

# Nuclear Reactor Materials and Fuels

**Massoud T. Simnad**

*University of California, San Diego*

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## GLOSSARY\*

**Alpha emitter** Element with a nucleus that loses excess energy by spontaneously releasing an alpha particle, which is a positively charged helium ion.

**Beta decay** Mode of radioactive decay in which a beta particle (electron or positron) is emitted from a nucleus.

**Blanket** Fertile or largely fertile material surrounding the cores of certain types of reactors, usually breeder reactors.

**Breeder reactor** Nuclear reactor that produces more fissionable atoms than it consumes; this is done by transmuting fertile material into fissionable material.

\*From Kaufman, A. R., ed. (1962). "Nuclear Fuel Elements," Wiley, New York.

**Burnable poison** High-cross-section neutron absorber material blended with reactor fuel or cladding that is gradually changed to a low-cross-section material under neutron radiation.

**Burnup** Measure of the number of fissionable atoms that have undergone fission. It is usually expressed as the atomic percent of the total uranium atoms that have fissioned in the fuel, as megawatt-days of energy generated per ton of uranium, or as gigajoules of energy per kg of uranium. Other definitions include fissions/cc or atomic percent of fissions per total atoms present in the fuel.

**Cladding** Protective material surrounding the fuel that acts as a barrier between the fuel and the coolant medium and also prevents escape of the fission products.

**Control rod** Device containing material with a high neutron absorption cross section that is used to govern the fission rate of a nuclear reactor by absorbing excess neutrons.

**Conversion ratio** Number of fissionable atoms produced per atom fissioned in a reactor.

**Cross section** Probability that a given nuclear reaction will occur between a nucleus and an incident particle (e.g., a neutron). It has the dimensions of area, and the unit of cross section, called a barn, is  $10^{-24}/\text{cm}^2$  in magnitude.

**Decay heat** Heat generated by radioactive material, particularly heat from the decay of fission products in irradiated fuel.

**Disintegration** Spontaneous nuclear transformation resulting in the emission of photons and/or particles from the nucleus.

**Enriched uranium** Uranium having a  $^{235}\text{U}$  isotope content greater than that of natural uranium (0.7115 wt. %).

**Fast breeder reactor** Nuclear reactor in which there is little moderation and where fission is induced primarily by fast neutrons.

**Fertile material** Material capable of being transmuted into a fissionable material by capture of a neutron ( $^{232}\text{Th}$ ,  $^{238}\text{U}$ ).

**Fission** The splitting of a fissionable nucleus ( $^{233}\text{U}$ ,  $^{235}\text{U}$ ,  $^{239}\text{Pu}$ ,  $^{241}\text{Pu}$ ) into two nuclides (fragments), each of which has about one half of the mass of the original nucleus. In addition to the fission fragments, neutrons and gamma rays are produced during fission.

**Fission product** Nuclide produced directly by the fission of a fissionable nuclide or by subsequent radioactive decay. Thirty five fission-product elements, from zinc through gadolinium, have been identified from slow neutron fission.

**Moderator** Material used in a nuclear reactor to decelerate neutrons from the high velocities at which they are released. Neutrons lose velocity by scattering collisions with nuclei of the moderator. A good moderator has high scattering cross section, low atomic weight, and low neutron-absorption cross section.

**Neutron fluence** Total number of neutrons passing through a unit surface area in a specified time period.

**Neutron flux** Number of neutrons (thermal or fast) passing through unit surface area per unit time, that is, neutrons/ $(\text{cm}^2 \text{ sec})$  or neutrons ( $\text{m}^2 \text{ sec}$ ).

**Reflector** Layer of material surrounding the core of a nuclear reactor that serves to deflect escaping neutrons and return many to the core.

**Thermal reactor** Nuclear reactor in which fission is induced primarily by thermal neutrons (those in equilibrium with the material of the core).

**THE SELECTION OF MATERIALS** and fuels for nuclear power reactors involves a multidisciplinary approach, including physics, chemistry, materials science and engineering, systems analysis, and economics. There is also a need to consider the environmental and political factors that have an important impact on the acceptance of nuclear power.

The continuing growth of nuclear energy (over 400 power reactors in 33 countries in 2000) has been made feasible by the successful development of reactor fuels and materials. The goals of low fuel-cycle costs and reliable performance in the fuel elements have been achieved. The materials and fuels have to accommodate the severe operating conditions set by the designs of the reactor cores, including thermal and mechanical stresses and prolonged exposure to the coolants and nuclear irradiation.

## I. SUMMARY OF NUCLEAR REACTOR MATERIALS AND FUELS

### A. Classification

Nuclear reactor materials and fuels can be classified as follows.

1. Fuel and fertile materials and their cladding and fuel elements and their structural components.
2. Fuel cycles and fuel systems, which include materials preparation, fuel element fabrication, fuel reprocessing, fuel element refabrication, and the management of nuclear wastes.
3. Moderator and reflector materials, which include liquids such as water and heavy water and solids such as beryllium, beryllium oxide, graphite, and metal hydrides.
4. Coolants, which may be liquids (water, heavy water, sodium, molten salts, and organics) or gases (helium and carbon dioxide).
5. Control materials and component, which use materials with high neutron-absorption cross sections, such as boron, cadmium, indium, silver, hafnium, and rare earths.
6. Shielding materials, which serve to attenuate neutrons and gamma rays. The internal shielding in the reactor vessel is generally provided by the moderating materials and steel, and the outer shielding is usually concrete.
7. Thermal insulation materials, which limit heat loss from the reactor core to surrounding structural materials and containment vessel. The insulator materials may consist of refractory compounds or metal foils.
8. Structural materials, which include duct or coolant channels, solid moderator and reflector blocks, core support grid structures, coolant piping, heat exchanger materials, reactor vessels, and containment structure.

## B. Power Reactors

The engineering designs of nuclear reactors are largely governed by materials properties. The choices of nuclear fuels and designs are limited by the characteristics of the reactor cores, namely, the fuel enrichment, the nature of the moderators and coolants selected, the operating temperatures and pressures in the core, the fuel burnup and exposure time, and the average neutron energy and fluence. The most important nuclear power reactor concepts at present include the following.

1. Light-water moderated and cooled reactors (LWR). These may be either pressurized-water (PWR) operating at about 14 MPa pressure and 300°C or boiling-water (BWR) operating at about 7 MPa and 300°C. In the PWR, the heat is transferred from the core to steam generators via intermediate heat exchangers, whereas in the BWR, the coolant water boils at the top of the core and furnishes steam directly to the turbines. The fuel consists of slightly enriched  $\text{UO}_2$ .

2. Heavy-water moderated reactors (CANDU). In these reactors, the heavy-water moderator is contained in a calandria, through which insulated pressure tubes containing the fuel elements circulate the pressurized light-water coolant at 15 MPa and 300°C to transfer the heat from the fuel elements to steam generators. The fuel is natural  $\text{UO}_2$ .

3. Carbon-dioxide gas-cooled graphite moderated reactors. The first generation of these reactors (Magnox) are cooled by circulating  $\text{CO}_2$  gas. The fuel elements consist of natural-uranium metallic fuel rods clad with a magnesium alloy. The second-generation advanced gas-cooled (AGR) reactors use stainless steel clad slightly enriched  $\text{UO}_2$  fuel rods, which permit steam generation at higher temperatures.

4. High-temperature helium gas-cooled reactors (HTGR). In these reactors, graphite serves as moderator, reflector, and core structure material. Coated-particle oxide or carbide fuel is used. The helium gas coolant (700–1000°C and 5–8 MPa) transfers heat to steam generators.

5. Liquid-metal cooled fast breeder reactors (LMFBR). Here the liquid sodium in the primary system transfers the heat from the core to an intermediate heat exchanger, from which sodium transfers heat to the steam generator. The fuel consists of (U, Pu) $\text{O}_2$  pellets contained in stainless steel cladding.

## II. NUCLEAR FUEL ELEMENT DEVELOPMENT

The low fuel-cycle costs and the high reliability of the fuel elements allow nuclear reactors to compete with other en-

ergy sources, in spite of the high capital costs for their construction. Above all, the fuel must meet the regulatory requirements for safety in the operation of the plants. The fuel elements must accommodate power cycles and meet the design objectives, such as adequate heat transfer, nuclear reactivity, retention of fission products, inherent safety under accident conditions, and retention of structural and mechanical integrity.

The plant costs have been reduced by increasing the thermal output of the core and using higher quality steam. Improvements in fuel technology and heat transfer have permitted the use of higher fuel heat flux, which has increased core performance. The use of burnable poisons in the fuel has enabled control of the large excess reactivity required at initial startup with high fuel exposure cores.

There have been successful developments to improve performance by means of better fuel management and fuel cycling, advanced fuel design, fuel-cycle cost reduction, and more reliable reactor components. The ability to predict fuel element performance based upon design modeling has been a major development in recent years. More accurate and extensive data are required on critical properties of the fuel and cladding to provide the needed engineering relationships. A most useful parameter for evaluating the performance of a fuel rod is the thermal power per unit length, which is directly related to the integral of the thermal conductivity of the fuel material from a permissible temperature at the center of the cylinder to the designed temperature at the edge.

The fuel materials that have been developed for use in power reactors include metals and alloys, oxides, carbides, nitrides, and hydrides. The configurations used include cylindrical pellets, long extruded rods (metal fuels only), spherical elements (graphite matrix with coated particle dispersion fuel for the AVR-HTGR), dispersions in a matrix material (cermets), coated particles, and fluids (molten salt reactor and aqueous homogeneous reactor experiments). The most widely used fuel material in power reactors is uranium dioxide in the form of cylindrical, cold pressed, and sintered pellets.

The stages in the development of fuel elements are listed in [Table I](#). The major components and materials in nuclear systems are summarized in [Table II](#).

The most extensively used ceramic fuels are the oxides, namely,  $\text{UO}_2$ , (U, Pu) $\text{O}_2$ , and  $\text{ThO}_2$ , all of which have the face-centered cubic fluorite structure and are completely miscible in solid solution. A number of reactors have also operated with the carbide fuels UC,  $\text{UC}_2$ , and (U,Pu)C, and  $\text{ThC}_2$ . Nitride fuels have been prepared and irradiated in test reactors. The properties of nuclear fuels that have been studied or used in fuel elements are summarized in [Table III](#).

**TABLE I Stages in Fuel Element Development<sup>a</sup>**

1. Define the reactor type: purpose, coolant, and performance.
2. Calculate fuel element dimensions, heat fluxes, design features, physics, and critical assemblies.
3. Consider the range of available fuels and cladding materials and pick the most suitable for the design.
4. Consider fuel and cladding properties, both out-of-reactor and in-reactor.
5. Examine fuel-cladding interactions (chemical and physical).
6. Develop a preliminary fuel element design.
7. Develop fabrication procedures for fuel, cladding, and fuel element if necessary.
8. Develop mathematical models of the fuel element; specify and obtain input data.
9. Test fuel elements: out-of-reactor (thermal-hydraulics), in-reactor (on increasing scale), and transient tests.
10. Analyze test: post-irradiation examination, failure mechanisms, run beyond cladding breach, feedback to models, and improvements in design.
11. Optimize via iterations of 8, 9, and 10. Write detailed design and manufacturing specifications.
12. Plan production: quality assurance, NDE, SPM assay, safeguards, safety, critically control, economics, and automation.
13. Establish interfaces with the rest of the fuel cycle: mining, enrichment, reprocessing, and waste management.
14. Obtain license for qualified cores.

<sup>a</sup> From Frost, B. R. T. (1982). "Nuclear Fuel Elements," Pergamon, New York.

The oxide ceramic fuels have a number of advantages and disadvantages compared with other forms of nuclear fuels. The advantages include high neutron utilization, excellent irradiation stability, exceptional corrosion resistance in conventional coolants, high melting point, compatibility with cladding, ease of manufacture, and high specific power and power per unit length of fuel pin. The disadvantages include low thermal conductivity, poor thermal shock resistance, and relatively low fissionable atom

density compared with metallic and carbide fuels. The relatively high melting points of the oxide fuels compensate partially for the low thermal conductivity.

The viability of the nuclear industry depends primarily on the lower cost of the nuclear fuel cycle compared with fossil fuels. The nuclear fuel-cycle cost includes the costs of the unit operations of extracting, preparing, reprocessing, and disposing of nuclear fuels and the credit allowed for reclaimed uranium and plutonium. The carrying charges during the residence time in the fuel cycle and the financing costs may reach 25% of the total cost. The fabrication costs of the fuel elements for LWRs correspond to about 20% of the total electricity generation cost.

The limitation set by the fuel burnup at discharge is governed by the irradiation behavior of the materials and/or the reactivity characteristics. The natural uranium required to prepare the initial in-core fuel loading that is required in an 1100-MW(e) reactor is approximately 580 tons for a light-water reactor, 450 tons for an HTGR, and 700 tons for a fast breeder reactor. The recycling of Pu in light-water reactors may decrease the uranium requirements by about one-third. Approximately 200 kg of Pu is produced per year in an 1100-MW(e) LWR.

Fuel management aims at the attainment of the most economical use of the fuel within the constraints set by the fuel design, the operation of the reactor, and the various cost items involved in the financing of the reactor. The cost of nuclear fuel must also include costs for the unique requirements of safety and safeguarding of enriched and irradiated fuels in processing and reprocessing facilities and costs for precautions against illegal diversion.

The judicious selection of materials and fuels for the reactor cores must consider the design, fabrication, and operation of the reactor. The effects of irradiation on the physical, mechanical, chemical, and isotopic changes during operation of the reactor must be known in advance.

**TABLE II Major Components and Materials in Nuclear Systems**

Reactor component	Reactor system material				
	BWR	PWR	CANDU	AGR	LMFBR
Core					
Fuel/cladding	UO <sub>2</sub> /Zircaloy	UO <sub>2</sub> /Zircaloy	UO <sub>2</sub> /Zircaloy	UO <sub>2</sub> /SS	UO <sub>2</sub> , 25 ± 5% PuO <sub>2</sub> /SS
Control materials	B <sub>4</sub> C/Type 304 SS	AgInCd alloy	B <sub>4</sub> C/SS	B <sub>4</sub> C/SS	B <sub>4</sub> C/SS
Breeding blanket	UO <sub>2</sub> -Gd <sub>2</sub> O <sub>3</sub> /Zircaloy 2	B <sub>4</sub> C-Al <sub>2</sub> O <sub>3</sub> ; borosilicate glass	NA	NA	UO <sub>2</sub> /Type 316 SS
Reactor vessel					
Shell	Low-alloy steel (SA533 Gr. B)	Low-alloy steels (SA533 Gr. B., SA508)	Zircaloy tubes in Al calandria	Prestressed concrete	Type 304 SS
Cladding	Type 308L SS (SA264)	Type 308 SS: Inconel 617			NA

**TABLE III Properties of Fuels**

Property	U	U-10% Mo	U <sub>8</sub> Si
Melting point, K	1405	1423	1203
Density, g/cm <sup>3</sup>	19.12	17.12	15.58
Heavy metal density, g/cm <sup>3</sup>	19.12	17.12	15.58
Crystal structure	<i>a</i>	<i>b</i>	bet
Thermal conductivity, W/cm-K	0.35 (670 K)	0.29 (870 K)	0.2 (to 1170 K)
Thermal expansion, 10 <sup>6</sup> /K	19 (to 920 K)	12.3 (to 670 K)	16 (to 1070 K)
Electrical resistivity, ohm-cm	35 × 10 <sup>6</sup> (298 K)	—	75 × 10 <sup>6</sup> (to 1070 K)
Specific heat, cal/g-K	0.026 (to 773 K)	0.035 (to 773 K)	0.043 (to 773 K)
Heat of fusion, cal/mol	4760	—	—
Vapor pressure, atm	5 × 10 <sup>6</sup> (2300 K)	5 × 10 <sup>6</sup> (2300 K)	—
Debye temperature, K	200 K	—	—
Free energy of formation, kcal/mol	—	—	—
Heat of formation, kcal/mol	—	—	—
Entropy, cal/mole-K	—	—	—
Poisson ratio	0.21	0.35	—
Modulus of rupture, MPa	—	—	—
Modulus of elasticity, MPa	1.7 × 10 <sup>6</sup>	10 <sup>6</sup>	—
Shear modulus, MPa	0.85 × 10 <sup>6</sup>	3 × 10 <sup>4</sup>	—
Tensile strength, MPa	400	300	600
Compressive strength, MPa	—	—	2000
Thermal neutron fission cross section, barns	4.18 (natural)	4.18 (natural)	0.159 (natural)
Thermal neutron absorption cross section, barns	7.68 (natural)	6.68 (natural)	0.293 (natural)
Eta ( $\eta$ ) <sup>d</sup>	1.34	1.34	1.34
	<b>UN</b>	<b>(U<sub>0.8</sub>Pu<sub>0.2</sub>)O<sub>2</sub></b>	<b>(U<sub>0.8</sub>Pu<sub>0.2</sub>)C</b>
Melting point, K	3035 (1 atm N <sub>2</sub> )	3023	2758 ± 25
Density, g/cm <sup>3</sup>	14.32	11.04	13.58
Heavy metal density, g/cm <sup>3</sup>	13.52	9.80	12.3 (2.6 Pu)
Crystal structure	fcc (NaCl)	Cubic (CaF <sub>2</sub> )	fcc (NaCl)
Thermal conductivity, W/cm-K	0.2 (1023 K)	0.027 (1270 K)	0.18 (to 1270 K)
Thermal expansion, 10 <sup>6</sup> /K	9.3 (to 1270 K)	10.3 (to 1270 K)	12.2 (to 1670 K)
Electrical resistivity, ohm-cm	1.75 × 10 <sup>4</sup> (298 K)	2 × 10 <sup>4</sup>	1.82 × 10 <sup>4</sup>
Specific heat, cal/g-K	0.049 (298 K)	0.10	0.047 (298 K)
Heat of fusion, cal/mol	12.750	—	10.920
Vapor pressure, atm	4.5 × 10 <sup>7</sup> (2000 K)	—	8.1 × 10 <sup>2</sup> (2000 K)
Debye temperature, K	—	—	—
Free energy of formation, kcal/mol	-64.75 (298 K)	—	21.00
Heat of formation, kcal/mol	-70.70 (298 K)	—	21.18
Entropy, cal/mole-K	15.0 (298 K)	—	14.80
Poisson ratio	0.263	0.28	0.295
Modulus of rupture, MPa	—	—	—
Modulus of elasticity, MPa	—	1.8 × 10 <sup>6</sup>	—
Shear modulus, MPa	1.01 × 10 <sup>6</sup>	0.53 × 10 <sup>4</sup>	0.78 × 10 <sup>6</sup>
Tensile strength, MPa	—	—	—
Compressive strength, MPa	—	—	—
Thermal neutron fission cross section, barns	0.143 (natural)	—	—
Thermal neutron absorption cross section, barns	0.327 (natural)	—	—
Eta ( $\eta$ ) <sup>d</sup>	—	—	—

<sup>a</sup> Orthorhombic (<936 K), tetragonal (936–1043 K), body-centered cubic (>1043 K).<sup>b</sup> Orthorhombic plus tetragonal (<838 K), body-centered cubic (>838 K).

(continues)

TABLE III (Continued)

U-Fs	UO <sub>2</sub>	UC	UC <sub>2</sub>
1275	3138	2780 ± 25	2773
18	10.96	13.61	12.86
18	9.65	12.97	11.68
bcc (>100 K)	fcc (CaF <sub>2</sub> )	fcc (NaCl)	fcc (CaF <sub>2</sub> )
0.33 (820 K)	0.03 (1270 K)	0.216 (to 1270 K)	0.35 (to 1270 K)
17 (to 820 K)	10.1 (to 1270 K)	11.6 (to 1470 K)	18.1 (1970 K)
—	1 × 10 <sup>4</sup>	40.3 × 10 <sup>6</sup> (298 K)	—
—	0.065 (700 K)	0.048 (298 K)	0.12 (298 K)
—	16.000	11.700	—
—	8.5 × 10 <sup>8</sup> (2000 K)	1.7 × 10 <sup>10</sup> (2300 K)	2.5 × 10 <sup>11</sup> (2300 K)
—	<600 K, 870 K	—	—
—	−218 (1000 K)	−23.4 (298 K)	—
—	−260 (to 1500 K)	−23.63 (298 K)	−23 (298 K)
—	18.6 (298 K)	14.15 (298 K)	16.2 (298 K)
—	0.3	0.284	—
—	80	—	—
6 × 10 <sup>6</sup>	1.8 × 10 <sup>6</sup>	2 × 10 <sup>6</sup>	—
—	0.75 × 10 <sup>6</sup>	0.873 × 10 <sup>6</sup>	—
270	35	—	—
—	1000	350	—
—	0.102 (natural)	0.137 (natural)	0.112 (natural)
—	0.187 (natural)	0.252 (natural)	0.207 (natural)
1.34	1.34	1.34	1.34
(U <sub>0.8</sub> Pu <sub>0.2</sub> )N	Th	ThO <sub>2</sub>	ThC
3053	2028	3663	2898
14.31	11.72	10.00	10.96
13.5 (2.7 Pu)	11.72	9.36	10.46
fcc (NaCl)	fcc < 1618 K < bcc	Cubic (CaF <sub>2</sub> )	Cubic (NaCl)
0.19 (to 1270 K)	0.45 (923 K)	0.03 (1270 K)	0.28 (to 1270 K)
9.8 (to 1270 K)	12.5 (to 923 K)	9.32 (to 1270 K)	7.8 (to 1270 K)
—	15.7 × 10 <sup>6</sup>	—	25 × 10 <sup>6</sup> (298 K)
0.046 (298 K)	0.038 (970 K)	0.07 (298 K)	0.043 (298 K)
12.590	3300	25.000	—
2.1 × 10 <sup>6</sup> (2000 K)	1.3 × 10 <sup>14</sup> (1500 K)	5 × 10 <sup>9</sup> (2000 K)	—
—	163.5	200 K	—
—	—	−279 (298 K)	−6.4 (298 K)
71.10	—	−293 (298 K)	−7.0 (298 K)
—	—	15.59 (298 K)	12.0 (298 K)
0.275	0.27	0.17	—
—	—	80	—
—	7 × 10 <sup>4</sup>	14 × 10 <sup>4</sup>	—
1.02 × 10 <sup>4</sup>	2.7 × 10 <sup>4</sup>	1 × 10 <sup>5</sup>	—
—	230	100	—
—	—	1500	450
—	—	—	—
—	7.56	—	—

<sup>c</sup> U containing 5% fission (0.22% Zr + 2.5% Mo + 1.5% Ru + 0.3% Rh + 0.5% Pd). U-5% fission is bcc above 10,000 K, bcc + monoclinic U<sub>2</sub>Ru between 825 K and 1000 K, and bcc + U<sub>2</sub>Ru + tetragonal below 825 K.

<sup>d</sup> Number of fission neutrons released per neutron absorbed.

The primary objectives in fuel management are not only to minimize the fuel-cycle costs but also to allow optimum utilization of the fuel and to assure availability of fuel resources. Fuel management includes (1) the out-of-core activities of planning, budgeting, purchasing, designing, and fabricating; (2) the planning of the in-core utilization of the fuel; and (3) the control of the fuel cycle.

The design of the fuel elements aims to achieve the goals of adequate heat transfer, nuclear reactivity, retention of fission products, inherent safety under accident conditions, and retention of structural and mechanical integrity. In addition, the important economic parameters must be considered, namely, reliability and high specific power and burnup, optimum fuel management, high neutron utilization, and realistic specifications for manufacture and quality assurance. A 1000-MW(e) LWR is fueled with about 9 million  $\text{UO}_2$  pellets contained in approximately 150 km of fuel rods, with 40 fuel rods per MW(e).

There is a tradeoff between the specific power and burnup limits of the fuel and the influence of these factors on the capital cost in relation to the core dimensions, components, pressure vessel, and containment sizes. The design of the core reflects the need to optimize the critical parameters by suitable choice of fuel enrichment, distribution of fuel, control rod and burnable poison distribution, and so forth. In LWRs, the peak rod power is about 19 kW/ft and up to 25 kW/ft under power transients. The ratio of peak to average power falls in the range 2.8–3.0.

Fuel performance predictions are based on design modeling, which includes both the results of experiments and analytical studies. The principal operating conditions governing fuel lifetime are the burnup (MWd/kgU) and specific rod power (kW/m). Also, the fission gas pressure, ratcheting between the fuel and cladding, and irradiation effects on the cladding (swelling, loss of ductility, irradiation-creep, and fission product corrosion) influence the behavior of the stressed cladding. Allowance is made for the released fission gases by means of a large plenum volume in the fuel rod.

The Th- $^{233}\text{U}$  cycle is the most advantageous of the fuel cycles in the thermal and epithermal regions. The thorium cycle also depends on the initial fissile charge of  $^{235}\text{U}$  or Pu to generate the fissionable  $^{233}\text{U}$ . The reactors that are based on the Th- $^{233}\text{U}$  cycle include the HTGR and the thermal breeders MSBR, HWBR, and LWBR. The thorium cycle is associated with significantly higher conversion ratios and longer reactivity lifetimes compared with the uranium cycle. However, the fuel inventory and fuel fabrication and processing costs are also higher for the uranium cycle. Hence, increased uranium costs and lower interest rates favor the thorium cycle.

The fuel elements in power reactor cores are distributed in zones of different uranium enrichments. The highest en-

richment is at the periphery of the core, to compensate for the lower neutron flux toward the periphery and thereby to achieve a flatter neutron flux profile and higher power output. At each refueling period (about once a year), the fuel elements are discharged from the central zone of the core, and the elements in the outer zones are moved inward. The fresh fuel elements are loaded into the vacated outer zone. The control rods are another core component that is periodically replaced. A 1000-MW(e) light-water reactor (LWR) has an initial fuel loading of low-enriched (2% to 3%) uranium of approximately 80,000 kg (80 metric tons) and a replacement fuel requirement of about 25,000 kg (25 metric tons) per year to make up the fuel that is consumed. Supplying the fuel for the 1000-MW(e) LWR requires the mining of  $21.8 \times 10^7$  kg (240,000 short tons) of uranium ore, the processing of about  $4.5 \times 10^5$  kg (500 tons) of uranium oxide into feed for the enrichment plants, and the fabrication of  $8.3 \times 10^4$  kg (92 tons) of the enriched uranium oxide into  $7.2 \times 10^4$  kg (80 tons) of reactor fuel elements for the initial core loading. The spent fuel elements contain several million dollars worth of unconsumed uranium and plutonium, as well as the fission products. The fuel reprocessing plants are designed to separate the fission products from the remaining fuel and to solidify the liquid radioactive waste for permanent disposal. The recovered fuel is recycled.

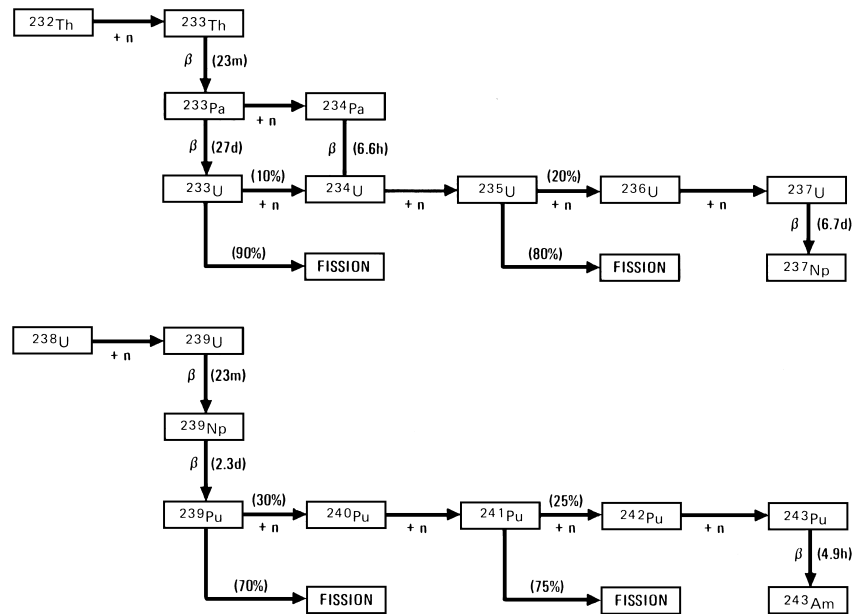
### III. NUCLEAR FUEL CYCLE

#### A. Fissionable Materials and Fission Products

The fissionable isotopes used in nuclear reactors include  $^{233}\text{U}$ ,  $^{235}\text{U}$ ,  $^{239}\text{Pu}$ , and  $^{241}\text{Pu}$ . The fertile isotopes are  $^{238}\text{U}$  and  $^{232}\text{Th}$ . The fertile isotopes are converted into fissionable isotopes by neutron absorption ( $^{238}\text{U}$  into plutonium isotopes and  $^{232}\text{Th}$  into  $^{233}\text{U}$ ). Natural uranium contains 0.71%  $^{235}\text{U}$ , 99.28%  $^{238}\text{U}$ , and 0.006%  $^{234}\text{U}$ . Fuel enriched in  $^{235}\text{U}$ ,  $^{233}\text{U}$ , or plutonium is used to provide greater latitude in selecting materials for use in the reactor system and to achieve higher burnup. Since  $^{233}\text{U}$  and plutonium must be produced from thorium and  $^{238}\text{U}$ , respectively, by neutron capture, the neutrons are provided initially by fission of  $^{235}\text{U}$  (Fig. 1).

The isotope  $^{239}\text{Pu}$  is present in minute quantities (1 part in 100 billion) in uranium ores. It is produced by neutron irradiation of  $^{238}\text{U}$  by the reactions shown in Fig. 1. Short periods of irradiation produce mostly  $^{239}\text{Pu}$ , and longer irradiations result in progressively more of the higher isotopes of plutonium, up to  $^{246}\text{Pu}$ . The odd-number isotopes of Pu are fissionable, whereas the even-number isotopes have high neutron-absorption cross sections.

The nuclear fuel cycle includes (1) production of nuclear fuel (mining, milling, and enrichment), (2)



**FIGURE 1** Nuclide chains originating with  $^{232}\text{Th}$  and  $^{238}\text{U}$ . [From M. T. Simnad and J. P. Howe (1979). In "Materials Science in Energy Technology" (G. G. Libowitz and M. S. Whittingham, eds.), Academic Press, New York.]

fabrication of fuel elements, (3) reprocessing and recycling of the spent fuel to recover and raise the uranium and plutonium content, and (4) storage of the radioactive waste (Fig. 2).

When the fissionable isotope content of the fuel is above 15%, special precautions must be taken to ensure that critical assemblies are not formed. Federal regulations require that the quantities of these materials in process are strictly controlled by administrative procedures and through appropriate design of the dimensions of the process equipment, as well as by placing neutron detectors at strategic points to warn of approach to criticality. Quality control is carried out by means of nondestructive and destructive evaluations. Nuclear fuels in their natural state have a low level of radioactivity and do not pose a significant hazard. However, irradiated fuel is highly radioactive and must be handled and treated in shielded facilities. Figure 3 and Table IV show the chain yields of fission products and their chemical states. Special precautions have to be taken to minimize dust formation and contamination in handling and fabricating ceramic fuels in powder or particle form.

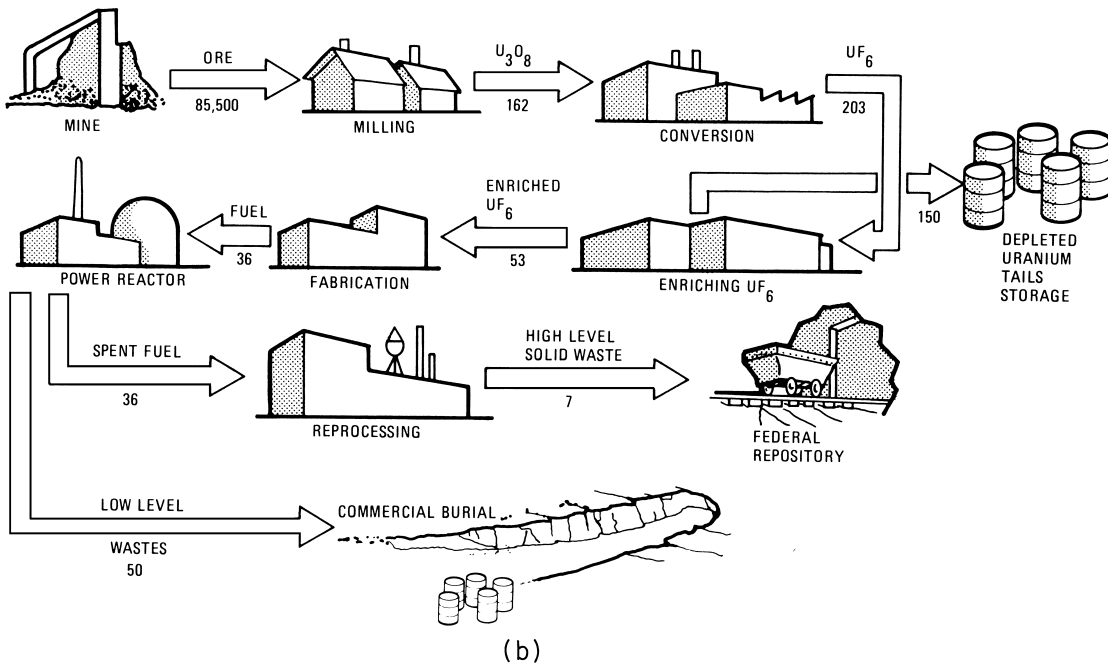
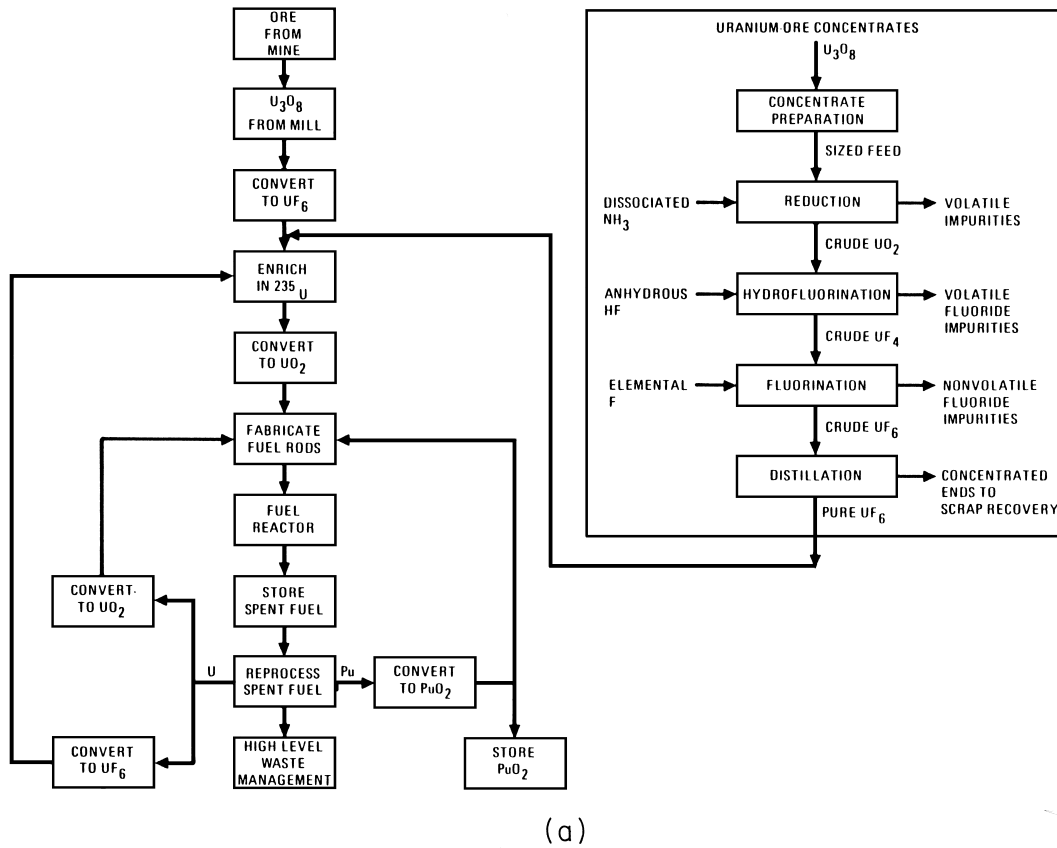
Enrichment of the fuel in the fissile isotope  $^{235}\text{U}$  is required for LWR, AGR, and HTGR power reactors. Hence, the uranium is extracted from the oxide in the form of the hexafluoride  $\text{UF}_6$ , which is processed through an isotope separation plant (Figs. 4 and 5). The plutonium produced in the fuel cycle is recycled in thermal or fast breeder reactors (Fig. 6).

Ceramic fuels can be fabricated into precise shapes (usually cylindrical pellets) that are clad in tubular thin-

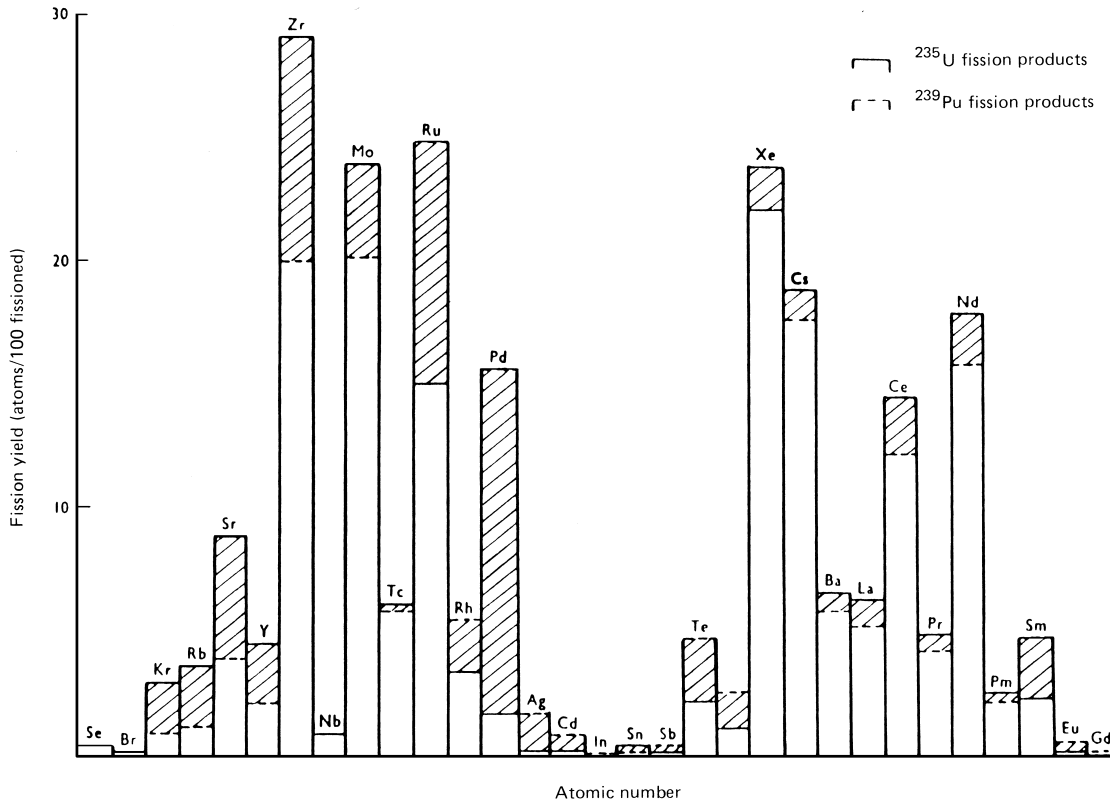
walled metal sheathing (cladding), which is back-filled with helium and endcapped. The cladding in water-cooled reactors is Zircaloy or stainless steel. It protects the fuel from the reactor coolant, retains the volatile fission products, and serves structurally to provide geometrical integrity. The clad fuel pins are assembled into fuel elements. The fuel elements are held in position by grid plates in the reactor core. The fuel burnup to which a reactor may be operated is expressed as megawatt-days per kilogram (MWd/kg), where MW(d) is the thermal output and kg the total uranium (sum of  $^{235}\text{U}$  and  $^{238}\text{U}$ ). Recently, the units GJ/kg M (gigajoules/kg metal) have been adopted. In light-water power reactors, the core may be operated to about 35 MWd/kg (about 3.5% burnup) before fuel elements have to be replaced. In fast breeder reactors (LMFBRs) and high-temperature helium gas-cooled reactors (HTGRs), the burnups may exceed 100 MWd/kg (about 10% burnup of the heavy metal atoms). Burnup conversion factors are given in Table V.

The production of uranium hexafluoride  $\text{UF}_6$  for the enrichment plants is carried out in conversion plants. The cost of this process is approximately 4% of the fuel-cycle cost. There are two commercial processes, namely, (1) the refining-fluoridation process (Kerr-McGee) and (2) the dry fluoride volatility process (Allied Chemical Co.). The refining-fluoridation process consists of solvent extraction of uranium from a nitrate solution, which is washed with water to remove impurities. The uranium is then reextracted into dilute nitric acid solution (0.01-N  $\text{HNO}_3$ ), and the uranium oxide formed is reduced with hydrogen to  $\text{UO}_2$ , which is converted first to  $\text{UF}_4$  (green





**FIGURE 2** (a) Overall refining process flow diagram with outline of complete uranium fuel cycle. (b) Annual quantities (tons) of fuel materials required for operation of 1000-MW(e) light water reactor. The depleted uranium storage is not required for the reactor, but these tails must be stored safely and have value for future breeder reactor blanket. [From M. T. Simnad and J. P. Howe (1979). In "Materials Science in Energy Technology" (G. G. Libowitz and M. S. Whittingham, eds.), Academic Press, New York.]



**FIGURE 3** Yield of major fission products for fast fission of  $^{235}\text{U}$  and  $^{239}\text{Pu}$ . [From M. T. Simnad and J. P. Howe (1979). In "Materials Science in Energy Technology" (G. G. Libowitz and M. S. Whittingham, eds.), Academic Press, New York.]

salt) by reaction with HF gas and then to  $\text{UF}_6$  with fluorine gas. The dry fluoride process involves fluid-bed reduction, hydrofluorination, and fluorination of  $\text{UO}_2$ . The  $\text{UF}_6$  is then double-distilled to produce the pure product. The enriched  $\text{UF}_6$  is reacted with aqueous ammonia to

**TABLE IVa** Chemical State of Solid Fission Products in Irradiated  $\text{UO}_2$

Fission product	Predicted chemical state	Remarks
Cs	Metallic	Volatile and insoluble in $\text{UO}_2$
I	Metallic	
Te	Metallic	Involatile and insoluble in $\text{UO}_2$
Mo	Metallic	
Tc	Metallic	
Ru	Metallic	
Rh	Metallic	
Ba	As oxides ( $\text{BaO}$ , $\text{SrO}$ ) and possibly zirconates ( $\text{BaZrO}_3$ , $\text{SrZrO}_3$ )	Insoluble in $\text{UO}_2$
Sr		
Zr	As oxides; some of Zr may exist as $\text{BaZrO}_3$ and $\text{SrZrO}_3$	Soluble in $\text{UO}_2$
Ce		
Nd		

yield ammonium diuranate (ADU), which is heated in an atmosphere of steam and hydrogen to yield  $\text{UO}_2$ .

The enrichment process involves the diffusion of  $\text{UF}_6$  vapor through a series of porous membrane barriers. Since the maximum theoretical separation per stage is governed by the ratio of the masses of gas molecules in the  $\text{UF}_6$ , namely, 1.00429, a large number of stages extending several miles are required. For example, to attain an enrichment of 4%  $^{235}\text{U}$ , a cascade of 1500 stages is required. At each stage, the gas that diffuses from the tube through the barrier is fed to the next higher stage, and the remaining portion, about 50%, is recycled to the lower stage.

The separative work in enrichment entails about one third of an average fuel-cycle cost. The separative work unit is a measure of the work required to carry out the separation of feed into tails. For example, the production of 1 kg of 3%  $^{235}\text{U}$  requires 4.306 units of separative work and uses 5.479 kg of uranium feed material (0.71%  $^{235}\text{U}$  to yield tails of 4.479 kg having a  $^{235}\text{U}$  content of 0.2%). The separative work costs are made up of power cost (49%), capital cost (35%), and operating, research, and development cost (16%). The three U.S. diffusion plants require 6000 MW(e) power capacity and consume 45 billion kWh of electric power. At full

**TABLE IVb Final Fuel Composition (in Atomic Percent) of (U<sub>0.85</sub>Pu<sub>0.15</sub>)O<sub>2</sub> Fuel Element in a Fast-Fission Environment at 10% Burnup**

Elements	State	Location	Concentration
Y	Oxide, solid solution	Columnar <sup>a</sup>	0.07
La	Oxide, solid solution	Columnar <sup>a</sup>	0.17
Ce	Oxide, solid solution	Columnar, equiaxed	0.44
Pr	Oxide, solid solution	Columnar <sup>a</sup>	0.16
Nd	Oxide, solid solution	Columnar <sup>a</sup>	0.51
Pm	Oxide, solid solution	—	0.06
Sm	Oxide, solid solution	—	0.11
Eu	Oxide, solid solution	—	0.02
Ba	Oxide, solid solution	Columnar, <sup>a</sup> equiaxed	0.21
Zr	Oxide, solid solution	Columnar <sup>a</sup>	0.68
Sr	Oxide, solid solution	Equiaxed	0.14
Nb	Oxide, solid solution	—	0.02
Mo	Metallic phase	Columnar <sup>b</sup> (inclusions)	0.66
Tc	Metallic phase	Columnar <sup>b</sup> (inclusions)	0.19
Ru	Metallic phase	Columnar <sup>b</sup> (inclusions)	0.69
Rh	Metallic phase	Columnar <sup>b</sup> (inclusions)	0.16
Pd	Metallic phase	Columnar <sup>b</sup> (inclusions)	0.41
Cs	Metallic phase	Columnar <sup>b</sup> (inclusions)	0.60
Rb	Metallic phase	—	0.07
Total concentration			5.37

<sup>a</sup> Primarily in columnar-grain matrix.

<sup>b</sup> Primarily near columnar-grain boundaries.

capacity these plants have a capacity of 17.2 million SWU per year.

Other enriching techniques include the centrifuge processes and laser separation. Both these methods are under intensive study and appear to have a potential for lower power requirements and capital costs and higher yields.

The characteristics of LWR-grade plutonium generated from three cycles of operation in a large reactor are as follows: the isotopic composition is 1% <sup>238</sup>Pu, 58% <sup>239</sup>Pu, 23% <sup>240</sup>Pu, 13% <sup>241</sup>Pu, and 6% <sup>242</sup>Pu. The isotopes <sup>239</sup>Pu and <sup>241</sup>Pu are fissile. The major sources of alpha radiation are <sup>239</sup>Pu, <sup>240</sup>Pu, and <sup>241</sup>Pu. The gamma-emitters are <sup>241</sup>Pu and the daughter products of <sup>241</sup>Pu (13-yr half-life), namely, <sup>241</sup>Am and <sup>237</sup>U. Also, neutrons are emitted by spontaneous fission from <sup>238</sup>Pu, <sup>240</sup>Pu, and <sup>242</sup>Pu.

The fission products present in irradiated oxide fuels consist of the following.

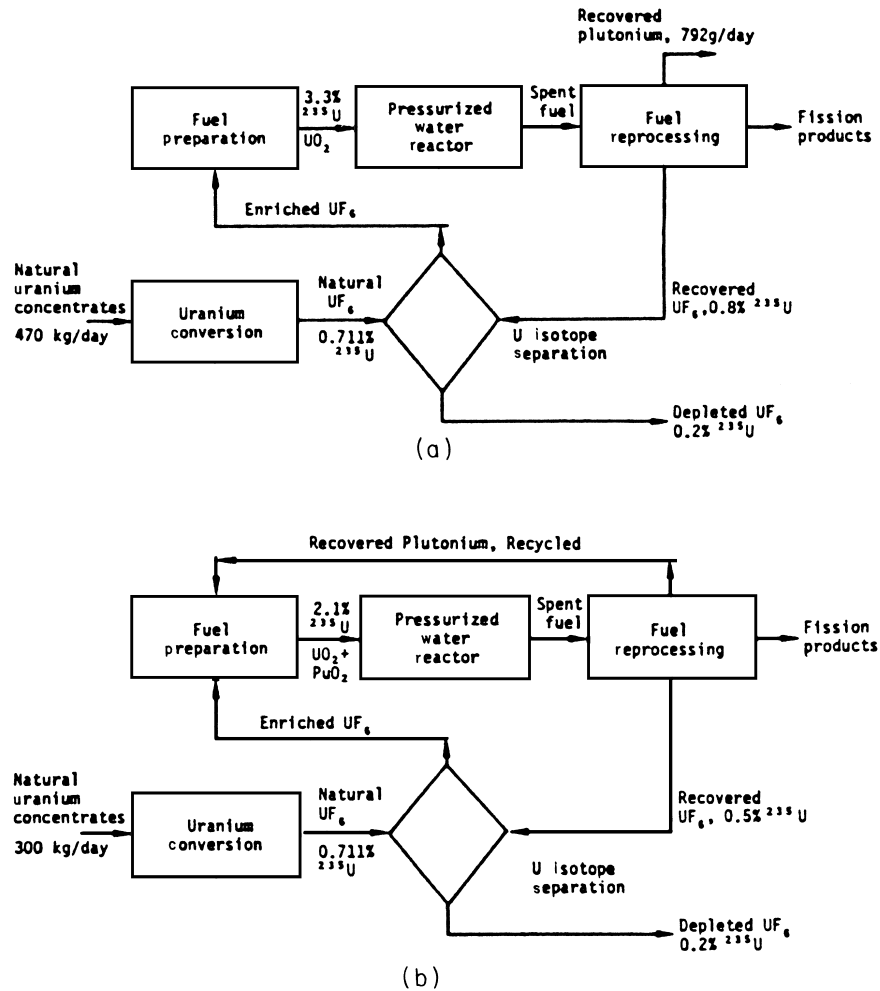
1. Volatile elements, which are Rb, Cs, I, Sb, Cd, and the inert gases Xe and Kr.
2. Zr and the rare earths, which form solid solutions with the oxide fuel.
3. SrO and BaO, which are present as occlusions dispersed in the fuel.
4. Noble metals—Mo, Ru, Tc, Pd, Rd, and Ag—which are in the unalloyed state and occur as white occlusions

in the equiaxed and columnar grains in the fuel. The Mo may form MoO<sub>2</sub> or MoO<sub>3</sub> in a region of high oxygen potential.

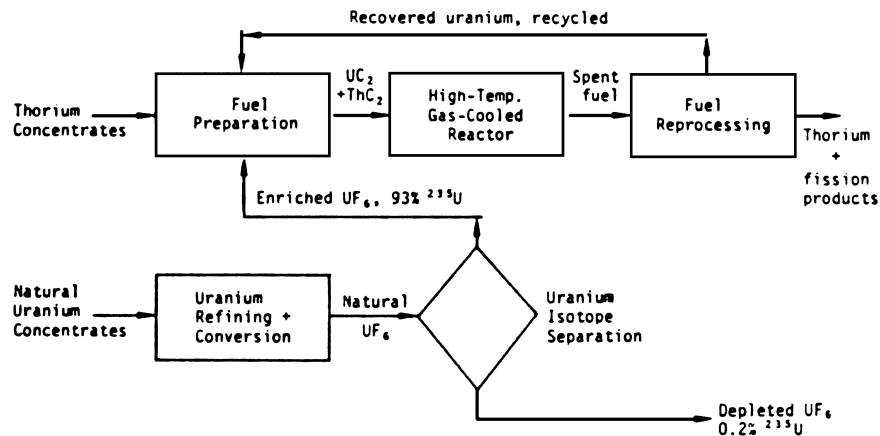
5. Noble metal alloys. The nominal composition of the alloy generally located in the central voids in the fuel is 20% Mo, 17% Tc, 48% Ru, 13% Rh, and 2% Pd.

## B. Reprocessing of Nuclear Fuel

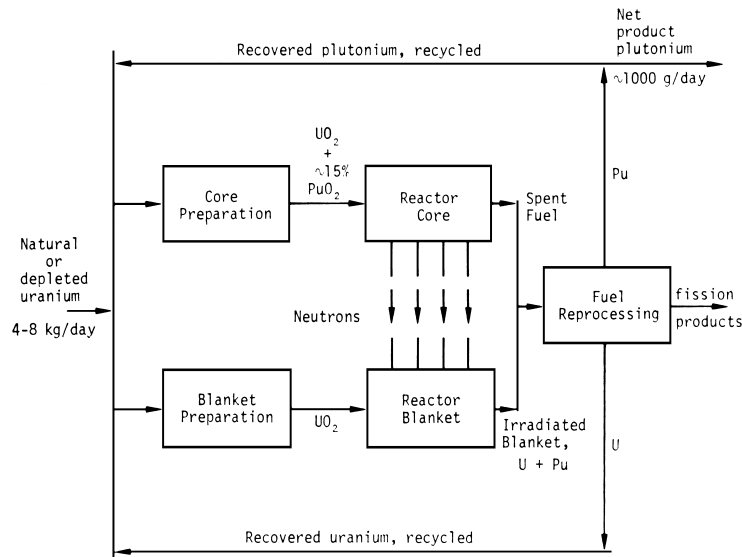
The reprocessing of LWR fuel assemblies would reduce the uranium needs and enrichment requirements by approximately 35%. The recycling of the plutonium for LWRs has been studied extensively and can now be used commercially. However, the institutional barriers to reprocessing in the United States have, in effect, eliminated this option for the time being in this country. Several other nations are proceeding to use reprocessed fuels in their LWRs. It should be pointed out that a typical core in a LWR derives about 50% of its power from the fissioning of bred-in plutonium isotopes near the end of an equilibrium cycle. The performance of the mixed-oxide recycle fuels (containing 3–6 wt. % PuO<sub>2</sub>) has been very impressive and generally superior to that of the uranium dioxide fuel. Other conservation measures include extended burnup of fuel and optimization of plant availability or capacity factor.



**FIGURE 4** Fuel processing flow sheets for 1000-MW(e) PWR: (a) without plutonium recycle and (b) with plutonium recycle. [From M. T. Simnad and J. P. Howe (1979). In "Materials Science in Energy Technology" (G. G. Libowitz and M. S. Whittingham, eds.), Academic Press, New York.]



**FIGURE 5** Fuel processing flow sheet for HTGR. [From M. T. Simnad and J. P. Howe (1979). In "Materials Science in Energy Technology" (G. G. Libowitz and M. S. Whittingham, eds.), Academic Press, New York.]



**FIGURE 6** Fuel processing flow sheet for 1000 MW(e) fast breeder reactor. [From M. T. Simnad and J. P. Howe (1979). In "Materials Science in Energy Technology" (G. G. Libowitz and M. S. Whittingham, eds.), Academic Press, New York.]

The reprocessing of spent fuel serves to reduce fuel-cycle costs. The basic process used for LWR fuels is the solvent extraction process. The fuel pins are first disassembled (about 4 months after removal from the reactor core) in a chop-leach step to remove the fuel from the clad. The fuel is dissolved in nitric acid and the solution is then subjected to solvent extraction (PUREX process) to strip first the Pu and then the U from the solvent. After purification cycles by means of subsequent solvent extractions [tributyl phosphate (TBP) in kerosene], the Pu is recovered as the nitrate in aqueous solution and the U as  $\text{UO}_2$  or nitrate in dilute nitric acid solution. The fission products in the waste solutions are stored for several years in cooled tanks to remove much of the decay heat and are then solidified. About 100–300 gal of fission product waste solutions are generated per ton of U fuel.

The four main solid fission product isotopes from spent reactor fuel are Sr, Cs, Ce, and Pm. It has also been proposed that the elements Ru, Rh, Pd, Xe, Kr, and tritium may be produced economically as by-product isotopes from fission products. Fission product yields are shown in Fig. 3. Their chemical states are listed in Table III.

A 1000-MW(e) LWR generates approximately 200 kg of Pu annually. The fabrication of recycled Pu poses problems of shielding arising from gamma radiation from  $^{241}\text{Pu}$  and the decay daughters  $^{237}\text{U}$  and  $^{241}\text{Am}$ , as well as neutrons from the spontaneous fission of  $^{238}\text{Pu}$ ,  $^{240}\text{Pu}$ , and  $^{242}\text{Pu}$ . A plant with 1700 tons capacity will provide the needs of 39 LWR power plants.

### C. Transportation, Safeguards, and Waste Disposal

The spent fuel from LWRs contains approximately 50% of fissile material that can be used for the reload batch. The fission product activity from a 3000-MW(t) core after 1-yr decay is approximately  $3 \times 10^8$  Ci. Decay heat of the discharged fuel is lowered by storing at the reactor site for a period of 3–4 months before shipment. The amount of fission product activity shortly after shutdown is about 10 Ci per thermal watt of power. The shipping cask for LWR spent fuel consists of an annular stainless steel shell with depleted uranium or lead in between for shielding. The decay heat is removed by means of cooling fins. The spontaneous fast neutrons from the  $^{242}\text{Cm}$  and  $^{244}\text{Cm}$  are shielded with a neutron moderator several centimeters thick. The cask may weigh up to 100 tons, but

**TABLE V** Burnup Conversion Factors

Material	Fissions/cm <sup>3</sup>	Percent burnup of heavy atoms	MWd/kg	
Uranium	$10^{20}$	0.209	U	$1.810$
	$4.78 \times 10^{20}$	1.0	$\text{UO}_2$	$8.650$
$\text{UO}_2$	$10^{20}$	0.411	U	$3.560$
	$2.43 \times 10^{20}$	1.0	$\text{UO}_2$	$8.650$
UC	$10^{20}$	0.305	U	$2.640$
	$3.28 \times 10^{20}$	1.0	UC	$8.220$

highway transportation is limited to under 20 tons (about 0.5 tons U fuel capacity). Hence, railroad transportation is required.

The safeguards on the fuel cycle are based on four methods: (1) accounting for the materials balance on a continuing basis by means of a computer program, NMIS (Nuclear Materials Information System), (2) surveillance, (3) nondestructive assay by remote detection systems (e.g., detecting the gamma radiation from  $^{239}\text{Pu}$ ), and (4) physical protection.

The assessment of the safety of nuclear reactors has been based on design basis accident (DBA) considerations. This approach identifies the events that can lead to the release of radioactivity and do harm to people and property. The reactor designs incorporate safeguards against the worst physically possible chain of events. It has been estimated that almost half the effort in the design and operation of nuclear reactors is related to safety features.

The principal fission products and other radionuclides in the reactor effluents for waste disposal are  $^3\text{H}$ ,  $^{58}\text{Co}$ ,  $^{60}\text{Kr}$ ,  $^{85}\text{Kr}$ ,  $^{89}\text{Sr}$ ,  $^{131}\text{I}$ ,  $^{133}\text{Xe}$ ,  $^{134}\text{Cs}$ ,  $^{137}\text{Cs}$ , and  $^{140}\text{Ba}$ . With 1000-GW installed capacity [about one thousand 1000-MW(e) plants], approximately 19,000 tons of spent fuel would be reprocessed per year. The volume of liquid waste would be 5.8 million gal/yr.

#### IV. PREPARATION AND PROPERTIES OF NUCLEAR FUELS

The processing of nuclear fuels requires the provision of strict accountability, safeguards, and criticality control. The fissionable isotopes are accountable to within 0.1 g. Also, personnel have to be protected from the toxicity and radioactivity of the fuel materials. Special gloveboxes and hot cells are utilized, with appropriate protective shielding and filters and fire prevention measures. Quality control and quality assurance must be exercised in all the stages of production.

Nuclear fuels are classified as metallic, ceramic, and dispersions. The metallic fuels are generally alloyed to improve their resistance to irradiation and corrosion. Ceramic fuels include the oxides, carbides, and nitrides. Dispersion fuels include two-phase metallic fuels and dispersions of ceramic fuels in metal or ceramic or graphite matrices.

##### A. Metallic Fuels

Uranium alloys have been used in the fuel elements in the carbon-dioxide cooled, first-generation nuclear power reactors in Britain (Calder Hall or Magnox reactors) and France and in fast breeder reactor prototypes (Dounreay, EBR-I and -II, and Fermi).

Metallic uranium is produced by the reduction of uranium tetrafluoride by magnesium or calcium in a pressure vessel. Uranium fuel rods are produced by casting, rolling, extrusion, machining, and heat treating. Uranium undergoes three phase changes up to its melting point, namely, the alpha (orthorhombic) up to  $666^\circ\text{C}$ , beta (tetragonal) from  $666$  to  $771^\circ\text{C}$ , and the gamma (body centered cubic) from  $771$  to  $1130^\circ\text{C}$  (melting point). Anisotropic alpha-uranium is subject to dimensional changes under both thermal cycling and nuclear irradiation. The changes are governed by the structure and composition as well as temperature and burnup.

Metallic uranium fuels are generally limited to operation below approximately  $600^\circ\text{C}$  maximum temperature and to relatively low burnups of about 5 MWd/kg U because of irradiation damage. Swelling and growth become excessive primarily because of fission gas bubbles at high temperatures and the formation of lattice defects (vacancies, interstitials, dislocation loops, etc.) at low temperature. Irradiation creep is also a problem at low temperatures. There is little swelling below about  $400^\circ\text{C}$ . The growth reaches a maximum in the range  $400$ – $600^\circ\text{C}$ . Above approximately  $700^\circ\text{C}$ , fission gas swelling predominates. The Magnox reactors used uranium adjusted with iron (260 ppm), aluminum (650 ppm), carbon (800 ppm), silicon (20 ppm), and nickel (50 ppm). The French EDF reactors used U–1% Mo in EDF-1, -2, -3, and -4 and Sicral alloy [uranium containing Al (700 ppm), Fe (300 ppm), Si (120 ppm), and Cr (80 ppm)] in EDF-5. These minor alloying elements result in grain-size refinement and very finely divided precipitates and the swelling diminishes by several orders of magnitude. These additions modify the  $\alpha$ – $\beta$  transformation and favor grain refinement and absence of preferred orientation upon quenching these alloys from temperatures in the beta range. Thus, heat treatment minimizes distortion of fuel elements due to either thermal cycling or irradiation growth, since induced intergranular stresses and strains are reduced, a typical grain size effect. These fuels were clad with magnesium alloys (Mg containing 0.8% Al, 0.002–0.05% Be, 0.008% Ca, and 0.006% Fe in the U.K., and Mg containing 0.6% Zr in France).

Metallic fuels for breeder reactors have been developed and studied at Argonne National Laboratory. An alloy of U–15% Zr–10% Pu has a solidus temperature of  $1155^\circ\text{C}$ . This fuel is satisfactory after irradiation to 16 at. % burnup when adequate void space is provided between the fuel and cladding to accommodate 25–30% swelling and a plenum for fission gases. The fuel is sodium-bonded to the cladding and has a smear density of 75%. It attained a power rating of 15 kW/ft and expanded to touch, but not strain, the cladding. The swelling rate was  $2$ – $\frac{1}{2}$ % per at. % burnup (the solid fission products accounted for 10%

of the dilation and the fission gas bubble swelling for 22–66%; 60–70% of the fission gases were released via cracks and fissures.) There was a marked effect of external pressure on swelling. For example, the swelling per 1 at. % burnup was 50% at 1 atm and 10% at 67 atm. The cast alloy U-5 wt, % fission (2.5% Mo, 2% Ru, remainder Si, Rh, Pd, Zr, and Nb) has been tested as a fuel in EBR-II. Swelling becomes marked above 500°C, and it can be exposed to a burnup of 1.2%. This fuel, when made into rods by centrifugal casting, developed a texture that resulted in excessive swelling. Over 4% burnup was achieved without rupture of the stainless steel cladding.

## B. Oxide Fuels

The dioxides of Th, U, and Pu have the face-centered cubic fluorite structure. They are completely miscible in solid solution. Uranium dioxide can take up oxygen interstitially to form hyperstoichiometric  $\text{UO}_{2+x}$ , where  $x$  may be as high as 0.25 at high temperatures. As the temperature is lowered, a phase having the composition  $\text{U}_4\text{O}_9$  precipitates. Hypostoichiometric oxides of uranium  $\text{UO}_{2-x}$  form under conditions of low oxygen partial pressure at high temperatures and revert to stoichiometric  $\text{UO}_2$  precipitating U on cooling. Unsintered, finely divided  $\text{UO}_2$  powders oxidize to  $\text{U}_3\text{O}_8$  at room temperature when exposed to air. The dioxides of Pu and Th form only the stoichiometric dioxides because of the stability of the  $\text{Th}^{4+}$  and  $\text{Pu}^{4+}$ . In  $\text{UO}_2$ – $\text{PuO}_2$  solutions,  $\text{Pu}^{4+}$  may be reduced to  $\text{Pu}^{3+}$ .

### 1. Uranium Dioxide

Uranium dioxide is the most widely used fuel material in nuclear power reactors, usually in the form of cylindrical, cold-pressed, and sintered pellets with densities in the range of 92–97% of the theoretical. The properties that combine to make  $\text{UO}_2$  such a unique fuel material are (1) high melting point (2800°C), (2) chemical stability in water cooled reactors, (3) compatibility with cladding (Zircaloy and stainless steel), (4) excellent irradiation stability, and (5) ease of fabrication.

Deviations of composition from stoichiometry have a profound influence on the properties of  $\text{UO}_2$ , diminishing the already low thermal conductivity, lowering the melting point and strength, increasing creep and fission product migration and release, and altering the complex irradiation behavior. The increase in oxygen activity with burnup can be very significant in leading rods in LWRs (5% burnup) and in fast breeder reactor fuels (over 10% burnup).

The allowable values of the thermal conductivity integral and the temperatures within pellets have been estimated from observation of microstructure; for example, the melting point boundary corresponds to 2865°C, columnar grain growth to 1700°C, and equiaxed growth

to 1500°C. The reported integral conductivity values from 500°C to melting range from 63 to 73 W/cm. The thermal conductivity of  $\text{UO}_2$  decreases as the O/U ratio is increased.

The melting point of stoichiometric  $\text{UO}_2$  is  $2865 \pm 15^\circ\text{C}$ . It drops to 2425°C at an O/U ratio of 1.68 and to 2500°C at an O/U ratio of 2.25. The lowering of the melting point to 2620°C at a burnup of  $1.5 \times 10^{21}$  fissions/cm<sup>3</sup> has been reported.

Particularly striking among the behavioral features of  $\text{UO}_2$  is the large increase, as the O/metal exceeds 2, in the rate of creep, sintering, diffusion, and other processes depending on mobile defects. Creep data on  $\text{UO}_2$  demonstrate this effect.

The uranium oxide (yellow cake) obtained from the milling operation must be purified before it can be used in nuclear fuels. The characteristics of the  $\text{UO}_2$  powder are largely determined by its method of preparation. The purification is accomplished by solvent extraction or by the hydrofluor process. In the solvent extraction method, the uranium oxide concentrate is dissolved in nitric acid, and the resulting solution is passed down through an extraction column through which 30% *n*-tributyl phosphate in kerosene or in hexane flows upward; that is, the solvent is the continuous phase, and the ratio of organic to aqueous is about 13:1. The uranyl nitrate is extracted into the organic solvent and is further purified by scrubbing with dilute nitric acid or water. The solution is then fed into a stripping column where the uranium is extracted into dilute (0.01 *N*) nitric acid solution. The stripped solvent is purified and recycled. The aqueous uranium nitrate solution is evaporated to dryness, and the resulting uranium nitrate is calcined at approximately 350–450°C to  $\text{UO}_3$  (orange oxide). The  $\text{UO}_3$  is reduced to  $\text{UO}_2$  by hydrogen at about 600°C. Alternately, the nitrate solution may be reacted with ammonia to precipitate ammonium diuranate, which is filtered, dried, calcined, and reduced by hydrogen to  $\text{UO}_2$ . The  $\text{UO}_2$  is converted to  $\text{UF}_4$  (green salt) by reaction with HF gas. The  $\text{UF}_4$  is a solid with a melting point of 960°C. It is shipped to uranium enrichment plants where it is reacted with fluorine gas. The reaction is highly exothermic, and the reactor towers are cooled during operation to a temperature between 450 and 550°C to form the volatile compound uranium hexafluoride,  $\text{UF}_6$ . The latter is used as the feed material in gaseous diffusion plants for the enrichment of the uranium. Sublimation of  $\text{UF}_6$  takes place above 56°C.

In the dry hydrofluor process, the  $\text{U}_3\text{O}_8$  concentrate (yellow cake) is ground and sized into feed material for a fluidized-bed unit, where it is reduced by hydrogen to  $\text{UO}_2$  at 540–650°C. The  $\text{UO}_2$  particles are then reacted in two successive fluidized-bed reactors with anhydrous HF at 480–540°C and 540–650°C, respectively, to produce  $\text{UF}_4$

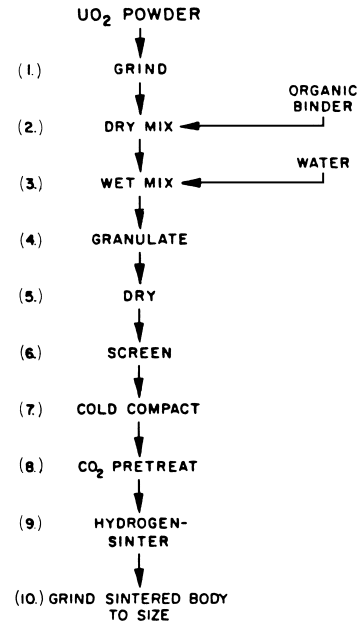
(green salt). The fluorination is carried out with excess fluorine, with an inert solid diluent,  $\text{CaF}_2$ , which serves to prevent caking and to distribute the heat of reaction. Next, the  $\text{UF}_4$  is reacted with fluorine gas at 340–480°C to produce  $\text{UF}_6$ , which is collected in cold traps (–15°C). Further purification (>99.97%) is accomplished by fractional distillation of the  $\text{UF}_6$  at a pressure of 0.35 to 0.7 MPa (50 to 100 psig).

Pure uranium dioxide is produced from  $\text{UF}_6$  by hydrolysis of the  $\text{UF}_6$  with water and precipitation of ammonium diuranate or ammonium uranyl carbonate by addition of ammonia or ammonium carbonate, respectively. The precipitate is filtered, dried at 175°C, and calcined and reduced at 800°C in hydrogen to  $\text{UO}_2$ . The characteristics of the powder influence the processing and properties of the finished fuel pellets as well as their performance. The  $\text{UO}_2$  is cooled under nitrogen and reduced to fine powder in wet, rubber-lined ball mills or by micronizing. The milling operation may be eliminated with ceramically active powder. It is important to add the correct amount of ammonia in the precipitation step to produce a sinterable product. Too much ammonia yields a gelatinous ammonium diuranate (ADU), which is difficult to filter, whereas with too little ammonia, the  $\text{UO}_2$  product is difficult to press and sinter. Sinterable  $\text{UO}_2$  is prepared by the rapid precipitation of ADU under conditions of low uranium solubility. The excess ammonia is programmed to adjust for the solubilizing and complexing action of the fluoride concentration, which increases as  $\text{UF}_6$  is fed into the system. Conditions of relatively low uranium solubility are desirable in order to maximize yields. For example, a concentration of 25 g/liter of fluoride may require an excess ammonia concentration of 5–15 g/liter to precipitate the ADU in a form that yields ceramically active  $\text{UO}_2$  powder. The occluded fluoride impurity in the precipitated  $\text{UO}_2$  is removed by passing steam over the ADU during calcining and reduction at 800°C. Hydrogen reduction is continued after the steam treatment is stopped.

Upon exposure to air, the  $\text{UO}_2$  powder partially oxidizes to  $\text{UO}_{2.03}$  to  $\text{UO}_{2.07}$ , and in extreme cases the powder may be pyrophoric and burn to  $\text{U}_3\text{O}_8$ . The highest oxygen forms ( $\text{UO}_3$  and  $\text{U}_3\text{O}_8$ ) are generally formed between 500 and 600°C. At higher temperatures, oxygen is released, and above 1100°C,  $\text{UO}_2$  is again the stable form.

The fuel for water-cooled power reactors is enriched to contain 2–4%  $^{235}\text{U}$ . Higher enrichments up to 93%  $^{235}\text{U}$  are used in fuels for fast breeder reactors, HTGRs, and certain research and test reactors.

The commercial method for producing  $\text{UO}_2$  fuel elements is to cold press and sinter cylindrical pellets of ceramic-grade  $\text{UO}_2$ , which are loaded into tubular metal cladding (Zircaloy or stainless steel). The cladding is sealed by welded end-plugs to form a fuel rod or fuel pin,



**FIGURE 7** Process flow diagram of principal operations for fabrication of  $\text{UO}_2$  fuel components. [From M. T. Simnad and J. P. Howe (1979). In "Materials Science in Energy Technology" (G. G. Libowitz and M. S. Whittingham, eds.), Academic Press, New York.]

and an assembly of the fuel rods into bundles constitutes a fuel element or fuel subassembly.

The main steps in the production of  $\text{UO}_2$  pellets consist of mixing the  $\text{UO}_2$  powder with binder and lubricant materials, granulation to form free-flowing particles, compaction in an automatic press, heating to remove the fugitive binder and lubricant, sintering in a controlled atmosphere, and grinding to final specified dimensions (Fig. 7). A large water-cooled reactor core contains several million fuel pellets.

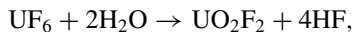
The granulated mixtures are compacted in automatic pellet presses that are double-acting cam-operated. The ends of the green pellets are dished by means of punches with slightly convex faces. The dished configuration provides space for thermal expansion of the pellet centerline during operating conditions. Chamfering of the pellet edges also improves performance. The length-to-diameter ratio of the compacts made in double-acting presses is usually limited to a maximum of 2:1 to minimize differences in density that would result in cracking due to differential shrinkage during sintering. The two-piece dies used to compact the highly abrasive fuel granules consist of a hard liner (tungsten carbide) and a soft steel shrink ring to reduce elastic die expansion. The punches are made of tungsten carbide.

A slight taper is introduced in the exit side of the die to prevent laminations in the compacts, by allowing a gradual elastic expansion during ejection from the die. For typical

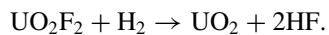


pellets of 1.0-cm diameter, the diametral clearance between die and punches is approximately 15–35  $\mu\text{m}$ . The binders and lubricants are removed from the green compacts by heating in a high flow of  $\text{CO}_2$  for several hours at 500–800°C, which also reduces the carbon content to below 50 ppm. The pellets are then sintered in a hydrogen atmosphere at 1550–1700°C. The sintered pellets may have densities ranging from 90 to 97% of theoretical density, depending upon the nature of the  $\text{UO}_2$  powder, the green compact density, and the sintering time, temperature, and atmosphere. Centerless belt grinding with silicon carbide abrasive is used to attain the specified dimensional tolerances in the sintered pellets.

Recent developments in the processing of  $\text{UO}_2$  pellets to improve the quality and lower the fabrication costs, include the double-cycle inverse (DCI) process used in France in which no additives are made to the  $\text{UO}_2$  powder except for a small amount of lubricant (0.2% zinc stearate). In this process the  $\text{UO}_2$  powder is produced from  $\text{UF}_6$  by pyrohydrolysis at 250°C:



followed by hydrogen reduction at 700°C,



The  $\text{UO}_2$  powder obtained by this process is readily granulated and sintered, without the addition of binders, to controlled densities. KWU (Germany) controls pore size distribution by addition of  $\text{U}_3\text{O}_8$  to the  $\text{UO}_2$  powder. The pellets have high stability (no further densification takes place during operation). The pellet density in the French (DCI) process is controlled by the cold compaction pressure in forming the green compacts. In Germany (KWU), the ammonium uranyl carbonate (AUC) process is used to produce  $\text{UO}_2$  powder that is free-flowing as calcined and does not require any pretreatment such as granulation before cold compaction.

The quality assurance activities in fuel fabrication are quite costly (as much as 30% of fuel fabrication costs), but this cost is more than compensated by the considerable improvements in fuel performance experienced when good inspection practices have been implemented. One of the most important quality requirements for fuel pellets is the need to minimize the moisture and fluorine contents (to <10 ppm each) to prevent internal corrosion failure of the cladding. The pellets should be stored in a dry environment and preferably heated in vacuum after loading into the cladding. A major fuel rod failure mechanism is mechanical interaction between the fuel pellets and the cladding in the presence of fission products (e.g., iodine, cesium, and tellurium), which results in stress corrosion or intergranular cracking of the cladding.

The serious problem of  $\text{UO}_2$  pellet densification under irradiation was experienced in pressurized water reactors in the early 1970s. This behavior causes the fuel materials to contract and leads to loss of integrity of the fuel rods by collapse of the cladding in axial gaps in sections of the fuel columns. The solution to fuel densification has been to control the manufacturing process so as to produce fuel pellets with higher density and stabilized pore structures (pore size and grain size). Prepressurizing the fuel rod with helium also avoids clad flattening.

In recent years there have been extensive studies to develop an alternate fuel fabrication technique in which crushed or spherical fuel particles are vibratory-packed directly into the cladding tubes, thereby avoiding the problems of pellet production. In this process the fuel fabrication operations can be carried out more economically and automatically by remote operation at room temperature. The gap between the fuel and cladding is eliminated, thereby relaxing the tolerance on the clad tube diametral dimensions. The results of irradiation tests of these fuel rods indicate improved performance over pellet fueled rods for equivalent exposures.

Spherical fuel particles produced by the wet chemical sol-gel process have been used in HTGRs and in test elements in water-cooled reactors and liquid-metal-cooled fast breeder reactors. The process consists of producing an aqueous solution or a hydrosol of the salts of the fissile and/or fertile materials, which is dispersed through spray nozzles into spherical droplets. Highly homogeneous mixed oxides are prepared by coprecipitation. The droplets are gelled by either an internal precipitation or dehydration reaction, washed and aged, and then heat treated to dry and sinter to produce high-density spherical particles (Fig. 8). The process is highly compatible with the shielded, remote-fabrication facilities required for irradiated recycle fuel and especially for the production of (U, Pu) oxides and carbides for fast reactors.

The packing efficiency of sphere-pac fuel is governed by the size ratios of the particles. It has been found that the cladding diameter should be at least ten times larger than the diameter of the coarse-sphere particles. Also, the size ratio among coarse, medium, and fine particles should be at least 77:7:1. A smear density of 90% of theoretical density has been achieved with a three-size mix containing 67% coarse, 23% medium, and 10% fine spheres, with diameter ratios of 77:7:1. The production methods for medium and fine spheres (50–550  $\mu\text{m}$ ) are well established. However, particles larger than about 500  $\mu\text{m}$  in diameter are difficult to fabricate. For the production of high-density fuel, a hybrid technique that combines the sphere-pac and pelletizing methods has been studied. In this approach the spherical sol-gel particles are first converted to  $\text{U}_3\text{O}_8$  at 600–800°C and then cold pressed and

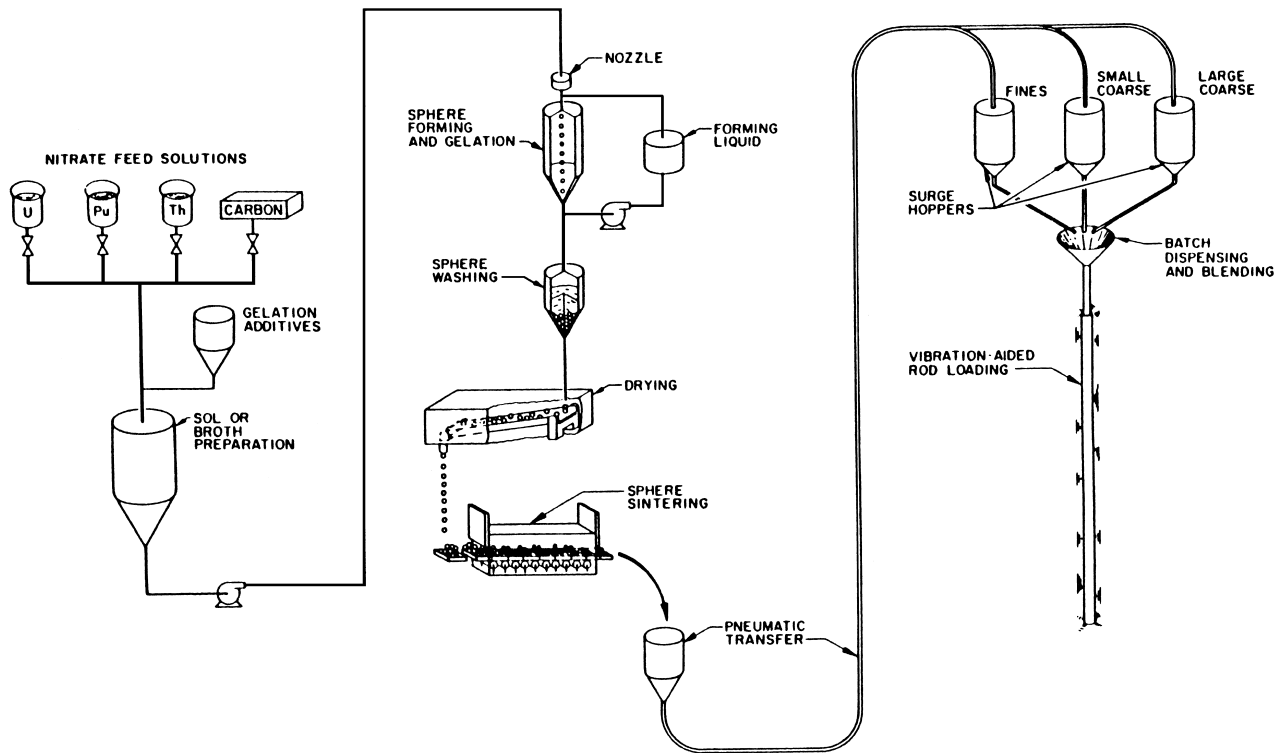


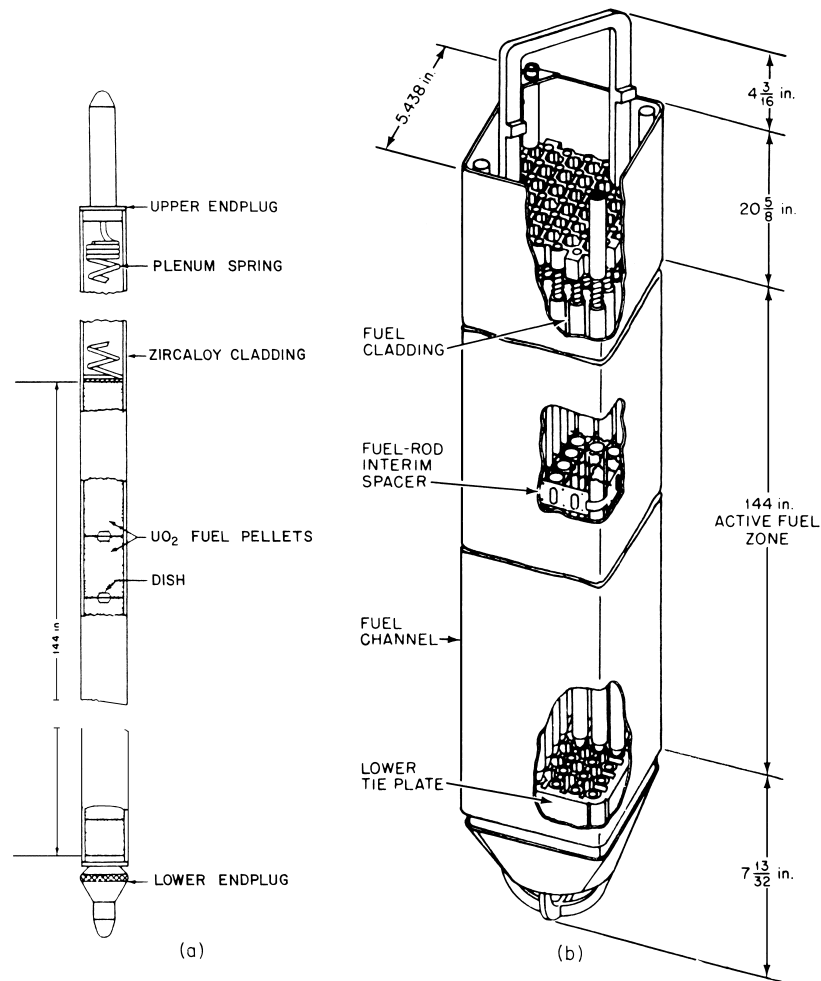
FIGURE 8 Major steps in the gel-sphere-pac process. [Courtesy of Oak Ridge National Laboratory.]

sintered in hydrogen at high temperature (1500–1700°C) to form pellets.

Most useful fuel elements are cylindrical, as are reactor cores, and for similar reasons. The exception is the spherical element for the experimental AVR helium gas-cooled reactor at Jülich, Germany. The overall active length of an element derives from the neutronic calculations that determine the size and fuel loading of the reactor. The diameter and number of the cylinders, usually called rods or pins, must satisfy two requirements: (1) the total volume of the pins must contain the required mass of fuel and fertile material and (2) the surface area multiplied by the local permissible heat flux and integrated over the reactor core must equal the required power. A third requirement trades minimizing fabrication costs against maximizing specific power and forces the diameter into the upper range permitted by the first two requirements. Cladding thickness, strength, and neutron absorption enter into these three requirements and are vital in a fourth, namely, fuel burnup and life. Prediction of fuel performance, life, probability, and mode of failure is the essence of nuclear fission fuel engineering. Implied in life and performance are stability of dimensions, tolerable corrosion, and confinement and management of fission products. For structural and handling purposes, fuel rods are grouped, spaced, and supported in conveniently sized bundles, or subassemblies.

The costs of fuel can be reduced primarily by higher burnups, lower fabrication costs, and an increase in the maximum specific power output of the fuel rods. Fuel assembly prices have not risen because fabrication costs have dropped and thus balanced the rising labor and materials costs. The specific fuel costs have actually decreased with the higher burnups.

A large [1000-MW(e)] LWR reactor core contains approximately 40,000 fuel rods arranged to form about 200 fuel assemblies. The fabrication of a fuel rod proceeds as follows (see Fig. 4). The cladding tube is thoroughly cleaned, and the first end-plug is pressed into the tube and welded. The  $\text{UO}_2$  pellets are loaded into the cladding tube, the plenum spring is placed on top of the fuel pellets, and the tube is back-filled with pressurized helium. The second end-plug is pressed into the tube and welded. A typical fuel rod and fuel assembly are shown in Figs. 9 and 10. The loaded and sealed fuel rod is then tested and inspected before final assembly, which includes dimensional inspection, helium mass spectrometer testing for leak tightness, radiography of the welds, and testing for surface defects on the cladding. Zircaloy-clad rods are etched in a nitric hydrofluoric acid bath and exposed for 3 days to high-pressure steam in an autoclave [400°C, 9.6 MPa (1400 psi)]. Acceptable rods are covered with a uniform black, lustrous oxide coating.



**FIGURE 9** (a) Fuel rod schematic for BWR. (b) Fuel assembly schematic for BWR. [From M. T. Simnad and J. P. Howe (1979). In "Materials Science in Energy Technology" (G. G. Libowitz and M. S. Whittingham, eds.), Academic Press, New York.]

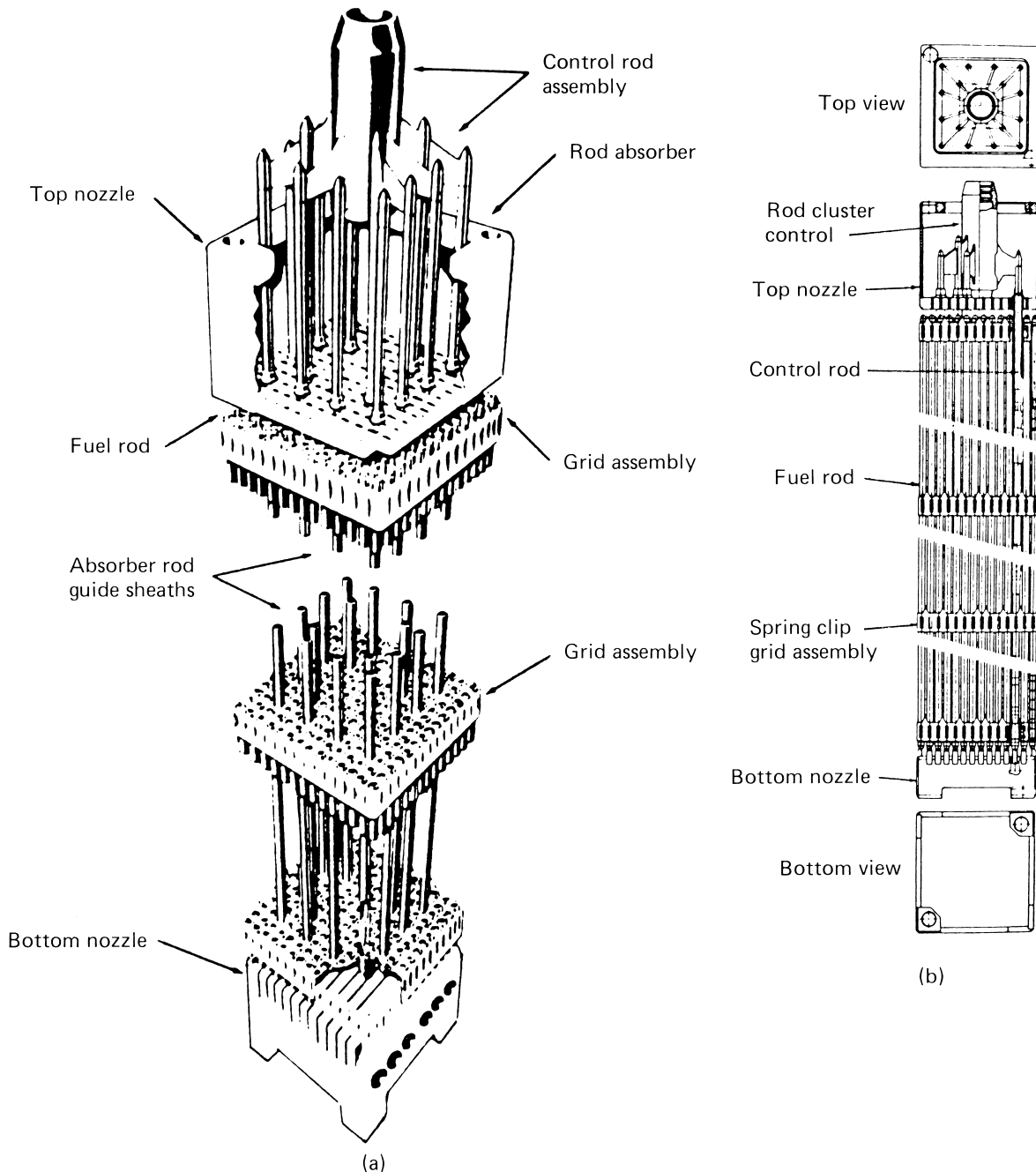
In the pressurized heavy-water reactors developed in Canada (PHWR CANDU), the main structural materials are zirconium and aluminum alloys. The use of heavy water as a moderator provides good neutron economy and permits a wide range of possible fuel cycles (including Th,  $^{233}\text{U}$  or U, Pu) and fuel management schemes. The  $\text{UO}_2$  fuel elements are positioned in Zircaloy-2 pressure tubes, which pass through an aluminum calandria containing the heavy water moderator (Fig. 11).

The advanced  $\text{CO}_2$  gas-cooled reactors in the United Kingdom are graphite moderated and fueled with slightly enriched  $\text{UO}_2$  fuel clad in stainless steel. The uranium dioxide fuel is in the form of sintered pellets [10.2 mm (0.40 in.) diameter], which are loaded into stainless steel tubes about 508 mm (20 in.) long with a 0.04-mm (0.015-in.) wall. A cluster of 21 fueled tubes is supported by stainless steel grids within a graphite sleeve to form a fuel element. In each channel several fuel assemblies are

joined together by a central tie bar to form a fuel stringer. The stainless steel alloy developed for the cladding has a 20% chromium, 25% nickel composition stabilized with niobium. This alloy is produced by a double vacuum melting technique, is free from sigma-phase formation, and has excellent resistance to oxidation in  $\text{CO}_2$  at temperatures as high as  $850^\circ\text{C}$ .

## 2. Plutonium Oxide Fuels

Plutonium is obtained by neutron capture from  $^{238}\text{U}$  because only an insignificant amount occurs in nature. Plutonium serves as a fissile fuel in both fast and thermal reactors. The fissile isotopes  $^{239}\text{Pu}$  and  $^{241}\text{Pu}$  produced from  $^{238}\text{U}$  can replace some of the  $^{235}\text{U}$  in thermal reactors. However, the most efficient and economical use of plutonium is in fast breeder reactors, where more  $^{239}\text{Pu}$  and  $^{241}\text{Pu}$  are produced than are fissioned in situ. Plutonium

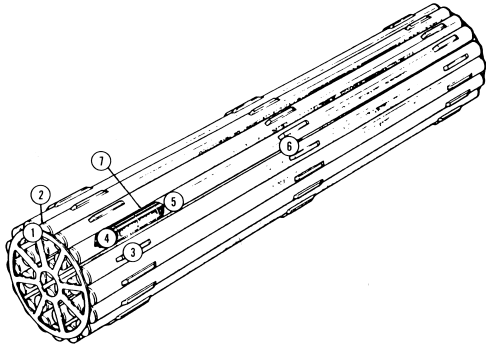


**FIGURE 10** (a) Pressurized water reactor rod-cluster control assembly. (b) Fuel assembly schematic for PWR. [From M. T. Simnad and J. P. Howe (1979). In "Materials Science in Energy Technology" (G. G. Libowitz and M. S. Whittingham, eds.), Academic Press, New York.]

is derived by chemical reprocessing from irradiated fuel containing  $^{238}\text{U}$ . The spent fuel is dissolved in nitric acid, and the plutonium is obtained as a nitrate in the solution. Precipitation of the plutonium is obtained as the hydroxide by adding ammonia, as the peroxide ( $\text{Pu}_2\text{O}_7$ ) by addition of hydrogen peroxide, or as the oxalate with oxalic acid.  $\text{PuO}_2$  is obtained by heating the hydroxide, peroxide, or

oxalate in hydrogen at  $500\text{--}800^\circ\text{C}$ . The  $\text{PuO}_2$  is mixed with  $\text{UO}_2$  for use in fast or thermal reactor fuels (15–20%  $\text{PuO}_2$  in fast reactor fuel, 3–5% in thermal reactors). The mixed oxide  $(\text{U,Pu})\text{O}_2$  can be prepared by coprecipitation or by mechanical mixing.

The large-scale production of plutonium-bearing fuels involves special mechanized equipment designs,



**FIGURE 11** Fuel bundle for CANDU reactor: 1, Zircaloy structural end plate; 2, Zircaloy end cap; 3, Zircaloy bearing pads; 4,  $\text{VO}_2$  pellets; 5, Zircaloy fuel sheath; 6, Zircaloy spacers; and 7, graphite coating. [From M. T. Simnad and J. P. Howe (1979). In "Materials Science in Energy Technology" (G. G. Libowitz and M. S. Whittingham, eds.), Academic Press, New York.]

improved shielding, rapid analyses, and continuous accountability. The major problems in the production of the mixed oxide fuels for fast breeder reactors are as follows.

1. Contamination or radiation exposure of personnel.
2. Criticality incidents and facility contamination.
3. Plutonium inventory and safeguards control.
4. Uniformity of plutonium enrichment.
5. Improved fuel closure methods and nondestructive tests.
6. Fuel assembly techniques.
7. Shipping methods for fuel assemblies and plutonium.
8. Systems for data storage and retrieval.
9. High costs and statistically insignificant information associated with initially low throughputs of plutonium fuel.
10. Lack of statistically significant data from well-characterized materials irradiated under well-known conditions.
11. Reactions between fission products and fuel cladding.
12. Fission product migration.
13. Fuel melting or slumping.
14. Transient performance of fuel and assemblies.
15. Fission gas release.
16. Inadequate knowledge of relationships of oxygen-to-metal ratio, grain size, density, and other properties to irradiation behavior.
17. Inadequate funding for many research and development activities.

Pellets of  $\text{UO}_2\text{-PuO}_2$  or  $(\text{U,Pu})\text{O}_2$  are prepared by cold pressing and sintering either a mechanical mixture of the oxides or, preferably, a chemically prepared solid-

solution powder, respectively (Table VI). Mechanical mixing should be done by wet ball milling. The important variables that influence the sintering process include the nature of the oxide particles (morphology and size distribution), the ratio of uranium to plutonium oxides, the sintering atmosphere, and the green density. The presence of up to 10%  $\text{PuO}_2$  particles reduces the sinterability of  $\text{UO}_2$  in a mechanical mixture. Sintering in an atmosphere of  $\text{CO-CO}_2$  mixture results in higher density pellets. However, with solid-solution oxide  $(\text{U,Pu})\text{O}_2$ , the sinterability in hydrogen is enhanced with  $\text{PuO}_2$  content and is better in hydrogen than in carbon dioxide or argon atmospheres. The optimum temperature for sintering the mixed oxide is  $1400^\circ\text{C}$ .

There are several methods for the production of the lower smear density fuel pellets (80–85% of theoretical) that are specified in fast breeder fuel designs to improve the irradiation stability of fuel pins. The composition of the sintering furnace atmosphere has to be carefully adjusted so as to control the oxygen-to-metal ratio in the hypostoichiometric range. The limited contact or remote operation equipment must be highly reliable, and maintenance, which can be time consuming and costly, must be minimum. The sintered pellets (about 5-mm diameter) are centerless ground to meet the required dimensional tolerances of 1%. Proper control of pellet production processes could minimize or even eliminate the grinding operation. The fuel pellets are inspected at the Hanford Engineering Development Lab (HEDL) by means of rapid (5 pellets/sec) test instruments, which perform complete characterization of 100% of the core loading of pellets (3 million in the Fast Test Reactor at the Hanford Engineering Lab).

The operational experience with mixed oxide  $(\text{U,Pu})\text{O}_2$  fuel in LWRs has been excellent. Fuel assemblies have exceeded 40 MWd/kg average and 70 MWd/kg peak burnups.

### 3. Thorium Oxide

$\text{ThO}_2$  is miscible with  $\text{UO}_2$  over the entire composition range. The low- $\text{UO}_2$  compositions used in the fuels are stable in air at elevated temperature because thoria is stable in oxygen up to its melting point ( $3300^\circ\text{C}$ ). The only stable oxide of thorium is  $\text{ThO}_2$ , and no higher oxides are formed. It has a cubic fluorite structure and low thermal conductivity.  $\text{ThO}_2$  fuel pellets can be fabricated by methods similar to those described for  $\text{UO}_2$ , and the densities achieved are sensitive to the characteristics of the starting powder material, which can be produced by thermal decomposition of the nitrate, oxalate, hydroxide, or carbonate. Higher densities at lower temperatures can be achieved with oxide powder derived from decomposition of the carbonate.  $\text{ThO}_2\text{-UO}_2$  mixtures are formed by coprecipitation

**TABLE VI Highlights of Typical Mixed-Oxide Fabrication Process (HEDL)**

PuO <sub>2</sub>	10–20 m <sup>2</sup> /gm surface area
Calcining	675°C soak, 60–75 min soak time, 200°C/hr rise, SS crucible
Screening PuO <sub>2</sub>	–325 mesh, 6–12 m <sup>2</sup> /gm surface area
Screening UO <sub>2</sub>	–100 mesh, 8 m <sup>2</sup> /gm surface area
Blending	(1) Hand premix through 20-mesh screen 6 times (2) V-blend 10 min
Ball milling	Low-ash rubber-lined mills, 12-hr cycle, tungsten carbide media, surface = 4–10 m <sup>2</sup> /gm
Binder addition	3 wt. % Carbowax 20 M in H <sub>2</sub> O (20 wt. % solution)
Drying	3–4 hr at 70°C
Granulation	–20 mesh
Re-drying	3 hr at 70°C
Prepressing	1/2 in. diameter die, 30–50 kpsi
Granulation	–20 mesh
Pellet pressing	20–30 kpsi, 53% theoretical density green density
Binder removal	
Atmosphere	Argon-8% H <sub>2</sub> 8 SCFH
Rate of temperature rise and cooling	120–140°C/hr (200°C/hr max)
Soak temperature	350–650°C
Soak time	4 hr
Batch size	3 kg max
Sintering	
Atmosphere	Argon-8% H <sub>2</sub> dried to <1 ppm H <sub>2</sub> O 1–6 SCFH
Soak temperature	1650°C
Soak time	4 hr
Batch size	6 kg max
Cycle	23 hr (The furnace is evacuated at 850°C during the cool-down to reduce gas and moisture content of sintered pellets.)
Gauging	Micrometers and dial indicators 0.001 in. accuracy
Grinding	Centerless (dry)
Pellet loading and fuel pin assembly	
Decontamination	
Closure welding	TIG weld, helium atm
Helium leak check	For cladding and weld integrity
Nondestructive testing	Gamma scan for fuel pellet placement and isotopic content
Cleaning and passivating	Caustic base cleaner and HNO <sub>3</sub> , passivating
Surface contamination test	For removable and fixed alpha
Packaging and storage	

of their salts or by mechanical mixing. Granulated mixtures of the oxides containing a binder (Carbowax) and lubricant and up to about 50% U<sub>3</sub>O<sub>8</sub> can be cold pressed into pellets and sintered in hydrogen or in air at 1750–1850°C to form the (Th,U)O<sub>2</sub> solid solution. The U<sub>3</sub>O<sub>8</sub> is prepared by heating UO<sub>2</sub> powder in air at 1000°C. The addition of about 1% CaO promotes the sintering of ThO<sub>2</sub> in air. (Calcium has a low neutron-capture cross section.) Sintered thoria exhibits good corrosion resistance in high-temperature water and in sodium.

The sol-gel process has been successfully used to prepare dense, spherical particles of ThO<sub>2</sub> and (Th,U)O<sub>2</sub> for

sphere-pac and coated particle fuels. The thoria is dispersed in water from nitrate solutions by slow heating and steam denitration to form a stable sol from which spherical particles are produced. The sol droplets are injected at the top of a tapered glass column containing an upward flow of 2-ethylhexanol (2-EH). The water from the sol particles is slowly extracted by suspension in the 2-EH, and the gelled spheres drop out of the column. Coalescence of the particles is prevented with surfactants in the 2-EH. The sol-gel spheres are dried in steam and argon at 220°C and sintered in hydrogen at 1300°C.

### C. Carbide Fuels

There are three compounds in the uranium–carbon system: UC,  $U_2C_3$ , and  $UC_2$ . The UC has the highest uranium density, has a face-centered cubic (fcc) structure, and is stoichiometric at a 4.8 wt. % carbon composition. At lower carbon contents, free uranium metal is present, generally at grain boundaries and as small particles within the grains. The hyperstoichiometric UC exhibits a Widmanstatten structure of  $UC_2$  platelets in the UC grains. The monocarbides of Th, U, and Pu have the fcc NaCl structure and are completely miscible. ThC and UC are stable to their melting points. The tetragonal  $CaC_2$  structure of  $UC_2$  transforms to a fluorite-type lattice at about 1700°C.

Compared with  $UO_2$ , UC has a higher uranium density, has at least five times greater thermal conductivity, and is almost as refractory.

The compatibility of UC with stainless steel depends on the stoichiometry and whether the gap between pellet and cladding is filled with gas or sodium. The cladding acts as a sink for carbon, and sodium enhances the transport of carbon from the fuel to the cladding. The decarburized fuel tends to crack, and the carburized cladding loses ductility quickly, even at 600°C. With a gas gap, there is no significant interaction with stainless steel cladding below about 800°C.

Mixed-carbide fuels have also been studied in order to broaden the single-phase field in UC so that the undesirable second phases are not present or are rendered harmless. Alloying UC with ZrC appears to provide the most promising combination, since ZrC additions increase the melting point and lower the vapor pressure. Both chromium and vanadium addition to UC have been reported to improve the compatibility of the carbide fuel with stainless steel cladding.

Uranium carbides may be prepared by a number of methods, including reaction of uranium with carbon, reaction of uranium dioxide with carbon in vacuum at elevated temperatures, or the reaction of uranium powder with a hydrocarbon such as methane.

The cold pressing is carried out in hardened steel dies. The carbide powder is first mixed with about 0.5–5% of binder lubricants, such as paraffin, camphor, Carbowax, cetyl alcohol, or beeswax dissolved in nonaqueous inert solvents such as benzene, isopropyl alcohol, or methyl alcohol. The bonded carbide powder is granulated by forcing through a screen and then loaded into the dies. The green density of the cold-pressed pellets may be as high as 80% of theoretical, and the sintered pellets may be densified to about 90% of theoretical. The optimum sintering condition is 1800°C for approximately 4 hr.

By using a feed of spherical particles of controlled particle sizes, fairly high density uranium carbide fuel pins

can be fabricated by means of vibratory packing directly into the cladding tube, as with sphere-pac oxide fuel.

Arc melting and casting of uranium carbide fuel rods have been achieved in large quantities. In the skull-melting procedure the uranium carbide is arc melted in a water-cooled crucible with a graphite-tipped electrode. The molten carbide is contained in the shell or skull of solid uranium carbide in the crucible and cast into suitable molds by tilt pouring or by centrifugal casting. The castings generally have very high densities (>99%).

The mixed carbides, UC–PuC, offer a significant improvement in breeding and a shorter doubling time through their higher metal-atom density and thermal conductivity. The disadvantages of the carbide fuels are the difficulty of control of composition (stoichiometry) to be compatible with the cladding and the sodium coolant and to minimize swelling, and the lack or adequate irradiation experience at high burnups and elevated temperatures. Cost studies indicate that carbide-fueled fast reactors have a fuel-cycle cost advantage over the oxide-fueled reactors.

Compared with mixed-oxide fuels, the mixed-carbide fuels have higher heavy-metal density (13 versus 9.7 g/cm<sup>3</sup>), better neutron economics, greater thermal conductivity (10 times greater), higher linear heat rate capability [1485 W/cm (45 kW/ft) for carbide] and specific power [up to 500 W/g (U + Pu)], improved breeding gain, and lower fuel-cycle cost when compared with oxide fuel at the same burnup.

With carbide fuels prevention of carbon transport from the fuel to the cladding material or vice versa requires control of the chemical potential of carbon in the fuel (e.g., by using stoichiometric UC composition: by stabilizing the fuel with small additions of Cr, V, or Mo; or by Cr plating the pellets). Both carbide and nitride fuels have good compatibility with sodium but relatively poor oxidation resistance.

### D. Nitride Fuels

Uranium mononitride UN has been studied fairly extensively as a reactor fuel but has not been used in any reactor. It possesses a combination of desirable properties: a FCC NaCl structure, a high melting temperature (2850°C for congruent melting at and above 2.5 atm of nitrogen), good thermal conductivity, high uranium density (14.32 g/cm<sup>3</sup>), compatibility with most potential cladding materials, and good irradiation stability and fission product retention. A disadvantage is the parasitic capture of neutrons in the transmutation of nitrogen atoms by the  $(n, \alpha)$  and  $(n, p)$  reactions and the release of nitrogen during the burnup of nitride fuel. The stability of UN in air is much higher than that of UC. The evaporation of UN has been studied under various conditions at temperature near 1700°C. Under dynamic vacuum conditions or sweep-gas conditions, the

rate of evaporation of nitrogen approaches that of uranium, resulting in the evaporation of UN without leaving an accumulation of liquid uranium on the surface of the UN.

Specimens of UN have been prepared by three fabrication methods: (1) hot isostatic pressing, (2) cold pressing and sintering, and (3) direct reaction of uranium with nitrogen through consumable arc-melting and casting procedures. The first two techniques use  $U_2N_3$  powder formed by reacting uranium with nitrogen at  $850^\circ C$  followed by decomposition to UN at about  $1300^\circ C$  in a dynamic vacuum.

## E. Fuel Element Cladding and Duct Materials

The reactor core is an assembly of fuel element bundles or subassemblies that contain the fuel rods. The cladding materials serve to maintain the design configuration of the fuel rods and to protect the fuel from the coolant medium. The cladding also prevents the fission products from entering the primary system of the reactor.

The fuel subassemblies contain spacers to maintain the coolant channel configuration. The ducts surrounding the fuel rods bundles direct the flow of coolant through the core. The ducts provide strength and support to the subassemblies and must not distort in service. The materials selected for the cladding, duct, and core structure must retain their integrity in the core environment and also have low neutron-absorption cross sections. The latter requirement limits the choice of materials to a very few, namely, aluminum, magnesium, zirconium, beryllium, graphite, and thin stainless steel for thermal reactors. In fast reactors, however, the neutron cross sections are lower, and stainless steels and nickel alloys are used extensively.

The principal stresses to which the cladding is subjected arise from the swelling of the fuel and the release of fission gases, as well as from the pressure of the coolant and the thermal stresses. There are also complex stresses resulting from fluctuating stresses at cracks in the fuel pellets and at pellet–pellet interfaces. The cladding material must possess adequate strength, ductility, and corrosion resistance. It must also be compatible with the fuel and be resistant to irradiation damage. Heat transfer considerations play an important role in the design of the cladding and may call for spiral fins or surface roughening or require spacers in the form of wire wrapped around the cladding in a spiral form or grids welded to the ducts.

## V. FUEL ELEMENT DESIGN AND OPERATION

### A. Design of Fuel Elements

The type and requirements of the reactor govern the design and the selection of the fuel elements and materials

for the reactor. The core design must include inputs from reactor physics, engineering (fluid flow, heat transfer, and stress analysis), materials science and technology, safety, and economics. This process is always based on an iterative procedure, whereby information from experimental results and operational experiences are factored into the refinement of the design.

The fuel rods are grouped together into subassemblies, which may be enclosed by metallic ducts that act as structural members and coolant-flow channels. In pressurized water reactors, the fuel rods are not enclosed by ducts but are spaced by means of metal grids placed at intervals down the subassemblies or by wire spacers wrapped around them.

The core designer must have an appreciation of the numerous complex phenomena that occur in fuel elements during operation. These include the results of the fission process in the fuel; the variations of temperature, fission rate, and neutron flux in the core; and the sensitivity of the fuel, cladding, and core structural materials to these factors. In addition, the problems of heat and mass transfer, corrosion, irradiation damage, and fuel–clad chemical and mechanical interactions must be assessed.

The temperature limitations in the reactor core are based upon factors such as the melting temperature of the fuel and cladding materials, phase changes in the fuel, corrosion rates of the cladding and structural materials, and maximum heat flux limits set to prevent continuous film boiling of liquid coolants and to retain the integrity of the cladding during accidental power transients.

The cost of fuel failures that lead to reactor shutdown is higher than the cost of avoidance of fuel failure because the purchase of replacement power adds a considerable incremental cost (about a million dollars per day for a large power reactor). The parameters that affect fuel costs include the following: incomplete burnup, leak testing and replacement of fuel pins, the increased storage capacity and shipping and reprocessing required for failed fuel elements, and derating of the fuel. Also, fuel failures increase the costs associated with operation and maintenance of the reactor, such as maintenance of radwaste systems and limiting personnel exposure to radiation. In recent years the typical rates of fuel rod failures in power reactors have been commendably low (less than 0.001%). The goal now is to design fuel rods that are more tolerant and forgiving of reactor operational procedures, particularly the rates of power increases and power cycles.

### B. Operational Factors

Operational experience with nuclear fuels in power, test, and research reactors is being continually evaluated. The



quality assurance system incorporates the various stages of design, fabrication techniques, and performance of the fuel elements. The quality assurance circuit for fuel elements includes the major tasks of fuel technology, namely, to determine the properties of the materials, develop fabrication techniques, and establish testing and inspection methods for quality control. The primary factors that limit the performance of fuel rods are pellet-clad interaction, fission gas release, and rod boxing. Much effort is being expended on the development of computer codes for fuel rod design and evaluation of the operational limits under steady-state and transient emergency conditions. The design codes have been benchmarked against operating experience and can be applied to a wide range of irradiation conditions and fuel parameters.

The important economic effects of fuel design, fuel fabrication methods, and quality control on nuclear power generating costs have been assessed in some detail. The major factors that reduce costs include decreasing fuel failure rates, increasing margin to thermal operating limits in the fuel elements, and improving fuel utilization. Thus, the performance and reliability of the fuel have a marked effect upon power generating costs. The fuel-cycle costs are approximately 25% of the nuclear operating costs. However, improved fuel performance does influence the costs of plant capital, operations, and maintenance and the total electrical system generation costs. For example, an increased core output and fuel reliability increases the plant capacity factor and thereby reduces the total system reserve requirements and costs, particularly by decreasing the need for costly replacement power.

The performance requirements for ceramic nuclear fuel elements include the following items:

1. Dimensional stability to high fuel burnups
2. Fission product retention
3. Corrosion resistance
4. Fabricability
5. Economic advantage
6. Inspectability
7. Chemical reprocessing and recycling

There are numerous variables that influence the complex relationships that govern the operating characteristics of oxide fuel elements. These include the configuration and dimensions of the fuel pellets, the compositions of the cladding, fabrication methods, fuel center temperatures, and heat fluxes. There has to be a compromise between the conflicting requirements of the materials scientist, the thermal designer, and the nuclear physicist. Long-term in-pile tests under simulated reactor operating environments are the principal means for evaluating the performance of fuel elements.

In addition to the microscopic crystal and defect structural features of the specific substances, both fuel and cladding, the macroscopic variables are neutron flux and fluence, fission rate and distribution, heat flow, mass flow, their conjugate thermal and chemical gradients and conductivities, temperature, chemical potentials, external pressure and other forces, coefficients of expansion, elastic moduli, creep coefficients, and other constitutive relationships. In spite of the complexity, empirical numerical relationships among some of the variables and processes have been devised and incorporated in computer programs that afford some degree of correlation and prediction of the performance of fuel elements and are of use in the design of reactors and of fuel element testing programs.

The practical effects on the performance and life of the fuel elements have to do largely with mechanical deformation, corrosion and failure of the cladding, and possible changes in the distribution of heat-producing fissionable materials. Five major mechanisms may move the fuel radially toward the cladding in an operating fuel element: thermal expansion, fuel swelling due to the accumulation of fission products, thermal ratcheting, mechanical ratcheting of cracked fuel, and thermal diffusion. These mechanisms are interdependent and must be evaluated for the full service life of an element. At the same time, the cladding undergoes changes in dimensions, ductility, and strength due to fast-neutron-induced voids and loops, dislocation tangles, helium bubbles at grain boundaries, and possibly, grain boundary attack by  $\text{Cs}_2\text{O}$ , Se, or Te; this corrosion depending on the chemical potential of oxygen.

The simplest effect of fission product accumulation is the expansion of the solid due to the relative atomic volume of uranium and the fission products, which depends on the chemical state (e.g., cesium metal has a larger atomic volume than cesium ions). Thus, the expansion of  $\text{UO}_2$  per at. % burnup ranges from 0.13 to 0.23% if cesium segregates as  $\text{Cs}_2\text{O}$  and to 0.54% if as Cs metal. In more dense UC, swelling is at least 1.2% per at. % burnup. The chemical state of fission products varies with the initial stoichiometry of the fuel and with burnup; that of some products is indicated in Table IV. In the ranges of higher temperature and temperature gradients, the products move toward some steady-state distribution more or less in accordance with our incomplete notions of the stability and vapor pressure of various species. The major volume changes are due to fission gases, and it is primarily their behavior that has been studied and modeled. Fifteen percent of the fission product atoms are the fission gases xenon and krypton, depending on neutron flux and spectrum; the fractions of the total fission gas atoms generated that are trapped and/or released depend on the

many factors mentioned and govern the behavior of the fuel element.

At low temperature the large krypton and xenon atoms are relatively immobile and are metastably housed singly and in small aggregates within defect structures ranging from one or two vacant sites per atom to voids and bubbles containing many atoms. Surface energy accounts for the confining forces, even for single atoms, and up to bubbles of the order  $1.0 \mu\text{m}$  in diameter where bulk yield and creep strengths prevail. Sufficient vacancies to permit equilibrium of the given bubble with surface forces are provided by the atom displacement mechanisms. In addition, displacement mechanism, both knock-ons and spikes, disperse and move the aggregates, the former termed radiation-induced resolution. Thus, in a reactor even in low-temperature regions, atoms and small bubbles may move fractions of a micrometer per day, resulting in some distribution of aggregate sizes.

However, the dominant effects are at temperatures where thermally activated motion of vacancies are higher. In this range, movement occurs of all sized aggregates of fission gases to traps such as dislocations and boundaries and thence to more stable states, the most stable being a segregated gas phase.

Recent studies of the effects of temperature, thermal gradients, and stress gradients on the nucleation and migration of bubbles have elucidated the influence of these factors on fuel swelling. The bubbles migrate up the thermal gradients toward the fuel center, being held and carried along by lattice defects (dislocations, grain boundaries, precipitates, and also defects by fission recoil damage) until they are large enough to escape from or migrate along the defects. Bubble migration has been postulated to be by Brownian motion for very small bubbles, by surface diffusion when they are larger, and by an evaporation–condensation process at elevated temperatures in very large bubbles (at  $r \approx 10^4 \text{ \AA}$ ). The phenomenon of fission gas resolution in irradiated fuel has been incorporated in the picture. If enough bubbles collect on a grain boundary to touch one another, continuous paths result for escape from the solid. In addition, the operating history of the fuel in the reactor must be considered, since cracks form in the fuel (in grain boundaries at high burnups) during power changes and release fission gases to the fuel–cladding gap. These are some of the processes that have been incorporated in computer codes that have been developed to predict fission gas release and swelling.

A nonsteady-state (or ratchetting) mode of mechanical fuel–cladding interactions during power changes appears to be a primary cause of diametral increases in fuel pins and end-of-life failure of LWR elements.

Fuel rod design requires a knowledge of the fraction of fission gases that is released and the fraction that is retained

in the fuel as gas bubbles. The principal stresses to which the cladding is subjected arise from (1) released fission gas pressure and (2) retained gas in the fuel in bubbles that are restrained by surface tension forces, by the hoop strength of the cladding, and by the creep strength of the fuel.

There are four competing mechanisms: (1) retention of the fission gases in the fuel lattice at low temperature, (2) diffusion and release of the fission gases to the free surface of the specimen at very high temperatures, (3) growth of closed pores at intermediate temperatures leading to swelling, and (4) fission gas resolution from bubbles into the matrix. Hence, the tendency to swell is maximum at some intermediate temperatures.

Segregation of many of the solid fission products takes place in the irradiated fuel. The concentrations of the fission products vary, depending on the isotope, the thermal gradients, and the chemical activity.

The swelling due to solid fission products has been evaluated on a thermodynamic basis by assigning a chemical form to each of the fission products and a corresponding molecular or atomic volume. The nonuniform distribution of the fission products in the fuel does not allow a more quantitative assessment of the swelling. For example, cesium contributes a very large proportion of the swelling, and if it is present as cesium oxide at the fuel–cladding interface, the solid fission product contribution reduces from 0.54% to about 0.23%  $\Delta/V/V$  per 1% burnup.

In very-high burnup mixed-oxide fuel at elevated temperatures, the migration of nongaseous fission products out of the fuel has been observed; this migration reduces the magnitude of the fuel swelling attributed to solid fission products.

Fission gas release from thermal and fast flux irradiations has been shown to be different because of the much larger flux depression in thermal flux irradiations. In a thermal flux, there is a higher local volumetric fission rate near the surface regions of the fuel than at the center, with the rate differing by a factor as high as two between the surface and the center. Hence, the fission gas concentration is larger in the cooler surface regions of the fuel body. In a fast flux, on the other hand, there is a relatively uniform volumetric fission rate and fission gas generation rate.

Another difference between thermal and fast flux irradiations is that the fission gas yield per fission is greater in a thermal flux than in a fast flux. In a thermal flux, the  $^{135}\text{Xe}$  captures a neutron to yield  $^{136}\text{Xe}$ , which remains gaseous instead of decaying to  $^{135}\text{Cs}$ . Hence, there is more fission gas present in fuel irradiated in a thermal flux. There is also a tendency toward lower fission gas release at lower linear power densities.

The fission products Cs and I combine to form caesium iodide, which migrates down the temperature gradients in the fuel rods to the fuel-clad gap and through the gap to the coolest regions. Problems of internal corrosion and strain deformation in the cladding have been ascribed to the presence of these fission products.

### C. Fuel Element Modeling

During the past decade a lot progress has been made in the computer modeling of nuclear fuel elements. This approach provides a quantitative basis for the design of fuel elements and allows a more rational planning and analysis of irradiation tests. However, it is essential to generate reliable input data on the properties of the fuels and materials for insertion into the many subroutines of the codes. The publication of data compilations for the light-water reactors (MATPRO) and for the fast breeder reactors (NSMH) has been an invaluable aid in code development studies.

Computer codes have been developed in the United States and Europe to describe fast breeder and light-water reactor fuels. They address the complex processes occurring during the life of operating fuel elements as functions of the power histories by rigorous analyses based on first principles. These codes have been well documented and are on file at the Argonne National Laboratory, Argonne, Illinois 60439, USA. They can be obtained on tape and IBM cards with user's manual.

The most challenging problem in the development of the fuel element modeling codes has been the complex effects of neutron irradiation on materials and fuels. The cladding and structural stainless steel alloys in fast reactor cores swell through void formation by migration of the vacancies formed by fast neutron irradiation. This leads to a movement of the cladding away from the fuel and thereby to a reduction of fuel-induced stresses. Radiation-induced creep could cause further movement of the cladding under the pressure of fission gases.

The ductility of the irradiated cladding is markedly reduced (to less than 1%), and little deformation can be accommodated by the cladding. The alloys also lose ductility through defect cluster formation and as a result of helium formation by  $(n, \alpha)$  transmutation reactions. The defect clusters are effective at the lower temperatures (0.2–0.5 melting temperature). The helium atoms segregate at grain boundaries and dislocations at elevated temperatures (above approximately 550°C), resulting in loss of ductility and creep strength. The swelling-temperature relationships follow a bell-shaped curve, with the peak swelling temperature for austenitic stainless steel being approximately 500°C. The nonuniformity of temperature distributions and neutron fluxes in the core can lead to severe

bowing of the cladding and the ducts. The factors involved in irradiation damage are illustrated in Figs. 12–17.

## VI. FUEL ELEMENT EXPERIENCE IN POWER REACTORS

### A. Light-Water Reactors

The fuel element designs attempt to meet the goals of economical fuel cycle costs within the framework of the regulatory requirements for safe plant operation. The power distribution and shutdown capability are maintained by means of control rod systems in the reactor core. A large PWR [1000 MWe] plant core contains about 200 fuel assemblies, consisting of Zircaloy-clad uranium dioxide pellets. The fuel assemblies are 3.8 m in length and are arranged within a 3.4 m diameter region. In the BWRs there are about three times as many assemblies because the fuel rods are larger in diameter than those of the PWR.

The remedies that have been applied to solve the fuels problems have been quite effective, resulting in marked improvements in fuel performance in recent years in the LWRs. An important example of this is the development of stable fuel pellets by control of their grain size, pore structure, and density and the back-filling of the fuel rods with pressurized helium to prevent cladding collapse and to improve the gap conductivity at high burnups. The improved reliability of the fuel elements, and the establishment of safe margins between the operating limits and the damage limits in the fuel, have been important factors in improving plant capacity factors and availabilities.

The property data for LWR fuel rod materials are available in the handbook *MATPRO*, which has been compiled with support from the U.S. Nuclear Regulatory Commission. Extensive studies have been in progress during the past decade to develop fuel designs that will achieve much higher burnups (over 4000 GJ/kg M), so as to allow longer fuel cycles (18-month cycles) with high reliability and to survive ramps to about 60 kW/m and 6–24-hr holds at peak power even after high burnups. The incorporation of a thin copper or zirconium barrier between the fuel and the cladding has been a successful means to attain this goal.

The basic design limits for the fuel elements in LWRs are set by heat transfer, clad strain, center melting of the  $UO_2$  fuel, and endurance of the fuel pin and element, including corrosion, fretting, vibration, and mechanical and metallurgical damage. Current BWR and PWR peak local burnups in fuel assemblies are on the order of 50 MWd/kg U and peak steady-state linear heat ratings of up to 630 W/cm, with a fission-gas release value of about 30%.

The most serious problem that has occurred in fuel element operational experience is fuel densification, which

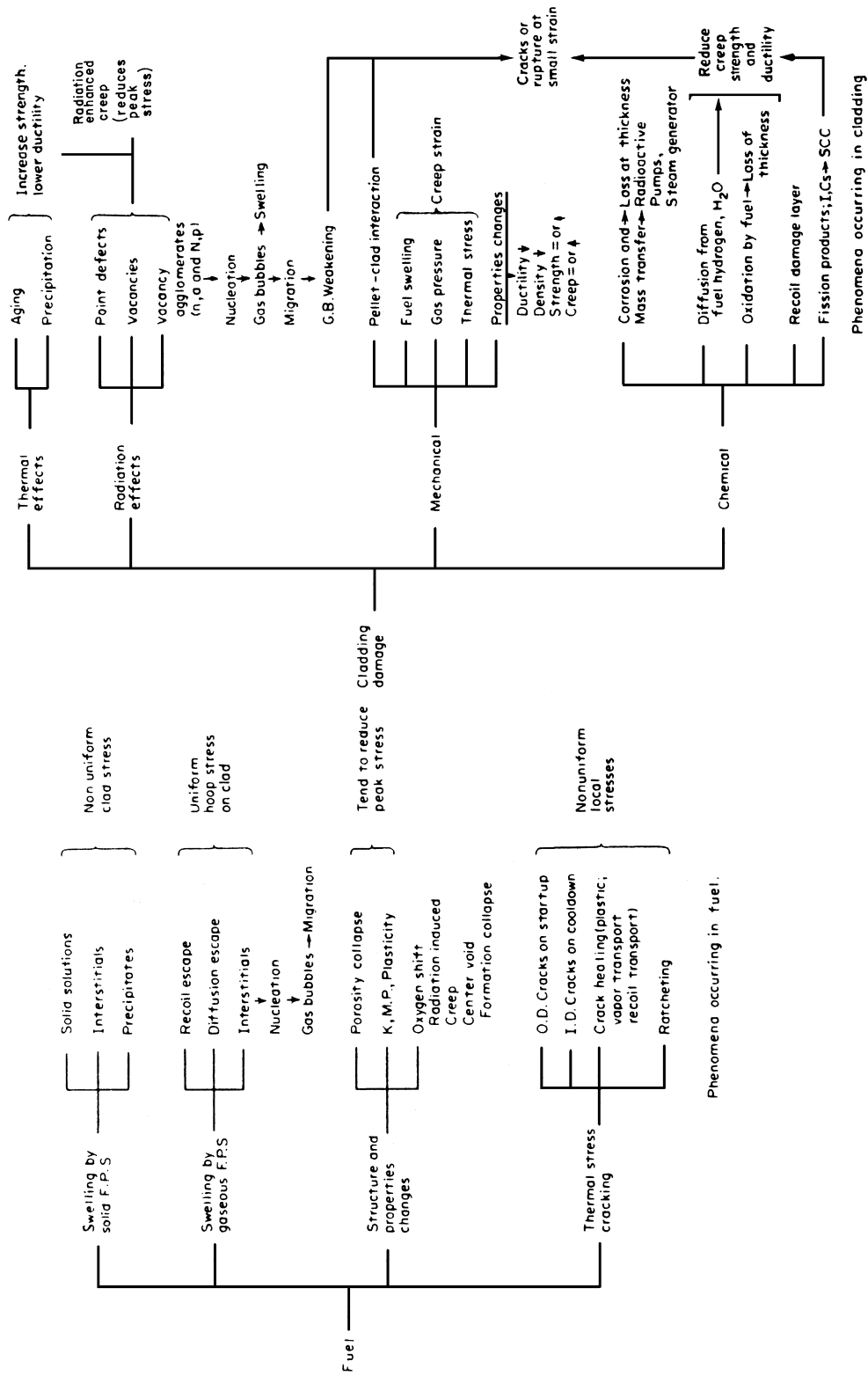
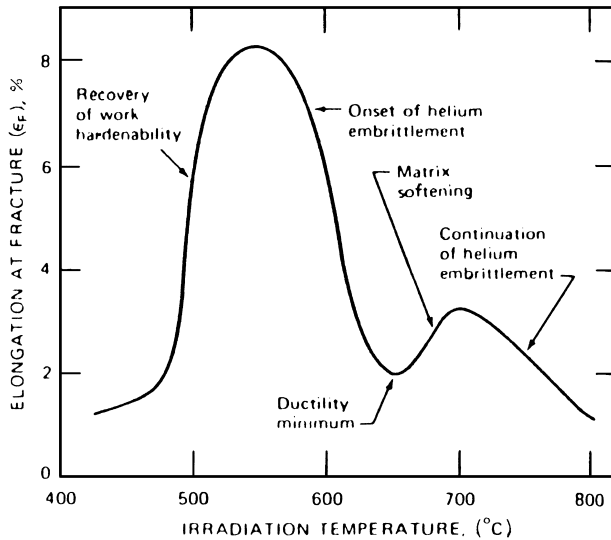


FIGURE 12 Phenomena occurring in cladding and fuel. [Courtesy of B. R. T. Frost.]



**FIGURE 13** Effect of irradiation temperature on the ductility of stainless steel. [Courtesy of D. Olander.]

results in collapsed sections in fuel rods. This effect was observed during 1972 in several large PWRs. The cladding collapses were found to have resulted from the occurrence of axial gaps in the fuel pellet columns within the rods. All of the rods with the flattened sections were of the unpressurized type. The inward creep of the cladding was not arrested where gaps in the fuel pellet column occurred until essentially complete flattening had taken place. Completion of the fuel densification process has required less than 2000 hr of reactor operation in the power range. The effects of fuel densification cause a decrease in the heat transfer and increase in the linear heat generation rate of the fuel pellet, resulting in local power peaking and increased stored energy in the fuel rod.

In-reactor fuel densification is ascribed to irradiation-induced reduction of porosity with radiation-enhanced vacancy diffusion in the  $\text{UO}_2$  fuel pellets, thermal sintering, and irradiation-enhanced creep of  $\text{UO}_2$ . Fuel structures



**FIGURE 14** Void structure in irradiated stainless steel. [From M. T. Simnad and J. P. Howe (1979). In "Materials Science in Energy Technology" (G. G. Libowitz and M. S. Whittingham, eds.), Academic Press, New York.]

(controlled pore size and grain size) have been identified that resist densification in-pile. Prepressurizing the fuel with helium also avoids clad flattening.

A gap is provided between the fuel pellets and the cladding to accommodate fuel expansion. Control of the pellet density near 90% and provision of concave or dished pellet ends, and possibly a central hole, also allow accommodation of fuel swelling.

The design limit for the plastic strain in the Zircaloy cladding is 1% (caused by swelling and thermal expansion of pellet). The linear power rating corresponding to this limitation is 930 W/cm.

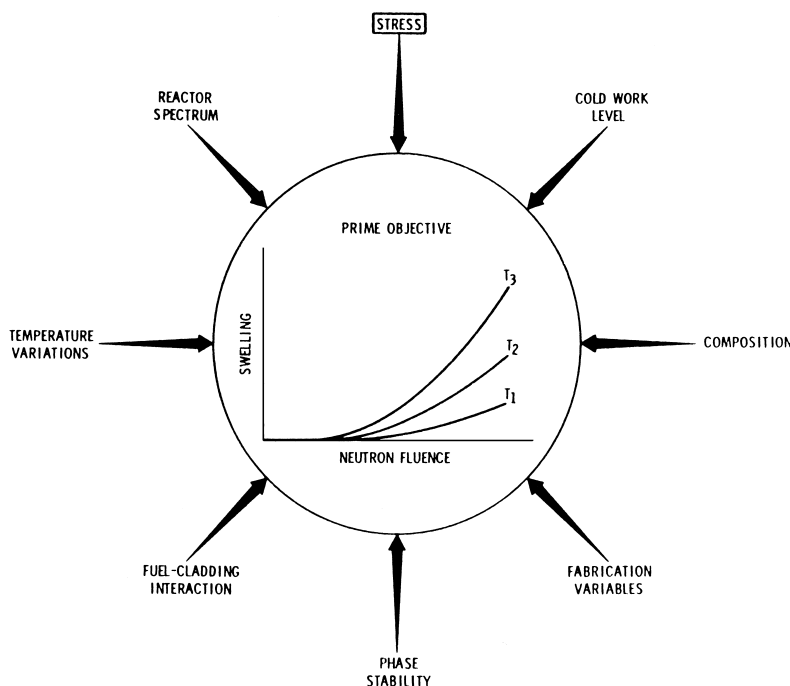
In LWRs the types of fuel failures that have been reported include the following.

1. Clad failure by excessive strain from fuel swelling and fuel-clad interactions
2. Internal corrosion of cladding resulting from presence of moisture, fluoride, or hydrogen in the fuel
3. Wear and fretting of clad by extraneous metallic pieces
4. Defects in the cladding or in the welds
5. Hot spots in the clad due to deposits of scale or poor heat transfer on corner rods

Zirconium alloys were developed for water reactors for fuel element cladding and pressure tubes because of their low neutron cross section, adequate strength in the operating temperature range, and satisfactory resistance to corrosion by water at high temperatures. In the United States, over three million Zircaloy-clad  $\text{UO}_2$  fuel rods have operated in LWRs.

The Zircaloy cladding must withstand thermal, bending, and hoop stresses and resist corrosion. The corrosion rate of the zirconium alloy and the hydrogen embrittlement accompanying excessive corrosion limit the coolant temperature and, hence, influence the thermal efficiency and capital cost of water reactors. The design criteria must make allowance for the degradation of heat transfer conditions and loss of ductility with time and temperature due to the buildup of the corrosion film, hydride formation (design limit 600 ppm), and crud buildup. The maximum allowable strain in the zirconium alloy cladding is set at 1% throughout the core life. One cause of low ductility is the precipitation of hydride platelets normal to the stress direction. The fission gas pressure is limited by means of a plenum space to accommodate the gases released from the fuel pellets (about 0.116 ratio of plenum void space to volume of fuel) (see Figs. 9 and 10).

The zirconium alloy claddings are also susceptible to hydriding on the internal surfaces from reaction with hydrogenous impurities in the fuel rod (e.g., adsorbed moisture, the presence of fluoride contamination, and



**FIGURE 15** Factors influencing swelling. [From M. T. Simnad and J. P. Howe (1979). *In* "Materials Science in Energy Technology" (G. G. Libowitz and M. S. Whittingham, eds.), Academic Press, New York.]

hydrocarbons). These impurities can be eliminated by drying the fuel in the cladding during fabrication (approximately 250°C for a day). In PWRs the corrosion rate (0.1–0.3 mg/dm<sup>2</sup>/day) at 300–350°C of Zircaloy is increased slightly by irradiation. In BWRs, there is a significant increase (up to tenfold) in the corrosion rate of Zircaloy because of the radiolytic oxygen in the BWR coolant, but the rate of hydrogen pickup is similar for both types of reactors.

## B. Heavy Water Reactors

In PHWR-CANDU and SGHWR reactors, the main structural materials are zirconium and aluminum alloys. The use of heavy water as a moderator provides good neutron economy and permits a wide range of possible fuel cycles (including Th–<sup>233</sup>U or U–Pu) and fuel management schemes. The UO<sub>2</sub> fuel elements are positioned in Zircaloy-2 pressure tubes that pass through an aluminum calandria containing the heavy water moderator (see Fig. 11).

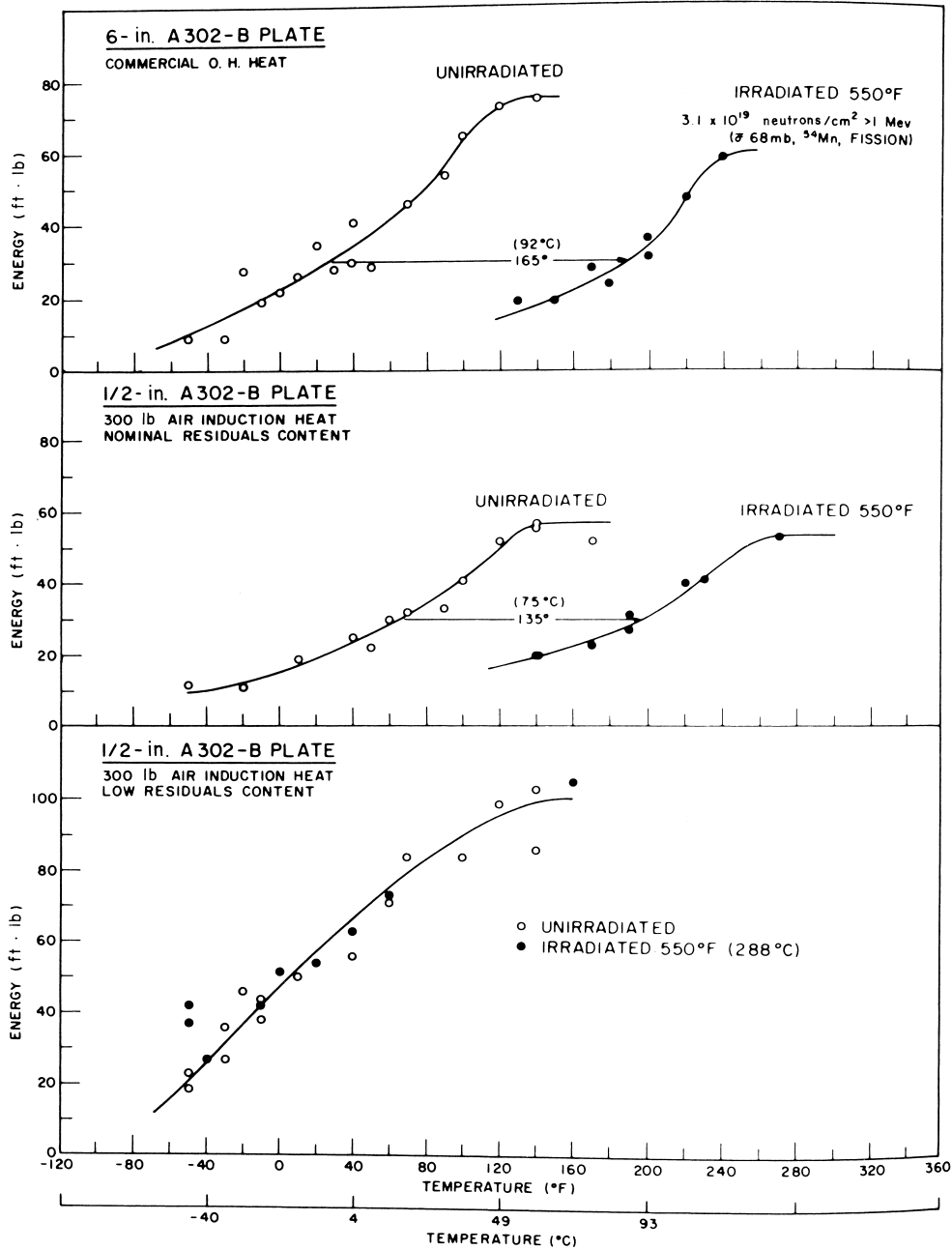
In the CANDU reactors the natural UO<sub>2</sub> pellet fuel is clad with Zircaloy-4, and the fuel rods are separated by Zircaloy-4 spacers brazed to the cladding. The fuel elements are made up of bundles of 28 rods. The maximum fuel rod rating is about 690 W/cm. The fuel temperature is 400°C surface and 2000°C center. The operational experience with the fuel elements in the CANDU reactor has

been highly satisfactory. A recent modification has significantly improved the fuel's performance. The new fuel rods include a thin graphite layer between the fuel and cladding, designated CANLUB fuel. This has decreased friction and the strain concentrations in cladding expanded over fuel fragments resulting from power cycling. The mean burnup in heavy water reactors is about 10.5 MWd/kg U, and the maximum specific fuel rod rating is about 20 kW/ft.

## C. Carbon Dioxide Gas-Cooled Reactors

The first generation of commercial nuclear power reactors in Britain and France were cooled by carbon dioxide gas. These reactors were graphite moderated and fueled with natural uranium metal rods clad in magnesium alloys, the performance of which has been covered. The first of these reactors (Calder Hall) started generating electricity in 1956. The second-generation CO<sub>2</sub>-cooled graphite moderated reactors in Britain (the AGRs) use slightly enriched UO<sub>2</sub> clad in stainless steel. These fuel elements can operate at higher temperatures to much greater burnups, giving higher efficiencies and ratings.

The magnesium alloy cladding in the Magnox reactors is finned to improve heat transfer. The "adjusted" uranium alloy fuel has antiratchetting grooves that lock the fuel to the cladding and minimize thermal cycling effects. The fuel temperature has to be kept below 665°C to avoid the phase transformation that occurs in uranium at this



**FIGURE 16** Radiation embrittlement sensitivities of pressure vessel steel. [From M. T. Simnad and J. P. Howe (1979). In "Materials Science in Energy Technology" (G. G. Libowitz and M. S. Whittingham, eds.), Academic Press, New York.]

temperature. These fuel elements have performed very well, allowing high plant capacity factors that tend to compensate for the low thermal efficiency and low burn up of the fuel.

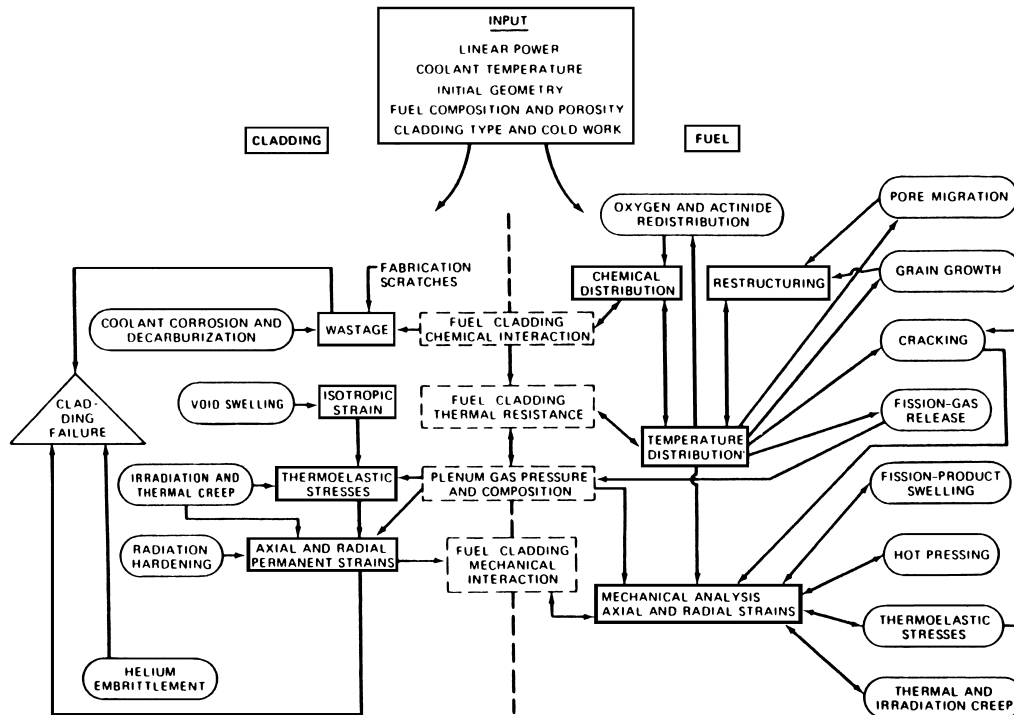
The AGR reactors use a super stainless steel (Fe-20%, Cr-25%, Ni-0.5%, Nb) alloy that has good high-temperature strength and oxidation resistance. The cladding is ribbed to enhance heat transfer. The fuel pellets

are in the form of hollow pellets to accommodate ramp-induced swelling.

#### D. Helium Gas-Cooled Reactors

The high-temperature gas-cooled reactors (HTGR) use helium gas at about 800°C and 5 MPa (685 psi) as the primary coolant, graphite as the neutron moderator and





**FIGURE 17** Interrelation of mechanical, metallurgical, and chemical processes in fuel element irradiation behavior. [Courtesy of D. Olander.]

fuel element structural material, and coated (Th-U) carbide or oxide fuel particles dispersed in a graphite matrix as the fuel. Currently TRISO-UC<sub>2</sub> and BISO-ThO<sub>2</sub> (Fig. 18) are the candidate fissile and fertile fuel particles, respectively, for the large commercial HTGRs being developed. The manner in which advantage may be taken of high-temperature materials deserves emphasis.

The choice of graphite as the moderator and core structural material is based on its unique chemical, physical, and mechanical properties at elevated temperatures and on its very low neutron cross section, satisfactory radiation stability, ease of fabrication, and low cost. The use of the graphite moderator as a diluent of the fuel permits much greater fuel dilution than would otherwise be possible and thereby minimizes radiation damage, increases specific power, and greatly extends the heat transfer surface.

The Th-<sup>233</sup>U standard fuel cycle (see Fig. 2) (with <sup>235</sup>U as the initial fissionable fuel) is used because of its potential for achieving a higher fuel utilization and lower power cost than any other thermal spectrum reactor system. The neutronic characteristics of <sup>233</sup>U are far superior to those of either plutonium or <sup>235</sup>U in thermal systems. A substantial portion of the power comes from fission of the <sup>233</sup>U converted from the fertile <sup>232</sup>Th. The carbon-to-thorium ratio is optimum at a value of 240. This concept promises a conversion ratio as high as 0.85, a steam-heat-power efficiency of about 39%, and a low fuel cost, even with

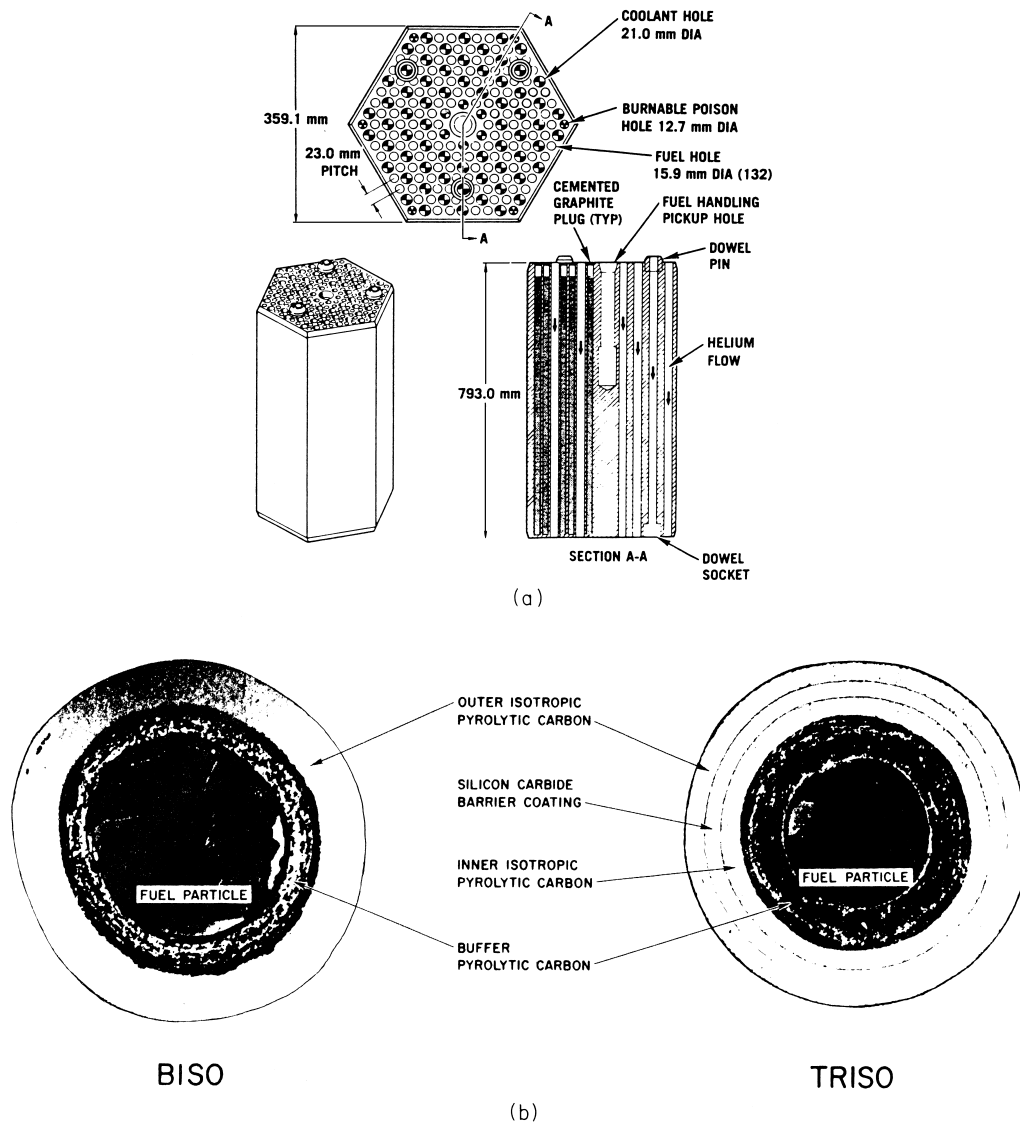
high ore costs. The annual uranium requirements for the HTGR are 30–40% less than for a pressurized-water reactor (PWR) with plutonium recycle operation. Enrichment requirements for the HTGR, but the total separative work commitment over the life of the reactor is about the same for the HTGR and PWR. Because it can use plutonium as a fissile nuclide and provide a burnup of over 100 MWd/kg, the HTGR can also use plutonium more efficiently than light-water reactors.

The use of coated-particle fuel allows the high-temperature operation of the core to very high burnup (80%) of the fissile fuel, with extremely high retention of the fission products. Also, the <sup>235</sup>U fissile particles are segregated from the <sup>233</sup>Np and can be separated during the fuel reprocessing operation. The average fuel burnup of 100 MWd/kg obtainable is by far the highest of all existing thermal reactor systems.

Inherent safety is achieved in the HTGRs by virtue of the single phase and inertness of the coolant, the high heat capacity of the fuel elements and moderator and their refractory nature, the negative temperature coefficient (which provides a safe shutdown mechanism) redundancy in the circulating systems, and assured retention of 4% of the coolant. The fission product plateout activity is limited to low levels that permit direct maintenance.

The fuel exposure, as measured in MWd/kg, is not an important constraint in the HTGR. The average exposure



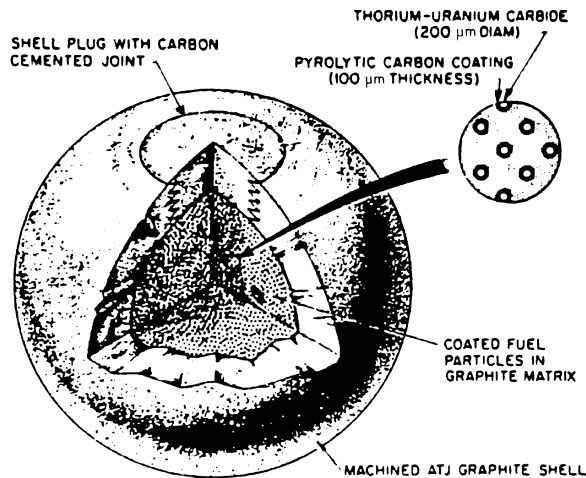


**FIGURE 18** (a) HTGR standard fuel element. (b) Typical coated fuel particles. [From M. T. Simnad and J. P. Howe (1979). In "Materials Science in Energy Technology" (G. G. Libowitz and M. S. Whittingham, eds.), Academic Press, New York.]

is about 95 MWd/kg, but the burnup in individual fuel particles in the HTGR reaches 0.75 fission per initial metal atom, or about 700 MWd/kg. The coatings on the fuel particles have been developed as a result of extensive studies on the production and properties of pyrolytic carbon coatings and irradiation tests on coated particles. The coatings are designed to retain the fission products and to withstand the effects of fuel burnup and irradiation. These include the internal pressure buildup due to fission gas accumulation, fission recoil damage, and stresses arising from fast neutron irradiation-induced dimensional changes in the pyrocarbon coatings. The inner buffer layer of low-density pyrocarbon serves to protect the outer layers from fission

recoil damage and provides void space to accommodate the fission gases, fuel swelling, and coating contraction. The silicon carbide layer in the TRISO coatings decreases the release of certain fission products that migrate readily through the pyrocarbon (e.g., barium, strontium, and cesium).

The pebble bed reactor, developed and built in Germany, is a helium gas-cooled, high-temperature reactor fueled with spherical, graphite matrix fuel elements surrounded by bottom and side graphite reflectors. The fuel elements consist of pyrolytic carbon coated (U,Th) $C_2$  spherical particles dispersed in a graphite matrix and encased in spherical graphite balls, 6 cm in diameter (Fig. 19). The



**FIGURE 19** Spherical AVR fuel element. [From M. T. Simnad and J. P. Howe (1979). In "Materials Science in Energy Technology" (G. G. Libowitz and M. S. Whittingham, eds.), Academic Press, New York.]

continuous on-load refueling is accomplished by removing used fuel from the bottom of the core and adding new fuel at the top.

The AVR reactor has certain basic characteristics that are similar to those of the other helium-cooled reactors. These include (1) the use of graphite both as structural material and moderator, (2) (U,Th)C<sub>2</sub> fuel particles coated with pyrolytic carbon coatings and dispersed in a graphite matrix, and (3) high gas temperatures that allow the use of modern steam cycles. This leads to high efficiency and good conversion of fertile elements into fissile materials (<sup>232</sup>Th into <sup>233</sup>U). The reactor is also compact as are other helium-cooled reactors. The AVR reactor is a prototype designed to yield construction and operation experience and to prove the feasibility of the pebble bed concept.

### E. Fast Breeder Reactor Fuel Elements

Fast breeder reactors increase fuel usage to over 70% of the uranium employed, compared with about 1% in thermal reactors. In a 30-yr period, a fast breeder reactor of 1000 MW(e) capacity would require about 23,000 kg (23 tons) of uranium compared with about 3 million kg (3000 tons) in a light-water-cooled reactor. The fuel-cycle cost is also expected to be significantly lower in fast breeder power reactors than in thermal reactors or fossil-fueled power stations. The cost of power is not strongly influenced by the cost of uranium in fast breeder reactors.

There will be an adequate supply of plutonium (about 600 tons) from LWRs by the year 2020, when commercial fast breeder reactors are expected to be available. This amount of plutonium is sufficient of fuel as many as 200

fast breeder reactors. The value of plutonium is much greater in a fast reactor than in a thermal reactor. Although the technical feasibility and advantages of the fast breeder reactor have been demonstrated, the goal of the fast reactor programs at present is to improve the technology so as to build economically viable fast breeder reactors in the next decade.

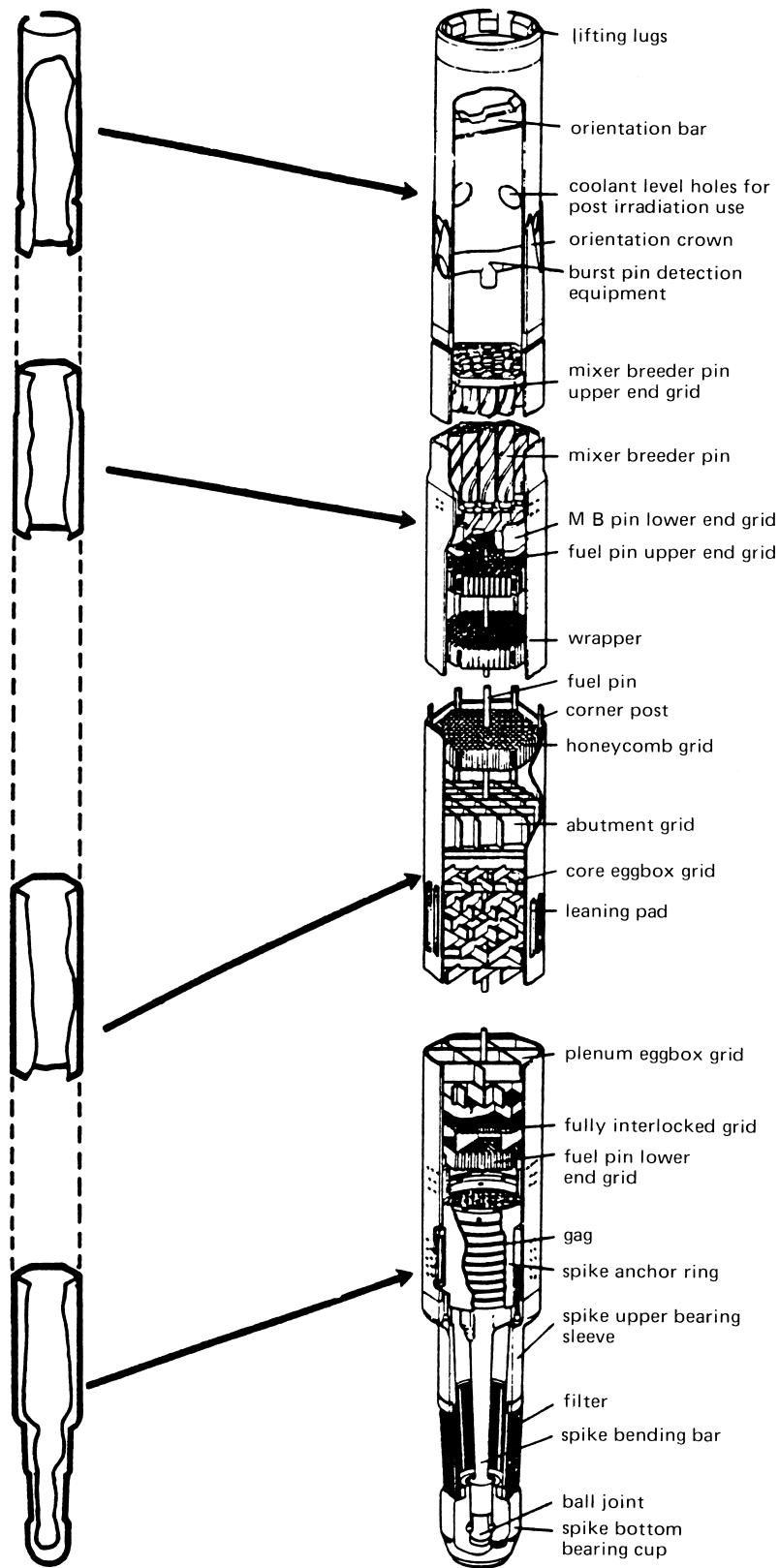
The fuel rods in fast breeder reactors consist of stainless steel clad, mixed-oxide (U, Pu)O<sub>2</sub> fuel. A major development in recent years has been the successful demonstration of the use of ferritic stainless steels and modified austenitic stainless steels, which exhibit adequate resistance to swelling and embrittlement under fast-neutron irradiation. The design of the fuel elements for fast breeder reactors is shown in Fig. 20, and the metallurgical and chemical processes in fuel element irradiation are depicted in Fig. 17.

In a fast breeder reactor, the fuel configuration consists of a highly enriched fuel surrounded both axially and radially by fertile blanket material (natural or depleted UO<sub>2</sub>) in which plutonium is bred. The enrichment required decreases with increasing size of the reactor, ranging from fully enriched fuel for small reactors to about 20% enrichment in a 1000-MW(e) reactor. The breeding process counteracts loss of reactivity with burnup, so that burnups of over 10% of heavy atoms of 100 MWd/kg can be achieved. The main limiting factor on burnup is degradation of cladding and duct materials by radiation damage.

The fuel elements are grouped into hexagonal sub-assemblies that are stacked together to form a compact cylindrical core. The fuel pins are spaced by wires wrapped around them or by grids. The power distribution in the core is flattened by means of zones of differing enrichment in the core. The fuel rods in the enriched region have small diameters to avoid excessive central fuel temperature with the high heat rating that is required. The components of fuel-cycle cost include the following items: fabrication, breeding credit, inventory, and capitalization charges.

Developments in the performance of advanced fuel and structural materials in fast breeder reactors were presented in international symposia (Lyons, France, 22–26 July 1985, and Knoxville, Tennessee, April 1985). The U.S. experience has been summarized in a series of papers from the Hanford Engineering Development Laboratory (HEDL), where the Fast Flux Test Facility (FFTF) has served as a powerful tool for irradiation testing of fuels and materials for commercial reactors. The following section is based upon the information presented in recent HEDL papers, which were kindly furnished by Drs. Ersel Evans and R. D. Leggett.

The FFTF is a 400-MW(t) sodium-cooled fast reactor with a peak fast neutron flux of  $7 \times 10^{15}$  n/(cm<sup>3</sup> sec). The



**FIGURE 20** Fuel assembly schematic for FBR. [From M. T. Simnad and J. P. Howe (1979). *In* "Materials Science in Energy Technology" (G. G. Libowitz and M. S. Whittingham, eds.), Academic Press, New York.]

reactor began routine, full-power operation in April 1982. In the 1000 equivalent full-power days (EFPD) since, the plant has demonstrated excellent performance and reliability. The complex irradiation testing program in the FFTF has yielded extensive technical data. The most encouraging test has been the successful irradiation of 125 standard driver fuel assemblies, containing over 27,000 commercially fabricated fuel pins, to the equivalent of the plant's one-year reference fuel system without a single cladding failure. The tests were continued to proof-test a long-lifetime core system with a number of 3–5-yr components, as well as to evaluate innovative plant improvements that are intended to reduce capital costs and to improve the LMFBR's economic potential. The reactor's on-mission time was 98%.

Important experiments were performed in the FFTF, which included fifty instrumented fuel assemblies. Mixed-oxide fuel, as well as two assemblies containing carbide fuel, have been irradiated in the FFTF. Peak burnup for the mixed-oxide fuel was 155 MWd/kg as of December 1986. The limits to fuel performance were established in these tests. The extended-life fuel systems were tested in the Core Demonstration Experiment, which can take advantage of improved materials that are more resistant to radiation damage and of knowledge gained of fuel assembly behavior in the FFTF. The extension of fuel and component life in the reactor core will result in important reductions in the costs associated with fuel fabrication and inventory, reprocessing and waste disposal, and operations and maintenance. It will also be necessary to reduce the fuel fabrication cost from \$4000/kg to \$3000/kg to reduce the annual fuel cost to less than the LWR. This should be feasible by process simplification, automation, and application of learning.

A special irradiation device in the FFTF, the materials open test facility (MOTA), served to test nonfuel materials in the reactor core under controlled temperature conditions. Over 3000 material samples have been irradiated in MOTA, including ferritic (HT-9) and modified austenitic stainless (D-9 and D-9I) steels to be used in the long-life demonstration test. The results of these tests indicate that mixed-oxide fuel clad with the stainless steel alloys HT-9, and D-9, or with dispersion-strengthened ferritic stainless steel, enclosed in an HT-9 alloy duct, can be expected to achieve the extended burnup goals of 3-yr in-core residence capability. The ferritic alloys appear to be the only clear candidate alloys capable of achieving the 5-yr residence objective, corresponding to 250 MWd/kg peak burnup and  $4.0 \times 10^{23}$  n/cm<sup>2</sup> ( $E = 0.1$  MeV) peak neutron fluence.

An automated, remotely-controlled fuel pin fabrication process was installed in the secure automated fabrication (SAF) facility at HEDL. This facility implements process

improvements and specifications and has produced mixed uranium–plutonium oxide fuel for the FFTF. The fabrication and support systems in this facility are reported to be designed for computer-controlled operation from a centralized control room. The throughput capacity was 6 MT/yr. The FFTF was shut down in 1995.

The inherent safety features of the mixed-oxide fuel in LMFBRs include a large negative Doppler coefficient, a dispersive rather than compactive behavior during design-basis hypothetical accidents, and a low-energy molten fuel–coolant interaction. The latter has been well demonstrated in the BR-5-10 test reactor in Russia, where a core was operated until cladding breaches had occurred in about 40% of the fuel assemblies. The reactor operation was stable, and only a small increase occurred in the level of radioactivity of the primary coolant system.

The operational experience with LMFBR reactors has been very encouraging in all the countries that have built these systems, namely France, Germany, Japan, United Kingdom, the former Soviet Union, and United States. A dozen LMFBRs have been in operation to date, ranging in power from 5 MW(t) to 3000 MW(t) and providing an experience range that now exceeds 70 yr of reactor operation.

## VII. NEUTRON MODERATOR MATERIALS

Moderator materials serve to slow down the high-energy neutrons liberated in the nuclear fission reaction, mainly as a result of elastic scattering reactions. These materials contribute to the conservation of neutrons in a thermal or epithermal nuclear reactor core by slowing them down to the energy levels at which the fission reaction occurs most efficiently. The most desirable properties in moderator materials are low atomic number, small cross section for neutron capture or adsorption, and large scattering cross section for neutrons.

The reactor core is generally surrounded by a neutron reflector, which also serves to conserve neutrons by backscattering the neutrons that have escaped from the core. The critical mass of the fissile nuclide is decreased by the use of a reflector. The same materials that are used as moderators may be used as reflectors in thermal and epithermal reactors. In fast reactors, where most of the fissions are caused by high-energy neutrons, the reflector consists of a dense element of high mass number to minimize moderation of the neutrons that are backscattered into the core. The most commonly used moderator and reflector materials include ordinary and heavy water (deuterium oxide), carbon (graphite), beryllium, and zirconium hydride. In fast reactors, which contain no moderator

in the core, the reflector may be steel and depleted uranium. The choice of moderator and reflector materials for a particular reactor is based upon nuclear considerations and upon operating conditions (e.g., temperature, irradiation damage properties, compatibility with coolant, and cladding). Solid moderator and reflector materials are considered here.

### A. Graphite

Graphite is the most extensively used solid moderator and reflector material for thermal reactors, although its nuclear properties are not as good as those of beryllium or heavy water. It is available in high purity and at reasonable cost. Its mechanical properties, high thermal conductivity, and thermal stability are good up to extremely high temperatures. However, at elevated temperatures, it is attacked by reactor coolants such as air, carbon dioxide, water vapor, and liquid sodium. It also carburizes cladding materials such as stainless steels and zircalloys at high operating temperatures.

The most stable commercial grade graphites are the near-isotropic materials, such as H-451, which is being evaluated for HTGRs. There are few experimental data above  $4 \times 10^{22}$  nvt ( $E > 0.1$  MeV) fluence range, the probable limit of usefulness of graphite in reactors.

The viscoelastic response of graphite materials in irradiation environments has been analyzed. In this approach, the effects of irradiation-induced creep and dimensional changes are considered in the stress analysis. The mechanical response of graphite is assumed to be viscoelastic, and the constitutive relations are inferred from measurements. A computer program has been developed for analysis of plane strain, generalized plane strain, and axisymmetric problems, using the finite element method. The material properties are considered to be temperature dependent as well as neutron flux dependent.

The dimensional-change behavior of nuclear graphites generally is in the pattern just mentioned. In extruded material there is first a contraction in the direction transverse to the extrusion direction and then a turnaround and rapid expansion. In the direction parallel to extrusion, there is a contraction at an increasing and then decreasing rate, followed by a turnaround and expansion. The rapid expansion is associated with porosity generation between filler particles; the isotropic and finer grained materials expand at a lower rate. The initial shrinkage rate is temperature dependent, decreasing up to 800°C and then increasing with increasing temperature up to 1200–1400°C.

The thermal conductivity of the graphites is primarily by phonons and is markedly reduced by irradiation at low temperature. The rate of reduction declines, and the conductivity approaches a saturation level, which in-

creases as the irradiation temperature increases. Eventually, when irradiation-induced expansion starts, the conductivity again decreases, probably because of internal cracking. The time constant for approach to saturation appears to increase linearly with irradiation temperature, whereas the conductivity after saturation increases exponentially with irradiation temperature.

The irradiation-induced creep of graphite has been studied. The transient creep strain and the steady-state creep constant increase with increasing irradiation temperature over the interval 500–1200°C. For different graphites, the transient creep strain and steady-state creep constant are both inversely proportional to Young's modulus. Creep strains up to 2.5% in tension and 5% in compression have been reported. However, there is some indication that in isotropic graphites compressive creep slows down or stops when the strain reaches 2–3%.

The new near-isotropic commercial graphites, which use isotropic petroleum coke as filler for improved radiation stability, have been fabricated in large sections and evaluated for use as core components in large HTGRs. These graphites are typified by grades H-451 (Great Lakes Carbon) and TS-1340 (Union Carbide Corp.).

### B. Zirconium Hydride

The atomic density of hydrogen in many metal hydrides is greater than in liquid hydrogen or in water. Metal hydrides are efficient moderators and neutron shielding materials and are particularly suitable for minimizing the core shield volume.

Examples of the use of metal hydrides as moderators include the following reactor systems. In the gas-cooled Aircraft Nuclear Propulsion (ANP) reactor program (General Electric) yttrium hydride was in the form of large, hexagonal-cross-section rods that were metal-clad and had central axial holes for fuel elements and coolant channels. These elements were capable of operation at 1000°C in air. The SNAP space power reactors (Atomics International) used uranium–zirconium hydride rods as a combination fuel-moderator element. A similar uranium–zirconium hydride fuel element was developed for the TRIGA research reactors (General Atomic). The sodium-cooled prototype reactor KNK (Interatom and Karlsruhe) contained metal-clad zirconium hydride as a moderator element for operation at temperatures up to 600°C. The hydride bodies should be clad to prevent significant loss of hydrogen at elevated temperatures. The rates of hydrogen loss through stainless steel cladding 250  $\mu\text{m}$  thick have been determined. A 1% loss of hydrogen per year occurs at about 500°C. Glass–enamel-coated metal cladding (about 76  $\mu\text{m}$  thick internal coating) has a very low permeability (about 10% of that of molybdenum)

and has been used successfully in the SNAP (space nuclear power) reactor UZrH fuel elements at temperatures up to 700°C.

Most of the irradiation experience to date is limited to the uranium–zirconium hydride fuels used in the SNAP and TRIGA reactors. The presence of uranium (about 8–10 wt. %) complicates the situation because of the damage resulting from fission recoils and fission gases. Transmission electron-microscope studies of irradiated samples indicated the presence of voids within the range of fission recoils in the vicinity of the uranium fuel particles, with the regions far from the fuel particles retaining a microstructure similar to unirradiated material. The UZrH fuel exhibits high growth rate during initial operation, the so-called offset growth period, which has been ascribed to the vacancy-condensation type of growth phenomenon over the temperature range where voids are stable. The voids are also associated with the delta–epsilon phase banding.

### C. Beryllium

Beryllium metal has been used as the moderator and reflector in a number of reactors, such as test reactors (MTR, ETR, and ATR); the Oak Ridge research reactors (ORR and HFIR); the Experimental Breeder Reactor (EBR-II); research reactors in France, Japan, and the Russia; and the SNAP reactors. Beryllium has many of the nuclear properties desirable for a moderator and reflector, such as low neutron-absorption cross section, high neutron-scattering cross section, low atomic weight, high melting point, high specific heat, and fairly good corrosion resistance in water. Its disadvantages are high cost, low ductility, toxicity, crystallite growth, and swelling under irradiation at high temperatures. These features combine to eliminate its use as a structural material in commercial reactors.

Beryllium has a close-packed hexagonal crystal structure, alpha form, with a  $c/a$  ratio of 1.5671 and lattice parameters  $a = 2.2866 \text{ \AA}$  and  $c = 3.5833 \text{ \AA}$ . The alpha form transforms to the body-centered cubic form at about 1250°C, with a lattice constant of  $a = 2.551 \text{ \AA}$ .

A number of parameters influence the mechanical properties of beryllium, such as orientation of the test specimen, purity, iron and BeO content, grain size and anisotropy, strain rate, temperature, method of production, surface condition, and irradiation.

Commercial beryllium has good resistance to atmospheric corrosion. It shows variable behavior in high temperature water. The oxidation of beryllium in air or dry oxygen follows a parabolic rate at temperatures up to about 700°C. However, at temperatures above 750°C a break-away reaction that is associated with the appearance of voids sets in after an induction period.

For each transmuted Be atom, two atoms of He and one Li atom are produced. Thus, for an exposure of  $10^{22} \text{ n/cm}^2$  about  $22 \text{ cm}^3$  He gas at STP, equivalent to 1 at. %, is present in the metal. The solubility of helium in beryllium is extremely low. Because of its high cross section, the Li soon reaches an equilibrium level, whereas the quantity of  $^3\text{He}$  increases with time. Both these isotopes have high neutron cross sections.

At temperatures below approximately 500°C, the rate of growth of irradiated beryllium is about 0.2% per  $10^{22}$  nvt ( $E > 1 \text{ MeV}$ ) up to a fluence of  $10^{22}$  nvt. The helium at low temperatures is in enforced solid solution in the beryllium lattice, and no gas bubbles are observed. At elevated temperatures (above 600°C), the helium gas migrates and agglomerates into gas bubbles, which results in marked swelling. The gas bubbles themselves can migrate by a surface diffusion mechanism and coalesce into larger bubbles.

The stresses arising from the inhomogeneous growth of beryllium can result in cracking even in the low-temperature range. Bowing, cracking, and swelling occurred in MTR reflector blocks subjected to fast neutron fluences in the range  $4\text{--}10 \times 10^{21}$  nvt.

The design thermal stress for beryllium reflectors has been limited to 12,000–15,000 psi. Considerable swelling occurs when beryllium is irradiated to high fluences (above approximately  $1 \times 10^{21}$  nvt) at high temperatures or is annealed at high temperatures after irradiation at low temperatures. The swelling threshold (or breakaway) temperature decreases as the fast neutron fluence increases. The lowest threshold temperature reported is 550°C for a fast fluence of  $1.6 \times 10^{22}$  nvt. However, there is evidence from yield strength measurements that suggests that helium mobility is significant at temperatures above 300°C.

## VIII. REACTOR CONTROL MATERIALS

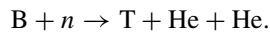
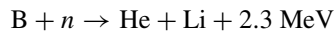
Reactor power control is accomplished by means of control rods and burnable poisons that contain neutron-absorbing materials. In PWRs a soluble chemical, boric acid, in the primary coolant also provides power control. The concentration of boric acid is varied to control reactivity changes caused by depletion of fuel and buildup of fission products.

### A. Boron Carbide

Boron carbide is the most extensively used control material. It is used in thermal and fast reactors. The data on boron carbide obtained from thermal reactors differ substantially from the results of fast neutron spectra irradiations. There have also been differences in irradiation behavior reported from experiments by different

groups, particularly in the relations between temperature and swelling and in the rates of release of tritium.

The absorption of neutrons by  $^{10}\text{B}$  results in the primary formation of  $^7\text{Li}$ , helium, and tritium by the following reactions:



The fast neutron capture cross section of the  $^{10}\text{B}$  isotope is greater than that of any other known isotope. The absorption cross section in a thermal neutron flux is much larger than that in a fast breeder reactor spectrum, resulting in considerable self-shielding in a thermal reactor flux and a sharply decreasing reaction profile. Hence, it is difficult to extrapolate thermal reactor irradiation data to predict the behavior of boron carbide in fast breeder reactor spectra, where there is virtually no self-shielding and where the reaction rates and irradiation are homogeneous throughout the absorber material.

Boron carbide has a boron concentration of 85% of that of elemental boron. Natural boron contains 19.8% of the high-cross-section isotope  $^{10}\text{B}$ , and the content of  $^{10}\text{B}$  in natural boron carbide is 14.7%. The thermal neutron absorption cross section of  $^{10}\text{B}$  is 4000 b and of natural  $\text{B}_4\text{C}$  about 600 b. The energy of the secondary gamma radiation is 0.5 MeV. The neutron-absorption cross section decreases with an increase in the neutron energy by the  $1/V$  relation for neutron energies below 100 eV. It remains fairly constant for energies between 100 eV and 0.1 MeV and has several resonances between 0.5 and 5 MeV. The cross section in a fast breeder reactor spectrum is about 1 b.

Boron carbide pellets and structures can be produced by cold pressing and sintering (70–80% density) or by hot pressing. The FFTF uses hot-pressed pellets of 92% density. In the hot-pressing operation, the  $\text{B}_4\text{C}$  powder is first cold pressed into pellet form and then hot pressed in graphite dies at temperatures from 2050 to 2300°C under pressure of 10.3 MPa (1500 psi). The density is controlled by varying the temperature and the pressure. Some reactors have used boron carbide in powder form, vibratory-packed in 20% cold-worked type 316 stainless steel cladding.

The British prototype fast reactor (PFR) studies on boron carbide compatibility covered the temperature range of 450–1000°C for test durations of up to 15 months. The reaction rate was determined to be acceptable up to 600°C. Copper coating (125  $\mu\text{m}$  thick on a 25- $\mu\text{m}$  nickel substrate coating) was used on the inside diameter of the M-316 stainless steel cladding to restrict the interaction. In heat treatment tests, no interaction has been found for exposure times of 10,000 hr at 850°C. No failure of the copper

plating occurred after thermal cycling 40 times between 400 and 750°C. In-pile tests have also been carried out in the Dounreay fast reactor (DFR). The density of the  $\text{B}_4\text{C}$  pellets in the DFR experiments is in the range 86–90% theoretical density.

The use of boronated graphite in HTGRs has been reported. Boronated graphites containing 23–43 wt. % boron as  $\text{B}_4\text{C}$  were successfully irradiated at 300–750°C to fast neutron fluences up to  $7 \times 10^{25}$  n/m<sup>2</sup> ( $E > 29$  fJ).

The interaction of  $\text{B}_4\text{C}$  graphite bodies with metal cladding (Hastelloy X and Incoloy 800) has been investigated. The reaction rate is found to be appreciable only above 800°C.

## B. Silver–Base Alloys

The combination of silver with 15 wt. % cadmium and 5 wt. % indium provides a control rod alloy with suitable neutron absorption properties over the spectrum of neutron energies present in pressurized light-water reactors. This alloy clad in stainless steel or Inconel has been used as control rod material in PWRs. However, with any significant increase in the price of silver, alternate materials would be under consideration.

## C. Hafnium

The successful use of hafnium as a control rod material in the Shippingport PWR and submarine reactors has led to work on its application in other LWR reactors. Hafnium can be used without excessive reactivity loss or damage over extended irradiation (approximately 40 yr) for the lifetimes of the plants. Cost considerations will govern the extent to which Hf will be used in control rods.

## D. Europium Hexaboride

There has been increasing interest in the use of europium hexaboride as an alternate control material to  $\text{B}_4\text{C}$  in fast breeder reactors.

## E. Europium Oxide

Europium oxide has been under development and is being considered as a neutron absorber material for use in the control rods of fast breeder reactors in the United States, Britain, Germany, and Russia. The BOR-60 fast breeder reactor (Russia) has operated satisfactorily since 1972 with europium oxide in one of the control rods. The principal difference in design results from the absence of gas generation in europium oxide under irradiation with its  $(n, \gamma)$  reaction, and longer reactivity lifetime. This allows the use of thinner wall cladding with no gas plenum.

With a pellet density of 93% and a diametral gap of 8 mils (200  $\mu\text{m}$ ) (to accommodate 1.5% swelling), the europium oxide assembly is expected to have at least the same nuclear worth (reduction of neutron multiplication) as the rods containing  $\text{B}_4\text{C}$ . The centerline temperature is calculated to be between 700 and 950°C, based on unirradiated thermal conductivity values. Lifetimes of at least two years are predicted, based on assessment of the probable changes in the reactivity of  $\text{Eu}_2\text{O}_3$  when exposed to fast neutrons, because the nuclides resulting from transmutation also have large cross sections. These studies indicate a rate of loss of reactivity worth with neutron exposure one-third that of control rods containing  $\text{B}_4\text{C}$ . The main areas of concern are determining actual nuclear worths, maintaining pellet dimensional stability, and accommodating decay heating.

### F. Burnable Poisons

Neutron-absorbing materials are also used in reactors to prevent power peaking in the early stages of operation of the core and to allow optimum burnup of the fuel and power shaping in the core. Boric acid solution in the primary coolant is used in PWRs as the burnable poison to provide power control. Ceramic pellets containing burnable poisons are included in the fuel rods in most power reactors. Examples of these materials are boron carbide dispersions in alumina, borosilicate glass, and gadolinium oxide dispersed in the uranium dioxide fuel.

## IX. STRUCTURAL MATERIALS

The structural components of nuclear reactor systems include the pressure vessel, piping, and valves, which are fabricated from a number of different materials. The components are joined by welding, and a large reactor contains thousands of welds and many kilometers of piping.

The pressure vessel in LWRs is constructed from welded heat-treated steel plate and forgings. The vessel is given a final postweld heat treatment at about 880 K. The wall thickness of the vessel is about 230 mm in a LWR and 165 mm in a BWR for a 1000-MW(e) system. In the sodium-cooled fast breeder reactors, a relatively thin-walled (75 mm) stainless steel tank is suitable because of the relatively low pressure (1 MPa).

The piping and valves are made of either cast or forged stainless steel or austenitic clad ferritic steel. However, the problems with stress corrosion cracking of austenitic stainless steels in the BWRs has led to the selection of carbon steel (unclad SA 106 Grade B and SA 333 Grade 6) in the most recent BWR designs.

A number of remedial measures have been developed to control stress corrosion cracking of welded piping in

the BWRs that contain the susceptible Type 304 stainless steel piping. Stress corrosion cracking in this material is governed by the degree of sensitization of the alloy, the tensile stress level, and the nature of the corrodant. The stresses arise from both applied and internal stresses and from grinding operations. The presence of even parts per billion of radiolytic oxygen in the BWR coolant water plays a very significant role in stress corrosion cracking. It is the interactions among these parameters that result in crack initiation and propagation.

The remedial actions that have been examined include solution heat-treating the weldments to eliminate weld sensitization; installing corrosion-resistant cladding to isolate the sensitized regions; induction heating the outer pipe wall at the weld region while water-cooling the inside surface so as to generate compressive stresses in the inside surface upon cooldown; and heat-sink welding, which also results in compressive stresses on the inside surface.

The materials employed in nuclear reactors are fabricated to special nuclear-grade specifications. Significant advances have been made in the design analysis methods and in the selection and development of structural materials for nuclear plants in recent years.

The design rules for the major nuclear components are defined by ASME Boiler and Pressure Vessel Code, Section III, Nuclear Power Plant Components. These rules generally apply to LWRs, where the components are designed to operate in the subcreep range of temperatures. For applications where the components operate in the creep regime, the ASME Code Case 1592 is applicable. This code provides creep stresses that limit the elastically calculated load-controlled stresses for the stainless steels Types 304 and 316, Alloy 800H, and 2-1/4 Cr-1 Mo ferritic steel. A factor of safety is applied to the analyses to account for defects in the materials (Section XI of the ASME Boiler and Pressure Vessel Code). The limits on the service degradation of materials properties are defined in the Code of Federal Regulations (10CFR50) and in the Regulatory Guides issued by the U.S. Nuclear Regulatory Commission (USNRC).

The Structural Integrity Plan is used to assess the effects of materials flaws quantitatively to preclude failures resulting from flaw instabilities. This plan considers the influence of flaw size and the mechanical properties (particularly fatigue, corrosion fatigue, and stress corrosion) by means of analytical techniques.

Nuclear power reactors are contained in two types of pressure vessels, namely, steel pressure vessels (for most types of reactors) or prestressed concrete pressure vessels (for many gas-cooled reactors). The exception to this is the use of Zircaloy pressure tubes in the heavy-water moderated reactors (CANDU and SGHWR). The steels used are ferritic low-alloy steels (Mn-Mo-Ni grades,



ASTM-type A302-B, A537B, and A533-B plates and ASTM-A508 Class 2 in the United States), which are lined with stainless steel in LWR applications.

The pressure vessel materials are subject to neutron irradiation during operation of the reactors. This results in significant effects on the mechanical properties of the steels used for the pressure vessels, primarily an increase of the yield strength, decrease of the ductility, a rise in the brittle-ductile transition temperature, and decreased fracture toughness.

The neutron exposures on the LWR vessels range from about  $5 \times 10^{18}$  n/cm<sup>2</sup> > 1 MeV to as high as  $5 \times 10^{19}$  n/cm<sup>2</sup> > 1 MeV. The important factors governing radiation embrittlement of pressure vessel steels are the sensitivity of the steel to embrittlement, the neutron fluence and energy spectrum, and the irradiation temperature. Much useful information is being accumulated from reactor vessel surveillance programs. The profound influence of minor constituents (tramp impurities), particularly copper and phosphorous, on the irradiation embrittlement of steel at elevated temperatures has been demonstrated at the U.S. Naval Research laboratory. The temperature range of transition can be raised by as much as 300°C by neutron irradiation.

The main criterion used in specifying the operational limitation of the pressure vessel steel is the nil-ductility transition temperature (NDT), which in the irradiated steel must not exceed 33°C below the lowest operating temperature. An important theoretical development in recent years has been the concept of the damage function, which evaluates the relative damage by a given neutron energy spectrum. There is no significant temperature effect from room temperature up to approximately 230°C, above which the damage diminishes with increasing temperature.

The fine-grained vacuum deoxidized steels with low impurity content (Cu < 0.1%, P and S < 0.012%) provide a material with remarkably good resistance to irradiation embrittlement.

Recent assessments of the engineering damage cross sections for neutron embrittlement of pressure vessel steels have concluded that most (~94%) of the neutron embrittlement is caused by neutrons of energies >0.1 MeV. It is recommended that the threshold of >0.1 MeV be adopted for use in assessment of neutron embrittlement of reactor pressure vessel steels and also that the computed damage-fluence values incorporating damage cross sections be used to account for the influence of neutron spectrum on embrittlement.

Prestressed concrete reactor vessels (PCRVR) have been used for the gas-cooled reactors in France, Britain, and the

United States. The PCRVR consists of concrete reinforced with bonded, deformed steel bars and unbonded prestressing systems. The main cavity, penetrations, and cross ducts are lined with a 20-mm-thick liner keyed to the concrete by anchors. The liner and closures form a leak-tight barrier for the primary coolant. The liner is cooled with water. Thermal insulation keeps the concrete within allowable temperature limits. The prestressing of the concrete acts to produce a net compressive stress on both the main cavity liner and the penetration liners, thereby making it highly unlikely that crack propagation could occur. The tendons that are in tension and that provide the confining strength are not irradiated. Moreover, they may be monitored and replaced if evidence of weakness is observed.

## SEE ALSO THE FOLLOWING ARTICLES

FISSION REACTOR PHYSICS • NUCLEAR FUEL CYCLES • NUCLEAR POWER REACTORS • NUCLEAR SAFEGUARDS • RADIATION PHYSICS • RADIOACTIVE WASTE DISPOSAL • SPACE NUCLEAR POWER

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