APPENDIX A:

CHEMICAL FORMS AND PROPERTIES OF URANIUM

CONTENTS (APPENDIX A)

TABLE

FIGURE

NOTATION (APPENDIX A)

The following is a list of acronyms and abbreviations, including units of measure, used in this appendix.

ACRONYMS AND ABBREVIATIONS

General

DOE	U.S. Department of Energy
PEIS	programmatic environmental impact statement

Chemicals

BrF_3	bromine fluoride
Cl_2	chlorine
F_2	fluorine
HF	hydrogen fluoride; hydrofluoric acid
HNO_3	nitric acid
H_2O	water
NH_3	ammonia
O_2	oxygen
S	sulfur
Se	selenium
TCE	trichloroethylene
UF_4	uranium tetrafluoride
UF_6	uranium hexafluoride
UH_3	uranium hydride
UO_2	uranium dioxide
UO_2F_2	uranyl fluoride
UO_3	uranium trioxide
U_3O_8	triuranium octaoxide (uranyl uranate)

UNITS OF MEASURE

atm	atmosphere(s)
°C	degrees Celsius
°F	degrees Fahrenheit
cm^3	cubic centimeter(s)
g	gram(s)
mPa	millipascal(s)
psia	pounds per square inch absolute

APPENDIX A:

CHEMICAL FORMS AND PROPERTIES OF URANIUM

The U.S. Department of Energy (DOE) is proposing to develop a strategy for long-term management of the depleted uranium hexafluoride (UF_6) inventory currently stored at three DOE sites near Paducah, Kentucky; Portsmouth, Ohio; and Oak Ridge, Tennessee. This programmatic environmental impact statement (PEIS) describes alternative strategies that could be used for the long-term management of this material and analyzes the potential environmental consequences of implementing each strategy for the period 1999 through 2039. This appendix describes the properties of the chemical forms of uranium that are relevant to the analysis in the PEIS.

Most depleted uranium in the United States is currently stored as solid UF_6 in steel cylinders that have a wall thickness of at least 5/16 in. and are located outdoors. Although UF_6 can be handled and stored safely in a well-managed industrial environment, other uranium compounds or uranium metal may be more appropriate for long-term storage, use, or permanent disposal. Potential compounds other than UF_6 include triuranium octaoxide (U_3O_8) and uranium dioxide (UO_2).

A.1 PHYSICAL PROPERTIES

The physical properties of the pertinent chemical forms of uranium are shown in Table A.1.

A.1.1 Uranium Hexafluoride

Uranium hexafluoride (UF_6) at ambient conditions is a volatile, white, crystalline solid. Solid UF_6 is readily transformed into the gaseous or liquid states by the application of heat. All three phases — solid, liquid, and gas — coexist at 147°F (64°C) (the triple point). Only the gaseous phase exists above 446°F (230°C), the critical temperature, at which the critical pressure is 45.5 atm (4.61 mPa). The vapor pressure above the solid reaches 1 atm (0.1 mPa) at 133°F (56°C), the sublimation temperature.

Figure A.1 is the phase diagram covering the range of conditions usually encountered in working with UF_6. It shows the correlation of pressure and temperature with the physical state of UF_6. The triple point occurs at 22 pounds per square inch, absolute (psia) and 147°F (64°C). These are the only conditions at which all three states — liquid, solid, and gas — can exist in equilibrium. If the temperature or pressure is greater than at the triple point, there will only be gas or liquid.

A large decrease in UF_6 density occurs when UF_6 changes from the solid to the liquid state, which results in a large increase in volume. The thermal expansion of the liquid with increasing

TABLE A.1 Physical Properties of Pertinent Uranium Compounds

Compound	Melting Point (°C)	Density (g/cm^3) Crystal/ Particle	Bulk[a]	Solubility in Water at Ambient Temperature
UF_6	64.1	5.1	5.1	Decomposes to UO_2F_2
UF_4	960 ± 5	6.7	2.0 – 4.5	Very slightly soluble
U_3O_8	Decomposes to UO_2 at 1,300	8.30	1.5 – 4.0	Insoluble
UO_2	2,878 ± 20	10.96	2.0 – 5.0	Insoluble
Uranium metal	1,132	19.05	19	Insoluble

[a] Bulk densities of UF_4, U_3O_8, and UO_2 are highly variable, depending on the production process and the properties of the starting uranium compounds.

Notation: UF_4 = uranium tetrafluoride; UF_6 = uranium hexafluoride; UO_2 = uranium dioxide; UO_2F_2 = uranyl fluoride; U_3O_8 = triuranium octaoxide.

temperature is also high. Therefore, it is important to maintain control of the total mass and physical state of UF_6 throughout an operational cycle. To avoid hydraulic rupture, when items with restricted volumes, such as traps and containers, are filled with UF_6, full allowance must be made for the volume changes that will arise over the working temperature range to which the vessels will be subjected.

For UF_6 to be handled as a liquid, the pressure must be in excess of 0.15 mPa (1.5 atm) and the temperature above 147°F (64°C) because the sublimation temperature lies below the triple point. Thus, any process using liquid UF_6 is above atmospheric pressure and is subject to a potential leakage of UF_6 to the environment, with vapor loss and cooling occurring simultaneously. Solidification occurs exothermically when the pressure falls below 1.5 atm (0.15 mPa). Thus, if a cylinder heated above the triple point is breached, a rapid outflow of the UF_6 occurs until the pressure drops sufficiently to start the solidification process. The rate of outflow then decreases but continues until the contents cool to about 133°F (56°C), which is the atmospheric sublimation temperature. Some release of material may continue, depending on the type and location of the breach.

UF_6 is hygroscopic (i.e., moisture-retaining) and, in contact with water (H_2O), will decompose immediately to uranyl fluoride (UO_2F_2). When heated to decomposition, UF_6 emits toxic fluoride fumes.

A.1.2 Uranyl Fluoride (Uranium Oxyfluoride)

Uranyl fluoride (UO_2F_2) is an intermediate in the conversion of UF_6 to an uranium oxide or metal form and is a direct product of the reaction of UF_6 with moisture in the air. It is very soluble

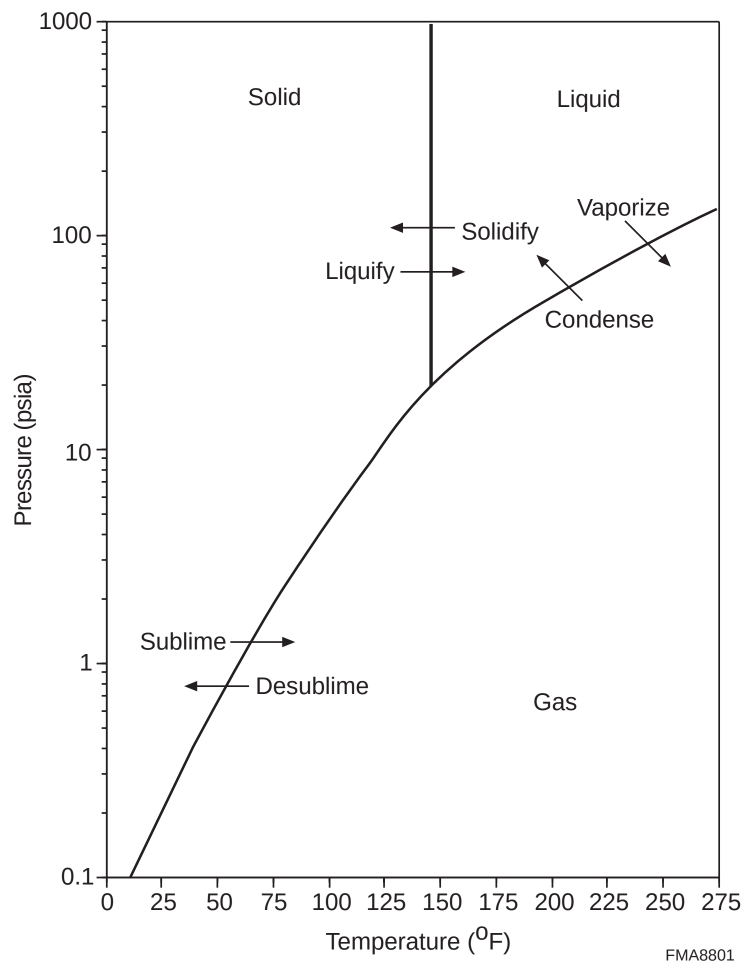

FIGURE A.1 Uranium Hexafluoride Phase Diagram

in water. Uranyl fluoride also is hygroscopic and changes in color from brilliant orange to yellow after reacting with water. Uranyl fluoride is reported to be stable in air to 570°F (300°C), above which slow decomposition to U_3O_8 occurs. When heated to decomposition, UO_2F_2 emits toxic fluoride fumes.

A.1.3 Uranium Tetrafluoride

Uranium tetrafluoride (UF_4) is a green crystalline solid that melts at about 1,760°F (960°C) and has an insignificant vapor pressure. It is very slightly soluble in water. It is generally an intermediate in the conversion of UF_6 to either uranium oxide (U_3O_8 or UO_2) or uranium metal. It is formed by the reaction of UF_6 with hydrogen gas in a vertical tube-type reactor or by the action of hydrogen fluoride (HF) on uranium dioxide. UF_4 can be readily converted to either uranium metal or uranium oxide. UF_4 is less stable than the uranium oxides and produces hydrofluoric acid in reaction with water; it is thus a less favorable form for long-term disposal.

A.1.4 Triuranium Octaoxide

Triuranium octaoxide (U_3O_8) occurs naturally as the olive-green-colored mineral pitchblende. U_3O_8 is readily produced from UF_6 and has potential long-term stability in a geologic environment. In the presence of oxygen (O_2), uranium dioxide (UO_2) and uranium trioxide (UO_3) are oxidized to U_3O_8. U_3O_8 can be made by three primary chemical conversion processes, involving either UF_4 or UO_2F_2 as intermediates. It is generally considered to be the more attractive form for disposal purposes because, under normal environmental conditions, U_3O_8 is one of the most kinetically and thermodynamically stable forms of uranium and also because it is the form of uranium found in nature.

A.1.5 Uranium Dioxide

Uranium dioxide (UO_2) is the form in which uranium is most commonly used as a nuclear reactor fuel. It is a stable ceramic that can be heated almost to its melting point, 5,212°F (2,878°C), without serious mechanical deterioration. It does not react with water to any significant level. At ambient temperatures, UO_2 will gradually convert to U_3O_8.

A.1.6 Uranium Metal

Uranium metal appears as a heavy, silvery white, malleable, ductile, softer-than-steel, metallic element. It is one of the densest materials known, being 1.6 times more dense than lead. Uranium metal is not as stable as U_3O_8 or UF_4 because it is subject to surface oxidation. It tarnishes in air, with the oxide film preventing further oxidation of massive metal at room temperature. Water attacks uranium metal slowly at room temperature and rapidly at higher temperatures. UO_2 and uranium hydride (UH_3) are formed while heat is evolved, and the metal swells and disintegrates.

A.2 CHEMICAL PROPERTIES

A.2.1 Uranium Hexafluoride

Uranium hexafluoride (UF_6) combines with water to form the soluble reaction products UO_2F_2 and HF. UF_6 is essentially inert to clean aluminum, steel, Monel, nickel, aluminum, bronze, copper, and Teflon™. Teflon is commonly used in the packing and cap gasket for cylinders storing depleted UF_6.

When released to the atmosphere, gaseous UF_6 combines with humidity to form a cloud of particulate UO_2F_2 and HF fumes. The reaction is very fast and is dependent on the availability of water vapor. Following a large-scale release of UF_6 in an open area, the dispersion is governed by meteorological conditions, and the plume could still contain unhydrolyzed material even after traveling a distance of several hundred meters. After hydrolysis, UO_2F_2 can be deposited as a finely divided solid, while HF remains as part of the gas plume.

In enclosed situations, the reaction products form a dense fog, reducing visibility for occupants of the area and hindering evacuation and emergency response. Fog can occur in unconfined areas if the humidity is high.

In a fire, the reaction of UF_6 with water is accelerated because of the increased UF_6 vapor pressure and the large quantities of water formed in combustion of organic materials or hydrocarbons. Reaction of liquid UF_6 with hydrocarbon vapors is extremely vigorous in flames, with formation of UF_4 and low-molecular-weight fluorinated compounds. More heat is generally released in these hydrocarbon interactions with UF_6 than in the corresponding reactions of hydrocarbons with oxygen.

A.2.2 Uranyl Fluoride

Uranyl fluoride (UO_2F_2) is a yellow hygroscopic solid that is very soluble in water. In accidental releases of UF_6, UO_2F_2 as a solid particulate compound may deposit on the ground over a large area.

A.2.3 Uranium Tetrafluoride

Uranium tetrafluoride (UF_4) reacts slowly with moisture at ambient temperature, forming UO_2 and HF, which are very corrosive.

A.2.4 Triuranium Octaoxide

Triuranium octaoxide (U_3O_8) has no hazardous chemical properties that are significant.

A.2.5 Uranium Dioxide

Uranium dioxide (UO_2) will ignite spontaneously in heated air and burn brilliantly. It will slowly convert to U_3O_8 in air at ambient temperature. Its stability in air can be improved by sintering the powder in hydrogen.

A.2.6 Uranium Metal

Uranium powder or chips will ignite spontaneously in air at ambient temperature. During storage, uranium ingots can form a pyrophoric surface because of reaction with air and moisture. Uranium metal will also react with water at ambient temperature, forming UO_2 and UH_3. The metal swells and disintegrates. Hydrogen gas can be released.

Solid uranium, either as chips or dust, is a very dangerous fire hazard when exposed to heat or flame. In addition, uranium metal can react violently with chlorine (Cl_2), fluorine (F_2), nitric acid (HNO_3), selenium (Se), sulfur (S), ammonia (NH_3), bromine fluoride (BrF_3), trichlorethylene (TCE), or nitryl fluoride and similar compounds.