

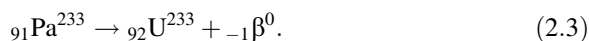
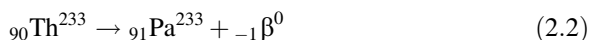
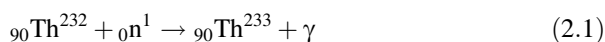
# Chapter 2

## Uranium

### 2.1 Introduction

The element uranium (U) was discovered by a German chemist Klaproth in 1789. Metallic uranium was first prepared by Peligot, who showed that the substance discovered by Klaproth was the oxide of uranium. Uranium is the basic (primary) nuclear fuel, since it contains the only naturally occurring fissionable material. In these nuclear applications the element uranium is of interest because of its nuclear properties, providing energy, fission products, and more fissionable material. Uranium may be present in fuel elements as a pure metal, an alloy, or an oxide or other compound. Uranium cannot be handled like the common metals (such as Fe, Cu, Al etc.), because of its chemical reactivity, radioactivity with consequent health hazards, and highly anisotropy. In spite of above difficulties, several tonnes of uranium metal are processed every year in different forms like rod, tube, sheet and plate.

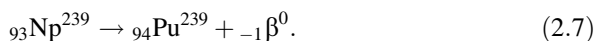
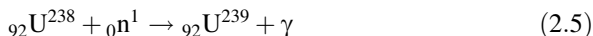
Uranium-235 ( $U^{235}$ ) is the only naturally occurring fissionable material. Artificial isotopes with mass numbers from 228 to 239 have been prepared. The most important of these is  $U^{233}$ , which is prepared from the reaction of neutrons with thorium-232 ( $Th^{232}$ ).



Uranium-235 captures a neutron to form uranium-236, which is most likely to undergo fission into a pair of atoms. Depending on the pair fission products, different numbers of neutrons are released.



$\text{U}^{238}$  is converted to the fissionable plutonium-239 ( $\text{Pu}^{239}$ ):



The plutonium and uranium-233 are separated from their respective precursors, uranium and thorium, by chemical means. The separation of the fissionable uranium-235 from natural uranium requires other methods.

## 2.2 Sources

Uranium is widely distributed in the upper crust of the Earth, albeit somewhat thinly. Uranium contained in the Earth's crust is about 2–4 ppm. It does not occur freely, it is always associated with other minerals. Table 2.1 shows the principal minerals of uranium. Pitchblende and uraninite occur in the form of veins or lodes, the uranium is present in the form of an oxide ( $\text{U}_3\text{O}_8$ ); associated with sulphides of silver, lead, nickel, cobalt and iron; and radioactive radium. The later is a degradation product of uranium, the two are always found together. As a secondary mineral, uranium is found associated with vanadates, phosphates, arsenates, etc., the most common is carnotite, a potassium uranyl vanadate, and autunite, a calcium uranyl phosphate, deposits contain averaging up to 1% uranium oxide.

Uranium-bearing ores have been discovered in India at the Singhbhum Thrust Belt (Jaduguda) of Bihar; a few small ones in Rajasthan, in the Himalyan regions of Himachal Pradesh, Uttar Pradesh, and Madhya Pradesh in India. Jaduguda (India) ore contains: 0.08%  $\text{U}_3\text{O}_8$ , 67%  $\text{SiO}_2$ , 15%  $\text{FeO}$ . Sea beach sands of Kerala and

**Table 2.1** Principal minerals of uranium

Mineral	Composition	Colour	Occurrence
Uraninite	Essentially $\text{UO}_2$ with $\text{UO}_3$ present as a result of oxidation	Black	Norway, South Africa
Pitchblende	$\text{U}_3\text{O}_8$	Black	Canada, Congo, India etc.
Carnotite	$\text{K}_2\text{O} \cdot 2\text{UO}_3 \cdot \text{V}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ ( $n = 1-3$ )	Yellow	USA, South Australia, Congo etc.
Autunite	$\text{CaO} \cdot 2\text{UO}_3 \cdot \text{P}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ ( $n = 8-12$ )	Lemon yellow–sulphur yellow	France, USA, etc.

Tamil Nadu contain a useful radioactive mineral, Monazite, which contains thorium, uranium oxides, phosphate and a large percentage of rare earth oxides (9% ThO<sub>2</sub>, 0.4% U<sub>3</sub>O<sub>8</sub> and 59% RE<sub>2</sub>O<sub>3</sub>), where RE represent the rare earth metals like scandium (Sc), neodymium (Nd), cerium (Ce), holmium (Ho) etc.

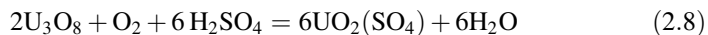
## 2.3 Extraction of Uranium from Ore

General flow diagram for production of natural and enriched uranium from ore (which contains 0.08% U<sub>3</sub>O<sub>8</sub>, 67% SiO<sub>2</sub>, 15% FeO) is shown in Fig. 2.1. The following steps are required for production of uranium metal from ore:

1. Acid leaching.
2. Ion exchange separation.
3. Production of reactor grade nitrate.
4. Production of uranium dioxide.
5. Metallothermic reduction of uranium compounds.

### 2.3.1 Acid Leaching

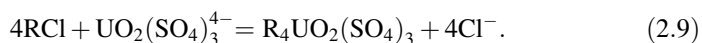
The leaching of the uranium valuable from the ore is done by sulphuric acid (H<sub>2</sub>SO<sub>4</sub>). The uranium goes into solution as uranyl sulphate:

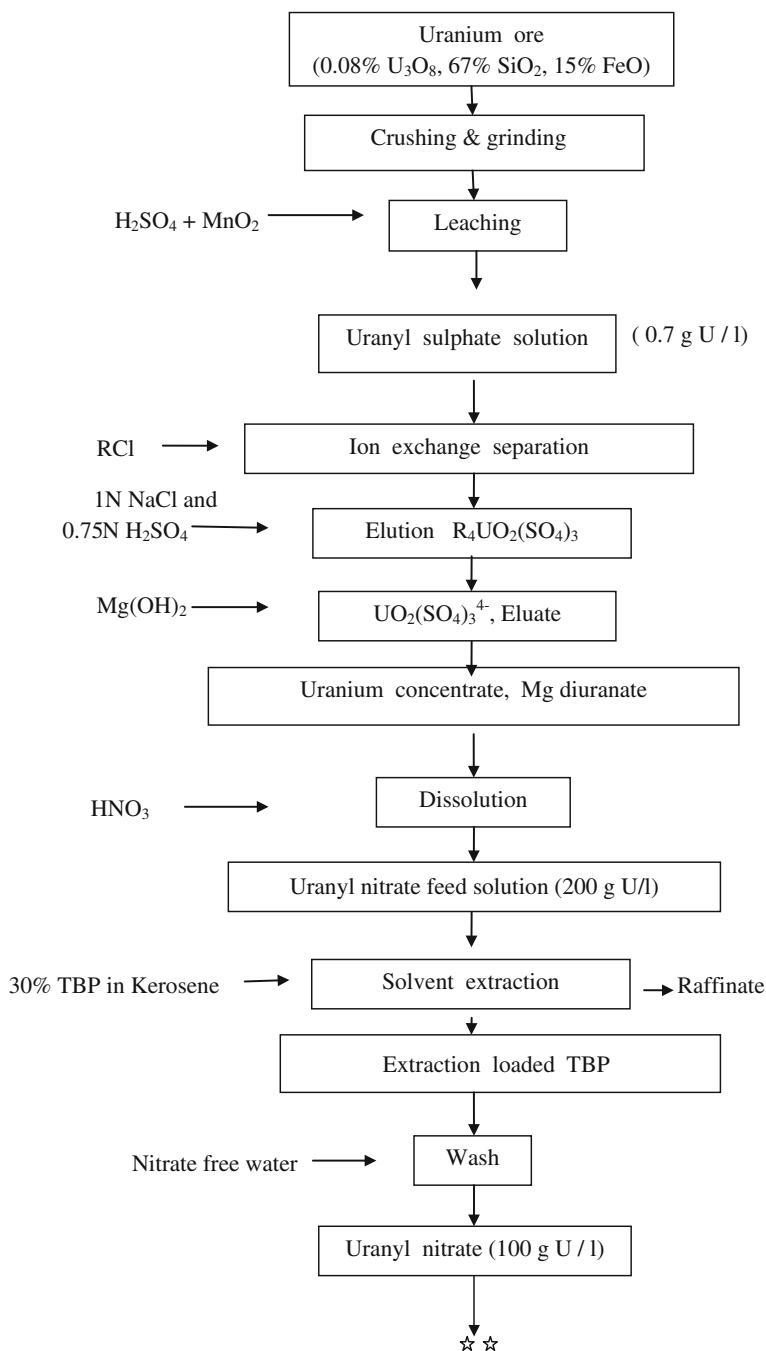


The oxygen required in the leaching process is indirectly supplied by the addition of pyrolusite (60–70% MnO<sub>2</sub>). The uranyl sulphate present in the lean liquor complexes with excess sulphate ions present in the solution and forms negatively-charged complexes like UO<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub><sup>4-</sup>, UO<sub>2</sub>(SO<sub>4</sub>)<sub>2</sub><sup>2-</sup>.

### 2.3.2 Ion Exchange Separation

An ion exchange process using the quaternary ammonium anion exchange resin which exhibits a high selectivity for the uranyl sulphate anions is employed to concentrate uranium from the sulphuric acid leach liquors:





**Fig. 2.1** General flow sheet for production of natural and enriched uranium from ore

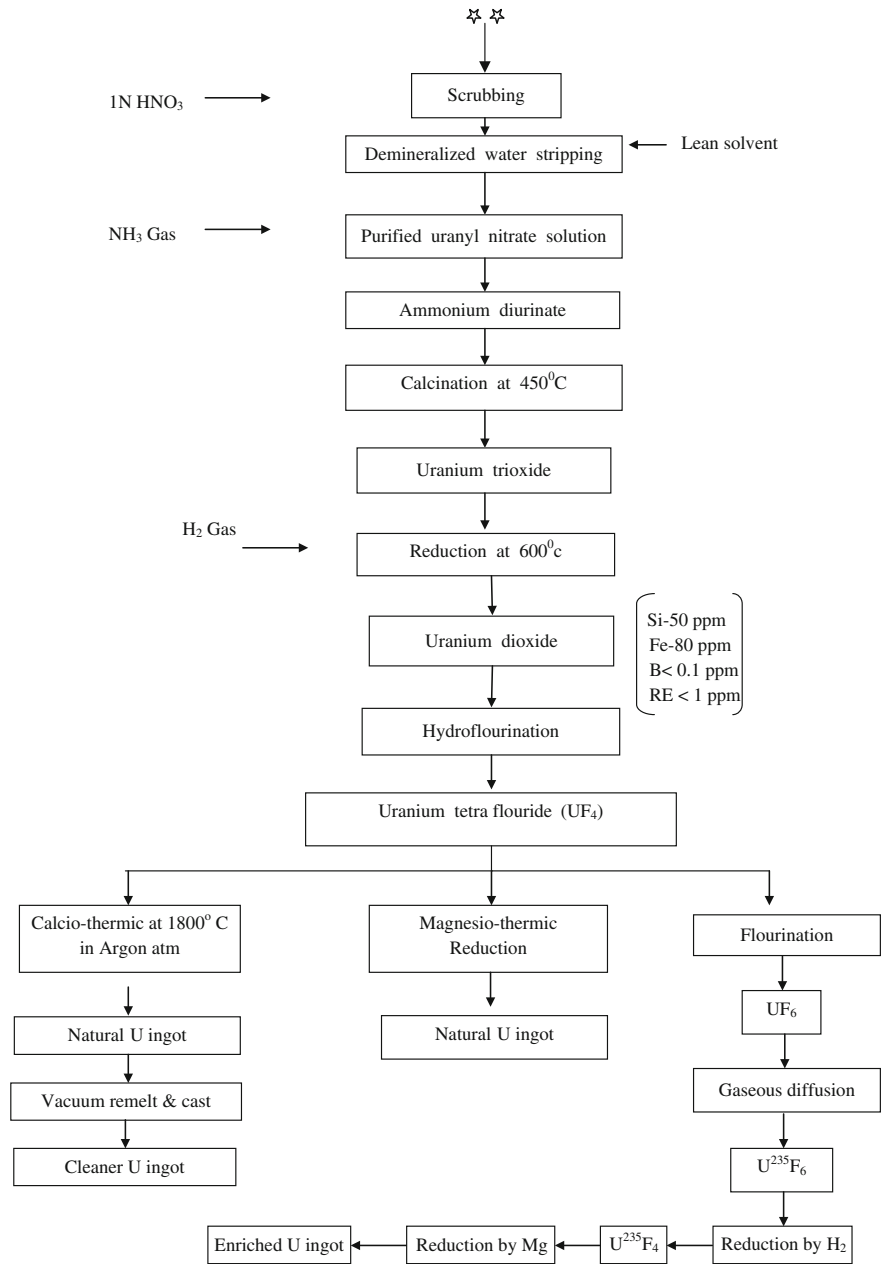
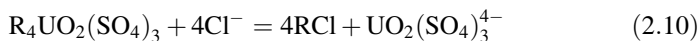


Fig. 2.1 (continued)

The uranium is adsorbed on the anion exchanger in fixed bed ion exchange columns. The adsorbed uranium is collected by passing a strong chloride (NaCl) solution through the saturated resin column:

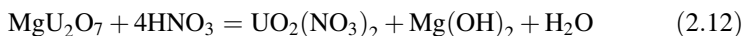


Magnesium diuranate is then precipitated from the eluate by the addition of  $Mg(OH)_2$ .

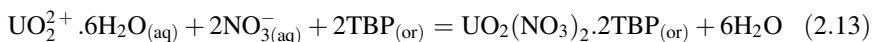


### 2.3.3 Production of Reactor Grade Uranyl Nitrate

The uranium concentrate is first dissolved in nitric acid to obtain a solution of uranyl nitrate  $[UO_2(NO_3)_2]$ .



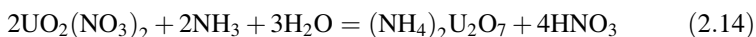
This compound is soluble in various organic solvents such as diethyl ether, methyl isobutyl ketone (hexone), and tributyl phosphate (TBP). TBP selectively forms neutral addition complex  $UO_2(NO_3)_2 \cdot 2TBP$  with uranyl nitrate.



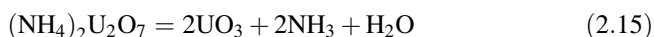
When the loaded TBP is washed with nitrate free water pure uranyl nitrate is obtained in the aqueous phase.

### 2.3.4 Production of Uranium Dioxide

This aqueous solution is again dissolved in nitric acid for scrubbing (i.e. cleaning) and stripping (i.e. removing) by water to form purified uranyl nitrate solution. Then by passing ammonia gas, ammonium diuranate  $[(NH_4)_2U_2O_7]$  is precipitated.



Now  $(NH_4)_2U_2O_7$  is calcinated at 450 °C to obtain uranium trioxide ( $UO_3$ ).



The uranium trioxide is then reduced by hydrogen at 550–600 °C to form uranium dioxide. This uranium dioxide contains 50 ppm Si, 80 ppm Fe, < 0.1 ppm B, and < 1 ppm RE.



### 2.3.5 Reduction of Uranium Compounds

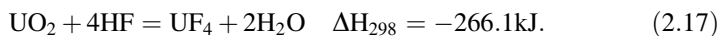
Pure uranium metal is difficult to prepare because the element has affinity for other elements such as oxygen, halogens, nitrogen and carbon. So, the reduction has to be performed in closed systems to avoid atmospheric contamination. The large negative free energy of formation of uranium dioxide ( $\text{UO}_2$ ) [–514.6 kJ/g-atom of  $\text{O}_2$  at 25 °C] shows the need for strong reducing agents if  $\text{UO}_2$  is to be used as starting material in the preparation of the metal. Hydrogen would require a very high  $\text{H}_2/\text{H}_2\text{O}$  ratio in the gas mixture and cannot be considered a practical reducing agent. Reduction with carbon requires a vacuum and leads to contamination by carbide formation.

Thermodynamically, uranium dioxide ( $\text{UO}_2$ ) can be reduced to uranium metal by the reducing agents calcium and magnesium. But the refractory oxides product does not melt in the process and uranium is obtained dispersed through the slag matrix as fine powder. The product is inconvenient to handle, impure and this method is not used to produce uranium.

Halides are more suitable than oxides as starting materials for metal preparation. Additional heat is evolved, and the halide by-product has a lower melting point. This halide therefore melts and permits the dense uranium metal to settle at the bottom. Fluoride reduction is therefore universally employed to obtain uranium metal. The fluoride can involve high heat of reaction yielding oxygen free consolidated uranium metal.

#### 2.3.5.1 Preparation of Uranium Tetrafluoride

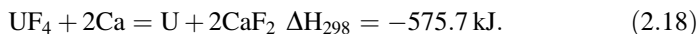
The uranium tetrafluoride is less hygroscopic and less volatile than the chloride and it is the preferred halide intermediate. The uranium tetrafluoride is prepared by hydrofluorination of uranium dioxide:



The reaction is highly exothermic and continuous hydrofluorination is presently carried out in magnesium-lined inclined rotary reactors. The reaction is carried out at 600 °C and the  $\text{UO}_2$  and HF feed rates are adjusted to obtain complete conversion of  $\text{UO}_2$  to  $\text{UF}_4$ .

### 2.3.5.2 Reduction of UF<sub>4</sub>

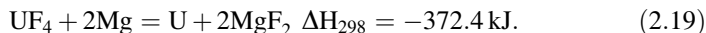
- (i) Calciothermic reduction of UF<sub>4</sub>: The reduction with calcium is simpler because of the high heat of reaction which raises the charge temperature to as high as 1800 °C.



Melting points of U and CaF<sub>2</sub> are 1132 °C and 1418 °C respectively, both are molten stages at 1800 °C; and so the slag-metal separation will be good. Calcium has a high boiling point (1494 °C) and hence the reaction takes place at normal pressure.

High purity UF<sub>4</sub> powder is intimately mixed with high purity vacuum distilled calcium and the mixture is charged in a tight stainless steel bomb reactor which is initially lined with dry CaF<sub>2</sub>. Calciothermic reduction of UF<sub>4</sub> is done in an argon atmosphere. Uranium ingots obtained are usually remelted in a vacuum electric furnace and cast into cleaner ingots.

- (ii) Magnesiothermic reduction of UF<sub>4</sub>: Magnesium is easier to get in high purity. Although the heat of the reaction is low and external heat supply is required for good slag-metal separation, Mg is still preferred for uranium production.



The boiling point of magnesium (1105 °C) is lower than the melting point of uranium (1132 °C). Hence, a high pressure develops during the reaction and a pressure vessel is required to carry out the reduction. To supplement the heat requirement of the process, potassium chlorate is added as a heat booster. The reduction vessel is lined with MgF<sub>2</sub>.

- (iii) Production of UF<sub>6</sub>: UF<sub>4</sub> is reacted with fluorine gas to form UF<sub>6</sub>:



By the gaseous diffusion to form U<sup>235</sup>F<sub>6</sub>, then reduced by hydrogen:





Then further reduction is done by magnesium to get enriched uranium:



### 2.3.6 High Purity Uranium Metal

Small ingots of massive pure uranium are made by vacuum melting of high purity crystals of uranium in uranium oxide crucibles. These crystals are prepared by electrolysis in an argon atmosphere. The anode is ordinary vacuum cast uranium and the cathode is molybdenum (Mo). The electrolyte is a fused salt, comprising a eutectic mixture of LiCl, KCl and 30%  $\text{UF}_4$  at 400–450 °C.

## 2.4 Properties

The uranium metal possesses a silver-grey luster when freshly prepared, but tarnishes readily on exposure to air owing to oxide formation. Uranium is a dense, moderately hard metal and has attractive properties such as high specific gravity and thermal conductivity. The atomic mass of uranium is 238.07. The radiation energy and half-life of natural uranium are shown in Table 2.2. The specific gravity of uranium depends on the amount of carbon and other low atomic number impurities present in uranium. The specific gravity for high purity uranium metal is 19.05 and for wrought uranium metal (variable purity) is 18.7–19.1. The melting point and boiling point of uranium are 1132 °C and 3813 °C respectively. It possesses a tensile strength of 63 kg/mm<sup>2</sup>, with reasonable ductility (10% elongation). The strength rapidly deteriorates above 400 °C. Thermal conductivity (0.0645 cal/cm °C) and electrical resistivity (30  $\mu\Omega$  cm at 25 °C) of uranium are increased with increasing temperature. Electrical resistivity show discontinuities at the phase transformation temperature, but thermal conductivity is continuous. Uranium can be cast and fabricated into desired shapes by conventional means such as rolling, extrusion and drawing. The metal is, however, very reactive and oxidizes at moderately high temperatures and as a consequence must be protected from air during fabrication.

**Table 2.2** Radiation energy and half-life of natural uranium

Mass no.	Radiation			% in natural uranium
	Type	Energy (Mev)	Half-life (years)	
234	$\alpha$	4.76	$2.48 \times 10^5$	0.0056
235	$\alpha$	4.39	$7.13 \times 10^8$	0.718
238	$\alpha$	4.18	$4.51 \times 10^9$	99.276

**Table 2.3** Phase transformation in uranium

Transformation	Temperature (°C)	Volume change ( $\Delta V/V$ ) %	$\Delta H$ , kJ/g-atom
$\alpha \rightarrow \beta$	667	1.06	2.93
$\beta \rightarrow \gamma$	775	0.736	4.81
$\gamma \rightarrow \text{Liquid}$	1132	5.0	19.66

Uranium has three allotropic forms (between room temperature and its melting point): (a) orthorhombic— $\alpha$  phase which is stable from room temperature to 667 °C; (b) tetragonal— $\beta$  phase, stable from 667 to 775 °C; and (c) BCC— $\gamma$  phase, stable from 775 to 1132 °C. Phase transformation in uranium takes place due to temperature change as shown in Table 2.3.

**Hardness:** The vickers hardness number (VHN) is commonly used as the scale for hardness of uranium. At room temperature, a hardness of about 220 VHN is found for uranium which has been either cast or  $\alpha$ —rolled and annealed. The hardness falls sharply as the temperature increases. The rate of decrease becomes more rapid at 350–400 °C, and a sharp rise in hardness due to transformation from  $\alpha \rightarrow \beta$ . The hardness of  $\beta$  decreases gradually with temperature, transformation to  $\gamma$  gives a very soft phase like lead (Pb) at room temperature.

**Alloys:** Uranium alloys are formed due to: (a) to obtain a finer grain size; (b) to improve mechanical properties; (c) to change its properties so that it can be fabricated with other metals; (d) to improve corrosion resistance; (e) to improve resistance to radiation damage; (f) to lower the melting point for liquid metal fuels or to improve castability for cast fuels.

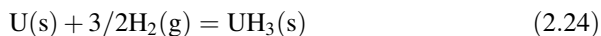
Uranium can be alloyed with metals like Zr, Si, Al, Nb, Mo, Cr, V and Ti.

- (i) Metals, those permitting  $\beta$ —U at room temperature, are: V, Nb, Cr, Mo, Mn.
- (ii) Metals, those permitting  $\gamma$ —U at room temperature, are: Nb, Mo, Zr.

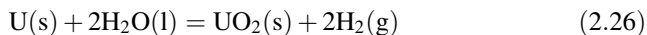
Certain alloying elements, when added to uranium, can increase its corrosion resistance in high-temperature water, presumable through the formation of denser and more tenacious oxide films than those formed on unalloyed uranium. The alloys may be grouped into four classes:

1. Supersaturated  $\alpha$  phase (martensitic) alloys, e.g. U—1.5 wt% Nb—5 wt% Zr.
2. Metastable  $\gamma$  phase alloys, e.g. U—7 to 15 wt% Mo or 9 to 20 wt% Nb.
3. Intermetallic compounds or intermediate phases, e.g.  $\epsilon$  phase—stoichiometric composition of  $U_3Si$ .
4. Uranium containing relatively small amounts of alloying elements such as Zr, e.g. U—2 wt% Zr, U—5 wt% Zr, U—7.5 wt% Zr etc.

**Corrosion:** Uranium reacts readily with air, oxygen, nitrogen, hydrogen, water and many other media. Ordinarily the rates of reaction increase rapidly with increasing temperature. Uranium reacts readily in air at room temperature, forming a layer of uranium oxide which at first is adherent but which eventually becomes loose and powdery. At elevated temperature the rate of reaction with air becomes faster.



Uranium reacts with water to form uranium oxide and release of hydrogen gas:



## 2.5 Applications

For use in atomic energy reactors (atomic energy is derived by virtue of the transformation of matter into energy) the uranium metal is cast into rods approximately 2.5 cm in diameter using vacuum melting technique in a high frequency electric furnace.

Since the discovery and isolation of plutonium and uranium-235 took place during a war period, it was natural that attention should have been directed to the military angle. As early as 1940, before the separation of U-235 had been achieved or the existence of plutonium had ever been imagined, scientists were giving attention to the possibility of producing an atomic weapon of unprecedented power.

The rapid growth and development of the nuclear industries has been in many ways unique. Today, many countries are either planning or already developing nuclear power programmes. Britain began operating the world's first industrial-scale nuclear power station in 1956.

Extraction of Nuclear and Non-ferrous Metals

Dutta, S.K.; Lodhari, D.R.

2018, XV, 247 p. 53 illus., 1 illus. in color., Hardcover

ISBN: 978-981-10-5171-5