrating odor is similar to that of a high concentration of ozone. The most powerful oxidizing element known, fluorine (a halogen) reacts readily with practically all organic and inorganic substances except inert gases, metal fluorides in their highest valence state, and a few pure and completely fluorinated organic compounds. However, even these few pure and fluorinated organic compounds may burn in a fluorine atmosphere if they are contaminated with a combustible material or are subjected to high flow rates of fluorine.

Hydrogen and fluorine combine with extreme violence, forming hydrogen fluoride. Fluorine also reacts explosively with most organic compounds. Moreover, it reacts with other halogen gases to form such compounds as ClF, ClF_3, BrF_3, and IF_5.

Although oxygen does not ordinarily react with fluorine, two oxygen fluorides, OF_2 and O_2F_2, do react with it. The extreme reactivity of fluorine demands that you properly clean and passivate a fluorine system prior to using fluorine in that system. An explosion and fire may result if proper procedures are not followed.

Health Hazards

Inhalation of fluorine gas can cause nose and throat irritation, respiratory tract and lung injury, unconsciousness, and even death. If fluorine makes contact with your skin or eyes, burns may result. These burns are caused by heat produced when fluorine or hydrogen fluoride (the result of fluorine reacting with moisture in the air) reacts with the moisture on the skin. Moreover, fluoride ions can penetrate deeply to the bone, replacing the hydroxide ions in the bone to produce injury.

Pain from injuries associated with fluorine exposures is often delayed especially if the fluorine is dilute. Therefore, if you even suspect you may have been exposed, rinse your skin and eyes with large amounts of water; continue rinsing for 20 min. Get immediate medical treatment. Appendix A to this supplement describes the proper emergency procedures to be followed in the event of exposure to fluorine.

Hygienic Standards. According to the U.S. Department of Labor Occupational Safety and Health Administration,[1] the allowable limit for an 8-h time-weighted average exposure to fluorine in a 40-h work week is 0.1 part per million (ppm). Fluorine gas is so irritating that humans will not tolerate excessive exposures to it. In one incident, brief inhalation of a concentration of 25 ppm caused acute toxic effects in humans. In a study on mice, the lethal concentration for 50% of the mice after 60 min of exposure was 150 ppm. Direct skin exposure to pure fluorine can cause severe burns in 0.2 s, and an exposure for as long as 0.6 s can result in thermal flash burns comparable to those produced by an oxyacetylene flame.

Precautions for the Safe Use of Fluorine

Engineering Controls. As stated in Pressure Vessel and System Design, Supplement 32.03 of the Health & Safety Manual, you must ensure that an Engineering Safety Note is attached to the OSP for all toxic or corrosive gas systems; this includes fluorine systems. Whenever a change is made to a system you must obtain a new or revised Engineering Safety Note documenting that change. Direct any questions regarding Engineering Safety Notes to the Pressure Safety Manager or your Safety Team.

You are responsible for establishing the following engineering controls to preclude the release of fluorine into the work area.

Isolation. Closed systems, constructed to prevent the escape of gas into work areas, must be used for all fluorine operations within a building.

Gas Storage Cabinets. All cylinders or containers in use or ready-to-use status need to be kept in ventilated gas storage cabinets. Cylinders must be moved with their caps on until they have been put into and secured in a gas storage cabinet. Gas storage cabinets are commercially available for cylinders in ready-to-use condition. These were developed for the semiconductor industry and can be used without modification for fluorine/inert gas mixtures containing <5% fluorine (10% fluorine/inert gas mixtures can be used to passivate these systems). Gas storage cabinets need the following features:

Eighteen gauge or thicker steel walls (minimum required by UFC Article 80) for fluorine/inert-gas mixtures containing $\leq$10% fluorine.

The smallest doors consistent with safe cylinder handling. The doors must be self-closing and need louvers so the cabinet will be under flowing suction ventilation at all times (see the next item for air flow specifications).

Self-closing and self-latching windows to make all routine valve adjustments other than those needed to remove old cylinders and install new ones. Air flow needs to be sufficient to maintain an inflow of air at an average velocity of 200 feet per minute (fpm) and never less than 150 fpm anywhere in the plane of the fully opened window. Test smoke released in the window plane must never flow outward.

Toxic gas detectors installed inside the cabinet. Cylinders must be rigidly clamped so that opening the supply valve will not cause torque to be transmitted to the regulator manifold (we have found that this can cause a leak). Cabinets used for pure fluorine, inert gas mixtures containing >10% fluorine, other gas mixtures, and oxidizing fluorides should have bare-finish stainless steel walls. Such cabinets also need:

Barricades to protect the operator. Valve handles that protrude through the cabinet wall to minimize the times when an operator must open the cabinet door or window and reach inside. Air velocities through the holes must be 500 fpm or more.

Delivery Hardware. Delivery pipes and tubes must be of all-welded construction or be double walled. The outer tubing must be under suction ventilation and be continuously monitored for gas leakage in a double-walled system. Double-walled and all-welded lines are recommended and may become mandatory in the future. All non-welded joints and fittings must be in enclosures that are under suction ventilation and monitored for gas leakage. The materials in all-welded lines and the inner tubes of double-walled lines must be made of compatible materials.

Compatible Materials. Compatible materials must be used. These are summarized in Appendix B for fluorine and fluorine/inert gas mixtures. Contact the material vendor for guidance about compatible materials for the material, temperature and pressure you will use. Additional guidance is available from your Hazards Control Field Team.

At room temperature, fluorine reacts slowly with many metals; this often results in the formation of a metal fluoride film that retards fluorine's effect on brass, iron, aluminum, magnesium, and copper. Hence, these metals are quite satisfactory for handling fluorine at room temperature. However, at higher temperatures, you must consult the manufacturer regarding the adequacy of the material to be used. For example, nickel and Monel are more resistant to corrosion from fIuorine at higher temperatures.

Passivation of Equipment. All equipment used in fluorine operations must be thoroughly cleaned, degreased, dried, and passivated. Never use pure fluorine to passivate fluorine equipment or systems. Several procedures can be used for passivation. See Appendix C for examples of cleaning and passivation procedures. The type of procedure will depend on the system to be installed. Contact your Safety Team or the Industrial Hygiene Group of the Hazards Control Department for information on procedures.

You must describe the passivation procedure in the OSP for your operation. A passivation procedure checklist unique to your operation is desirable.

All systems must be flow tested ("dry-run") with dry, inert gas before passivation of the assembled system begins if such testing is feasible.

Discharging Fluorine or Fluorine-Like Materials to the Atmosphere. NEPA/CEQA requirements mandate discharging fluorine, any fluorine mixture, or reactive fluoride to the atmosphere in a controlled manner. See Supplement 12.03 of the LLNL Health & Safety Manual for further details about how to plan atmospheric discharge controls. The area Industrial Hygienist will specify the controls needed. Possible controls include:

Rock salt beds. Useful for concentrated streams. The fluorine displaces the chlorine so chlorine remover is needed just downstream. Chlorine is less reactive and somewhat less toxic.

Caustic scrubbing followed by precipitation for large gas streams.

Tall stacks for emergency releases. Tall stacks are used only for discharging unplanned releases or when other controls for planned releases are not practical! Use the cylinder leak time specified by the vendor, if possible, or assume a cylinder filled with liquefied gas voids in 30 min and a cylinder containing gas only will void in 5 min when planning for emergency releases.

Cylinder size limits. Cylinder size limits can be used to reduce the height of a stack needed for emergency releases. Activated carbon was used for removing fluorine gas. This technique is no longer acceptable because it has been found that the fluorine can react explosively with the carbon. Keep any used carbon beds on hand in secure locations away from heat and call Hazards Control for guidance about disposal of them.

Purging. Any equipment that has contained fluorine must be thoroughly purged with dry, inert gas (such as nitrogen) and evacuated at least once before opening or refilling it. Purging by a sequential evacuation and inert gas backfill is preferred; backfill locations need to be as close to the fluorine/fluoride source as possible. Automated purge controllers need to be used whenever possible for sequential evacuation/ backfill purging to reduce the risk of human error during this tedious but critical process.

Gas Monitoring. Gas monitoring is needed where people are or could be present. Contact your Hazards Control Field Team for guidance about available sensors, alarms, and alarm annunciation requirements.

Labels and Signs. Labels need to be conspicuously posted near entrances to areas where fluorine is stored or used. Equivalent signs are needed for oxidizing fluorides (contact your Hazards Control Field Team to get these signs). In addition to the signs, information concerning the quantity of fluorine in use in the area should be posted at the entrance, along with emergency procedures to be followed in case of an accident. "No smoking" signs should also be posted where fluorine is stored or used. Lines carrying fluorine must be labeled once every 20 ft, at wall penetrations, and in concealed spaces. (It's a good idea never to run fluorine lines through concealed spaces!)

Inactive Gas Storage. Containers that are not in use or ready to be used (i.e., cylinders with valves shut and caps on and thoroughly sealed containers of materials such as XeF_6 need to be stored in protected outdoor locations or dedicated-use buildings where they are protected from temperature extremes, contact with rain or condensed moisture, and direct sunlight. Indoor storage spaces need to be vented at a rate of 1 cfm/ft^2 or 10 air changes per hour, whichever is greater. These storage areas must be normally locked and unoccupied, and entrances need to be posted with appropriate warning signs. Combustible/flammable materials and reducing agents cannot be stored in the same area.

No part of the cylinders should be subjected to temperatures higher than 52°C (125°F); therefore, place them away from radiators and other heat sources that could cause an excessive rise in temperature. CAUTION: Never allow flame to come in contact with any part of a compressed-gas cylinder. Fluorine cylinders are not equipped with pressure-relief devices.

Additional Design Precautions. Below are additional design precautions that you must take when working with a fluorine system.

Pipes and Fittings. Weld the pipes and fittings of lines that are not to be dismantled. Socket-weld fittings are preferable to butt-weld fittings because they are easier to keep free of slag and foreign matter during joining. However, butt-weld fittings are acceptable if shielded arc techniques are used.

Where welding is impractical, use threaded joints or tube fittings, as long as these fittings are contained in an exhaust ventilation enclosure. Permatex #2, manufactured by Loctite, is recommended as a pipe dope; apply it only after the first few threads of the male fitting are engaged. Parker Aircraft, Swagelok, or Cajon fittings (or equivalent) may be used where small connections in the system are broken frequently.

Pressure Regulators. Regulators must be used on a high-pressure fluorine source to facilitate the safe handling of pressure. Using a double-valving system alone to control pressure is not acceptable.

The Instrument Shop will not supply a fluorine regulator unless you present the appropriate Engineering Safety Note or authorization from the Pressure Safety Manager. Ensure that all regulators are inspected and pressure tested by the Instrument Shop and are labeled with the LLNL pressure-tested label shown on page 17 of Pressure Vessel and System Design, Supplement 32.03, of the Health & Safety Manual.

Pressure-Relief Protection. For low-pressure work (3 psi or less), blow-out traps, similar to laboratory test tubes, are recommended to warn of blocked lines or vessels when spring-loaded valves or rupture disks are not available. These traps are filled with chlorotrifluoroethylene (Kel-F) polymer oil. The head of oil should not exceed a nominal 6 in. The trap(s) should be placed in a ventilated enclosure that can exhaust any accidentally vented fluorine. If a blow-out trap is needed, contact the Matheson Company, East Rutherford, NJ.

All components of fluorine systems using pressures above those protected by blow-out traps must have a rated working pressure above the maximum pressure that could accidently occur in the system. A safety factor of 5 to 8 shall be used in the system design.

When the maximum fluorine pressure could exceed the rated working pressure of any system component because of the pressure supply source or the heat involved in the operation, the system must be protected by a spring-loaded pressure-relief device or a rupture disk. When using a pressure-relief device, ensure that device is acceptable for use in a fluorine system. When using a rupture disk, the discharge from the disk must be directed into a local exhaust ventilation system or extended into an area where it can discharge safely. You must establish a regular program for replacing rupture disks to prevent corrosion from weakening the disks and causing them to fail prematurely.

Use of a three-disk system is recommended: the inner disk protects the center disk from corrosion by direct contact with gas. The center disk is rated to rupture at a designated pressure, and the outer disk protects the center disk from moisture corrosion.

Valves. All valves for fluorine service must have dissimilar metal-to-metal seating to prevent galling. They shall be provided with packless stem sealing and Monel or stainless-steel bodies. If packed valves are used, tetrafluoroethylene polymer shall be used in the stuffing box.

Gauges. Gauges with Monel or stainless-steel Bourdon tubes passivated for fluorine service shall be used. Gauges should be appropriate for indicating up to two times the pressures expected at the gauged points in the system.

Hydrogen Fluoride Traps (Optional). Hydrogen fluoride impurities can be removed from commercial fluorine using a trap containing sodium fluoride.

Flow Meters. Flow meters must be constructed of materials acceptable for use in a fluorine system.

Purge System. A purge system is required for experiments or operations using fluorine. The purge system must include an inert gas supply. This gas supply shall be protected from the fluorine system by use of fluorine-compatible check valves.

It may be desirable to treat the fluorine purged from the system rather than release it to the atmosphere. Your Safety Team will determine this need during the design phase of the system and will recommend procedures for treating fluorine exhaust.

Vacuum Pumps. Vacuum pumps compatible with fluorine systems must be used. To protect the pump, a soda-lime tower followed by a dryer shall be included in the vacuum line to pick up trace amounts of fluorine. Vacuum pump systems using LN_2 traps shall have a relief device vented to a local exhaust ventilation system.

Eyewash and Safety Shower Facilities. You are responsible for ensuring that eyewash and safety shower facilities are located within 10-s travel time or 100-ft walking distance of your fluorine operation.

Administrative Controls

The minimum quantity needed to do a job must be used to minimize dangers to safety. Using minimum quantities of materials such as XeF_6 will also minimize the amount of material left over that must be disposed of as expensive hazardous waste. The lowest fluorine concentration that will do the job also needs to be used.

Two key administrative controls are OSPs and training.

- OSPs. OSPs for fluorine operations need to specify:
- The quantity, concentration, and type of material in storage and in use and where it will be stored and used.
- Personal protective equipment (including respirators).
- Passivation and cleaning procedures (also required in the Engineering Safety Note).
- Safety checklist.
- Procedures for dismantling and disposing of used equipment. Fluoride salts may be left over in lines and ducts being removed, but they are only modestly toxic and irritating so disposable lab coats and disposable respirators will often offer adequate protection from these salts (but not the gas). Exposures to massive amounts of fluoride residues will require whole body coveralls and more protective respirators. Fluorides are environmentally hazardous so fluorides and fluoride-contaminated items will need to be disposed of as hazardous waste. Residual fluorine, all fluorine mixtures, or reactive fluoride gases will need to be purged from systems and the fluorine/fluoride sources sealed (this means shutting the valves of cylinders and capping them). Contact your Hazards Control Field Team for guidance.

Training. Personnel need to take H5-503, "Pressure Safety Orientation," H5-504, "Intermediate Pressure Safety," and H5-512, "Fluorine Safety" before starting such work. Personnel also need to take the following before starting such work:

- H5-511, "Installers Practical Test" (for those who build or repair or assemble the system).

- H5-506, "Pressure Seminar for Engineers" (for those who prepare Engineering Safety Notes and design the system).

- Review the applicable OSP, Engineering Safety Note and this Supplement. Personnel preparing OSPs should also take H5-32, "Preparing an Operational Safety Procedure."

Fluorine users must also be aware of and follow these administrative controls:

- Personnel who transport or handle cylinders of pure fluorine, inert gas mixtures, containing >10% fluorine, other fluorine mixtures, and oxidizing fluorides need to be be warned that dropping, shocking, or striking cylinders could cause an incident.

- Cylinders of fluorine, inert gas mixtures containing >10% fluorine, other fluorine mixtures, and oxidizing fluorides need to be transported in the back of an open truck.

    - Personnel should never work alone when handling fluorine, including fluorine mixtures. Another person should always be within your sight and earshot, although not necessarily in the immediate area. (See Section 26.15, "Working Alone," of the Health & Safety Manual.)

    - All components to be used in a fluorine system must be clean and free of organic material and bagged (or otherwise closed off to ensure system cleanliness until final assembly).

    - All lines and equipment to contain fluorine should be pretested for leaks with dry nitrogen or helium.

    - Repeated bending or excessive vibration of piping or equipment should be avoided. Either can cause the fluorine film that has developed in the system to flake and corrode valves and other system components. Excessive thermal cycling can also cause this problem.

Procedures and checklists must be agreed upon by your Safety Team, Industrial Hygienist, Pressure Safety Manager, and all other concerned parties before the system can be initially activated or reactivated after disassembly or modification.

- Systems containing fluorine under pressure must be inspected for leaks at frequent intervals. If you detect a leak, purge the system immediately and repair the leak. You can detect leaks using one of three methods:

    1. Purge fluorine from the system and introduce helium.

    2. Expel ammonia vapor at suspect leak points from a squeeze bottle containing ammonium hydroxide. A white mist will be observed if fluorine is leaking.

    3. Use long metal tongs or forceps to place filter paper moistened with potassium iodide solution near suspected leaks. The paper will turn brown if fluorine is leaking.

- A regular program must be established for replacing rupture disks when such disks are used in the system.
- The possibility of valves freezing should be minimized by following these rules:
  - Never use a regulator or manual control as the on-off control.
  - When shutting down operations for any extended period, always close the cylinder valve and bleed the pressure in the regulator or manual control to atmospheric pressure.
  - When the regulator or manual control is removed from the cylinder, replace the metal or plastic cylinder valve outlet cap originally provided.
  - Use the proper wrench when opening or closing cylinder valves.
  - Store cylinders in a dry, cool, well-ventilated area.
  - While the cylinder is in use, rotate the valve stem at least once a day to break up any forming corrosion products.
  - Use traps or check valves to prevent reverse flow.
  - Obtain cylinders of a size that will ensure consumption in a short time. Suppliers usually carry a wide range of sizes to meet this need.
  - Flush the regulator or manual control valve with dry nitrogen or dry air after use.

Returning Fluorine Cylinders. Before you return your cylinders to Industrial Gases, they must be inspected by an Industrial Hygienist or a Health and Safety Technician. Cylinders in good condition are returned by Industrial Gases to the gas supplier. Be sure to return the cylinders to Industrial Gases as soon as possible, and do not overstock cylinders. Try not to keep these cylinders for more than one year from original delivery to you.

Affix a return tag for toxic/corrosive gases to each cylinder before returning it to Industrial Gases. For additional questions on proper return procedures, refer to the Compressed Gas Cylinder Return and Disposal Procedure, which is available from your Safety Team, Industrial Gases, or the Pressure Safety Manager.

Disposing of Leaking or Damaged Fluorine Cylinders. When you find a leaking or damaged fluorine cylinder, notify the Fire Department immediately (ext. 2-7333). They will assess the situation, take action necessary to rescue or protect personnel, and ensure appropriate action is taken to contain the hazard. Hazards Control and Hazardous Waste Management will advise you on how to dispose of a leaking cylinder.

DISMANTLING FLUORINE SYSTEMS**. CONSULT YOUR SAFETY TEAM PRIOR TO DISMANTLING A FLUORINE SYSTEM. THE PROCEDURE FOR DISMANTLING THE SYSTEM MUST BE DOCUMENTED IN THE OSP FOR THE EXPERIMENT OR A SPECIAL OSP BEFORE DISMANTLING CAN TAKE PLACE.**

Procedural Controls

Experimenters need to:

- Prepare an OSP per Chapter 2 of the LLNL Health & Safety Manual and an Engineering Safety Note per Supplement 32.03 of the LLNL Health & Safety Manual.
- Prepare a revised Engineering Safety Note and have it approved when a system handling fluorine, any fluorine mixture, or oxidizing fluoride is changed.
- Arrange to have all unusual experiments involving fluorine peer-reviewed in a manner similar to that used in planning HE experiments.

Requestors need to:

- Order elemental fluorine and all mixtures of it in cylinders with CGA 679 connections with valve closure torques not to exceed 50 ft-lb (state the closure torque limit in the procurement document).
- Have all orders signed by the Industrial Hygiene Group before the material can be delivered to the requestor. Direct deliveries to requestors are not permitted.
- Receive shipments personally and sign a receipt.
- Do not allow incoming shipments to remain in hallways, unoccupied rooms and uncontrolled areas.

The Industrial Gas Section:

- Receives and logs in all incoming shipments at the gas dock, Building 518.
- Delivers it to the requestor and obtains a signed receipt of delivery.
- Stores it properly if it cannot be delivered on the day it arrives at LLNL.
- Puts an expiration date tag on a cylinder along with an LLNL Delivery Tag.

PERSONAL PROTECTIVE EQUIPMENT

Protective equipment is routinely required; that is:

- Wear clean neoprene gloves when directly handling equipment that contains fluorine or has recently contained fluorine.
- Wear neoprene coats and boots to afford overall body protection for short intervals of contact with low-pressure fluorine. This clothing should be designed and worn so that it can be shed immediately.
- Wear safety glasses at all times. Metal frames are preferable to the customary plastic to eliminate the possibility of the frames catching fire. Never wear contact lenses when working around fluorine.

- Wear face shields made of chemically resistant polymers whenever you change cylinders or manipulate systems containing fluorine under pressure.

- You may also need to wear special respiratory protective equipment. Requirements for this special equipment will depend on the nature of the fluorine system installed and the special circumstances necessitating such equipment. Consult your Safety Team about these requirements.

- Personal protective equipment required for a fluorine operation must be detailed in the OSP. In addition, you must know the location of all personal protective equipment specified for your operation (including respiratory protective equipment) and the proper use and care of that equipment.

References

1. General Industry OSHA Safety and Health Standards (26 CFR 1910), U.S. Department of Labor Occupational Safety and Health Administration, Washington, D.C., OSHA 2206 (1983).

2. Chemical Hazards of the Work Place (J. P. Lippincott Co., Philadelphia, Pa., 1978), p. 271.

3. Chemical Hazards of the Work Place (J. P. Lippincott Co., Philadelphia, Pa., 1978), p. 271.

4. The Matheson Company Gas Data Book, 6th ed. (Matheson Gas Products, Inc., Secaucus, NJ., 1980) p. 331.

Appendix A
Fluorine Emergency Procedures

Calling for Help

In all accidents involving fluorine, notify the Fire Department using the emergency number for assistance: 911.

Rescuing the Exposed Victim

Do not attempt to rescue a victim unless you are trained in emergency rescue, are adequately protected from any hazard, and have another trained and equipped person standing by. If you enter a heavily contaminated area, you must wear skin protection and use self-contained breathing apparatus or approved air-line equipment.

Treating the Exposed Victim

If That Victim is Someone Else

Skin and Eyes. Remove the victim from the contaminated area as soon as possible. Cleanse the fluorine from skin and eyes by flushing with copious amounts of water. Continue flushing for 20 min. As you flush, remove any contaminated clothing from the victim.

Inhalation. If you suspect a person has inhaled fluorine, move that person into the fresh air. If that person has stopped breathing, apply mouth-to-mouth resuscitation at once. Also treat the victim for eye and skin exposure by flushing the eyes and skin with large amounts of water. Do not delay emergency treatment; have someone else dial the emergency number.

Refer all affected persons to the Health Services Department, even when the immediate injury seems slight, and give the physician a detailed account of the accident.

If That Victim is You

Skin and Eyes. If your eyes are exposed to fluorine, do not rub them. Flush them with water for at least 20 min, lifting the upper and lower eyelids frequently to ensure complete washing.

If fluorine comes in contact with any part of your body or with your clothing, get into a safety shower immediately and flush your body with large amounts of water for 20 min. Wash thoroughly under your nails. Strip off any contaminated clothing as you wash.

Inhalation. If you have inhaled fluorine, leave the area immediately. Treat yourself for eye and skin exposure by flushing with large amounts of water.

No matter how slight the injury may seem, report it to the Health Services Department immediately, using the Fire Department for transportation. Emergency response personnel will ensure your clothing is washed before returning it to you.

Evacuating the Contaminated Area

In the Event of Leaks

If fluorine cylinders or equipment leak, evacuate the area immediately and dial the emergency number for assistance. Ensure no other personnel enter the area until the Fire Department arrives.

In the Event of Fire

Evacuate the area immediately and call for emergency assistance. Do not attempt to extinguish a fluorine fire. Ensure no other personnel enter the area until emergency response personnel arrive.

Appendix B
Accepted Materials for Fluorine System Components

Table B-1 consists of information on materials acceptable for use in fluorine systems. It is adapted from a table presented in the Handbook of Compressed Gases, 2nd ed. (Compressed Gas Association, Inc., 1981). This table is not intended to list all materials acceptable and available for use in fluorine systems.

When selecting system components for an operation, consult the manufacturer to ensure that those components selected are acceptable for use under the intended temperatures and pressures. At high temperatures, nickel or Monel is the material of choice. Teflon is the preferred gasket material. Air Force Manual 161.30, Volume II has useful information about halogen halides.

Appendix C
Fluorine System Cleaning and Passivation Procedures

System Cleaning

System cleanliness and passivation are critical to the successful handling of fluorine. All equipment, lines, and fittings intended for fluorine service must be leak-tight, dry, and thoroughly cleansed of all foreign matter before use. The following procedure should serve as a minimal guideline to system cleaning. Experimental requirements may dictate a more thorough procedure, particularly for use with pure fluorine and reactive fluorides.

1. Wash and rinse thoroughly with hot water. Do not allow to dry.

2. Rinse with acetone.

3. Degrease with Freon TFE (Fr-113); vapor degrease where possible.

4. For polymers (Teflon or Kalrez), squirt Freon TFE onto a clean, lint-free wipe and then wipe the polymer clean.

5. Dry with clean, oil-free, dry air or nitrogen, or in a vacuum oven.

6. Assemble system and check for leaks at working pressure with an inert gas. A vacuum check is also desirable.

7. Evacuate the system to 4-5 µm or less, and at the same time heat to at least 120°C, or 10–20°C above operating temperature. Hold for 1 hr after base pressure is obtained.

Documentation that the system has been cleaned to at least these guidelines shall be maintained by the responsible individual/designer.

Passivation

The corrosion resistance of all materials used with fluorine depends upon the passivation of the system. This operation is intended to remove the last traces of foreign matter from the system and to form a passive fluoride film on the metal surface. At room temperature, fluorine reacts vigorously with most metals to form this protective fluoride film; however, further reaction may be obtained by raising the temperature. For this reason, passivation must be accomplished at the working temperature and pressure of the system or a few degrees higher. Using the standard regulator manifold as an example, the following can serve as a guideline to system passivation. This procedure may be used for passivation with dilute fluorine mixtures:

CAUTION! Dropping, striking, or shocking the fluorine cylinders may result in an exposure incident.

1. Wear protective gear: safety goggles, full-face shield, flame-retardant gloves, and apron. A second person should be present.

2. Ensure the vent blower system is operating. Ensure the active fluorine detector is operating, if applicable.

3. Make a careful visual inspection of the exterior of the cylinder, valve, and CGA connection. Check for corrosion or mechanical problems. Verify the cylinder pressure tag at 500 psi or less.

4. Check the tightness of the packing nut--should be 40 ft-lb, nominally right-hand thread.

5. Slowly loosen the outlet cap. CAUTION! A cross-seat leak may have pressurized the outlet.

6. Check the valve outlet and system inlet for foreign material (solid or liquid).

CAUTION!
Two connections are in general use in the fluorine industry: CGA670 and CGA679. Make certain that you have a match between the standard regulator manifold and the supply valve outlet.

7. Install a new gasket (degreased, dried, and lint free).

8. Ensure that the air-operated valve is closed and the regulator on the manifold is backed out.

9. Attach the cylinder to the regulator manifold.

10. Clamp the cylinder to prevent torque from being applied to the regulator manifold upon opening the valve.

11. Attach a remote cylinder valve handle and close the barricade.

Remote temperature and pressure monitoring capabilities are desirable during the passivation process because pressure surges and rapid temperature rises are indicative of possible system failure.

1. Check the supply cylinder and upstream connections to the regulator for leaks at 500 psig with an inert gas source. Check the downstream connections for leaks at the working pressure.

2. Vent and evacuate the leak-check gas.

3. Close all valves and back off the regulator.

4. Open the fluorine-supply cylinder valve as gently as possible and close it immediately. Monitor the temperature in the exposed region.

5. After 10 min, or when the temperature is ambient, open the air-operated valve. Note the pressure, and monitor the temperature in the newly exposed region.

6. After 10 min, or when the temperature is ambient, set the regulator to 5 psig. Note the pressure drop on the supply gage, and monitor the temperature in the newly exposed regions. Back off the regulator, and monitor the 100-psi gage.

7. After 5 min, or when the temperature and pressure are stable, set the regulator to 5 psig. The user may start passivating the system by opening the system valve on the regulator manifold. The user must follow the guidelines of slowly exposing sections of the system to increasing concentrations of fluorine until working conditions are achieved.

8. When the supply gage indicates approximately 50 psig, back off the regulator. Open the vent valve and vent the system to atmospheric pressure. Close the vent valve.

9. Gently open and immediately close the fluorine-supply valve. The supply gage should read the approximate cylinder pressure. Monitor the temperature and pressure as before.

10. After 5 min or when the temperature and pressure are stable, set the regulator to 10 psig.

11. After 5 min or when the temperature and pressure arc stable, set the regulator to 15 psig. Monitor the temperature and pressure.

12. After 5 min or when the temperature and pressure are stable, set the regulator to 20 psig. Monitor the temperature and pressure.

13. Back off the regulator. Vent the downstream system to atmospheric pressure. Close the vent valve.

14. Gently open the fluorine-supply valve. The supply gage should read the cylinder pressure.

15. Set the regulator to 10 psig. Wait 5 min, or until the temperature and pressure are stable.

16. Set the regulator to 20 psig. Wait 5 min, or until the temperature and pressure are stable.

17. Set the regulator to 30 psig. Wait 5 min, or until the temperature and pressure are stable.

18. The manifold is now passivated for 30 psig maximum operating pressure and room temperature conditions.

19. If higher operating temperatures are to be used, repeat steps 8 through 16 at 25–50°C intervals.

CAUTION! Avoid vibration and bending of passivated surfaces. This may cause flaking or spalling of the fluoride film, exposing unpassivated surfaces and fouling valve seats. Avoid exposing system to air or any gas containing water or organic materials.

Systems may also be passivated with pure fluorine by a slow and gradual exposure to increasing concentrations. Much smaller pressure increases must be used in conjunction with greater pressure measurement resolution, as shown in this example.

All increases must be added slowly. The supply source must be valved out of the system between additions (to minimize the available fluorine if the reaction goes out of control). If operating temperatures are to be above room temperatures, repeat the above procedure at 25–50°C intervals to 10–20°C above the operating temperature.