APPENDIX A:
CHEMICAL FORMS AND PROPERTIES OF URANIUM
CONTENTS (APPENDIX A)

NOTATION ............................................................. A-iv

A.1 PHYSICAL PROPERTIES ............................................. A-1

  A.1.1 Uranium Hexafluoride ........................................ A-1
  A.1.2 Uranyl Fluoride ............................................. A-2
  A.1.3 Uranium Tetrafluoride ...................................... A-3
  A.1.4 Triuranium Octaoxide ...................................... A-4
  A.1.5 Uranium Dioxide ............................................ A-4
  A.1.6 Uranium Metal .............................................. A-4

A.2 Chemical Properties .............................................. A-4

  A.2.1 Uranium Hexafluoride ....................................... A-4
  A.2.2 Uranyl Fluoride ............................................. A-5
  A.2.3 Uranium Tetrafluoride ...................................... A-5
  A.2.4 Triuranium Octaoxide ...................................... A-5
  A.2.5 Uranium Dioxide ............................................ A-5
  A.2.6 Uranium Metal .............................................. A-6

TABLE

A.1 Physical Properties of Pertinent Uranium Compounds ................. A-2

FIGURE

A.1 Uranium Hexafluoride Phase Diagram ................................ A-3
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

BrF₃ bromine fluoride
Cl₂ chlorine
F₂ fluorine
HF hydrogen fluoride; hydrofluoric acid
HNO₃ nitric acid
H₂O water
NH₃ ammonia
O₂ oxygen
S sulfur
Se selenium
TCE trichloroethylene
UF₄ uranium tetrafluoride
UF₆ uranium hexafluoride
UH₃ uranium hydride
UO₂ uranium dioxide
UO₂F₂ uranyl fluoride
UO₃ uranium trioxide
U₃O₈ triuranium octaoxide (uranyl uranate)

UNITS OF MEASURE

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Unit Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>atm</td>
<td>atmosphere(s)</td>
</tr>
<tr>
<td>°C</td>
<td>degrees Celsius</td>
</tr>
<tr>
<td>°F</td>
<td>degrees Fahrenheit</td>
</tr>
<tr>
<td>cm³</td>
<td>cubic centimeter(s)</td>
</tr>
<tr>
<td>g</td>
<td>gram(s)</td>
</tr>
<tr>
<td>mPa</td>
<td>millipascal(s)</td>
</tr>
<tr>
<td>psia</td>
<td>pounds per square inch absolute</td>
</tr>
</tbody>
</table>
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 (UF₆) 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 UF₆ in steel cylinders that have a wall thickness of at least 5/16 in. and are located outdoors. Although UF₆ 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 UF₆ include triuranium octaoxide (U₃O₈) and uranium dioxide (UO₂).

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 (UF₆) at ambient conditions is a volatile, white, crystalline solid. Solid UF₆ 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 UF₆. It shows the correlation of pressure and temperature with the physical state of UF₆. 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 UF₆ density occurs when UF₆ 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

<table>
<thead>
<tr>
<th>Compound</th>
<th>Melting Point (°C)</th>
<th>Crystal/Particle</th>
<th>Bulk(^a)</th>
<th>Solubility in Water at Ambient Temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td>UF(_6)</td>
<td>64.1</td>
<td>5.1</td>
<td>5.1</td>
<td>Decomposes to UO(_2)F(_2)</td>
</tr>
<tr>
<td>UF(_4)</td>
<td>960 ± 5</td>
<td>6.7</td>
<td>2.0 – 4.5</td>
<td>Very slightly soluble</td>
</tr>
<tr>
<td>U(_3)O(_8)</td>
<td>Decomposes to UO(_2) at 1,300</td>
<td>8.30</td>
<td>1.5 – 4.0</td>
<td>Insoluble</td>
</tr>
<tr>
<td>UO(_2)</td>
<td>2,878 ± 20</td>
<td>10.96</td>
<td>2.0 – 5.0</td>
<td>Insoluble</td>
</tr>
<tr>
<td>Uranium metal</td>
<td>1,132</td>
<td>19.05</td>
<td>19</td>
<td>Insoluble</td>
</tr>
</tbody>
</table>

\(^a\) Bulk densities of UF\(_4\), U\(_3\)O\(_8\), 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\(_2\)F\(_2\) = uranyl fluoride; U\(_3\)O\(_8\) = 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\(_2\)O), will decompose immediately to uranyl fluoride (UO\(_2\)F\(_2\)). When heated to decomposition, UF\(_6\) emits toxic fluoride fumes.

A.1.2 Uranyl Fluoride (Uranium Oxyfluoride)

Uranyl fluoride (UO\(_2\)F\(_2\)) 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
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 U₃O₈ occurs. When heated to decomposition, UO₂F₂ emits toxic fluoride fumes.

A.1.3 Uranium Tetrafluoride

Uranium tetrafluoride (UF₄) 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 UF₆ to either uranium oxide (U₃O₈ or UO₂) or uranium metal. It is formed by the reaction of UF₆ with hydrogen gas in a vertical tube-type reactor or by the action of hydrogen fluoride (HF) on uranium dioxide. UF₄ can be readily converted to either uranium metal or uranium oxide. UF₄ 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 (U₃O₈) occurs naturally as the olive-green-colored mineral pitchblende. U₃O₈ is readily produced from UF₆ and has potential long-term stability in a geologic environment. In the presence of oxygen (O₂), uranium dioxide (UO₂) and uranium trioxide (UO₃) are oxidized to U₃O₈. U₃O₈ can be made by three primary chemical conversion processes, involving either UF₄ or UO₂F₂ as intermediates. It is generally considered to be the more attractive form for disposal purposes because, under normal environmental conditions, U₃O₈ 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 (UO₂) 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, UO₂ will gradually convert to U₃O₈.

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 U₃O₈ or UF₄ 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. UO₂ and uranium hydride (UH₃) are formed while heat is evolved, and the metal swells and disintegrates.

A.2 CHEMICAL PROPERTIES

A.2.1 Uranium Hexafluoride

Uranium hexafluoride (UF₆) combines with water to form the soluble reaction products UO₂F₂ and HF. UF₆ 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 UF₆.

When released to the atmosphere, gaseous UF₆ combines with humidity to form a cloud of particulate UO₂F₂ and HF fumes. The reaction is very fast and is dependent on the availability of water vapor. Following a large-scale release of UF₆ in an open area, the dispersion is governed by
Chemical Forms of Uranium

meteorological conditions, and the plume could still contain unhydrolyzed material even after traveling a distance of several hundred meters. After hydrolysis, $\text{UO}_2\text{F}_2$ 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 $\text{UF}_6$ with water is accelerated because of the increased $\text{UF}_6$ vapor pressure and the large quantities of water formed in combustion of organic materials or hydrocarbons. Reaction of liquid $\text{UF}_6$ with hydrocarbon vapors is extremely vigorous in flames, with formation of $\text{UF}_4$ and low-molecular-weight fluorinated compounds. More heat is generally released in these hydrocarbon interactions with $\text{UF}_6$ than in the corresponding reactions of hydrocarbons with oxygen.

A.2.2 Uranyl Fluoride

Uranyl fluoride ($\text{UO}_2\text{F}_2$) is a yellow hygroscopic solid that is very soluble in water. In accidental releases of $\text{UF}_6$, $\text{UO}_2\text{F}_2$ as a solid particulate compound may deposit on the ground over a large area.

A.2.3 Uranium Tetrafluoride

Uranium tetrafluoride ($\text{UF}_4$) reacts slowly with moisture at ambient temperature, forming $\text{UO}_2$ and HF, which are very corrosive.

A.2.4 Triuranium Octaoxide

Triuranium octaoxide ($\text{U}_3\text{O}_8$) has no hazardous chemical properties that are significant.

A.2.5 Uranium Dioxide

Uranium dioxide ($\text{UO}_2$) will ignite spontaneously in heated air and burn brilliantly. It will slowly convert to $\text{U}_3\text{O}_8$ 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 $\text{UO}_2$ and $\text{UH}_3$. 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.