Chapter 16 Nuclear Reactor Chemistry

One of the most important applications of nuclear and radiochemistry is in the area of nuclear power. Chemistry and chemical processes are intimately involved in reactor operation, the preparation and processing of reactor fuel, and the storage and ultimate disposal of radioactive waste. In this chapter, we shall examine some of the most important chemistry associated with nuclear power.

16.1 Introduction

The basic principles behind nuclear reactors and the current design of light water reactors are discussed in Chapter 14. The two types of light water reactors, the pressurized water reactor (PWR) and the boiling water reactor (BWR) are shown schematically in Figure 14-2. In these light water reactors, the reactor fuel is enriched to ~3% in $^{235}$U and ordinary water is used as the coolant and moderator. In a PWR, the reactor core is encased in a steel pressure vessel filled with water under a pressure of ~150 bar or greater. The water does not boil due to this high pressure even though the temperature of the water is as high as 350°C. It passes through a heat exchanger where its heat is used to boil water in the secondary coolant loop. The steam is dried and used to drive a turbine, then condensed and returned to the boiler. The water in the primary loop usually contains boron (as 0.025 M boric acid, $\text{H}_3\text{BO}_3$) to control the reactivity of the reactor.

In a BWR, the water passing through the reactor core is allowed to boil because it is at a lower pressure, ~75 bar. The steam produced is passed through a turbine, condensed and returned to the reactor.
In PWRs, the fuel is UO$_2$, enriched typically to 3.3% $^{235}$U; while for BWRs, the fuel is UO$_2$, enriched to 2.6%. (Natural uranium is 0.72% $^{235}$U). The fuel elements are clad in Zircaloy, a zirconium alloy that includes tin, iron, chromium, and nickel that prevents fission product release and protects them against corrosion by the coolant. The control material in BWRs is B$_4$C, while PWRs have Ag-In-Cd or Hf control materials.

The nuclear fuel cycle is a set of steps in the processing of the reactor's fissile materials that begins with the mining of uranium and extends through the final disposition of the waste from the reactor. These steps are referred to as a cycle because it is possible that the material taken from the reactor after use can be recycled. A schematic diagram of the nuclear fuel cycle is shown in Figure 16-1.
Figure 16-1 A schematic diagram of the nuclear fuel cycle.

This diagram shows two possible paths for this cycle, *i.e.*, with and without fuel reprocessing. The majority of reactors in the world and all US reactors operate with a once-through cycle without reprocessing. Some countries, particularly France, do fuel reprocessing with reuse of the plutonium from spent fuel. The portions of the
cycle that precede the introduction of the fissile material into the reactor are referred to as the front end of the cycle while the back end includes those steps that occur after the removal of the fuel from the reactor. The details of this cycle and the chemistry involved are discussed below.

16.2 Fission Product Chemistry

In the chemistry of the fuel cycle and reactor operations, one must deal with the chemical properties of the actinide elements, particularly uranium and plutonium and those of the fission products. In this section, we focus on the fission products and their chemistry. In Figures 16-2 and 16-3, we show the chemical composition and associated fission product activities in irradiated fuel. The fission products include the elements from zinc to dysprosium, with all periodic table groups being represented.
Figure 16-2 The chemical composition of the fission products in irradiated fuel as a function of decay time after a two month irradiation. [From J. Prawitz and J. Rydberg, Acta. Chem. Scand. 12, 393 (1958)]
The inert gases (Group 18) are represented by isotopes of Kr and Xe. These isotopes are generally short-lived and will decay before fuel reprocessing. As inert gases, they are unreactive and consequently they are isolated using cryogenic techniques.

The alkali metals (Group 1) are represented by Rb and Cs where long-lived $^{137}$Cs ($t_{1/2} = 30$ y) is the most important nuclide. Their solution chemistry is that of the generally soluble +1 cation. The alkaline earths (Group 2) are represented by the high yield nuclides $^{140}$Ba, $^{90}$Sr and $^{91}$Sr. These nuclides can be separated using ion exchange or solvent extraction or gravimetric techniques. 28-year $^{90}$Sr is an important radiation hazard in aged spent fuel while 12.8-day $^{140}$Ba frequently determines the shielding requirements for fuel for the 10-100 day cooling period.

Group 3 contains Y and the lanthanides. These elements are chemically similar. They can be separated from one another by ion exchange while their separation from U and Pu can be done using solvent extraction with tri-butyl phosphate (TBP). These elements have soluble nitrates, chlorides and sulfates while their fluorides and hydroxides are insoluble. LaF$_3$ is frequently used as a carrier for this group. They form stable complexes with strong chelating agents such as DPTA, EDTA, etc. The Group 4 element in fission product mixtures is zirconium whose chemistry is that of the +4 oxidation state. The principal nuclide of interest is the 63
d $^{95}$Zr and its 35-day daughter, $^{95}$Nb. The chemistry of Zr can be tricky as it readily forms complexes and does form colloids, which can lead to poor separation factors.

The Group 5 element niobium occurs as a decay product, $^{95}$Nb, of $^{95}$Zr. Like its zirconium parent, $^{95}$Nb forms colloids and is readily hydrolyzed. The principal Group 6 fission product is $^{99}$Mo ($t_{1/2} = 67$ h), which is important at short cooling times because of its high yield but is insignificant in aged fuel. The most important Group 7 fission product is the long-lived (2.1 x $10^5$ year) $^{99}$Tc. Its chemistry is that of the pertechnate ion TcO$_4^-$.

The Group 8,9,10 elements are important because of their activity and in the case of ruthenium and its multiple oxidation states and the slow interconversion kinetics, the chemistry can be troublesome. RuO$_4$ can be volatilized leading to the loss of Ru in radiochemical procedures. The chemistry of the Group 11 element, Ag, is straightforward (+1 cation, forming insoluble compounds) and the Groups 12 and 13 elements, Zn, Ga, Cd and In have low yields and small activities. The Group 14 and 15 elements, Ge, As, Sn and Sb, also have low activities in aged fuel. The Group 16 element, Te, is present in the form of 30-100 day activities but most interest is focused on 78 h $^{132}$Te which decays to short-lived $^{132}$I which is volatile and can be released in rapid processing of fuel. The halogens, Br and I, are not important in fuel reprocessing due to their short half-lives but can be important in reactor operation due to their volatility.

16.3 Radiochemistry of Uranium

16.3.1 Uranium Isotopes
Natural uranium is 99.274 atom percent $^{238}$U, 0.7205 atom percent $^{235}$U and 0.0056 atom percent $^{234}$U. The $^{234}/^{238}$ ratio is exactly the ratio of their half-lives as expected for nuclei in secular equilibrium. The isotope $^{233}$U is produced by neutron capture on $^{232}$Th, followed by $\beta^-$ decay. $^{232}$U is a short-lived ($t_{1/2} = 72$ years) nuclide that is a contaminant in $^{233}$U samples (from fast neutron reactions). The daughters of $^{232}$U are hard $\gamma$-ray emitters that make working with $^{232}$U containing samples difficult. $^{236,237,239}$U are produced by neutron captures on $^{235}$U and $^{238}$U. $^{236}$U is long-lived but $^{237,239}$U are short-lived and decay to $^{237}$Np and $^{239}$Pu, respectively.

### 16.3.2 Metallic Uranium

Metallic uranium can exist in three different solid phases with differing densities, depending on temperature. At room temperature, the $\alpha$ phase is observed with a density of 19.07 g/cm$^3$ and a melting point of 1132°C. Metallic uranium is a very reactive metal that is silvery in color. (Frequently a surface oxide layer makes metallic uranium look black). Uranium powder is pyrophoric. When uranium metal is cut or scratched in the laboratory, a shower of sparks is sometimes observed due to the creation of small particles that ignite. Uranium metal with an oxide coating will burn at 700 °C to form $\text{U}_3\text{O}_8$. Uranium reacts with hot water to produce $\text{UO}_2$ and $\text{UH}_3$. In reactors, uranium is alloyed with zirconium to resist corrosion and radiation damage. Metallic uranium can be produced by the reduction of $\text{UF}_4$, i.e.,

$$\text{UF}_4 + 2 \text{ Mg} \rightarrow 2 \text{ MgF}_2 + \text{ U}$$

### 16.3.3 Uranium Compounds
Uranium exists in the +3, +4, +5 and +6 oxidation states. The +5 state disproportionates to the +4 and +6 states and is of little importance. Trivalent uranium reduces water and therefore there is no stable aqueous chemistry of U³⁺ although compounds do exist.

The most important uranium compounds are the oxides. UO₂ is the compound used in reactor fuel. It is a stable refractory material that is brown-black in color and is non-reactive with H₂O. It has density of 10.97 g/cm³ and can be prepared by the reduction of UO₃ with hydrogen. U₃O₈ (UO₂•2UO₃) is a green-black solid that occurs in the mineral pitchblende. It has a density of 8.38 g/cm³, is soluble in HNO₃ and can be prepared by oxidizing UO₂ or reducing UO₃. UO₃ is a yellow-orange solid ("orange oxide") and is important as an intermediate in the production of UO₂ or UF₆.

Uranium hydride, UH₃, is a reactive black powder. It is a powerful reducing agent and is pyrophoric. A mixture of uranium and zirconium hydrides is used as the fuel for the TRIGA research reactors.

Uranium halides exist in the +3 oxidation state (UF₃, UCl₃, UBr₃, UI₃), the +4 oxidation state (UF₄, UCl₄, UBr₄, and UI₄), the +5 oxidation state (UF₅, UCl₅) and the +6 oxidation state (UF₆, UCl₆).

UF₄ ("green salt") is an intermediate in the production of U and UF₆. It can be made by reacting UO₂ with excess HF as

\[ \text{UO}_2 + 4\text{HF} \leftrightarrow \text{UF}_4 + 2\text{H}_2\text{O} \]

or, for laboratory use, by the reaction
\[ U^{4+} + 4 \text{F}^- \rightarrow UF_4 \downarrow \]

(Uranium tetrafluoride precipitated from aqueous solutions exists as $UF_4\cdot5H_2O$ and it is difficult to remove the waters of hydration so that the dry reaction above is preferred.) $UF_4$ is frequently used to make accelerator targets of uranium by vacuum volatilization.

$UF_6$ ("hex") is the only readily available uranium compound that is volatile at room temperature. It is a colorless solid that is used in the uranium enrichment process. It sublimes at room temperature without melting. $UF_6$ is rapidly hydrolyzed by water and is a fluorinating agent. This latter property means that one must carefully choose the materials to contain $UF_6$.

**16.3.4 Uranium Solution Chemistry**

The solution chemistry of uranium is that of the +4 and +6 oxidation states, *i.e.*, $U^{4+}$ and $UO_2^{2+}$. The formal reduction potential of uranium in aqueous solution (*i.e.*, 1 M HClO$_4$) is

\[
\begin{array}{c}
UO_2^{2+} \overset{+0.063}{\rightarrow} UO_2^+ \overset{+0.58}{\rightarrow} U^{4+} \overset{-0.031}{\rightarrow} U^{3+} \overset{-1.70}{\rightarrow} U
\end{array}
\]

U (IV) chemistry is similar to that of Th$^{4+}$, except for the charge/radius ratio of the ions. $U^{4+}$ solutions are green in color, stable and slowly oxidized by air to $UO_2^{2+}$. Solutions of $U^{4+}$ are generally prepared by reduction of solutions of the uranyl ($UO_2^{2+}$) ion. U (IV) forms complexes with many anions ($C_2O_4^{2-}$, $C_2H_3O_2^-$, $CO_3^{2-}$, $Cl^-$ and
The chlorides and bromides of U (IV) are soluble while the fluorides and hydroxides are insoluble. In aqueous solution, U (IV) hydrolyzes via the reaction,

\[ \text{U}^{4+} + \text{H}_2\text{O} \rightarrow \text{U(OH)}^{3+} + \text{H}^+ \quad \text{K}=0.027 \]

U (VI) can be prepared by dissolving UO₃ in acid or U metal in HNO₃. Solutions of the uranyl ion show a characteristic yellow-green color and are very stable. U (VI) shows complex solution equilibria due to the occurrence of hydrolysis which leads to \([\text{UO}_2\text{OH}]^{3+}, [\text{UO}_2\text{OH}_2]^{2+}, \text{and } [\text{UO}_2\text{OH}_4]^{2+}\) mixtures. Because of hydrolysis reactions, aqueous solutions of uranyl salts are slightly acidic. Addition of base to uranyl solutions results in precipitation beginning at a pH between 4 and 7.

Uranyl ions form complexes in solutions with most anions. Uranyl sulfate and carbonate complexes are especially strong and are used in extracting uranium from its ores. Of great practical importance are the complexes of the uranyl ions with nitrate that are soluble in organic liquids such as alcohols, ethers, ketones and esters. One of the most important of these reactions is that involving the extraction of uranyl nitrate into TBP (the Purex process)

\[ \text{UO}_2^{2+} (\text{aq}) + 2 \text{NO}_3^- (\text{aq}) + 2\text{TBP (org)} \leftrightarrow \text{UO}_2(\text{NO}_3)_2 \cdot 2\text{TBP (org)} \]

Neglecting activity coefficients, the distribution coefficient for the distribution of uranium between the organic and aqueous phases is written as

\[ D = \frac{[\text{UO}_2(\text{NO}_3)_2 \cdot 2\text{TBP}]}{[\text{UO}_2^{2+}]} = K(\text{NO}_3)^2 (\text{TBP})^2 \]

where K is the equilibrium constant (K \(\sim\) 15-60). One can use the concentration of a salting agent such as \(\text{NO}_3^-\) to control the extraction process. (In the Purex process,
these salting agents ultimately leave the cycle with the fission products, contributing to the problem of these wastes).

16.4 The Nuclear Fuel Cycle—The Front End

The nuclear fuel cycle (Figure 16.1) begins with the mining of uranium ore. Uranium is by no means rare. Its overall abundance in the earth’s crust is ~ 4 ppm (which is more abundant than Ag, Hg, Bi or Cd). There are ~ 10^4 tonnes of uranium in the earth’s crust. The problem is one of concentration in that most uranium deposits contain < 0.001% uranium.

16.4.1 Mining and Milling

Uranium ore can be classified as high grade (1-4% U), medium grade (0.1-0.5% U) and low grade (<0.1% U). In the high grade deposits, in Zaire and Canada, uranium is found as pitchblende or uranite, materials of general composition xUO_2\cdot yUO_3 where 0 < y/x < 2. The medium grade ores are found in places such as the Colorado plateau of the US, where uranium is incorporated in carnotite (K_2O\cdot 2UO_3\cdot V_2O_5\cdot x H_2O) or autunite (CaO\cdot 2UO_3\cdot P_2O_5\cdot x H_2O). Low grade sources include the gold ore residues of S. Africa, seawater where the nominal uranium concentration of 3 ppb corresponds to a reservoir of ~ 10^{10} tonnes of uranium or the fertilizer by-products of the phosphate fields of Florida and Idaho, Tennessee shale, or the lignites of Wyoming and the Dakotas. The average uranium content of the ores used in the nuclear fuel cycle in the US in recent years is ~ 0.24%.
After mining, the uranium must be concentrated before further operations are carried out. This is done in the mills, which are located near the mines. Here the uranium ore content is increased from a few tenths of a percent (in the ore) to 85-95% (in a semi-refined concentrate known as “yellowcake”), while eliminating other elements that are present (the “tailings”).

While very high-grade pitchblende deposits can be concentrated by physical techniques involving their specific gravity, most concentration of uranium involves chemical leaching from the ore. The ore is prepared for leaching by crushing and roasting (to destroy organic material). It is then subjected to chemical leaching followed by a separation of the liquids and solids, followed by concentration/purification and final product recovery.

The normal choice (~80% of all US ores) for chemical leaching is acid leaching with sulfuric acid (due to its low cost and great availability). For the ores that have high carbonate content, an alkaline leach with Na$_2$CO$_3$ is used to prevent high acid concentration.

The problem in acid leaching is that only U (VI) dissolves in H$_2$SO$_4$. Any U (IV) present must be oxidized to U (VI) prior to leaching. The chemical steps can be summarized by the equations

\[
\text{FeS}_2, \text{Fe} + \text{H}_2\text{SO}_4 \rightarrow \text{Fe}^{++} + \text{H}_2 + \text{SO}_4^{2-}
\]

\[
2\text{Fe}^{++} + \text{MnO}_2 + 4\text{H}^+ \rightarrow 2\text{Fe}^{+++} + \text{Mn}^{++} + 2\text{H}_2\text{O}
\]

or

\[
6\text{Fe}^{++} + \text{NaClO}_3 + 6\text{H}^+ \rightarrow 6\text{Fe}^{+++} + \text{NaCl} + 3\text{H}_2\text{O}
\]

leading to
\[
\text{UO}_2 + 2\text{Fe}^{3+} \rightarrow \text{UO}_2^{2+} + 2\text{Fe}^{2+}
\]

\[
\text{UO}_3 + \text{H}_2\text{SO}_4 \rightarrow \text{UO}_2^{2+} + \text{SO}_4^{2-} + \text{H}_2\text{O}
\]

\[
\text{UO}_2^{2+} + 2\text{SO}_4^{2-} \Leftrightarrow [\text{UO}_2(\text{SO}_4)_2]^{2-} \Leftrightarrow [\text{UO}_2(\text{SO}_4)_3]^{4+}
\]

The final product thus appears in three chemical forms, \(\text{UO}_2^{2+}\), \([\text{UO}_2(\text{SO}_4)_2]^{2-}\) and \([\text{UO}_2(\text{SO}_4)_3]^{4+}\).

In alkaline leaching of high carbonate materials, one takes advantage of the unique solubility of \([\text{UO}_2(\text{CO}_3)_3]^{4+}\). One begins with finely divided material and must also deal with the oxidation of any U (IV) that is present. The basic reaction (pun intended) is

\[
\text{UO}_2 + \text{(oxidant, Ox)} + 3\text{CO}_3^{2-} \rightarrow [\text{UO}_2(\text{CO}_3)_3]^{4+} + \text{Ox}^{2-}
\]

After leaching, a concentration/purification is done to get rid of other materials leached from the ore. This can be done by ion exchange or solvent extraction. In the ion exchange method, three steps are employed: (a) the absorption of uranium from the leach liquor onto the resin (b) the selective elution of uranium from the resin and (c) the re-generation of the resin. Anion exchange is the preferred method of ion exchange with the relevant chemical equations for acid leach being

\[
[\text{UO}_2(\text{SO}_4)_3]^{4+} + 4\text{RX} \Leftrightarrow \text{R}_4[\text{UO}_2(\text{SO}_4)_3] + 4\text{X}^{-}
\]

and for alkaline leach

\[
[\text{UO}_2(\text{CO}_3)_3]^{4+} + 4\text{RX} \Leftrightarrow \text{R}_4[\text{UO}_2(\text{CO}_3)_3] + 4\text{X}^{-}
\]

The eluant is usually 1 M \(\text{NO}_3^{-}\) in the form of \(\text{NH}_4\text{NO}_3\). The physical method for carrying out the extraction can involve: (a) a fixed resin bed, (b) a “resin in pulp”
technique where resin in baskets is passed through a stream of pulp or slurry from the leach process or (c) a moving bed of resin.

Concentration/purification by solvent extraction usually involves four steps: (a) extraction of uranium from the leach liquor in a solvent (b) scrubbing to remove impurities from the solvent (c) stripping to remove uranium from the solvent and (d) regeneration of the solvent. The solvent in solvent extraction will contain the extractant which complexes uranium to make it soluble in the organic phase, a diluent, an inexpensive material to dilute the extractant, and a modifier to improve the solubility of the extractant in the diluent. Typical extractants are amines with isodecanol acting as a modifier to improve the amine solubility in a diluent such as kerosene. The typical chemistry of the extraction would involve the reactions

\[ 2R_3N(\text{org}) + H_2SO_4 \rightarrow (R_3NH)_2SO_4(\text{org}) \]

\[ 2(R_3NH)_2SO_4(\text{org}) + [UO_2(SO_4)_3]^+(\text{aq}) \rightarrow (R_3NH)_4[UO_2(SO_4)_3](\text{org}) + 2SO_4^{2-}(\text{aq}) \]

with the stripping reactions being

\[ (R_3NH)_4[UO_2(SO_4)_3](\text{org}) + 4NH_4OH \rightarrow 4R_3N(\text{org}) + 4H_2O + [UO_2(SO_4)_2]^{2-} + 4NH_4^+ + SO_4^{2-} \]

Following solvent extraction, uranium is precipitated from the solution by the addition of gaseous ammonia with the yellowcake product (Figure 16-4) being collected, packaged in 55 gallon drums and shipped to a refinery for further purification and conversion to UF₆ for enrichment.
Alkaline leach mills will use NaOH for final product recovery (in the form of sodium uranate, Na$_2$U$_2$O$_7$). Often these uranium ore concentrates (yellowcake) are transformed into U$_3$O$_8$ by drying at 200 °C to remove water and calcining, *i.e.*, heating until decomposition.

**16.4.2 Refining and Chemical Conversion**
Following milling, the yellowcake is shipped for refining and conversion. In most refineries, the uranium ore concentrates are purified by solvent extraction and then converted to UF₆ for enrichment. (A schematic diagram for this process is shown in Figure 16-5).

![Diagram of the refining and conversion of uranium ore concentrates](image)

**Figure 16-5** A schematic diagram of the refining and conversion of uranium ore concentrates. From Benedict, Pigford and Levi [4].

The yellowcake is dissolved in nitric acid. Uranyl nitrate is separated from metallic impurities in the dissolver by solvent extraction with TBP in some organic hydrocarbon, such as hexane. The organic extract is scrubbed with 1 M nitric acid...
and uranium is stripped from the organic phase by back-extraction with 0.01 M HNO₃. The uranyl nitrate-hexahydrate, UO₂(NO₃)₂•6H₂O or UNH is converted to UO₃ (orange oxide) in two steps, a concentration by evaporation and a de-nitrification by heating. UO₃ is reduced to UO₂ (brown oxide) using hydrogen via the overall reaction

\[ UO₃ + H₂ \rightarrow UO₂ + H₂O \]

UO₂ is hydrofluorinated via the reaction

\[ UO₂ + 4HF \rightarrow UF₄ + 2H₂O \]

using anhydrous HF gas to produce green salt, UF₄. This green salt can be burned in F₂ to produce UF₆. UF₄ can also be reduced to metallic uranium.

16.4.3 Enrichment

As discussed earlier, natural uranium is 0.72 atom percent ²³⁵U and the fuel used in light water reactors is typically 3% ²³⁵U. This means the refined uranium must be enriched in the lighter 235 isotope prior to fuel fabrication. This can be done by a variety of physical approaches that take advantage of the small mass difference between ²³⁵U and ²³⁸U. We shall discuss four of these methods, gaseous diffusion, gas centrifuges, electromagnetic separation, and laser enrichment.

In gaseous diffusion, one takes advantage of the fact that in a gas, the lighter molecules have a higher velocity. If we assume the average kinetic energy of all gas molecules at a given temperature is the same, then we can write

\[ \text{average kinetic energy} = \frac{mv^2}{2} \]
For $^{235}\text{UF}_6$ and $^{238}\text{UF}_6$, we have

$$m_{235}v_{235}^2 = m_{238}v_{238}^2$$

$$v_{235}/v_{238} = \left(\frac{m_{238}}{m_{235}}\right)^{1/2} = \left(\frac{314}{311}\right)^{1/2} = 1.0043$$

If we send a stream of UF$_6$ gas into a vessel with porous walls (Figure 16-6), then the lighter 235 molecules will pass through the pores more frequently (due to the greater number of impacts on the walls per time). The maximum separation factor is 1.0043, but, in practice, this is not achieved and the less enriched part of the gas stream is recycled. Typically if one starts with natural uranium (0.72% $^{235}\text{U}$) and with tails depleted to 0.3%, about 1200 enrichment stages are needed to get a 4% enrichment. In practice, several million 10-100 nm pores/cm$^2$ of the membrane are used and the process must be carried out at elevated temperatures, dealing with UF$_6$, a strong fluorinating agent that decomposes upon contact with water. Most enrichment is done using this technique.

![Diagram](image)

Figure 16-5 A schematic diagram of the operation of a gaseous diffusion cell. From R.E. Leuze in [3].
In *gas centrifuges*, (Figure 16-7), one takes advantage of the fact that the centrifugal force will push the heavier \(^{238}\text{UF}_6\) molecules to the wall of the centrifuge and the gas near the center will be enriched in \(^{235}\text{UF}_6\). The gas flow pattern allows the heavier gas to be collected near the top and the lighter gas near the bottom. Separation is more efficient than in the gaseous diffusion method, requiring only about 10 stages to enrich \(^{235}\text{U}\) from 0.72 to 3\% with a 0.2\% tail.

![Figure 16-7](https://example.com/fig16-7.png)

Figure 16-7  A schematic diagram of a gas centrifuge. From R.E. Leuze in [3].

In *electromagnetic separation*, one uses the fact that when ions of differing mass in the same charge states are accelerated through a potential difference, their energy is the same and the radius of curvature in a magnetic field is proportional to
Thus the material to be separated is ionized, accelerated, and passed through an analyzing magnet that separates the isotopes into separate beams and a collector for the relevant beams. The technology is straightforward, but the cost is high for processing macroscopic amounts of material and so this technique has largely been abandoned although it was used recently in Iraq in an attempt to obtain enriched uranium for nuclear weapons.

In *laser enrichment*, one takes advantage of the fact that the atomic energy levels of different isotopes differ slightly. This is due to the differing reduced electron masses for the different isotopes and the change in the overlap between the wave functions of the inner electrons and the nucleus, due to isotopic differences in nuclear radii. Lasers can be tuned to excite $^{235}$U atoms, but not $^{238}$U atoms, to higher energy levels. The excited atoms are then ionized with another laser beam. The resulting ionized $^{235}$U atoms can be separated electromagnetically. To date, the feasibility of this technique has been demonstrated but there are no commercial applications.

### 16.4.4 Fuel Fabrication

The enriched UF$_6$ is converted into UO$_2$ at the fuel fabrication plants. The UF$_6$ is reacted with water to produce a solution of UO$_2$F$_2$ and HF

$$\text{UF}_6(g) + 2\text{H}_2\text{O} \rightarrow \text{UO}_2\text{F}_2 + 4\text{HF}$$

Ammonium hydroxide is added to the uranyl fluoride solution to quantitatively precipitate ammonium diuranate
\[ 2\text{UO}_2\text{F}_2 + 6\text{NH}_4\text{OH} \rightarrow (\text{NH}_4)_2\text{U}_2\text{O}_7 + \text{NH}_4\text{F} + 3\text{H}_2\text{O} \]

This product is collected, calcined in air to produce \( \text{U}_3\text{O}_8 \) and heated with hydrogen to make \( \text{UO}_2 \) powder. The \( \text{UO}_2 \) powder is pressed into pellets, which are sintered, ground to size and loaded into zircalloy tubing filled with helium. The tubes are sealed and assembled into fuel bundles.

### 16.5 The Nuclear Fuel Cycle—The Back End

At one point in the history of nuclear power, the concept of reprocessing spent reactor fuel to recover its plutonium content to fuel other reactors was considered central to reactor development. The idea of an energy source that could generate its own fuel was very appealing. But, as outlined earlier, most fuel is not reprocessed/recycled but used in a “once-through’ manner. The reasons for this are complex, \textit{i.e.}, no shortage in near-term uranium supply, low uranium prices, some technical problems in reprocessing and a concern that reprocessing would make plutonium too readily available for use in weaponry. Nonetheless there are operating plants for reprocessing reactor fuel and the overall fate of spent fuel is of great concern and interest.

#### 16.5.1 Properties of Spent Fuel

Periodically a portion of the fuel in a nuclear reactor is removed and replaced with fresh fuel. In the past, the average lifetime of fuel in the reactor was three
years with 1/3 of the fuel being removed each year. More recently, attempts are being made to extend fuel lifetimes.

Initially the radioactivity levels of the irradiated fuel are very high (Figure 16-8). Chemically, the $^{235}$U content has been reduced from its initial 3% to 1% while the $^{238}$U content has been reduced from 97 to 94% (Figure 16-9). $^{239}$Pu and other Pu isotopes are produced along with the fission products.

![Graph showing the radioactivity and heat output of spent fuel over time.](image)

**Figure 16-8** The radioactivity and heat output of spent fuel as a function of time.

From Bodansky[6].
Figure 16-9 Changes in the chemical composition of irradiated fuel. From Murray [8].

The original plan for this spent fuel was to store it for about 150 days and then transfer it to other facilities for disposal as waste or reprocessing. In the US, this transfer has not occurred and most of the fuel has remained in cooling ponds at the reactor sites, for times that have exceeded 20 years. In this case, a closer look at the properties of irradiated fuel is justified.

In Figure 16-8, we show the activity and heat output for spent fuel, beginning one year after discharge from the reactor. (During the first year, the activity drops to 1% of its initial value and drops another factor of 5 in a ten year period) The
“waste disposal problem” begins at the ten-year point. Interpreted in this light, the dominant activities over the long term in un-separated waste are $^{90}$Sr, $^{137}$Cs, $^{241}$Pu, $^{241}$Am (from the decay of $^{241}$Pu), $^{239,240}$Pu, $^{99}$Tc and $^{237}$Np. The activity level of the waste decreases faster than the heat output due to the shorter half-lives of the beta emitters, which do not contribute as much to the heat output as the longer-lived alpha emitters. The heat output of the waste is sufficiently large to require care in waste storage.

### 16.5.2 Fuel Reprocessing

Fuel reprocessing has three objectives: (a) to recover U or Pu from the spent fuel for re-use as a nuclear reactor fuel or to render the waste less hazardous (b) to remove fission products from the actinides to lessen short term radioactivity problems and in the case of recycle of the actinides, to remove reactor poisons and (c) to convert the radioactive waste into a safe form for storage. Fuel reprocessing was/is important to produce plutonium for weapons use.

The Purex process is used for almost all fuel reprocessing today. Irradiated UO$_2$ fuel is dissolved in HNO$_3$ with the uranium being oxidized to UO$_2$(NO$_3$)$_2$ and the plutonium oxidized to Pu(NO$_3$)$_4$. A solution of TBP in a high-boiling hydrocarbon, such as n-dodecane, is used to selectively extract the hexavalent UO$_2$(NO$_3$)$_2$ and the tetravalent Pu(NO$_3$)$_4$ from the other actinides and fission products in the aqueous phase. The overall reactions are:

$$\text{UO}_2^{++}(aq) + 2\text{NO}_3^-(aq) + 2\text{TBP (org)} \rightarrow \text{UO}_2(\text{NO}_3)_2 \cdot 2\text{TBP (org)}$$
or

$$\text{Pu}^{4+}(aq) + 4\text{NO}_3^-(aq) + 2\text{TBP} \text{(org)} \rightarrow \text{Pu(NO}_3)_4(\text{TBP})_2(\text{org})$$

(These equilibria can be shifted to the right (i.e., improved extraction) by increasing the TBP concentration in the organic phase or increasing the [NO$_3^-$](aq).) In a second step, the TBP solution is treated with a dilute nitric acid solution of a reducing agent, such as ferrous sulfamate or U (IV), which reduces the plutonium to a trivalent state but leaves the uranium in a hexavalent state. Plutonium will then transfer to the aqueous phase, leaving uranium in the organic phase. The uranium is stripped from the organic phase.

The only fission fragments that extract during the Purex process are Zr, Ru, Nb and Tc, with the most troublesome being Zr and Ru. Zr forms a number of complex species with the most important being [Zr(NO$_3$)$_4$•2TBP]. The formation of this complex is inhibited by the addition of F$^-$ whereby

$$\text{Zr(NO}_3)_4\cdot2\text{TBP} + 6 \text{F}^- \leftrightarrow \text{ZrF}_6^{2-} + 4 \text{NO}_3^- + 2 \text{TBP}$$

An overall schematic view of the Purex process is shown in Figure 16-10. Detailed descriptions of the process can be found in the works by Benedict, Pigford and Levi [4] and Wymer and Vondra [3]. We shall briefly summarize the important steps. The first step is to prepare the irradiated fuel for dissolution by mechanically chopping it into small pieces ($\sim 1$–5 cm). This opening of the cladding causes the release of $\sim 10\%$ of the Kr and Xe fission products as well as some $^3$H and volatile fission products. These off-gases are combined with those from the dissolution step.
In the dissolution step, the fuel pieces are dissolved in near boiling 10 M HNO$_3$. This step, which takes a few hours, dissolves the uranium, plutonium, and fission products, leaving the cladding to be recovered. From the off-gas of steam, air
and NO₃, the Kr and Xe are recovered. The chemical reactions for the dissolution of uranium involve processes like

\[ 3 \text{UO}_2 + 8 \text{HNO}_3 \rightarrow 3 \text{UO}_2(\text{NO}_3)_2 + 2 \text{NO} + 4 \text{H}_2\text{O} \]

and

\[ \text{UO}_2 + 4 \text{HNO}_3 \rightarrow \text{UO}_2(\text{NO}_3)_2 + 2 \text{NO}_2 + 4 \text{H}_2\text{O} \]

The plutonium is oxidized to Pu(IV) and Pu(VI), while the neptunium ends up in the pentavalent or hexavalent states. Small amounts of plutonium and fission products may not dissolve and they can be leached with acid solutions containing the oxidant Ce⁴⁺.

The off-gas treatment involves primarily iodine, krypton and xenon. There are a variety of processes for capturing the iodine and disposing of it. Kr and Xe are captured by either cryogenic techniques or selective absorption, such as absorption in chlorofluoromethane. Most of the off-gas volume is due to Xe (~800 L/Mg fuel) with the activity being mostly 10.7-year ⁸⁵Kr (~11,000 Ci/Mg fuel).

The dissolver solution is treated with chemicals to adjust the acidity, valence and concentrations of the species involved. The HNO₃ concentrations are ~2-3 M, the UO₂(NO₃)₂ concentrations are ~1-2 M and the Pu is stabilized as Pu(IV) using N₂O₄ or hydroxylamine. In these and subsequent manipulations of these solutions, attention must be given to criticality control. This is done by regulating the solution geometry, the concentrations of fissile materials and the addition of neutron absorbers such as Gd.

The primary separation of plutonium and uranium from the fission products involves a solvent extraction with 30 volume percent TBP at room temperature.
The activity levels in this separation are quite high (~1700 Ci/L for the fission products) and the aqueous waste, which contains 99% of the fission products, is a high-level waste. Am and Cm are not extracted and Np is partially extracted. Because of the high radiation levels, there are radiolysis problems with TPB, leading to solvent degradation. Primary products of the radiolysis of TBP are the dibutyl- and monobutylphosphoric acids along with phosphoric acid. These degradation products are removed in the solvent purification steps.

Following decontamination of the uranium/plutonium from the fission products, the plutonium is separated from the uranium. This is done by reducing the Pu (IV) to non-extractable Pu (III), leaving uranium in the hexavalent state. In the older Purex plants, this was done using Fe^{2+} while the newer plants add U^{4+}. The plutonium thus ends up in an aqueous phase while the uranium remains in the organic phase.

Uranium is back-extracted (and thus removed from the organic phase) with 0.01 M HNO₃. It is purified by a series of solvent extraction cycles until the Pu/U ratio is < 10⁻⁸ and the total βγ activity is less than twice that of aged natural uranium.

### 16.6 Radioactive Waste Disposal

Radioactive waste management began with the advent of nuclear energy and has been studied since then, with the expenditure of billions of dollars. Despite this Herculean effort, great uncertainty remains about when and how, many aspects of
waste disposal, especially high-level waste, will be understood and dealt with effectively.

16.6.1 Classification of Radioactive Waste

The simplest way to classify radioactive waste is by its physical state, *i.e.*, whether it is a gas, liquid or solid. Gaseous waste arises from gas evolution, during nuclear fuel reprocessing and by activation of air during reactor operation. The principal gaseous activation product is 1.8 hr \(^{41}\)Ar, which is usually dispersed into the atmosphere from a stack whose height insures safe ground level concentrations of the released gas.

The off-gases from fuel reprocessing are the largest contributors to the gaseous waste. The fission products krypton and xenon escape when the fuel elements dissolve. Molecular iodine and ruthenium tetraoxide can also be released. Iodine and ruthenium are removed from the waste stream by trapping. Radio xenon has mostly decayed after a cooling time of about one year, while \(^{85}\)Kr is trapped cryogenically. While small quantities of \(^{14}\)C are formed in reactors, the release of this \(^{14}\)C as CO\(_2\) is an important component (~ \(\frac{1}{2}\)) of the public dose due to the fuel cycle.

The most important liquid wastes are the high level effluents, containing fission products from fuel reprocessing. They contain > 99% of the fission products in the fuel with small quantities of U and Pu. Medium level liquid waste has an activity of ~ 4 GBq/L and results from various steps in fuel reprocessing. Low level
(<0.1 GBq/m$^3$) is treated or concentrated. Liquid organic waste is usually incinerated or chemically destroyed.

Solid waste comes from the mining and milling of uranium ore, and the sludge from spent fuel storage. It also includes contaminated equipment and structures. High-level solid waste includes the hulls from the dissolving of spent fuel, ion exchange resin, etc.

Radioactive waste may also be classified as to origin (defense or commercial waste), the material present (transuranium waste, spent fuel) or the level of radioactivity present (high, medium, low). The principal categories of waste using this classification scheme are: high level waste (HLW) resulting from spent fuel reprocessing and consisting mainly of fission products and a small portion (<0.5%) of the original U and Pu; spent nuclear fuel (SNF) which is irradiated fuel that has not been reprocessed; transuranic waste (TRU) which is $\alpha$-emitting waste with $>100$ nCi/g of the transuranium nuclei; low level waste (LLW) which is waste with small amounts of radioactivity (non TRU) arising from a variety of sources and mill tailings, a special type of LLW that contains $\alpha$-emitting radionuclides resulting from uranium mills. This finely ground sandy material contains U daughters. Waste may contain “hazardous” waste (i.e., carcinogens, flammable materials, etc.) as well as “radioactive” waste. Such waste is referred to as “mixed” waste.

16.6.2 Amounts and Associated Hazards
The volume and activity of this waste, as of 1996, is summarized in Table 16-1.

Table 16-1 1996 US Radioactive Waste Inventory

<table>
<thead>
<tr>
<th>Type/Origin</th>
<th>Volume ($10^3 m^3$)</th>
<th>Activity (M Ci)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Military</td>
<td></td>
<td></td>
</tr>
<tr>
<td>HLW</td>
<td>347</td>
<td>853</td>
</tr>
<tr>
<td>LLW</td>
<td>3474</td>
<td>16</td>
</tr>
<tr>
<td>SNF (MTHM)*</td>
<td>2483</td>
<td>9980</td>
</tr>
<tr>
<td>TRU</td>
<td>238</td>
<td>1.3</td>
</tr>
<tr>
<td>Mill Tailings</td>
<td>28,000</td>
<td>0.08</td>
</tr>
<tr>
<td>Commercial</td>
<td></td>
<td></td>
</tr>
<tr>
<td>HLW</td>
<td>2</td>
<td>26</td>
</tr>
<tr>
<td>LLW</td>
<td>1782</td>
<td>8</td>
</tr>
<tr>
<td>SNF(MTIFM)*</td>
<td>34,252</td>
<td>12537</td>
</tr>
<tr>
<td>Mill Tailings</td>
<td>11,870</td>
<td>0.03</td>
</tr>
</tbody>
</table>

*By convention, the quantity of spent fuel is reported in mass units (MTHM, or MTIHM, metric tons of heavy metal or metric tons of initial heavy metal)
The largest volume, but lowest activity is the mill tailings which have a specific activity of ~1.8 nCi/g, mostly due to the $^{238}\text{U}$ decay series daughters ($^{230}\text{Th}$, $^{226}\text{Ra}$, $^{222}\text{Rn}$, $^{210}\text{Pb}$, $^{210}\text{Bi}$, $^{210}\text{Po}$, etc). Of special concern is gaseous $^{222}\text{Rn}$. Most of the activity associated with radioactive waste is in the unprocessed spent fuel. The military high level waste tends to have larger volumes than the commercial HLW because the latter has been compacted. Most of the commercial spent fuel is stored at the reactor sites while most of the military/USDOE waste is stored at a few major production facilities.

One measure of the hazard associated with this waste is the water dilution volume ($\text{m}^3$). The water dilution volume is the volume of water needed to dilute a radionuclide to its maximum permissible concentration in water. A plot of the water dilution volume (WDV) for spent fuel is shown in Figure 16.11.
Figure 16.11 The water dilution volume for radionuclides in PWR spent fuel.


Though the activity of the spent fuel falls by more than a factor of 1000 in the first thousand years (Fig 16.3), the WDV falls more slowly. This is due to the hazards posed by the long-lived $\alpha$-emitters in the spent fuel. For times greater than 500 years, the actinide radio toxicity prevails. On a time scale of $10^4 - 10^6$ years, the WDV values approach those of the original ore used to make the reactor fuel. (There are limitations to this measure of hazard because of how radionuclides enter the biosphere and are concentrated)

16.6.3 Storage and Disposal of Nuclear Waste
What does one do with the radioactive waste described in the previous section? Clearly the most important component of the waste is the spent fuel. Currently most spent fuel assemblies are held in cooling ponds at the reactor sites, although one cannot do this indefinitely. In a few reactor sites, dry storage of the spent fuel is used. The fuel rods are transferred to special casks when the heat output and activity are such that air-cooling will suffice.

Because a permanent disposal strategy has proven illusive due to technical and political considerations, plans have been made for interim storage facilities where the fuel is stored in a retrievable manner until a permanent storage facility is developed.

The favored method for permanent storage of radioactive waste is deep geologic repositories. This option is the only option for unprocessed spent fuel assemblies and for most HLW. (An alternative, supplemental strategy discussed below is to remove some of the actinides in the HLW by chemical separations prior to geologic storage).

In general terms, the goal of long-term waste storage is to isolate the radioactive waste from humans and the environment. The prevailing design strategy for waste repositories is that of multiple barriers (Fig-16.12)
The first barrier is the form of the waste, which will immobilize the radioactive materials. The waste form should not be damaged by heat or radiation nor be attacked by ground water. The waste is placed in a steel canister, which is resistant to leaching. The canister is surrounded by packing materials that prevent radioactivity from escaping and the entire repository is backfilled with a material that absorbs or resists chemical intrusion. The final barrier is the host medium that separates the repository from the surrounding area.

The host medium can be bedded salt, salt domes, granite, basalt or volcanic tuff. Each medium has advantages and disadvantages with regard to resistance to water intrusion, site availability and political considerations. Each medium can work and the most important factor is how the local site is designed.
An additional factor is the position of the repository relative to the groundwater table, with most repositories being below the water table. The US has chosen the Yucca Mountain region in Nevada, near the Nevada nuclear weapons test site, as its location for permanent geologic storage. The Yucca Mountain area features welded volcanic tuff as the host medium. Welded volcanic tuff is a material of low permeability, and the Yucca Mountain site is above the water table.

The biggest concern with respect to radionuclides in a waste repository is their movement in the ground water. Attention is focused on the horizontal motion of the groundwater not the upward motion, as the repositories are several hundred meters below the surface. The repositories and their boundaries and locations are such that the biosphere is 10-100 km away from the center of the repository. The velocity of the ground water in typical geologic media proposed for repositories ranges from 0.01 to 10 m/y. The velocity of radionuclides in ground water is smaller than the velocity of the groundwater due to sorption phenomena. This sorption can be expressed by a retardation factor R where R is the ratio of the groundwater velocity to the average radionuclide velocity. R can be expressed by an approximation as

\[ R \approx 1 + 10 K_d \]

where \( K_d \) is the ratio of the radionuclide concentration in the rock of the repository to that in the ground water. Retardation factors for radionuclides in geologic media of interest as repository sites range from 1 to 3000 and depend strongly on the ion being sorbed [12]. For \(^{239}\text{Pu} \), \( R = 200 \) for volcanic tuff. The Yucca Mountain groundwater velocities are \( \sim 0.025 \) m/y, meaning that \(^{239}\text{Pu} \) will decay before it migrates 6
km. A similar conclusion can be reached for the transplutonium nuclei and $^{90}\text{Sr}$.

From this standpoint, special concern is given to $^{99}\text{Tc}$ and $^{237}\text{Np}$, whose long half-lives can allow geologic transport.

16.6.3.1 **Spent Fuel**

The largest single radioactive waste disposal problem is the spent fuel from military and commercial reactors. As discussed earlier, the spent fuel from commercial reactors is stored in water ponds at the reactor sites. The spent fuel storage facility consists of a cooling and cleanup system for the water along with equipment to safely transfer the fuel rods from the reactor to the storage area. A typical pool will have a volume of ~ 400,000 gallons. The water will contain ~ 2000 ppm boron that acts as a neutron absorber and will be maintained at a temperature of < 70 °C.

The long-term fate of the spent fuel is geologic storage. The spent fuel assemblies are packaged in canisters with a stabilizing material (powder or sand) in the canister. The fuel canisters are placed in the geologic storage site and covered by a backfill to impede water movement.

16.6.3.2 **HLW**

The high level waste (HLW) consists primarily of liquid waste from fuel reprocessing. It contains all the fission products from the spent fuel along with all
the neptunium and transplutonium nuclei and less than 1% of the uranium and plutonium. HLW is intensely radioactive with a high heat output (Fig. 16.8). The hazard potential of this waste is much greater than the time scale of nuclear energy use. In addition to its radiological hazard, it is very corrosive, being up to 7M in HNO₃ and containing ~250g/L salt. This waste is ultimately to be stored in geologic repositories after solidification of the liquid waste. The volume of the solidified waste is modest in that a commercial nuclear power reactor plant running for 1 GW-year will produce about 2 m³ of solidified waste after reprocessing.

The liquid waste is stored for at least six years prior to solidification to reduce the decay heat (Fig. 16.8) by a factor of ten or more. The first US military fuel reprocessing wastes were stored as neutralized waste in mild steel tanks at the Hanford reservation in E. Washington. These steel-lined, reinforced concrete tanks were 500,000 – 1,000,000 gallons in capacity with provisions for removal of waste heat and radiolysis products. Corrosion of several tanks occurred with the release of waste. Fortunately the soil around these tanks retarded nuclide transport. A better (and more expensive) design for storage tanks was implemented at the Savannah River site in South Carolina consisting of a steel tank inside of a Hanford tank. The storage of acid waste in these tanks has not encountered the corrosion problems seen with the Hanford tanks.

The solidification of waste takes place in two steps, a calcining step and an incorporation of the calcined material into borosilicate glass. Calcining can be done in various ways but primarily involves the removal of volatile products like water or NO₃⁻ and conversion of all species in the HLW to solid stable oxides. The oxides are
then mixed with SiO$_2$, B$_2$O$_3$, etc. to make a borosilicate glass, which is then prepared for geologic storage (Fig. 16.13)

Figure 16.13 Schematic diagram of the final steps in putting vitrified waste into a geologic repository.
16.6.3.3 Transuranic Waste (TRU)

Transuranic waste (TRU) results from fuel reprocessing and fuel fabrication facilities, the production of nuclear weapons and the decommissioning of nuclear reactors or fuel cycle facilities. TRU includes clothing, equipment, etc. from reprocessing facilities along with plutonium and other transplutonium elements removed in fuel reprocessing. Because of the relatively low activity levels of this waste, the primary processing steps prior to storage involve volume reduction. In the US, this waste is stored in an interim storage facility, the Waste Isolation Pilot Plant (WIPP), an underground salt-bed facility near Carlsbad, New Mexico.

16.6.3.4 Low Level Waste (LLW)

Low-level waste (LLW) consists of contaminated dry trash, paper, plastics, clothing, organic liquids such as liquid scintillation samples, etc. LLW is produced by any facility that handles radioactive materials such as nuclear power plants, medical facilities, colleges, etc. In the US, commercial LLW is sent to one of three disposal sites (Barnwell, S. Carolina; Richland, Washington and Clive, Utah). Due to the limited size of these sites (and similar disposal sites through the world) and steeply escalating costs for waste disposal, the primary goal of LLW treatment prior to disposal is volume reduction, either by incineration or compaction, followed by immobilization. For noncombustible solids, volume reduction can be achieved by
mechanical disassembly, crushing, melting or dissolution. For noncombustible liquids, evaporation, calcination, filtration or concentration on ion exchange resins are used for volume reduction. Combustible material is oxidized to ashes. Mechanical techniques of volume reduction reduce volume by 5 - 10 x, while combustion reduces volume by 50 -100x. The products of volume reduction are immobilized using absorbents (vermiculite, clay, etc.), cement or salt matrices.

16.6.3.5 Mill Tailings

The tailings from uranium mining and milling contain all the daughters of uranium present in the original ore. The mill tailings thus have ~ 70% of the original activity of the ore. This activity decays with the half-life of $^{230}$Th, $\sim 8 \times 10^4$ y. The radiological hazard is mostly in the $^{226}$Ra and its daughter, $^{222}$Rn. The inert gas $^{222}$Rn can escape from the tailings and can create a radiological inhalation risk. Other radionuclides, such as $^{230}$Th or $^{226}$Ra, etc. can be leached from the tailings by water, being transferred to the biosphere. The tailings themselves are finely divided sandy material that can be dispersed by wind. Remediation of sites containing mill tailings involves covering the tailings by a clay or earth overburden that is 3-8 m thick. This overburden reduces Rn release, minimizes leaching and prevents wind dispersal.

16.6.3.6 Partitioning of Waste
As discussed earlier, for a variety of reasons, the nuclear fuel cycle is operated in a “once-through” mode in the US and for the majority of reactors worldwide. The long-lived transuranium nuclides are thus mixed with the shorter-lived fission products in the HLW and SNF. As concern about the lack of long-term, widely-accepted programs to deal with this waste mounts, attention is being focused on partitioning (chemically separating) the transuranium nuclei from the waste and transmuting it to nuclides of shorter half-life by irradiation in high neutron fluxes. These waste destruction steps also can be incorporated into advanced design reactor systems or advanced fuel cycle designs. Other targets of partitioning are troublesome fission products such as $^{99}$Tc, $^{129}$I, $^{90}$Sr and $^{134,137}$Cs.

At the outset, one should comment that there is a division [4,6] among scientists as to whether the gains in reduced radiotoxicity of the waste offset the additional cost and risk of further treatment and handling of the waste. Removal of the actinides from a waste repository gives a small reduction in risk because the actinides migrate so slowly through the repository. Several additional problems would be created by partitioning and transmutation such as: a greater volume of wastes, the need for large, expensive processing facilities, an increase in the neutron flux coming from the waste, necessitating increased shielding and the possibility of additional releases of radioactivity to the environment. A US study has suggested 99.9% removal of the actinides and 95% removal of Tc and I is a minimum requirement to justify the effort.

Nonetheless, the US and other nations have been developing additional chemical separation processes to bring about these goals. Strontium and cesium can
be removed from HLW by extraction with crown ethers, such as
ditertiarybutyldicyclohexanone-18-crown-6, which can also extract $^{99}$Tc. In the US,
a variation of the Purex process is being developed to reprocess spent fuel. This
modification of the Purex process is such that only U and Tc are extracted from the
fission products and TRU nuclei (Np, Pu, Am, Cm). It is called the UREX process
(Uranium Extraction). It is intended to recover >99.9% of the U, >95% of the Tc
and leave >99.9% of the TRU nuclei in the acid waste. All chemicals used in the
process are converted to gases in subsequent processing to minimize waste. A
Purex separation is carried out using 30% TBP in kerosene working on a 1 M HNO$_3$
solution of spent fuel and then acetohydroxamic acid (AHA), an analog of
hydroxylamine, is used to reduce Np (VI) to non-extractible Np (V) and to complex
Pu(IV) and Np (IV) preventing their extraction. Figures 16.14 and 16.15 show the
flowsheet for the UREX process and its place in the total, new proposed treatment of
spent fuel. Other work on pyrochemical processes involving electrochemical
reduction steps in molten salt baths is also underway.
16.6.3.7 Transmutation

Transmutation is the term used in connection with waste management to describe a nuclear process in which long-lived nuclides are changed into shorter-
lived nuclides by nuclear reactions. Possible sources of bombarding particles are neutrons from reactors or accelerators that have been configured to produce large neutron fluxes, by reactions, such as spallation. Fast neutrons are preferred as the bombarding particle because some of the relevant isotopes of the actinides Np, Am and Cm are not thermally fissionable. $^{129}$I and $^{99}$Tc, on the other hand, are readily destroyed in thermal fluxes. Transmutation can also be used to destroy plutonium from dismantled nuclear weapons. Of course, the resulting fission or reaction products from transmutation are radioactive and do constitute radioactive waste, albeit with shorter half-lives.

Current attention is centered on methods using charged particle accelerators for transmutation. In a typical scheme, an accelerator is used to produce a 10-200 mA beams of 1 GeV protons. The proton beam strikes a liquid lead or lead-bismuth eutectic target giving rise to 30-40 fast neutrons/proton, via spallation. These fast (1-10 MeV neutrons) are slowed down in a graphite moderator surrounding the Pb target. Some designs produce fast (75-225 keV) neutrons in the moderator while other designs thermalize the neutrons. The actinides and fission products to be transmuted are dissolved in molten salts or other media allowing high heat transfer in channels passing through the moderator. The neutron flux in the channels is $\sim 10^{15}$- $10^{16}$ n/cm$^2$-sec.

Typical heat production in the moderator-fuel blanket is $\sim$750 – 1500 MW. The excess heat is used to generate electricity that helps to pay for the operation of the facility. The transmuted material will have $\sim$20% of the original plutonium and minor actinides of the input material and will contain significant fission product
activities. This transmuted material can be put into geologic storage, reducing the long-term hazard of the repository material.

### 16.7 Chemistry of Operating Reactors

A complex set of chemical processes occurs during the operation of a nuclear reactor. Up to now, we have concentrated our attention on the chemical, physical and nuclear processes occurring in the fuel and their consequences. Now we turn our attention to the coolant, the moderator and the reactor materials and the changes in them due to the hostile chemical environment. The reactor environment has coolant temperatures up to 350°C, pressures of ~75-150 atmospheres and intense neutron and gamma radiation. Further complications are introduced by the two phases present in BWRs and the use of chemical shims like B to control the reactivity of PWRs. Both reactor types exhibit potentially serious possibilities of corrosion.

#### 16.7.1 Radiation Chemistry of Coolants

About 2% of the total neutron and γ-ray energy released in a nuclear reactor is deposited in the cooling water. The situation is of special concern in BWRs where the neutron and γ-ray fluxes near the core are ~ $10^9$ R/hr of neutrons and $10^8$ R/hr of photons. (There is a hydrogen gas overpressure in PWRs suppressing to some extent water decomposition or oxygen gas production). Due to radiolysis of the
coolant water, this energy deposit produces an oxidizing environment with 100-300 ppb oxygen and hydrogen peroxide, with lesser concentrations in the vapor phase.

The primary process is

$$H_2O \rightarrow H\cdot + OH\cdot$$

These radicals react to form $H_2$ or $H_2O_2$ by

$$H\cdot + H\cdot \rightarrow H_2$$
$$H\cdot + OH\cdot \rightarrow H_2O$$
$$OH\cdot + OH\cdot \rightarrow H_2O_2$$

Molecular $O_2$ is generated by

$$H_2O_2 + OH\cdot \rightarrow HO_2\cdot$$
$$HO_2\cdot + OH\cdot \rightarrow H_2O + O_2$$
$$HO_2\cdot + HO_2\cdot \rightarrow H_2O_2 + O_2$$

and destroyed by

$$O_2 + H\cdot \rightarrow HO_2\cdot$$

16.7.2 Corrosion

The oxygen and radiolysis products attack the outer layers of the stainless steel or nickel based alloys used in the reactor structure, forming a thin oxide layer on these components. Corrosion products are released from this thin oxide layers by the cooling water and become activated as they pass near the reactor core. These products can deposit on fuel surfaces, in coolant channels, and on reactor materials.
These deposits are referred to as *crud* (Chalk River Unidentified Deposits). In PWRs the chemical composition of the crud is Ni$_x$Fe$_y$O$_4$ where $x/y = 0.25$ and $x + y = 3$. In PWRs, the crud that also contains boron compounds causes a phenomenon known as “axial offset anomaly” (AOA), which is an unexpected deviation from predictions of the core axial power distribution during operation. Because it is not well understood, AOA limits the operating power of several PWRs, at great cost to the utilities.

Attempts are made to minimize corrosion by controlling the chemistry of the coolant water. Adding $^7\text{LiOH}$ raises the pH to 8. One can use oxygen scavengers such as hydrazine to reduce the oxygen concentration.

### 16.7.3 Coolant activities

When corrosion products are deposited on the fuel surfaces, they become activated by neutron capture. Some of the most prominent of these activities are $^{55}\text{Fe}$, $^{63}\text{Ni}$, $^{60}\text{Co}$, $^{54}\text{Mn}$, $^{58}\text{Co}$ and $^{59}\text{Fe}$. These radionuclides will then be found in the reactor coolant.

Fission products can be released from defects in the fuel rods or from tramp uranium on the fuel cladding. Of special importance are the volatile fission products $^{131-135}\text{I}$ ($^{89}\text{Kr}$, $^{137,138}\text{Xe}$ in BWR steam). Cations include the Sr and Cs isotopes, which are present along with $^{129}\text{I}$ and $^{99}\text{Tc}$. One can use the ratio of short/long-lived isotopes such as the ratio of $^{133}\text{I}/^{131}\text{I}$ to measure the source of the fission product
release, by assuming the short-lived species can only result from tramp fuel or large cracks in the fuel assembly.

Impurities in the water and water activation products also contribute to the radioactivity of the coolant water. Tritium is produced as a low yield (~ 0.01%) fission product that can diffuse out of the fuel, by activation of boron or $^6$Li impurities in PWRs. $^{24}$Na and $^{38}$Cl are produced by neutron activation of water impurities. In BWRs, the primary source of radiation fields in the coolant and steam systems during normal operations is 7.1s $^{16}$N. This nuclide is produced by $^{16}$O(n, p)$^{16}$N reactions from fast neutrons interacting with the coolant water. This $^{16}$N activity can exist as NO$_2^-$, NO$_3^-$ in the coolant and NH$_4^+$ in the steam.

Problems

1. Define or describe the following terms or concepts: (a) crud (b) axial offset anomaly (c) accelerator transmutation of waste (d) UREX process (e) LLW (f) TRU (g) HLW (h) SNF (i) Purex process (j) back end of the fuel cycle (k) pyroprocessing

2. Define or describe the following terms or concepts: (a) yellowcake (b) orange oxide (c) green salt

3. Since UO$_2$ can be converted directly to UF$_6$, why is it first converted to UF$_4$ and then to UF$_6$?
4. Write balanced chemical equations for three different methods to produce metallic uranium.

5. Nitric acid readily dissolves UO$_2$. Why doesn’t hydrochloric acid?

6. Given a $G$ value of 1.59 for the production of hydrogen gas by the irradiation of TBP with 1 MeV electrons, calculate the rate of hydrogen gas evolution in a liter of TBP irradiated for 1 hour at a dose rate of 200 watts/L. Assume STP conditions.

7. Draw a flowsheet for the Purex process like Figure 16-10. Estimate the relative volumes of all streams in the process using data from the references cited in the text.

8. Discuss the disposal of the following examples of radioactive waste:

   (a) water solutions containing 1 mCi of $^3$H from a research lab.

   (b) Gas escaping from the dissolution of 1 kg of irradiated reactor fuel

   (c) The ion exchange resin used to purify the cooling water of a 1 MW research reactor.
9. 500 grams of natural uranium is irradiated in a neutron flux of $10^{13}$ n/cm$^2$-sec for one year. What is the heat output of this material after cooling for one week? One month? One year?

10. What is the theoretical maximum separation factor for separation by gaseous diffusion of $^3$He and $^4$He?

11. If a gaseous diffusion plant produces uranium with a 235/238 ratio of 5, what is the expected 234/235 ratio in the resulting material?

12. Discuss quantitatively the relative merits of using LiOH, NaOH or KOH for pH control in reactor coolant water.

13. In reactors based on a Th fuel cycle, $^{233}$Pa is produced. Discuss the radiochemistry of this radionuclide.

References


