Chapter 16. Materials of Nuclear Power Plants: Oxide fuels

DRAFT

Function of the fuel (create and transfer fission heat; first fission product barrier)
Comparison with other fuel types (metals, carbides, nitrides, hydrides)
Fuel pellet diagrams – purposes of various fuels
Fabrication of oxide fuels, including MOX
Mechanical properties
Review of properties (recall material in earlier chapters)

LWR Fuel: UO₂

There is no leeway in selecting the element that provides energy by fission; ²³⁵U is the only naturally occurring fissile nuclide, and undergoes fission by reaction with neutrons according to:

\[ ²³⁵U + n_{\text{th}} \rightarrow 2\text{FP} + 2n_f \quad (16.1) \]

where \( n_{\text{th}} \) denotes a neutron in thermal equilibrium with the water coolant (\( E \approx 0.1 \text{ eV} \)) and \( n_f \) represents a “fast”, or high-energy neutron produced by the fission process (\( E \approx 1 \text{ MeV} \)). The fluxes of the thermal and fast neutrons in an LWR are about \( 4 \times 10^{13} \text{ n/cm}^2\cdot\text{s} \) each. The two fission products (FP in Eq (16.1)) are born with about 100 MeV of energy each. The energy they lose by interaction with the electrons in the fuel material is converted to heat which is conducted through the fuel and ultimately is deposited in the flowing coolant.

Natural uranium contains only 0.71% of the fissile isotope \( ²³⁵\text{U} \), an amount that is insufficient for sustaining a chain reaction in the presence of ordinary water. As a result, the uranium in LWRs is enriched to \( ²³⁵\text{U} \) concentrations up to 5%. The other uranium isotope, \( ²³⁸\text{U} \), does not fission readily with thermal neutrons. However, it can be converted to \( ²³⁹\text{Pu} \) by absorbing thermal neutrons. The sequence is:

\[ ²³⁸\text{U} + n_{\text{th}} \rightarrow ²³⁹\text{U} \rightarrow ²³⁹\text{Np} \rightarrow ²³⁹\text{Pu} \quad (16.2a) \]

The initial absorption product, \( ²³⁹\text{U} \), decays to the neptunium isotope with a 23-minute half-life, and \( ²³⁹\text{Np} \) decays to \( ²³⁹\text{Pu} \) with a half-life of 56 hours. The plutonium isotope is relatively stable (lifetime of 24,000 years), but fissions efficiently in a thermal neutron flux:

\[ ²³⁵\text{Pu} + n_{\text{th}} \rightarrow 2\text{FP} + 2n_f \quad (16.2b) \]

The thermal energy produced by the fission products from the combination of reactions (16.2a) and (16.2b) increases with time. At the end of life of the fuel (up to 6 years), this route contributes as much as reaction (16.1) to the reactor power. By growing in slowly,
$^{239}\text{Pu}$ fission partially offsets the loss of nuclear reactivity caused by the exponential decrease in the $^{235}\text{U}$ concentration with time. Spent fuel removed from the core of a large LWR generates approximately 1000 kg/yr of fission products and 250 kg/yr of plutonium.

The chemical form of uranium in the fuel is the oxide, $\text{UO}_2$. The oxygen in this compound serves no nuclear purpose, but neither is it detrimental to neutron economy. Its main purpose is to provide a chemically inert fuel form that is also relatively resistant to radiation damage, has a high melting point, and maintains the same cubic crystal phase throughout its entire solid range. Compared to all of these criteria, $\text{UO}_2$ is superior to uranium metal except for the uranium atom density and thermal conductivity. On the negative side, the oxygen in $\text{UO}_2$ decreases the density of uranium in the fuel by a factor of two compared to the metallic form, with a corresponding increase in the size of the reactor core.

Plutonium (as $\text{PuO}_2$) can be added to $\text{UO}_2$ during fabrication to produce a mixed oxide (MOX) fuel. The plutonium for this purpose originates either from reprocessed spent $\text{UO}_2$ fuel or from decommissioned nuclear weapons.

The quantity that most directly controls the reactor power, the fuel temperature, and the rate of production of fission products and neutrons is the *fission density*, $\dot{F}$. This is the rate at which reactions (16.1) and (16.2) proceed. It is proportional to the concentrations of the fissile nuclides and the neutron concentration expressed as the thermal neutron flux $\phi_{th}$:

$$\dot{F} = (\sigma_{\text{fU}^{235}} N_{\text{U}^{235}} + \sigma_{\text{fPu}^{239}} N_{\text{Pu}^{239}}) \phi_{th}$$

(16.3)

The rate constants are the fission cross sections for the reaction of the two fissile species with thermal neutrons. Because the thermal neutron flux varies with position in the reactor core, so does the fission density. A typical value of $\dot{F}$ is $10^{13}$ fissions/cm$^3$-s.

The fission density is a measure of the rate of fission. The cumulative fissions for an irradiation time $t$ is called the *burnup*, $\beta$. This quantity has two equivalent definitions. The fractional burnup is the ratio of the number of fissions to the number of initial uranium atoms (of both isotopes):

$$\beta = \frac{\dot{F}}{N_U} t$$

(16.4)

where $N_U = 2.5 \times 10^{22}$ atoms/cm$^3$ is the uranium density in $\text{UO}_2$. In LWRs, 1% burnup is accumulated per year of full-power operation.

The second measure of burnup is defined in terms of the energy produced per unit mass of initial uranium. This measure is the product of the fractional burnup of Eq (16.4) and the energy per fission:

$$\beta = 950 \frac{\text{MWd}}{\text{kg fissioned}} \times \frac{\dot{F} t}{N_U} \frac{\text{kg fissioned}}{\text{kg U}}$$

(16.5)
A typical burnup of fuel discharged from LWRs is 4%, or 40 MWd/kgU.

**Fabrication of Fuel Pellets**

The standard fuel pellet is a solid cylinder of polycrystalline uranium dioxide 1 cm or less in diameter. The two variants of the LWR, the boiling water reactor (BWR) and the pressurized water reactor (PWR) use slightly different pellet sizes, with that for the BWR being larger in diameter. The pellet height in both fuels is between 1 and 2 cm.

Fabrication of fuel for LWRs consists of two distinct processes. In the first, uranium hexafluoride is converted chemically into uranium dioxide powder. In the second, high-density pellets are produced from the starting UO₂ powder.

A flowsheet of the conversion process is shown in Fig. 16.1a. The feed material is UF₆, which is the chemical form that is used in the isotope enrichment plants. It arrives as a liquid at elevated pressure and is vaporized by reducing the pressure and warming slightly. The resulting UF₆ gas is fed into a chemical reactor along with steam and hydrogen in nitrogen as an inert carrier gas. The following chemical reaction produces a fine power of UO₂ as reaction product:

\[
UF₆(g) + 2H₂O(g) + H₂(g) \rightarrow UO₂(s) + 6HF(g)
\]  

(16.6)

The steam serves as the source of oxygen for the oxide product. Hydrogen reduces hexavalent U in UF₆ to the tetravalent state in UO₂. The hydrofluoric acid gaseous product is neutralized by NaOH, leaving relatively benign NaF as the sole waste stream.

The remainder of the flow sheet in Fig. 16.1a consists of steps that modify the UO₂ into a powder form that is easily made into a pellet in subsequent processing. In these steps, dry nitrogen cover gas prevents oxidation of UO₂. A lubricant such as stearic acid is added to aid in pressing pellets from the powder. A substance called a poreformer is also added to help control the quantity and shape of the voids that remain in the finished pellet.
The product of the conversion process constitutes the feed to the pellet fabrication process depicted in Fig. 16.1b. The first step is pressing the powder into “green” pellets that are 50 – 60 percent of the theoretical density of the crystalline material (this is abbreviated as %TD). The following high-temperature sintering step serves four functions. First, it drives off the lubricant added to the powder to assist pressing (care must be taken not to decompose the lubricant to carbon, which, along with fluorine, is an undesirable impurity in the final product).

Second, the void spaces between the particles in the green pellets are nearly completely eliminated by annealing at high temperature for several hours. This process is called sintering.

The porosity of the sintered pellets consists almost exclusively of closed spherical cavities called closed porosity with negligible open porosity. The latter takes the form of interconnected channels that communicate with free surfaces of the pellet. Most fuels are 95 - 96% TD. Retention of few percent porosity is desirable. The pores serve as sinks for
fission gases and lessen their release. Swelling of the fuel due to solid fission products is also reduced by filling in the internal voidage.

**Fig. 16.1b Pellet Fabrication flow sheet**

Third, the time and temperature of the sintering step also affect the size of the grains in the final polycrystalline pellets. Simply eliminating porosity during sintering leaves grains of the same size as the starting powder particles. More extensive annealing increases the average size of the grains by a process termed *grain growth*. The usual pellet fabrication process produces polycrystals with grain diameters about 8 μm. Both sintering (porosity reduction) and grain growth occur naturally at temperatures high enough to give reasonably rapid kinetics (see Chap. ...). However, both processes can be enhanced by additives introduced in the preparation of the feed powder.

The forth function accomplished during sintering is control of the oxygen-to-uranium ratio. This characteristic of the fuel is controlled by the temperature and the ratio of H₂ to H₂O in the gas fed to the sintering furnace (see Chap 7). Oxygen in excess of the 2:1 ratio of stoichiometric UO₂ is to be avoided. The excess oxygen in UO₂+x (even when x ≅ 0.01) is corrosive towards the cladding. Hyperstoichiometry also produces undesirable physical property changes in the fuel. Excess oxygen reduces the thermal conductivity, thereby increasing the fuel temperature during operation. Hyperstoichiometric fuel also enhances the mobility of the fission products, making their release easier. The composition of the oxide in typical reactor fuel is UO₂0.005.

The step following sintering in Fig. 16.1b is a grinding operation designed to smooth the outer surface of the pellet and closely control its diameter. The latter is important because, along with the cladding inside diameter, it determines the thickness of the gap between the fuel and the cladding in the finished fuel rod. This gap is gas-filled and constitutes a significant thermal resistance to heat removal from the pellet during operation.
The final step in Fig. 16.1b is a low-temperature vacuum drying step intended to reduce the concentration of adsorbed water on fuel surfaces to less than 10 ppm by weight. Improperly dried fuel can cause cladding failure by reaction of desorbed water with Zr to produce both ZrO₂ and ZrH₂. The latter embrittles the cladding and has been responsible for numerous fuel failures during the past several decades.

Figure 16.2 shows a photomicrograph of polycrystalline UO₂ after sintering. To obtain this picture, the pellet is first cut with a diamond saw, then polished with fine abrasives, and finally briefly exposed to an etching solution. Chemical etching reveals most of the grain boundaries as the thick irregular lines enclosing individual single-crystal grains. The grain boundaries are the intersections of the planar cut through the specimen with the faces of the polycrystalline grains that make up the solid. (the straight lines that cross grain boundaries are polishing scratches). The grain diameters are roughly 8 µm. The junctions almost always consist of three grain boundaries intersections called triple points. The third grain-boundary trace is sometimes missing from a few triple points in Fig. 16.2, possibly because of inadequate etching during specimen preparation. The porosity visible in the photomicrograph is all of the closed variety and is visible as
roughly circular black spots. The pores are less than one micron in diameter and occupy 7% of the total specimen volume.

In UO₂ destined for reactor fuel, the size of the pores is as important as the total porosity. In operation, very fine pores (<1 μm) are eliminated by a process called radiation densification. In essence, the pores are converted to their component vacancies, which are then removed by sinks in the microstructure such as dislocations and grain boundaries. This process causes an initial rapid reduction of the pellet diameter and concomitant collapse of the cladding on the shrunken fuel. This potential problem is solved by removing fine pores during the sintering step of fuel fabrication.

Over time, the standard cylindrical fuel pellet design has been modified in numerous ways, as shown by the gallery in Fig. 16.3. The standard pellet is shown in (a). During operation, the temperature distribution in the pellet and the resultant nonuniform thermal expansion causes its shape to change to the "hourglass" shape shown in (b). The edges of the top and bottom pellet surfaces deform the cladding with high local strains and stresses, risking perforation. Cladding subjected to this type of deformation resembles a stalk of bamboo. To avoid this type of cladding deformation and to minimize chipping during manufacturing and handling, the fuel pellets are chamfered as shown in (c). Additional void space to accommodate fission product swelling and axial thermal expansion of hot pellet centers is provided by “dishing” the top and bottom pellet surfaces.

In a solid pellet, fission heat generation and removal creates differences in temperature between the centerline and the pellet surface as large as 1000°C. This is undesirable for a number of reasons, the principal one being release of fission gases from the hot center. To reduce the centerline temperatures at the same linear power (i.e., power produced per unit fuel height), the designs shown in (d) and (e) have been developed. Both move the heat source closer to the heat sink (the coolant) than in the standard fuel pellet. In (d), the outer radial zone of the pellet is more highly enriched in U-235 than the inner zone, thus reducing heat production near the center and lowering the centerline temperature. In (e), the center is removed entirely, resulting in an annular pellet. To produce the same power, this pellet must contain a higher enrichment than the standard solid cylindrical pellet. However, the temperature at the inner surface of the annular pellet is significantly lower than that of the standard cylindrical pellet for the same linear power. Annular pellets are standard in the Russian VVER reactors.

In two designs, urania is mixed with other oxides for reasons related to the nuclear processes. In (f), the additive is Gd₂O₃. Gadolinium acts as a burnable poison that allows a longer irradiation time without excessive reactivity held in control rods at beginning-of-life.

In (g), UO₂ is mixed with PuO₂ to produce mixed oxide (MOX) fuel. The plutonia is in the form of small particles in a matrix of UO₂. Since Pu is the principal fissionable nuclide, these particles are hotter than the rest of the fuel. Despite this nonuniformity of temperature, MOX fuel behaves very similarly to standard UO₂ fuel in reactor. In (h), the
microstructure of the fuel is purposely altered to increase the grain size from 8 μm to as much as 40 μm by using oxides such as Nb₂O₅ as a fuel additive. Niobium promotes grain growth during the sintering process. The objective of the large grains is to reduce fission product release by increasing the length of the
Fig. 1.3 Ceramic Oxide Pellet Designs

(a) classic
(b) hourglassing at power
(c) dished and chamfered
(d) zoned enrichment
(e) annular (high U-235)
(f) Urania-gadolinia
(g) MOX
(h) large grain size
(i) non-fertile
diffusion path from the grain interior to the grain boundary.

So-called “nonfertile” or “inert matrix” fuel depicted in panel (i) is a response to the desire to burn excess plutonium without simultaneously producing this element from a U-238 component, as is the case with MOX fuel. Nonfertile fuels contain PuO$_2$ dissolved in a matrix such as (Zr,Eb)O$_2$. Erbium also serves as a burnable poison like gadolinium.