NUCLEAR MATERIALS

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INDIAN ASSOCIATION OF NUCLEAR
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About IANCAS

The Indian Association of Nuclear Chemists and Allied Scientists (IANCAS) was founded in 1981 with an objective of popularizing nuclear sciences among the scientific community in the country. Under its mandate, IANCAS is continuously promoting the subject of nuclear and radiochemistry, and use of radioisotopes & radiation sources in education, research, agriculture, medicine and industry by organizing seminars, workshops and publishing periodical thematic bulletins. With its enthusiastic Life Members from all over the country and overseas, IANCAS has become one of the popular platforms for popularizing the subject of nuclear and radiochemistry across the country. The Association's activities can be seen on its website: www.iancas.org.in.

IANCAS brings out quarterly thematic bulletins on the topic of relevance to the nuclear science and technology with the financial support from BRNS. The Association's popular book on "***Fundamentals of Nuclear and Radiochemistry***", "***Introduction to Radiochemistry***" and "***Experiments in Radiochemistry"*** is widely sought amongst the academia, researchers and students of DAE, non-DAE units and Universities. Another popular book of INCAS is "***Nuclear Materials***" which has been translated into Arabic, Hindi, Marathi and Telugu. Till March 2023, IANCAS has published 71 Thematic Bulletins and several special Bulletins. All IANCAS Books and Bulletins are available for free download on its website: www.iancas.org.in.

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To encourage scientists / researchers actively pursuing activities in this discipline, IANCAS has instituted several awards. ***Dr. M.V. Ramaniah Memorial Award*** is conferred annually to an outstanding scientist for their significant contributions and lifetime achievements in the field of nuclear and radiochemistry. **Dr*. Tarun Datta Memorial Award*** is given annually to a young scientist (below 45 years of age) with minimum 5 years of research experience in the field of nuclear and radiochemistry and applications of radioisotopes. IANCAS also gives ***Prof. H.J. Arnikar Best Thesis Award*** annually for the Ph.D. research in the nuclear and radiochemistry area. Additionally, IANCAS also gives about 20 best paper awards to young researchers for presetting their work in NUCAR symposia.

To achieve the excellent in its cause for popularizing the nuclear sciences through electronic media, IANCAS has its own website (www.iancas.org.in) which is updated regularly. Information about the workshops, Awards and various activities of IANCAS are available on the website. All the publications of IANCAS including bulletins and books are available in free downloadable form.

Seraj A. Ansari
General Secretary, IANCAS
March, 2023

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Chapter 1

The Structure of Matter

Discovery and exploitation of various forms of energy are intimately linked with the advancement of civilization. Mankind began to use wood, coal and oil for producing energy much before understanding the mechanism by which this energy is released. On the other hand, the use of atomic/nuclear energy was a result of the knowledge obtained, by a very large number of scientists, during their efforts in understanding the nature of matter. In the ancient times, philosophers speculated about the nature of matter and gave various theories. The concept of 'Anu' (atom) and 'Panchatatvas' (5 elements) is a part of the Hindu philosophy. Similar philosophical ideas were in vogue in Greece. There is a steady evolution of the concept of matter from the Greek philosophy to the modern science and it is fascinating to recapitulate some salient features.

Elements and Atoms

Pythagoras (582-497 BC) was the first to propose that the matter was composed of four elements: fire, air, water and earth. Empedocles (490-430 BC) suggested that these elements interact with forces of love and hate to give rise to the various forms of matter. Democritus (460-380 BC), a contemporary of Socrates, gave an alternate concept of matter in which the world is made up of vacuum, or empty space, and fullness of matter. All matter consisted of individual particles 'Atomos' (that cannot be cut) which are so small that nothing smaller could be imagined. He mentioned that atomos differ in physical shape and this allows them to form different substances. His reasoning that there was no such thing as spirit led to the non-acceptance of this materialistic concept of matter and adherence to the elemental concept for almost 2000 years. Galileo Galilee (1564-1642 AD) revived atomism and suggested that atoms of different matter have different weight, shape and velocity. Until this period, all theories were speculative in nature and devoid of any experimental support. Robert Boyle (1627-1691) developed the technique of chemical analysis and defined that element was a material which can be identified by scientific experiment and cannot be broken down further into still simpler substances. He was thus responsible for combining the concept of the element and the atom in a subtle way. Benjamin Franklin (1706-1790 AD) postulated positive and negative electricity and showed that lightning was due to the interaction of these electrically charged entities accumulated in the clouds. He reasoned that electricity was a subtle fluid that could exist either in excess or in deficient quantities in matter. Antoine Laurent Lavoisier (1743-1794 AD) is quite often called the father of Modem Chemistry along with Robert Boyle. Building on the ideas suggested by Boyle, Lavoisier proved that air was made up of oxygen and nitrogen, and that fire was not an element. He also showed that any form of matter has a total mass which remains constant, a principle which was extremely valuable in further investigations on matter. In 1789, Henry Cavendish proved that water was made up of hydrogen and oxygen. These discoveries led to the search for new elements by scientists and many were discovered in the coming decades.

Joseph Lewis Proust (1754-1826 AD) analyzed many compounds and proved that the elements combined in definite proportions to form compounds. John Dalton (1766-1844 AD) proposed a theory in 1803 and is considered as the father of Modem Atomic Theory. According to this theory, all matter is made up of relatively small number of chemical elements and each element consists of small, indivisible and identical atoms. The atoms of different elements combine in definite proportions to form compounds. He also established the idea of relative atomic weights of elements. Amedeo Avogadro (1776-1856 AD) clearly distinguished between atoms and molecules and corrected the atomic weights proposed by Dalton. His concept that a fixed volume of any gas, at a given temperature and pressure, always contains a fixed number of molecules was extremely beneficial for the subsequent development of atomic theory.

In 1800, Italian Physicist, Alessandro Volta (1745-1827) devised a combination of metals and solutions that could produce a steady electric current. Around the same time, it was observed that some substances when dissolved in water gave electrically charged atoms called ions. Michael Faraday (1791-1867

AD) studied the transport of ions under the influence of electric field provided by positive electrode (anode) and negative electrode (cathode) of a voltaic cell and developed the laws of electrolysis. These laws established a correlation between the electricity and the atom leading to the concept of atomic unit of electricity. That is to say, an electrically charged atom or molecule must always carry an integral number of electric charges.

By 1850 a large number of elements had been discovered and their atomic weights were determined. The atomic weights, which were determined earlier with respect to hydrogen atom, were subsequently determined with respect to oxygen atom. With the discovery of such a large number of elements, scientists were looking for possible ways in which these elements could be arranged into definite groups based on chemical and physical properties. The best classification was proposed by Dmitri Ivanovich Mendeleyev (1834-1907 AD) who published his Periodic Table of elements in 1869. He continued to improve the periodic table and in 1871, published a Periodic Table, shown in Fig. 1.1, having gaps for four undiscovered elements.

Table 1.1: Mendeleyev's periodic Table II proposed in 1871

Period	Group I R^2O	Group II RO	Group III R^2O^3	Group IV RO^2	Group V R^2O^5	Group VI RO^3	Group VII R^2O^7	Group VIII RO^4
1.	H 1							
2.	Li 7	Be 9.4	B 11	C 12	N 14	O 16	F 19	
3.	Na 23	Mg 24	Al 27.8	Si 28	P 31	S 32	Cl 35.5	
4.	K 39	Ca 40	?— 44	Ti 48	V 51	Cr 52	Mn 55	Fe, Co, Ni, Cu 56, 59, 59, 63
5.	Cu 63	Zn 65	?— 68	?— 72	As 75	Se 78	Br 80	
6.	Rb 85	Sr 87	Y 88	Zr 90	Nb 94	Mo 96	?— 100	Ru, Rh, Pd, Ag 104, 104, 106, 108
7.	Ag 108	Cd 112	In 113	Sn 118	Sb 122	Te 122	I 127	
8.	Cs 133	Ba 137	Di 138	Ce 140	—	—	—	
9.	—	—	—	—	—	—	—	
10.	—	—	Er 178	La 180	Ta 182	W 184	—	Os, Ir, Pt, Au 195,197,198,199
11.	Au 199	Hg 200	Te 204	Pb 207	Bi 208	—	—	
12.	—	—		Th 231	—	U 240	—	

The classification was essentially based on atomic weights and it was observed that properties of elements were repeated resulting in classification of elements into groups and periods. In all, 64 elements were classified by Mendelyeev into 8 groups and 12 periods. In each group, the combining capacity of the element with respect to oxygen was fixed ranging from 0.5 to 3.5 oxygen atoms per atom of the element.

Electrical Nature of the Atom

The concept that the atom is an indivisible particle of matter was to be soon modified by the discovery of cathode rays and radioactivity. Michael Faraday had noted in 1832 that a given quantity of electricity seemed to liberate the same number of atoms for a variety of elements, though in some cases it liberated just half the expected number or in a few cases just a third. Scientists began to speculate that electricity like matter might consist of tiny units and attach to atoms in integral numbers. By now, conduction of electricity through metals, solutions and across small gaps was known and investigations were started to study its conduction through vacuum i.e. spaces without any air. In 1876, Eagen Goldstein (1850-1931 AD) sealed two electrodes in a glass tube and evacuated the same. He applied high voltage across the two electrodes and observed that some rays were produced at the cathode (negative electrode) and traveled towards the anode (positive electrode). He named them cathode rays. By 1885, William Crookes (1832-1919 AD) showed that cathode rays could be made to turn a small wheel kept in their path which indicated that the rays consisted of a stream of small atom like particles. He further observed that the rays could be bent by a magnet which meant that the rays carried electric charge. In 1897, Joseph John Thomson (1856-1940) showed that cathode rays could be bent in the presence of electrically charged objects and that they carry a negative charge. Thomson assigned the name electron (previously used to describe unit of electricity) to the particles making up the cathode rays. Assuming that the charge of an electron is equal to the minimum charge observed by Faraday, he concluded that the electron was a very light particle. The ratio of weights of hydrogen atom and electron was later found to be 1837.

Just around that time, another scientist Wilhelm Conrad Roentgen (1845-1923 AD) was also working on cathode rays. In 1895, he found that when cathode rays struck the glass at the other end, the glass fluoresced and a new radiation was produced. This radiation could penetrate glass, black paper and flesh. He called them 'X-rays' which, all of us know, found tremendous applications in the field of medical science.

Radioactivity

The discovery of X-rays attracted the attention of many scientists. Some scientists thought that X-ray emission might be linked to fluorescence and among them was Antoine Henri Becquerel (1852-1908 AD). He started investigating whether fluorescent salts emitted X-rays. He took potassium uranyl sulphate which glowed after being exposed to sun-light. He was using a photographic plate for detection of radiation but soon observed that the salt was giving penetrating X-ray-like radiation whether it was exposed to sun-light or not. He observed that like cathode rays, a part of the radiation emitted could be deflected by magnetic field. While working with Becquerel, the husband-wife team of Pierre Curie (1859-1906 AD) and Marie Curie (1867-1934 AD) showed that uranium atom was the source of radiation and called the phenomenon of continuous emission of radiation as 'radioactivity'. Uranium was the first element found to be radioactive. Very soon, it was observed that thorium was also radioactive. Careful experimentation on uranium ores by Curies led to the discovery of two new radioactive elements which were named as 'radium' and 'polonium'. Only very small amounts of these elements were present in the uranium ore and they had to process tonnes and tonnes of ore to obtain a fraction of a gramme of radium. They observed that the intensity of radiation emitted per gramme of radium was several thousand times more than that of uranium. Radium was to play a very crucial role in a number of discoveries in the coming years. Presence of radium was also found to make some salts fluorescent and hence it was used for painting watch dials which could be seen in the dark. In honour of Marie Curie, unit of radioactivity was named as Curie and is equal to 3.7×10^{10} disintegrations per second.

Ernest Rutherford (1871-1937 AD), while studying the nature of the emitted radiation by uranium and thorium, discovered that they consisted of positively charged particles and negatively charged particles which he called 'alpha rays' and 'beta rays' respectively. In 1900, Paul Villard discovered a third component that was not deflected by electric and magnetic fields and this was called 'gamma rays'. Beta rays were found to be like electrons. In 1906,

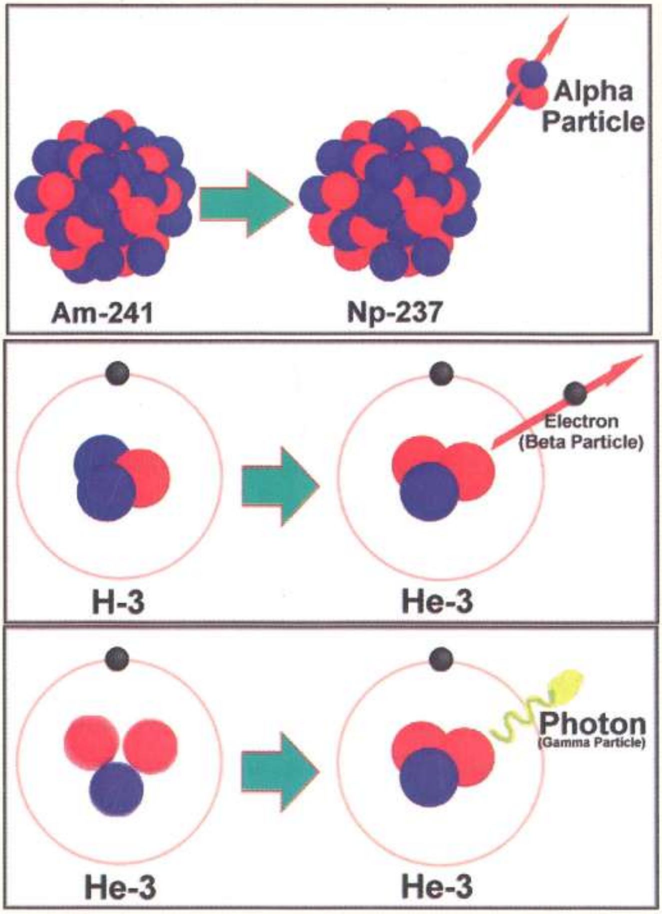
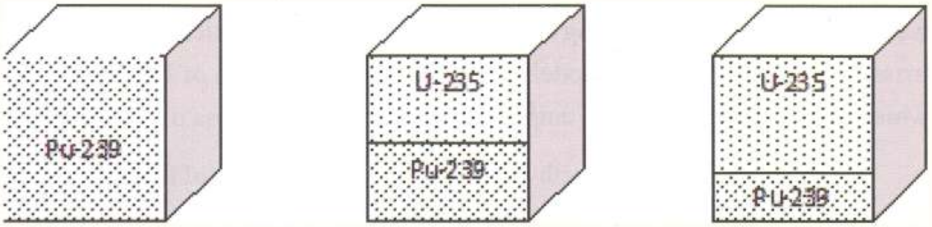


Fig. 1.1 Spontaneous Disintegration of Radioactive Atoms.

Rutherford discovered that alpha rays were also particles and carried two units of positive charge and were much more massive compared to electrons, in fact as massive as helium atoms. However, as alpha particles could penetrate through thin foils which helium atoms could not, their size was postulated to be much smaller. Fig. 1.1 depicts the spontaneous disintegration of an unstable atom.

Radioactive atoms may emit either alpha rays or beta rays. Emission of gamma rays quite often follows alpha or beta emission. Radioactive decay is a first order reaction. The rate of decay of radioactive atoms (-dN/dt) is proportional to the number of atoms N present,

$$-\frac{dN}{dt} = \lambda N$$



$$1\text{g}\ {}^{239}\text{Pu} \xrightarrow[\alpha]{24110\text{ y}} 0.5\text{g}\ {}^{239}\text{Pu} + 0.5\text{g}\ {}^{235}\text{U} \xrightarrow[\alpha]{24110\text{ y}} 0.25\text{ g}\ {}^{239}\text{Pu} + 0.75\text{g}\ {}^{235}\text{U}$$

Fig. 1.2 Radioactive decay of Plutonium-239 (In the figure weight loss due to alpha/beta particle emission is ignored. The figure also ignores the decay of Uranium-235, in the time span depicted, due to its long half life

where λ is the decay constant. Each radioactive species is characterized by a half life i.e, the time in which half the atoms originally present would be converted to atoms of another element. This is schematically illustrated in Fig 1.2.

Structure of the Atom

J. J. Thomson, on the basis of discovery of the electron and other available information, felt that since atom as a whole is neutral, the electrons must be exactly compensated by a positive charge in an atom. He postulated that an atom was a sphere of uniform positive electrification with tiny electrons uniformly studded in it. This idea led to the unification of the concept of electricity and atom. Thomson also discovered the positive rays which gave additional proof regarding this model of atom. This, however, had many drawbacks and was therefore, replaced by a model subsequently proposed by Rutherford and others.

By 1906, Rutherford was studying the interaction of a beam of alpha particles with thin sheets of metal using a strong radium source (1 g radium emits 37 billion alpha particles per second). He and his colleagues noted that while bulk of the alpha particles passed through the foil as if most of the space in the foil was empty, a few of them were deflected and a tiny fraction bounced back. Rutherford said, "It was about as credible as if you had fired a 15 inch shell at a piece of tissue paper and it came back and hit you". In 1911, he announced his results to the world in which he suggested that essentially all the mass of the atom was concentrated in a very tiny space at the centre of the atom. He called it nucleus. He also concluded that nucleus is positively charged. The diameter of the nucleus was only 1/10,000 of the diameter of the atom. The rest of the atom was filled with electrons having charge equal to that of the nucleus but very little mass. One notices that this model is a tribute to the thoughts of Democritus in which matter was made up of emptiness of spaces and fullness of matter.

At this stage, it may be worthwhile to know about the size of the atom. If we assume that the size of a person is equal to the size of hydrogen atom and all people in India (1290 millions) stood in a queue, the line would be only 12.9 centimeters long. That means 100 hydrogen atoms can be accommodated in a millionth of a centimeter. Heavier atoms would occupy 2 to 3 times more space compared to the hydrogen atom. The nucleus, as we have seen, is 10,000 times smaller than the atom. But each atom as tiny as it may be, displays all the properties of the element. Atom thus continues to remain the smallest chemical unit.

When Rutherford proposed his atomic model, Henri Gwyn Jeffreys Moseley (1887-1915 AD) was carrying out experiments on energy spectrum of X-rays emitted by various elements. He observed that in addition to a broad continuum, there were X-rays characteristic of each element. He observed that greater the atomic weight of the element shorter the wave length (higher the energy) of characteristic X-rays emitted by it. He also observed that the change in wave length, of these characteristic X-rays, from one element in the periodic table to the next was very regular. He postulated that the positive charge of elements increases in regular steps. From his data, he calculated the charge on various nuclei and observed that this charge, in most cases, agrees with the serial number of the atom in the periodic table. The number of units of charge in an atom was called its atomic number and Moseley correctly postulated that the atomic number is a more fundamental property of an atom than the atomic weight. The arrangement of the periodic table based on atomic numbers helped in solving certain anomalies in the Mendeleyev's periodic table and the currently accepted periodic table is given in Fig. 1.3. The results of Moseley were confirmed during 1920-1925 by precise alpha particle scattering studies.

The nucleus of hydrogen atom was called a proton. The hydrogen atom is thus made up of a proton and an electron. For many years, all atoms were thought to be made up of electrons and protons. However, it was noted that, in general, the charge on the nucleus was only half its atomic weight. Thus the nucleus had to contain either electrons to neutralize the charge of some of the protons or have

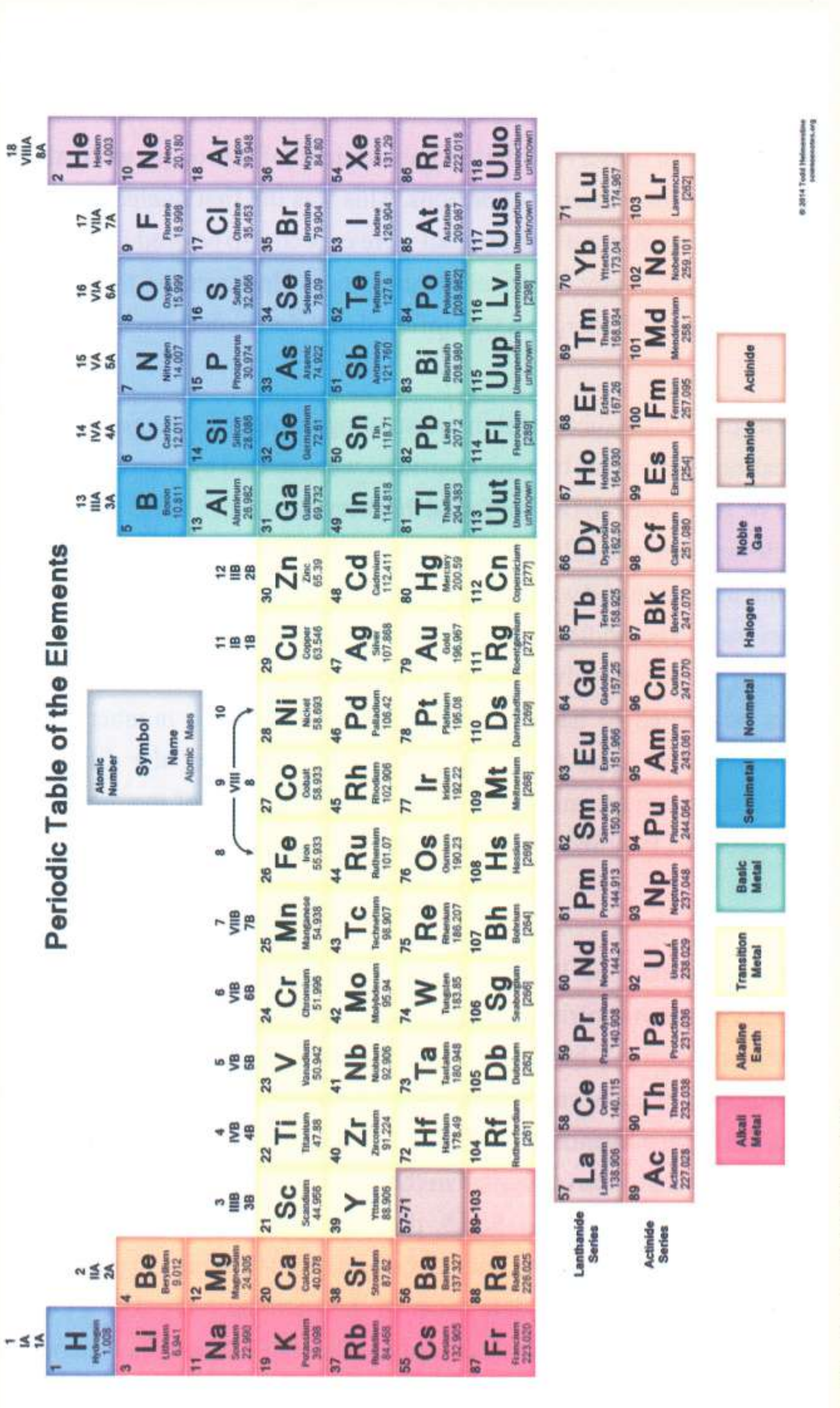


Fig. 1.3 The Periodic Table of Elements.

massive uncharged particle/particles. In fact, Rutherford proposed that uncharged particles should be present in the nucleus and named them as neutrons. During the studies on interaction of alpha particles with various elements, Rutherford observed that bombardment of nitrogen with alpha particles resulted in the emission of protons. This was the first nuclear reaction observed. As very few atoms of the product were expected to be produced, it was not possible to carry out any chemical identification. However, on the basis of conservation of mass and charge, it was inferred that the second product was an oxygen atom.

Rutherford was thus successful in transmuting nitrogen to oxygen. Studies on transmutation of elements by alpha particles were started by many scientists and in 1930 W. Bothe and H. Becker found that beryllium when bombarded with alpha particles emitted a highly penetrating radiation particles having the mass of a proton but no charge and were in fact neutrons proposed by Rutherford more than 10 years back. The riddle of atomic nucleus having mass almost double the atomic number was thus solved by the discovery of neutrons. The atomic nucleus was postulated to have protons equal to the atomic number of the element and neutrons equal to the nearest whole number of the difference between the atomic weight and the atomic number. The sum of the number of protons and neutrons is called the mass number.

Isotopes

Another co-worker of Rutherford, Frederick Soddy (1877-1956 AD) proposed that when uranium gives off an alpha particle, a new element is formed. This new element emits a beta particle and forms another element and this process of emission of alpha and beta particles continues till stable element lead is produced. This phenomenon of a chain of radioactive elements undergoing alpha and beta decay was also observed in the cases of thorium and actinium. In the course of these investigations, Soddy detected 40 to 50 different elements with different radioactive half lives but, on the basis of their chemical properties, it was not possible to accommodate them in the periodic table. On a closer scrutiny, however, he observed that the decay product of uranium had chemical properties similar to thorium. He therefore, suggested that these elements with two different masses (234 and 232) should be fitted 'in the same place' as thorium since they are chemically similar. Such elements were called isotopes

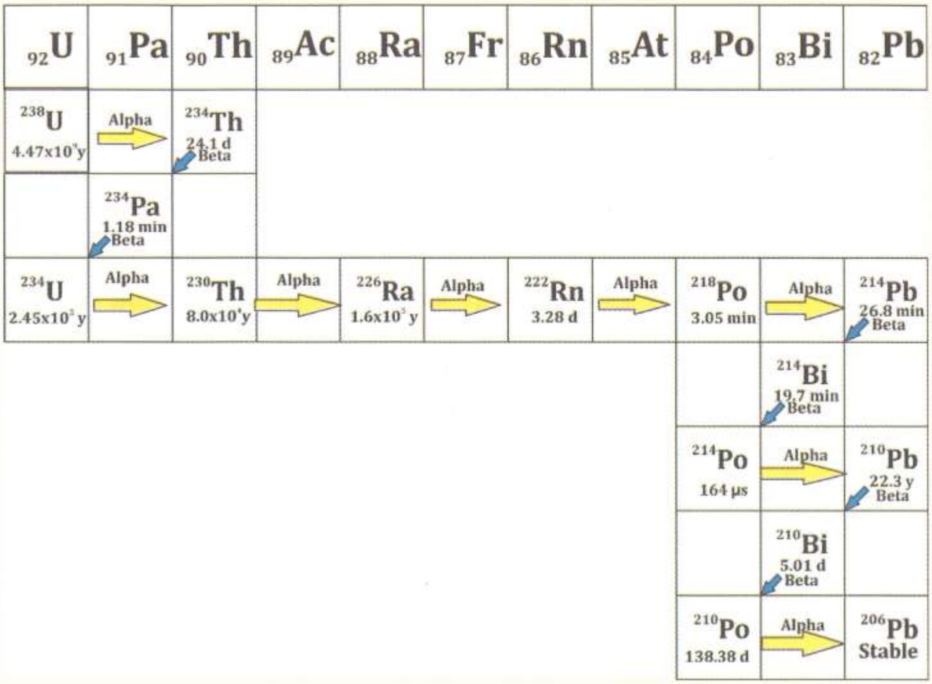


Fig. 1.4 Radioactive Decay of Uranium and its Daughter Products.

meaning the same place. Similarly it was realized that uranium, thorium and actinium series would end up in lead isotopes having respectively masses of 206, 208 and 207 which was confirmed experimentally by Soddy in 1914. These were the three isotopes of lead obtained as the end products from radioactive decay of three different elements. The natural lead has an atomic mass of 207.2, quite different from the lead obtained from any of the radioactive decay series. Decay series of uranium-238 and thorium-232 are shown in Figs. 1.4 and 1.5 respectively.

Most of the atomic weights of elements were close to whole numbers but some were substantially different. For example, inert gas neon has an atomic weight of 20.2. The possibility that this was due to the presence of two isotopes of neon was considered by Thomson. He carried out experiments on deflection of neon ions in electric and magnetic fields and proved that natural neon contains two isotopes, one with mass 20 and other with mass 22. More precise measurement by F.W. Aston (1877-1945 AD) proved that natural neon contained 90.51 % of neon-20, 0.27% of neon-21 and 9.22% of neon-22. Aston used his mass Spectrograph to determine the mass numbers of isotopes of many

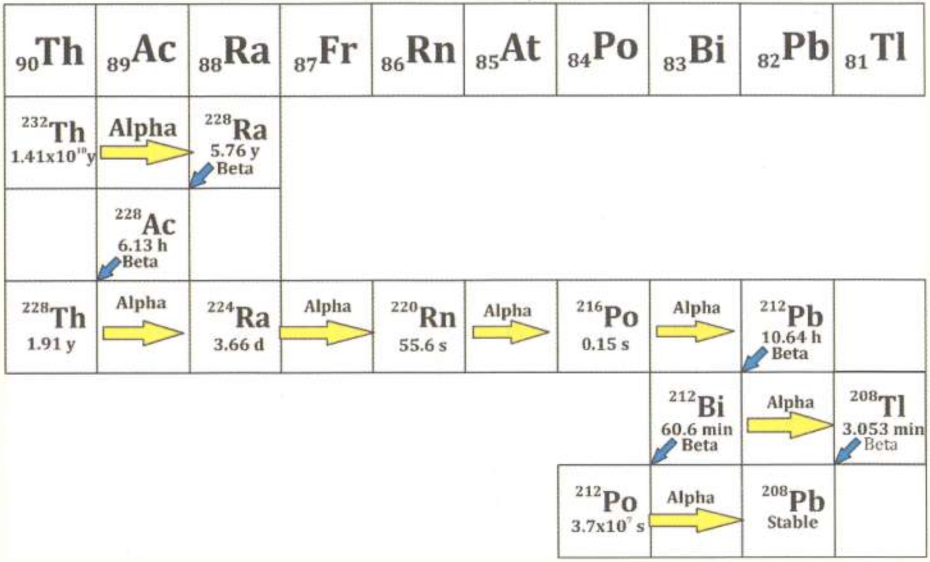


Fig. 1.5 Radioactive Decay of Thorium-232 and its Daughter Products.

elements. An astonishing fact is that Aston was responsible for the discovery of 212 isotopes out of the total of 288 naturally occurring isotopes. The element tin has the largest number of stable isotopes with mass numbers 112, 114, 115, 116, 117, 118, 119, 120, 122 and 124. Elements like beryllium (mass number 9) and sodium (mass number 23) have only one stable isotope. The discovery of neutron revealed that isotopes of an element have identical number of protons but the number of neutrons is different. For example, in the case of tin isotopes, the number of protons (as also the number of electrons) is 50 whereas the number of neutrons are 62, 64, 65, 66, 67, 68, 69, 70, 72 and 74. In addition, the radioactive isotopes of a number of elements have been identified and the total number of isotopes is about 1500.

With the discovery of isotopes, it became necessary that the atomic mass should be defined with respect to one of the isotopes. In 1962, atomic mass of carbon-12 was taken as 12.0000 atomic mass units and all other atomic masses were defined with respect to this mass. The mass of each atom of carbon can be determined by dividing 12 g by the Avogadro number (6.023×10^{23}). Accordingly, the masses of some of the fundamental particles are as follows:

Atomic mass unit (amu) = 1.660566 x 10^{-24} g
Mass of a proton = 1.007277 amu
Mass of an electron = 0.000549 amu

A notation was also evolved to represent the atomic number and mass number of each element. Accordingly, $^{112}_{50}$Sn, $^{114}_{50}$Sn etc., represent tin isotopes with mass number as superscript and atomic number as subscript.

Electronic Structure of the Atom

With the model proposed by Rutherford the possibility of negatively charged electron falling into the positively charged nucleus existed because opposite charges attract each other. To overcome this problem, Rutherford postulated that just as the planets (Mars, Earth, Venus etc.) do not fall towards the Sun, in spite of the gravitational pull, by moving around in fixed orbits, the electrons also must be revolving around the nucleus in a similar manner balancing the force of electrostatic attraction by the centrifugal force. This theory did not take into account the postulate, enunciated by James Clark Maxwell, that accelerating electrons should continuously emit radiation. However, atoms are known not to emit any radiation unless they are heated or excited by other means. Niels Bohr, postulated that electrons revolve in stationary orbits and the diameter of a stationary orbit depends upon the charge on the atomic nucleus. Electrons can only jump from one orbit to the other by absorption or emission of energy in the form of radiation. This model could explain the typical colour (frequency) of the radiation emitted by different elements when heated or excited. Broad features of the spectra of radiation emitted by an atom could be explained by Bohr's theory. Many refinements were proposed before the final model emerged. Erwin Schrodinger in 1926 applied the principles of quantum mechanics and postulated that in place of definite orbits there are orbitals where the probability of finding electrons is the highest. These orbitals are characterized by four quantum numbers: principal quantum number n, angular momentum quantum number *l*, magnetic quantum number m and spin quantum number s. This has led to the theory of electronic structure of the atom. Certain rules were also proposed. Each electron of an atom is expected to have a unique set of quantum numbers and two electrons of the same atom cannot have all the four quantum numbers identical. Principal quantum number n can have only positive integer values 1, 2, 3 etc. For each principal quantum number n, angular momentum quantum number l can have positive integer values from 0 to n-l i.e. 0,1,2,3,— (n-l). For each value of angular momentum quantum number l, the magnetic quantum number m can have (2l + 1) integer values from l to -l, including zero, i.e. l, l-1, l-2,……..0…..-(l-2), -(l-1), -l. Spin quantum numbers has only two values + 1/2 or -1/2. For example, if n=3, the corresponding l values are 0, 1 and 2. For l = 0, m = 0, For l = 1, m has three values -1, 0, +1, whereas for l = 3, m has five values, -2, -1, 0, +1, +2. In each case the electron can have spin +1/2 or -1/2. Using these rules, it is possible to write the electronic structure of atoms, e.g. sodium has atomic mass of 23 and atomic number 11. It, therefore, has 11 protons and 12 neutrons in the nucleus and 11 electrons in the orbitals. These electrons are arranged in different orbitals as shown in Table 1.2.

Table 1.2: Electronic Configuration of Sodium Atom

First Orbital n = 1

n	l	m	s	Electrons	Total
1	0	0	+1/2, -1/2	2	2

Second Orbital n = 2

N	l	m	s	Electrons	Total
2	0	0	+1/2, -1/2	2	8
1	1	1,0,-1	+1/2, -1/2	6	

Third Orbital n = 3

n	l	m	s	Electrons	Total
3	0	0	+1/2, -1/2	2	18
	1	1,0,-1	+1/2, -1/2	6	
	2	2,1,0,-1,-2	+1/2, -1/2	10	

From Table 1.2 it is clear that, the first orbital can have only two electrons with quantum numbers 1, 0, 0, +1/2 and 1, 0, 0, -1/2. The first orbital is called K shell. The second orbital has eight electrons with the following quantum numbers: [2, 0, 0, +1/2], [2, 0, 0, -1/2], [2, 1, 1, +1/2], [2, 1, 1, -1/2], [2, 1, 0, +1/2], [2, 1, 0, -1/2], [2, 1, -1, +1/2] and [2, 1, -1, -1/2]. This is called L shell. Similarly the third orbital will have 18 electrons and is called M shell.

Sodium has only one electron left after filling first and second orbitals, which is in the M shell with quantum numbers 3,0,0,+1/2. The electronic structure of sodium can thus be written as 2, (2,6), 1. In modern terminology the angular momentum quantum number of an electron is indicated by the terms s, p, d, f, g corresponding to the *l* values of 0, 1, 2, 3, 4 respectively. Thus the electronic configuration of sodium is $1s^2$, $2s^2$, $2p^6$, $3s^1$, where superscript indicates the total number of electrons that occupy the orbital. Electrons occupy various orbitals around the nucleus in order of decreasing energy and the energy of the orbital decreases with increasing quantum number. Electrons in the first orbital are most tightly bound and the force of attraction between the nucleus and electrons decreases with increasing value of n. A schematic representation of electronic structure of iron atom is given in Fig 1.6. It is seen that 3d orbit has

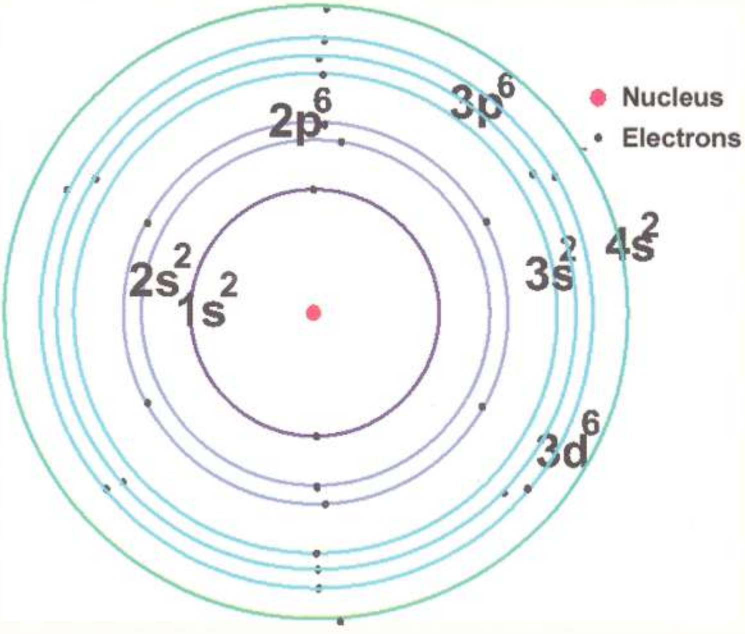


Fig. 1.6 Electronic Configuration of Iron.

only six electron, as against the possibility of ten electrons, and 4s orbit has two electrons. It is observed that rather than n, the energy of electrons is approximately a function of (n+*l*). Because of this, sometimes, the electrons start going to higher orbitals before the lower orbitals are completely filled. In some elements of the periodic table, not one but two or three of the outer orbitals may be incompletely filled. For example 6s orbital is occupied in lanthanides before 4f orbital is completely filled. It is now recognized that electrons in the outermost orbitals are responsible for its chemical properties. This explains why the properties of atoms display periodic nature when arranged according to atomic number. The modern periodic table (Fig 1.2), is in fact arranged as per the electronic structure of atoms.

Chapter 2

Nuclear Energy

Nuclear Binding Energy

The nucleus consists of protons and neutrons. As the protons are positively charged, they would be expected to repel one another and come out of the nucleus. However, the protons as well as the neutrons, referred to as nucleons, are held together in the nucleus by nuclear forces. Nuclear forces, therefore, should be strong, attractive and short ranged. The binding energy can be calculated from the energy required for separating these into individual particles. Conversely, if an element of mass number A is made by combining Z protons and A-Z neutrons, a corresponding amount of energy would be released. This in fact is happening all the time in the sun where hydrogen, which constitutes about 72% of the mass of the sun, is continuously converted to helium and other heavier elements with the release of energy. What is the source of this energy? Careful examination shows that for each isotope of an element, the atomic mass is lower than the total mass of constituent protons, neutrons and electrons. Apparently, energy equivalent to the mass difference is released during the formation of these elements from the constituent particles. Albert Einstein (1879-1955 AD) proposed that mass and energy are inter-convertible and the relation for the inter-conversion of mass and energy is:

$$\text{Energy} = \text{mass x (velocity of light)}^2 \qquad (2.1)$$

In the sun, about 4.6×10^6 tonnes of mass is being continuously converted into energy every second during the process of formation of helium and other elements. Even then, the mass of the sun is so large that this process is expected to continue for more than 20 billion years to come. Earth receives only a small fraction of energy released by the sun which is equivalent to 1.8 kg of mass per second. Energy on the atomic scale is expressed in units of electron volt (eV)[1]. One atomic mass unit (amu) is equal to 931.5 million electron volts (MeV) of energy. We can calculate the binding energy of some of the atomic nuclei. Hydrogen atom has one proton and one electron and we can visualize the atom of an element of mass A to be made up of Z hydrogen atoms (mass 1.007825 amu) and A-Z neutrons (mass 1.008665 amu). For example, the mass of sodium with A=23 and Z=11 is 22.989771 amu. The sum of mass of 11 hydrogen atoms and 12 neutrons is 23.190055 amu. The binding energy of sodium nucleus can, therefore, be calculated as follows:

$$\begin{aligned}\text{Binding energy} &= 23.190055 - 22.989771 = 0.200284 \text{ amu} \\ &= 0.200284 \times 931.5 \text{ MeV} = 186.564 \text{ MeV} \qquad (2.2)\end{aligned}$$

If we consider that the binding energy is contributed by all the nucleons, then the average binding energy per nucleon works out to be 8.111 MeV. Average binding energy (B) for a number of isotopes is plotted as a function of number of nucleons (mass number) in Fig. 2.1. It is seen from this figure that B is the largest (approximately 8.8 MeV) around mass number 60 and decreases on either side, being 2.22 MeV for deuterium and 7.57 MeV for uranium. The nuclei with mass number around 60 i.e. iron, nickel and cobalt isotopes are most stable. In principle, therefore, the lighter elements could fuse and the heavier elements breakup to yield more stable elements in the region of mass number 60. For example, two neon nuclei could fuse to form ^{40}Ca releasing 24 MeV of energy but this reaction does not occur because of the coulombic repulsion between the neon nuclei. Similarly, breaking of atoms like uranium would release significant quantities of energy.

To explain the observed systematics in the characteristics of nuclides such as stable isotopic abundance of some elements, nuclear fission and nuclear decay characteristics, various nuclear models have been proposed, of which two are important. Bohr in 1936, proposed that the nucleus is similar to a charged liquid drop with nucleons held together by strong nuclear forces. This model could successfully predict the binding energy of nuclei, energetics in β-decay and explain the mechanism of many nuclear reactions. Another model is single particle shell model, proposed in 1952, independently by Mayer, and Haxel,

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[1] Electron volt is the energy acquired by an electron when it is accelerated by a potential difference of one volt

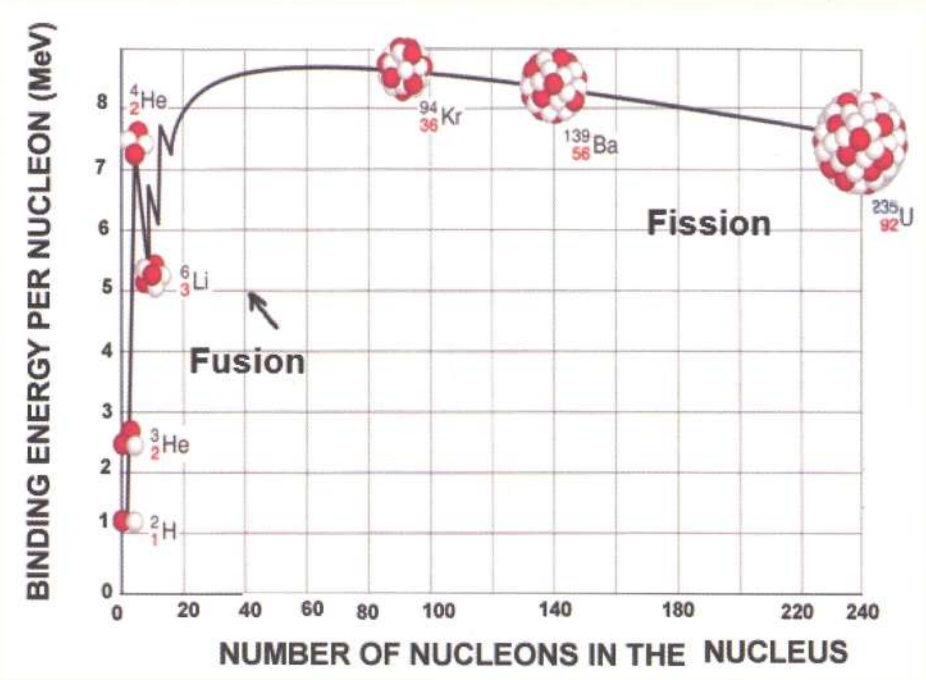

Fig. 2.1 Variation of Average Binding Energy as a function of Nucleon Number (Mass Number).

Jensen and Suess, in which nucleon-nucleon interactions were considered weak and nucleons occupy discrete energy states. This model explained the existence of many stable isotopes for Sn, discrete gamma energies and some other mechanical properties such as spin, parity and magnetic moments.

Nuclear Reactions

The decay of radioactive elements is a spontaneous nuclear process. In laboratory, the era of nuclear reactions began when Rutherford, in 1919, bombarded nitrogen with alpha particles which resulted in the formation of protons and oxygen. By 1924, he had demonstrated that alpha particles could knock protons out from almost all the elements up to potassium. Interaction of alpha particles with beryllium later led to the discovery of neutrons. However, it was not possible to have nuclear reactions of this type with heavier elements because they have high nuclear charge and the repulsive forces (coulomb barrier) between the alpha particle and the nucleus were much more than the kinetic energy of alpha particles (4 to 6 MeV) obtained from natural sources (radium, polonium etc.). In 1934, husband- wife team of Frederic Joliot-Curie (1900-1958 AD) and Irene Joliot-Curie (1897-1956 AD) bombarded ^{27}A1 with alpha particles and observed that the emission of neutrons was accompanied by the formation of an artificial radioactive isotope ^{30}P. The discovery of artificial radioactivity caused excitement in the scientific community. In order to overcome coulomb barrier, scientists were already working on machines to produce high energy charged particle projectiles.

Ernest Orlando Lawrence (1901-1958 AD) in 1930, constructed a special device called cyclotron. John Douglas Cockroft (1897-1967 AD) and Ernest Thomas Sinton Walton (1903-1995) constructed an electrostatic accelerator in 1932. Both the machines were used for producing high energy protons and alpha particles for the study of nuclear reactions.

The discovery of neutrons, however, opened a new chapter in nuclear sciences. As neutron does not have electric charge, it would not be repelled by the nucleus. Neutron induced nuclear reactions would thus be possible with almost all elements/isotopes. O. D'Augestino Enrico Fermi (1901-1954 AD), therefore, made a neutron source by taking beryllium powder and alpha emitting radon in a sealed tube. This source gave a million neutrons per second. By 1934, Fermi had discovered that slowing down (moderation) of neutrons with paraffin or water enhanced their interaction probability. This was just the opposite of what was observed with alpha particles. Fermi started bombarding many metals including uranium with neutrons with a hope to produce new elements, particularly transuranium elements. In 1935, Fermi and his colleagues had succeeded in transmuting platinum into gold as shown below:

$$^{198}_{78}\mathrm{Pt} + ^{1}_{0}\mathrm{n} \xrightarrow{\gamma} ^{199}_{78}\mathrm{Pt} \xrightarrow[31\ \mathrm{min}]{\beta} ^{199}_{79}\mathrm{Au} \qquad (2.3)$$

Thus it is possible to produce higher Z elements using neutron induced nuclear reactions.

In 1937, C. Perrier and E. Segre used a similar reaction of Mo (Z=42) with neutrons leading to the discovery of first artificial element Technetium (Z=43). When Fermi and his colleagues used neutrons to bombard uranium, the results were highly confusing. Absorption of neutrons by uranium was found to yield beta particles with four different half lives. As emission of beta particles implied increase in the charge of the nucleus by one unit, Fermi and co-workers proposed the formation of element 93 and subsequent higher transuranium elements. Other physicists, who repeated Fermi's experiment, also obtained products emitting a variety of beta particles but could not explain the reaction mechanism. Among those working on the problem were Otto Hahn (1879-1968 AD) and Lise Meitner (1878-1968 AD) who were trying to chemically identify the reaction products. They observed that a fraction of the radioactivity was getting precipitated with barium (Z=56) indicating that one of the products of the reaction had properties similar to barium. Radium (Z=88) was known to be chemically similar to barium and it was thought that neutrons might have induced the emission of two alpha particles from uranium leading to the formation of radium. In March 1938 Meitner had to escape from Germany because of her Jewish background. Hahn and his student Fritz Strassmann carried out careful experiments to separate barium from the postulated radium and were not successful. It then occurred to them that the product might be barium itself. This would imply that uranium nucleus had been split into two fragments by a slow moving neutron. They confirmed this by fractional crystallization of Ba and Ra fractions, and to their surprise, all the activity was found with Ba fraction. Hahn and Strassmann published the results in January 1939 and also conveyed these astonishing results to Meitner in Copenhagen. She discussed the matter with her nephew Otto Frisch and postulated that the neutron could excite the uranium nucleus which could undergo division into two fragments of nearly equal mass (Fig. 2.2). This process was named as nuclear

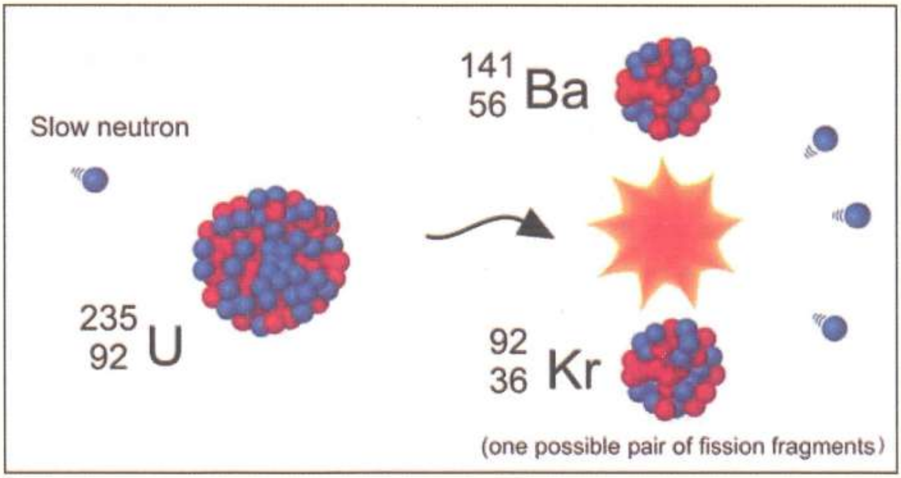

Fig. 2.2 The Fission of Uranium-235 Nucleus.

fission, just like the division of a living cell. If we assume that one of them is barium (Z=56) then the other must be krypton (Z=36). This explanation was also published in January 1939.

The Fission Chain Reaction

Every day we encounter chemical chain reaction when we light the gas burner. A spark initiates the burning of a few molecules of gas and the heat produced in turn initiates similar reaction in many more molecules. The reaction quickly builds up till we have a large flame consuming all the gas coming through the burner nozzle. The chemical reaction for burning of methane gas can be represented by the following reaction:

$$CH_4 + 2O_2 \xrightarrow{-212.7\ \text{kcal mol}^{-1}} CO_2 + 2H_2O \qquad (2.4)$$

16 g of this gas (1 mole) burns to release 212.7 kilocalories of heat. As there are 6.023×10^{23} molecules in each mole, the energy released per molecule works out to be 3.5×10^{-19} calories which is equivalent to 9.26 electron volts. Let us compare this with the energy released in the fission of uranium nucleus. We have seen that the average binding energy of a nucleon in uranium is 7.6 MeV and that for nuclei in the mass region of 100 to 140 is approximately 8.5 MeV. The fission of each atom of uranium would, therefore, release approximately 238 x (8.5-7.6) MeV i.e., 214 MeV of energy. The energy released in nuclear fission per atom is more than a million times the chemical reaction energy released in the burning of methane. While the chemical reaction of a gas requires only oxygen, which is always present in the environment, the fission of uranium would require neutrons. How could one sustain a nuclear chain reaction without a powerful neutron source? Leo Szilard (1898 -1964) a Hungarian physicist who had migrated to UK because of his Jewish background, was working on the possibility of nuclear chain reaction during the war period. One of the schemes which he imagined was the emission of two fast neutrons from a nucleus when bombarded by a fast neutron.

The two neutrons liberated could, in turn, cause the liberation of four neutrons and so on, leading to billions of nuclear reactions. However, he could not identify a reaction which would make this possible. Fermi while attending the first conference featuring the discussion on fission suggested that neutrons should be released during the process of fission since neutron to proton ratio in uranium is higher than that in the elements in the mass region of 100 to 140. The release of neutrons in fission reaction was soon experimentally verified by a number of physicists including Leo Szilard. A nuclear chain reaction was thus thought feasible.

Niels Bohr, while working on the theory of fission, predicted that only ^{235}U, which constitutes 0.715% of natural uranium, would undergo fission with slow neutrons. This was confirmed by subsequent experimental observations. ^{238}U was in fact observed to absorb slow neutrons without undergoing fission and in this way interfered with the fission chain reaction. Fission of each uranium atom was accompanied by the release of 2 or 3 neutrons (approx average 2.4) and the reaction can be represented as follows:

$$^{235}_{92}\mathrm{U} + ^{1}_{0}\mathrm{n} \rightarrow ^{236}_{92}\mathrm{U} \rightarrow ^{137}_{56}\mathrm{Ba} + ^{97}_{36}\mathrm{Kr} + 2^{1}_{0}\mathrm{n} + 200\ \mathrm{MeV} \qquad (2.5)$$

The buildup of chain reaction would require more than one neutron released, during each fission, to cause fission in other ^{235}U nuclei. A fission chain reaction is schematically shown in Fig. 2.3.

Equation 2.5 represents only one of the many possible modes in which uranium undergoes fission. In fact, a variety of fission products are produced and

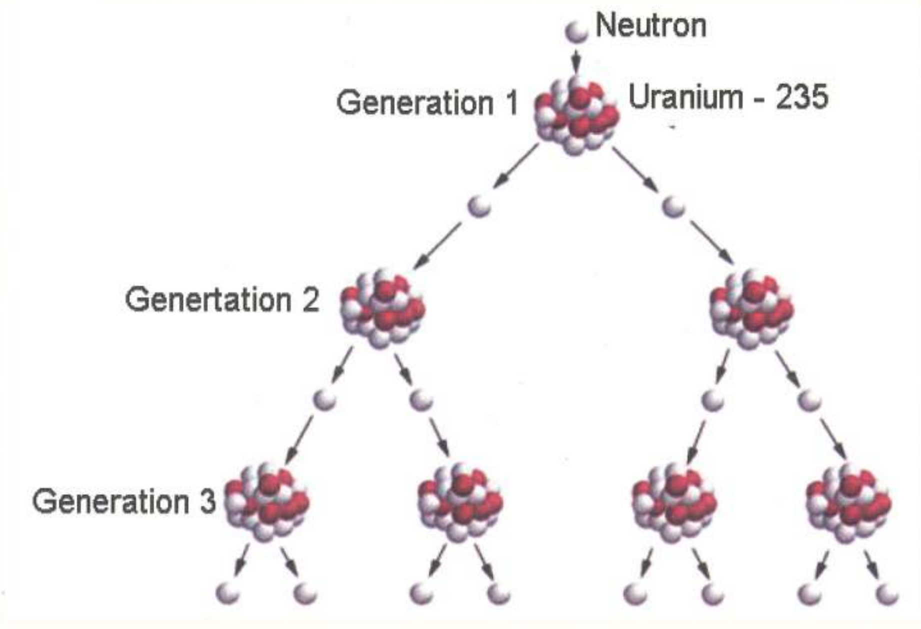

Fig. 2.3 Fission Chain Reaction

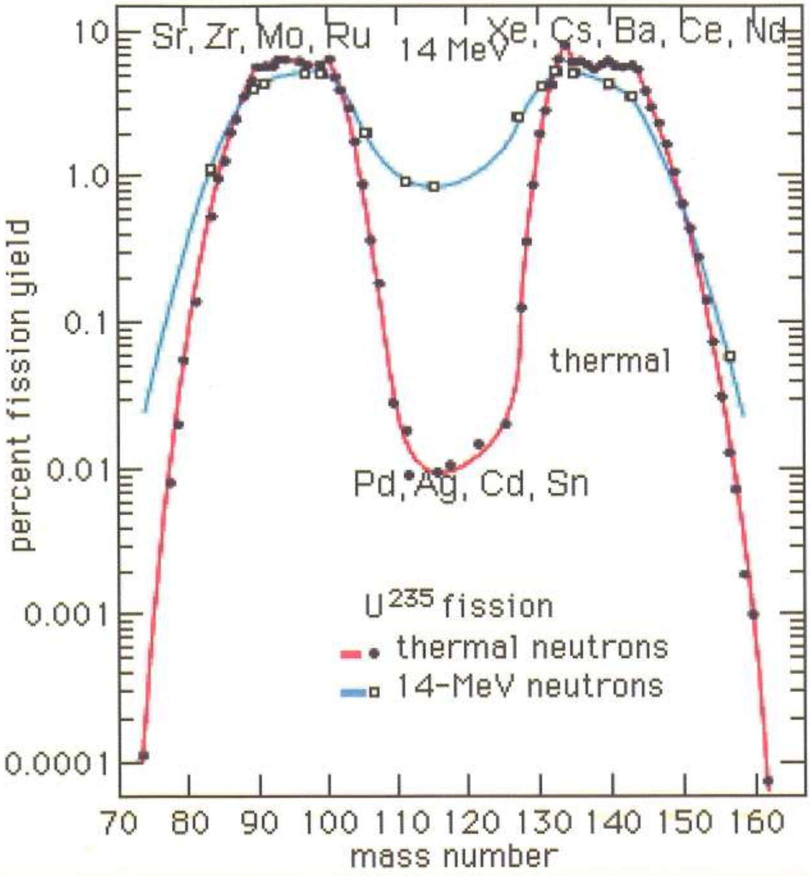

Fig. 2.4 Mass Yield Curve for Long Lived and Stable Fission Products in Thermal and 14 MeV Neutron Fission of ^{235}U.

the yield of various fission products as a function of mass number is given in Fig. 2.4. It is seen from this figure that the mass yield curve is asymmetric with two peaks around 97 and 135 mass units and the width is about 10 mass units at half maximum yield. The fission products are neutron rich, highly unstable, and undergo beta decay. The fission process thus leads to the formation of highly radioactive products. The fission fragments are formed in highly excited state and therefore, the neutrons released have considerable kinetic energy (En) their average speed being fifty million kilometers per hour (En=1.1 MeV). This may be compared with the average speed of 1650 kilometers per hour (0.025 eV) of the gas molecules in the air.

The energy of neutrons released by radium beryllium source also lies in the MeV region and Fermi had achieved the slowing down of neutrons to a speed of about ten thousand kilometers per hour by collision with carbon and hydrogen atoms in paraffin or with hydrogen atoms in water. Fission reaction, however, is sometimes possible only with fast neutrons. The possibility of a self sustained fission chain reaction was demonstrated by Fermi in August 1942 by setting up of the world's first nuclear reactor at Chicago.

The Fissile and Fertile Nuclides

The probability of a nuclear reaction, called the reaction cross section (σ), is measured in units of barn (b) which is equal to 10^{-28} m^2. With neutrons having energies greater than 1.6 MeV, both ^{235}U and ^{238}U undergo fission with similar probability (σ = 1-3 b). However, when neutron energy is decreased to thermal region (0.025 eV) the probability of fission for ^{235}U goes up by several times (σ = 535 b) whereas it becomes zero for ^{238}U. It has been observed, that among uranium and transuranium isotopes, those having odd number of neutrons and even number of protons, absorb neutrons of all energies to form compound nuclei (e.g. ^{236}U) which undergo fission. Those isotopes which can readily sustain a fission chain reaction are called the fissile nuclides. Uranium-235 is the only naturally occurring fissile nuclide. Uranium-238 which is always present along with ^{235}U and is also useful because the absorption of slow neutron results in the formation of ^{239}U which decays to a fissile isotope ^{239}Pu as per the following equation:

$$^{238}_{92}\mathrm{U} + {}^{1}_{0}\mathrm{n} \rightarrow {}^{239}_{92}\mathrm{U} \xrightarrow[23.45\ \mathrm{min}]{\beta} {}^{239}_{93}\mathrm{Np} \xrightarrow[2.3565\ \mathrm{d}]{\beta} {}^{239}_{94}\mathrm{Pu} \qquad (2.6)$$

Therefore, ^{238}U is called a fertile isotope. Plutonium-239 nucleus absorbs a neutron to form ^{240}Pu nucleus, in an excited state, which dexcites either by fission or gamma decay. Fission cross section of ^{239}Pu, with thermal neutrons, is 742 barns which is more than that for ^{235}U. ^{241}Pu, another isotope of plutonium produced in nuclear reactors, is also fissile (σ_f = 1010 b). A fissile isotope, of great importance to India is ^{233}U. This is produced by exposing another fertile material thorium to neutrons in a reactor.

$$^{232}_{90}\mathrm{Th} + {}^{1}_{0}\mathrm{n} \rightarrow {}^{233}_{90}\mathrm{Th} \xrightarrow[22.3\ \mathrm{min}]{\beta} {}^{233}_{91}\mathrm{Pa} \xrightarrow[26.967\ \mathrm{d}]{\beta} {}^{233}_{92}\mathrm{U} \qquad (2.7)$$

Thus we can summarize that there are 4 fissile isotopes namely ^{233}U (half life : 1.59 x 10^5 years), ^{235}U (half life : 7.04 x 10^8 years), ^{239}Pu (half life : 2.41 x 10^4 years) and ^{241}Pu (half life : 14.4 years). These isotopes are reasonably long lived for application in production of power. The two naturally occurring fertile isotopes which lead to the production of artificial fissile isotopes are ^{238}U and ^{232}Th.

Materials for Nuclear Reactors

Nuclear reactor is a device in which the fission chain reaction is allowed to take place in a controlled manner for the generation of energy and/or neutrons for research and isotope production. The essential materials used in a nuclear reactor are:

(i) Nuclear fuel for sustaining the fission chain reaction.
(ii) Moderator for slowing down the neutrons such that the fission reaction takes place with enhanced probability.
(iii) Cladding for the fuel such that the radioactive fission products produced during the reaction are not released to the environment.
(iv) Coolant for the removal of heat produced by the fission reaction.
(v) Control elements for absorption of neutrons to control the rate of fission chain reaction.

Fuel Materials

Nuclear fuel is the heart of the nuclear power reactor and great attention is devoted to its design. The fuel once charged into the reactor is not expected to fail during one to three year period of its stay in the reactor. Bulk of the energy in a nuclear reactor is produced by the fission of ^{235}U or $^{239,241}Pu$. During the process of energy production, 0.5 to 10% of uranium/plutonium undergoes fission (depending on enrichment). The fuel material is encased in the cladding to prevent the release of fission products to the coolant system. By a proper choice of fuel material and cladding alloy, the chemical and physical compatibility of the two is ensured. Uranium dioxide and uranium metal are the fuel materials of choice in most of the reactors. The physical appearance of spent fuel is identical to that of the fresh fuel. The main objective of the fuel design is to extract maximum power as well as energy from the fuel without any fuel failure. Present fuel designs have ensured that no gross fuel failure takes place and efforts are continuously being made to decrease the minor defects which occur in less than 0.05% of the fuel pins.

The rate at which the energy has to be extracted from a particular fuel is called its specific power and is measured in terms of megawatts of thermal power (MWt) produced per tonne of the fuel. Specific power is thus a measure of the amount of fuel used in a reactor. Thus the fissile inventory is lower if the specific power is higher. The fuel elements are normally in the form of cylindrical rods in which energy would be produced due to fission throughout the cross section of the element. The rate of energy production would depend on the density of the fuel and the fissile atom concentration. The energy produced in the fuel element is removed by the coolant from the outer surface of the cladding. Even though the surface of the fuel element is cooled, the central part can be quite hot. As per design the central part of the fuel should not undergo melting or other phase changes during power production, as phase changes can sometime involve large stresses on the cladding tube[2]. As the central part of the fuel is the hottest, its temperature has to be kept below the melting point or phase transition temperatures.

Moderator Materials

It has been mentioned that thermal neutrons are more efficient in sustaining a fission chain reaction. Thermalization is achieved by using moderators which slow down the neutrons by inelastic/elastic collisions. Moderator atoms of small mass are more efficient in thermalization provided they do not absorb neutrons in the process. The prominent moderators used in nuclear reactors are light water (H_2O, i.e. natural water), heavy water (D_2O) and graphite. Slowing down of fission neutrons, with most probable energy of 1 MeV, to thermal energy of 0.025 eV requires 18 collisions with H atoms, 24 collisions with D atoms or 111 collisions with C atoms. Light water, though very efficient in slowing down the neutrons, is not the best moderator as hydrogen has a neutron absorption cross section σ_a of 0.33b. Because of this, H_2O is not a suitable moderator for natural uranium fuelled reactors. In contrast, D with $\sigma_a = 0.0005$ b and C with $\sigma_a = 0.003$ b can be used as moderator with natural uranium. Beryllium with $\sigma_a = 0.0095$ b is

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[2] You might have experienced that a cold drink bottle left in the freezing chamber can lead to the formation of solid ice, which has lower density, and the extra volume leads to cracking of the glass bottle.

also a good moderator but has been used only in some reactors because of its toxic nature.

Cladding Materials

Uranium metal in the form of a rod or uranium dioxide in the form of pellets is encased in metallic clad tubes. Essential properties for a clad material are : (i) high strength, (ii) good chemical compatibility with fuel and the coolant and (iii) low neutron absorption cross section. Aluminium alloys are often used to clad fuel in research reactors. In power reactors, alloys of magnesium (Magnox) and zirconium (zircaloy 2 and zircaloy 4) have been extensively used as clad materials. Even though stainless steel has high neutron absorption cross section ($\sigma_a = 2.7$ b), it is also used as a clad material, particularly when the fuel operating temperature is above 350°C.

Coolant Materials

The requirement of coolant materials are : (i) good thermal capacity for heat removal, (ii) chemical compatibility with fuel, clad and structural materials and (iii) low neutron absorption cross section. Helium and carbon dioxide have been used as gaseous coolants. Light water is quite often the coolant and moderator though, some reactors use it only as coolant with other moderators. Similarly heavy water acts as a coolant in a large number of power reactors. Liquid sodium metal is used as coolant in reactors which operate at high temperature (> 350°C) and when moderation is not desirable.

Control Materials

In most reactors, the fuel cannot be replaced as it is consumed. Consequently each cycle of reactor operation starts with about 30% more fuel than required for its initial criticality. Without proper control the excess fuel may take the power to unacceptable levels. Control of power is achieved by having rods which contain neutron absorbing materials. The power of a nuclear reactor is controlled, and its shut down can be achieved, by the use of control rods. The rods normally contain boron ($\sigma_a = 759$ b) or cadmium ($\sigma_a = 2450$ b). Boron is most often used in the form of boron carbide. Cadmium as metal or as Ag - 15% Cd - 5% In alloy is used. Hafnium with $\sigma_a = 105$ b is also used in metallic form. The rods are withdrawn away from the fuel to start a chain reaction and increase power.

History of Reactors

The possibility of setting up a system for fission chain reaction was being explored by Joliot-Curie and co-workers in 1940 using uranium metal as fuel and light water as well as heavy water as moderators. The studies were, however, discontinued in June 1940 with the occupation of Paris by the German army. Just at that time, Otto Frisch was in UK and predicted that it should be possible to make a nuclear bomb using highly enriched ^{235}U. The British Government set up a committee to verify the prediction of Frisch and the report published in July 1941 confirmed the possibility of a bomb. The report also predicted the possibility of using nuclear energy for power production and the production of fissile isotope ^{239}Pu from ^{238}U.

The main thrust of work on nuclear fission was in the United States where Fermi and his team, which included Leo Szilard, were planning to set up a facility for the demonstration of the fission chain reaction. It was realized that in the interest of neutron economy, it would be essential to use the highest purity materials and prevent the loss of neutrons due to absorption by impurities. They decided to use graphite as the moderator and place uranium in the graphite matrix forming a cubical lattice of uranium. Since high purity uranium metal was not available, in the initial stages, uranium oxide was used as fuel. From July 1941 to July 1942 about 30 small assemblies were made to obtain data required for setting up the reactor. The final assembly was made by piling alternate layers of graphite bricks and graphite bricks with holes for accommodating uranium oxide spheres of 3.25 inch diameter. High purity uranium metal bricks became available by November 1942 and were used in setting up of the reactor. The reactor used about 36.6 te of uranium oxide and 5.6 te of uranium metal. Cadmium was used to control the fission chain reaction. The possibility of sustained fission chain reaction was established in this reactor on December 2, 1942. The reactor power was about 200 watts and therefore, cooling arrangement was not required at this stage.

The first application of sustained fission chain reaction was not for energy production, but for the production of plutonium. The first reactor for this purpose was set up in November 1943 at Oak Ridge National Laboratory, USA which used 35 tonnes of uranium metal as fuel and produced 3.8 MW of heat. This reactor was cooled with air. About 4 g of plutonium per day was formed in this reactor. Subsequently, reactors for producing plutonium were set up at various sites in the United States and as well as in UK, France and erstwhile USSR.

Following the second World War, the emphasis of reactor technology shifted towards the development of reactors for other applications. In 1953, USA launched a nuclear powered submarine named 'Nautilus' . The first reactor to produce electricity was commissioned in Moscow in June 1954. This was a 5 MWe reactor using uranium oxide as fuel, graphite as moderator and water as coolant. The first reactor to supply electricity for commercial applications was installed in UK in August 1956. This reactor was of 50 MWe capacity using uranium metal as fuel, graphite as moderator and carbon dioxide gas as coolant. The main purpose of this reactor, however, was the production of plutonium required for the military programme. The first reactor solely devoted for civilian application was set up in the USA in 1957 at Shipping Port. This reactor was of 20 MWe capacity with uranium oxide as fuel, and light water as moderator and coolant. The use of nuclear power reactors in ship propulsion was initiated by the then USSR in 1959 by launching the ice breaker Lenin which had three 90 MWe reactors. Currently, out of the large number of reactors operating in the world, several hundreds are being used for submarine and ship propulsion. There are about 350 research reactors which are used for studies involving neutrons and for production of isotopes. Research reactors are simpler in design as there is no need for high temperature and high pressure which is essential for power reactors.

India set up its first research reactor APSARA in 1956. It was a 1MWt swimming pool reactor and the core could be seen from top of the swimming pool. It was shut down in 2010 after 54 years of successful operation. A view of Apsara reactor is shown in Fig. 2.5. It is in the process of being upgraded to a higher capacity research reactor.

Power Reactors

There are 438 nuclear power reactors operating in the world and 67 more reactors are under construction. Operating reactors produce about 11% of the world's electricity (Table 2.1). Power reactors are quite often classified on the basis of the type coolant used. Some of the prominent types which are in

Table 2.1: Installed Capacity of Nuclear Power Plants in the World (Nuclear Power Reactors in the World, IAEA-RDS-2/35, IAEA, Vienna (2015))

Country	Nuclear MWe	Types of Reactors	% of Electricity TW(e) h
Argentina	1, 627	3 PHWR	4.1
Belgium	5, 927	7 PWR	47.5
Brazil	1, 884	2 PWR	2.9
Bulgaria	1, 926	2 PWR	31.8
Canada	13, 500	19 PHWR	16.8
China	19, 007	1 FBR, 20 PWR, 2 PHWR	2.4
Czech Republic	3, 904	6 PWR	35.8
Finland	2, 752	2 PWR, 2 BWR	34.7
France	63, 130	58 PWR	76.9
Germany	12, 074	9 PWR	15.8
Hungary	1, 889	4 PWR	53.6
India	5, 308	18 PHWR, 2 BWR, 1 PWR	3.5
Japan	42, 388	24 BWR, 24 PWR	0.0
Korea, Rep. of	20, 717	19 PWR, 4 PHWR	30.4
Pakistan	690	2 PWR, 1 PHWR	4.3
Russia	24, 654	1 FBR, 18 PWR, 15 LWGR	18.6
Slovakia	1, 814	4 PWR	56.8
Spain	7, 121	7 PWR	20.4
Sweden	9, 470	7 BWR, 3 PWR	41.5
Switzerland	3, 333	3 PWR, 2 BWR	37.9
United Kingdom	9, 373	15 GCR, 1 PWR	17.2
The United States	98, 639	65 PWR, 34 BWR	19.5
Ukraine	13, 107	15 PWR	49.4
Total Including Others	376, 216	277 PWR, 80 BWR, 15 GCR, 49 PHWR, 15 LWGR, 2 FBR Total: 438	~ 11

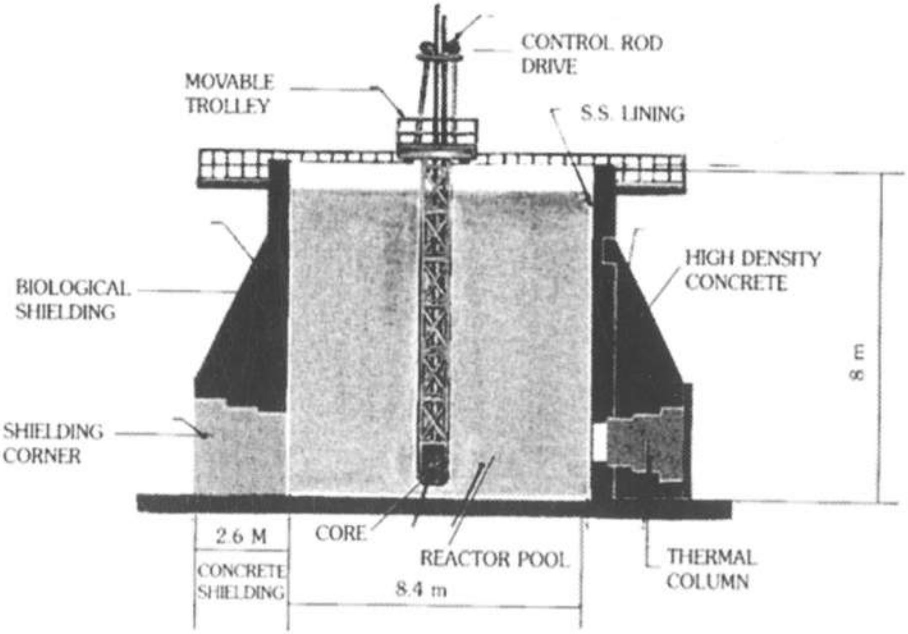


Fig. 2.5 A view of the Apsara reactor and its core

operation forth production of electricity in the world are given below along with the total, net electrical capacity.

1. Boiling Water Reactors (BWR) – 75,462 MWe
2. Pressurized Water Reactors (PWR) – 257,231 MWe
3. Pressurized Heavy Water Reactors (PHWR) – 24,549 MWe
4. Light Water Cooled Graphite Moderated Reactors (LWGR)- 10,219 MWe
6. Gas Cooled Reactors (GCR/AGR)- 8,175 MWe
7. High Temperature Gas Cooled Reactors (HTGR) None at present
8. Liquid Metal Cooled Fast Breeder Reactors (LMFBR)- 580 MWe

The reactors which use light water as moderator/coolant require enrichment of uranium e.g. BWR, PWR and LWGR. Similarly, if the cladding material used absorbs neutrons, enrichment of uranium is required, e.g. GCR/AGR.

The Boiling Water Reactor (BWR)

BWR uses uranium oxide fuel having 1.5 to 3% of ^{235}U. Zircaloy is used as cladding and the reactor is housed in a strong stainless steel vessel. Water flowing through the reactor is used as coolant as well as moderator and is

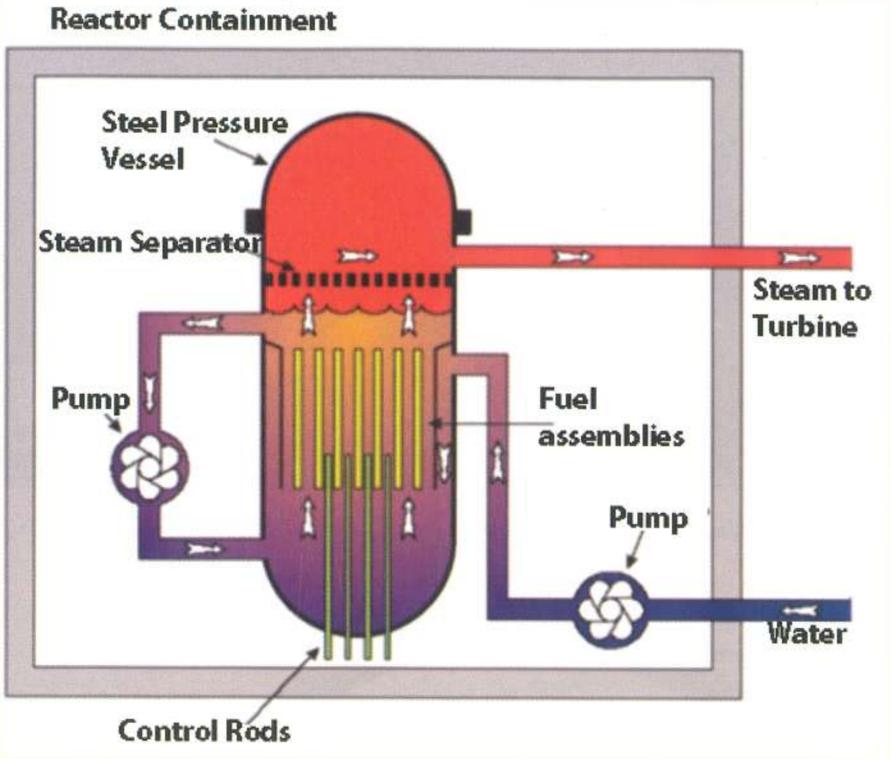


Fig. 2.6 Boiling Water Reactor (BWR).

pressurized to 70 atm pressure so that the water boils at about 285°C to get steam at high temperature. This high temperature improves the efficiency of conversion of thermal energy to electrical energy in the turbine. Total installed capacity for this type of reactors in the world is about 75,462 MWe. A schematic view of the reactor is shown in Fig. 2.6. In India, the reactors at Tarapur Atomic Power Station are Boiling Water Reactors and a view is shown in Fig 2.7.

The Pressurised Water Reactors (PWR)

In a PWR the fuel and cladding are similar to the BWR. In this case, however, the pressure in the reactor is kept at 145 atm such that water does not boil in spite of reaching a temperature of 310°C. The reactor vessel, therefore, should be stronger than that used for BWR. This super-heated water is transported to a heat exchanger to produce high temperature steam and water is returned back to the reactor. The steam generated in the heat exchanger is used for producing electricity. A schematic view of this reactor is given in Fig. 2.8. This is the most popular reactor type in the world and the total present installed

Fig. 2.7 A partial view of the Tarapur Atomic Power Station.

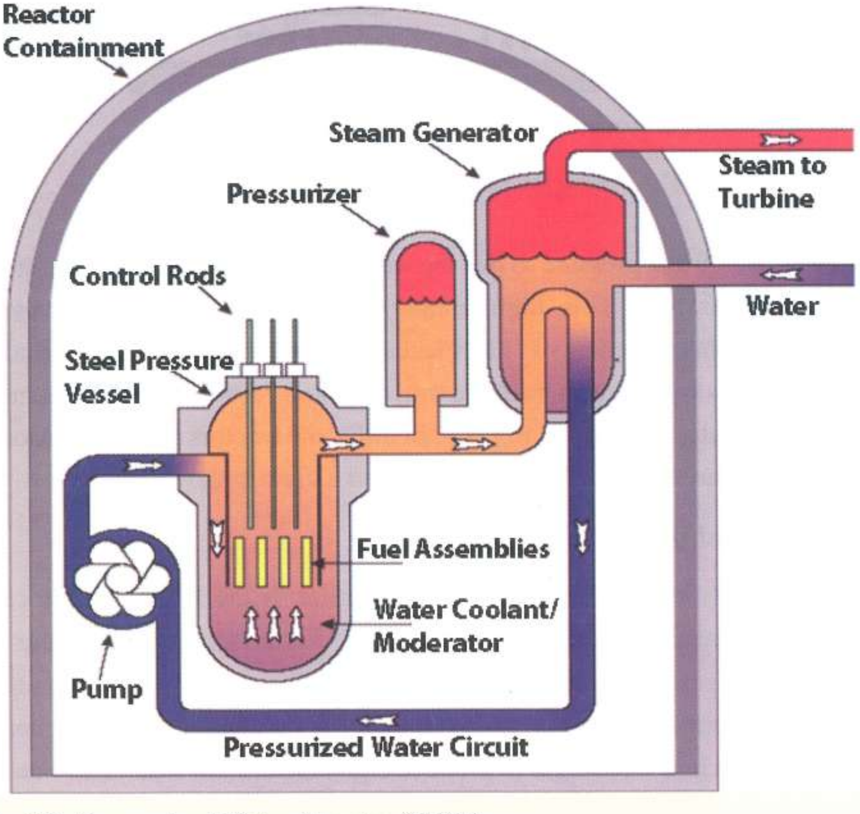


Fig. 2.8 Pressurized Water Reactor (PWR).

Fig. 2.9 Kudankulum Nuclear Power Station.

capacity is 257,231 MWe. India's reactors at Kudankulum are of this type and a view of these reactors is shown in Fig. 2.9.

Pressurised Heavy Water Reactor (PHWR)

PHWR is based on the use of natural uranium oxide fuel with zircaloy cladding. Unlike the two concepts discussed in the previous paragraphs, this concept does not make use of a large pressure vessel for containing the core components. Instead, the fuel is contained in a number of pressure tubes which are installed in a large vessel called 'Calandria'. The heavy water used for moderating the neutrons is filled in the Calandria and is kept cooled (< 85°C). The control rods are installed on the Calandria. Heavy water used for cooling the fuel circulates through the pressure tubes at a pressure of 85 atm and a temperature of about 300°C. A schematic view of this reactor is shown in Fig. 2.10. Total installed capacity of this type of reactors is presently 24,549 MWe. Most of the reactors in India are of this type, and a schematic view of reactors at Kaiga Atomic Power Station is shown in Fig. 2.11.

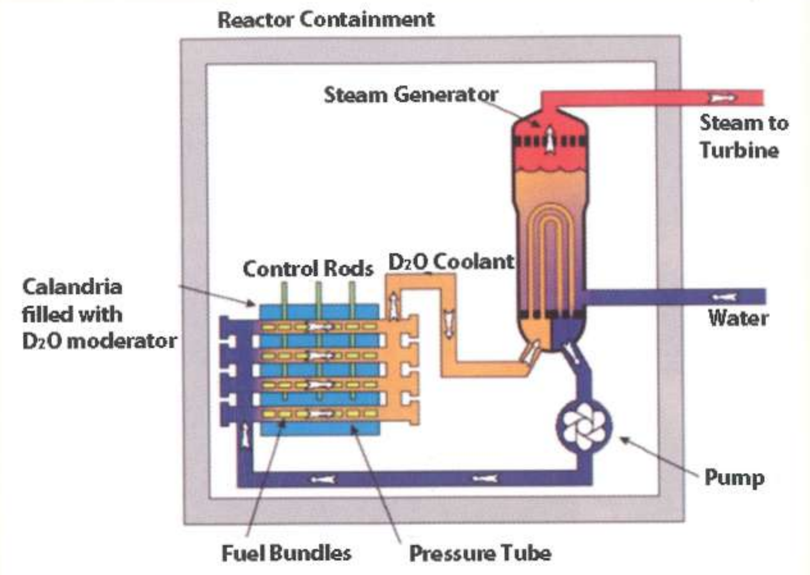


Fig. 2.10 Pressurized Heavy Water Reactor (PHWR).

Fig. 2.11 Kaiga Atomic Power Staion (Four Units).

Light Water Cooled Graphite Moderated Reactor (LWGR)

LWGR was the first reactor which produced electricity in the then USSR. This reactor is also a pressure tube type reactor just like PHWR but the pressure tubes are vertical. Uranium oxide enriched to 1.5 to 2% is used as fuel and Zr is used as cladding. Graphite blocks stacked together constitute the moderator and light water flowing through the pressure tubes is used as coolant. This reactor concept is used only in the USSR and the present operating capacity is 10,219 MWe. The reactor in the infamous accident at Chernobyl was of this type. Even though this reactor has been very successfully operated for many years, it has some inherent unsafe features and would not be licensed for operation in India or many other countries.

Gas Cooled Reactors (GCR)

GCR was developed in UK and France based on the experience of plutonium production reactors. In this concept, natural uranium clad in a magnesium alloy is used as fuel. These reactors are, therefore, sometimes called Magnox reactors. Graphite is used as a moderator and carbon dioxide gas as a coolant. Average temperature of the coolant is 400°C and the pressure is 20 atmospheres. All reactors of this type have been decommissioned.

Building on the concept of Gas Cooled Reactors, UK developed the Advanced Gas Cooled Reactor. This reactor also uses carbon dioxide as the coolant and graphite as moderator. However, the fuel is made from UO_2 pellets having 1.2 to 2.3% of ^{235}U and clad in stainless steel tubes. The outlet temperature of coolant gas in this reactor is 650°C and the coolant pressure is 40 atm. These reactors are operated only in UK and the present installed capacity is approximately 8,175 MWe.

High Temperature Gas Cooled Reactor (GCR)

HTGR concept is different from the other reactor concepts in that it does not use conventional metallic cladding. The fuel is in the form of microspheres (~0.2 mm dia) of $(U,Th)C_2$ or $(U,Th)O_2$ which are coated with layers of graphite and silicon carbide as cladding. These microspheres are mixed with carbon as well as a binder and made into fuel elements of desired shape. Graphite and helium are respectively used as moderator and coolant. Uranium enrichment is in the range of 20 to 90%. The outlet temperature of helium coolant is 740°C and the pressure

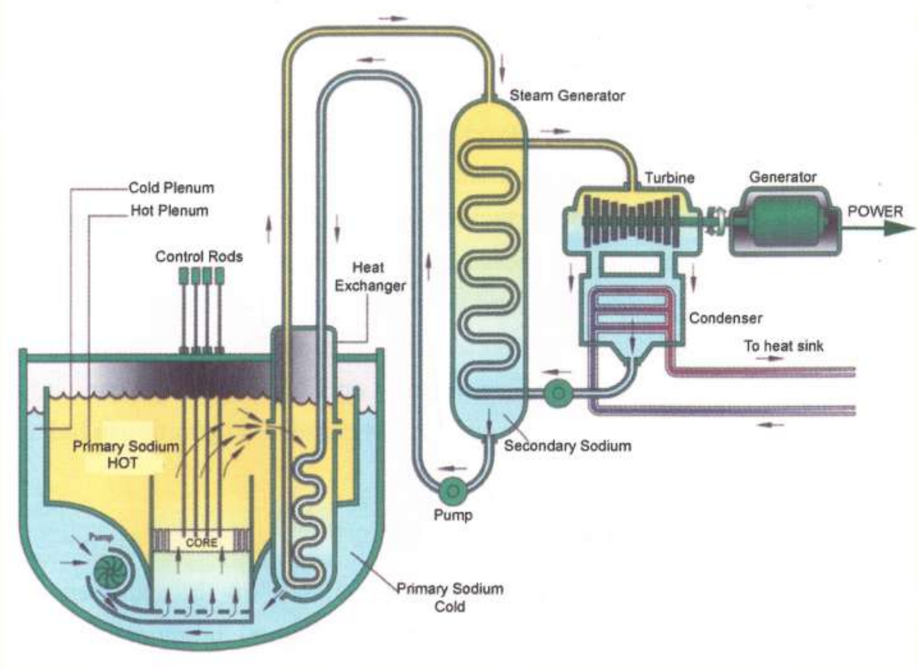
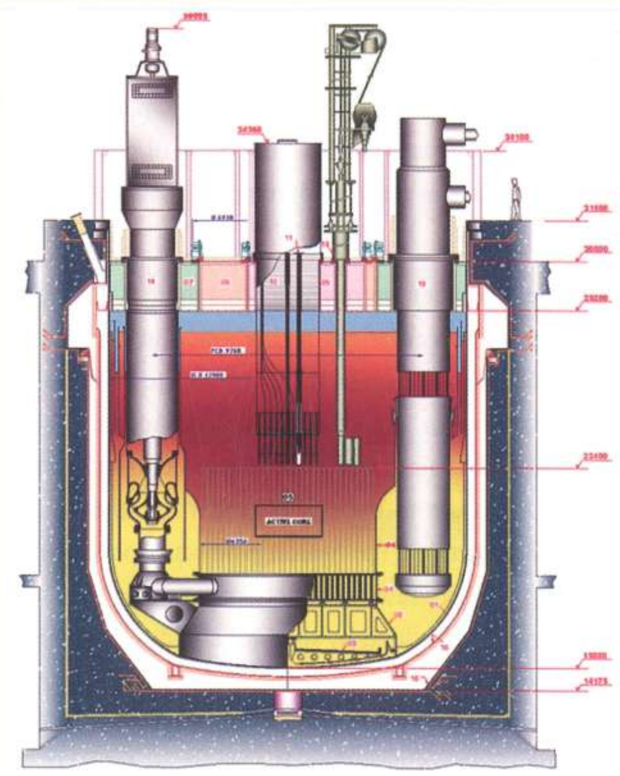


Fig. 2.12 Sodium Cooled Fast Breeder Reactor (FBR).

is about 50 atm. Only two power reactors of this type have operated in the world : one of 330 MWe capacity in the USA and another of 300 MWe capacity in Germany.

Liquid Metal Cooled Fast Breeder Reactor (LMFBR)

LMFBR is based on the use of fast neutrons and, therefore, no moderator is required. The use of fast neutrons permits more efficient conversion of ^{238}U to ^{239}Pu. The reactors in which amount of fissile material produced is more than the amount of fissile material consumed are called breeder reactors. As no moderator is used in the reactor, the fissile material concentration has to be significantly higher and currently, a mixed oxide of uranium and plutonium containing 20-25% of plutonium oxide is used as fuel. This fuel is clad in stainless steel tubes and cooled by liquid sodium metal. Sodium coolant temperatures and pressures are respectively 620°C and 3 atm. The central part of the reactor called core is surrounded by elements containing UO_2 blanket for efficient breeding of plutonium. A schematic view of this reactor is shown in Fig. 2.12. Countries which pioneered research in this area, include the United States, United Kingdom, France and USSR. Fast Breeder power reactors were installed



01	Main Vessel
02	Core
03	Core
04	Grid Plate
05	Core
06	Inner Vessel
07	Roof Slab
08	Large
09	Small
10	Control Plug
11	CSRDM /
12	Transfer
13	Intermediate
14	Primary
15	Safety
16	Reactor

Fig. 2.13 A schematic cross section of PFBR core.

in France (250 MWe and 1200 MWe) and United Kingdom (250 MWe). Russia is currently operating a reactor with 560 MWe capacity. China is operating a small reactor of 20 MWe capacity. India has a Fast Breeder Test Reactor of 40 MW_t capacity at Kalpakkam and installation of a new reactor Proto Type Fast Breeder reactor (PFBR), of 500 MWe capacity, is nearing completion at the same site. Fig 2.13 gives some details for PFBR core

Inherent Safety Features of Reactors

In power reactors, control rods have to be operated frequently to maintain the power generation as per the demand of electricity or to compensate for the depletion of fissile isotopes. Control rods are slightly withdrawn from the reactor in order to increase the power. The growth of power in the reactor is very rapid and, therefore, very fast acting control rods are provided for safe operation of the reactor. In addition, the design is suitably optimized so that any sudden increase in power would be opposed by inherent properties of the fuel, moderator and coolant systems. All reactors are thus designed to have a negative temperature coefficient of power which implies that any sudden increase in temperature, due to increased reactivity, would be opposed and lead to a decrease of power. This ensures that at no stage, the nuclear reaction goes out of hand and safe conditions are always maintained.

The design features of a nuclear power reactor ensure that there is no release of radioactivity to the environment. Nevertheless a tiny fraction of the fuel rods/pins do develop some defects which release radioactivity to the coolant stream. Heavy water used as moderator also becomes radioactive due to conversion of deuterium to tritium. The reactor design is mandated to ensure that this release of fission products or tritium to the environment is minimal and controlled. There are many barriers to prevent the fission products from entering the environment. The fuel matrix itself provides the first barrier for the release of fission products. The second barrier is provided by the fuel cladding. The third barrier is provided by the closed circuit coolant system which normally carries away any released activity to the pool of water used for cooling the fuel. The fourth barrier is provided by the pressure vessel or the pressure tube. If the radioactivity comes out of the pressure vessel or the pressure tubes, into the reactor building, it cannot escape from there because these buildings are of leak tight construction. Only controlled release takes place through properly filtered and monitored routes. The reactor building itself has an isolation zone of 1.6 km and a buffer zone of 5 km radius so that in the very unlikely event of any release of radioactivity from the reactor building, there is no danger to the population in the vicinity. The distance of 5 km provides adequate dilution of radioactivity in the event of its release.

The nuclear reactor is thus provided with adequate design and other safety features which ensure that the common man is not exposed to radiation even in the unlikely event of an accident. The exposure due to radiation released from the nuclear reactor during its normal operation is an insignificant fraction of the radiation received by man from natural environmental radionuclides. Every hour a total of 30,000 atoms of radium, polonium, bismuth and lead decay in our lungs, 0.4 million secondary cosmic ray particles traverse our body and about 15 million ^{40}K atoms, which are part of the overall potassium in our body, decay in our body. Besides this, we receive radiation due to terrestrial natural radioisotopes, medical check up etc. which are not known to cause any harmful effects. From experience at Tarapur, Kota and Madras atomic power stations, it has been observed that in the neighborhood of these reactors, the contribution to the radiation by the power reactors is less than one percent of the natural background. This is insignificant considering that the natural background itself may vary by more than 100% from place to place.

Chapter 3

Uranium

Introduction

Uranium, the heaviest element available in nature, is one of the largest resources of energy for mankind. Natural uranium has three isotopes and all of them decay by alpha emission. Uranium-238 having a half life of 4.5 x 10^9 years makes up 99.28% of the natural uranium. Uranium-235 with a half life of 7.00 x 10^8 years constitutes 0.715% and ^{234}U with a half life of 2.35 x 10^5 years is a minor isotope (0.005 %) which is mainly formed in the process of decay of ^{238}U. The products of decay of ^{238}U with the half lives are shown in Fig. 1.4 in Chapter 1. Similar details for ^{235}U are given in Fig. 3.1. Uranium-235 is the primary source of nuclear energy and ^{238}U is valuable for its conversion to ^{239}Pu. Because of the difference in the half lives of the two major isotopes of uranium, their relative amounts have been changing as a function of time. It is estimated

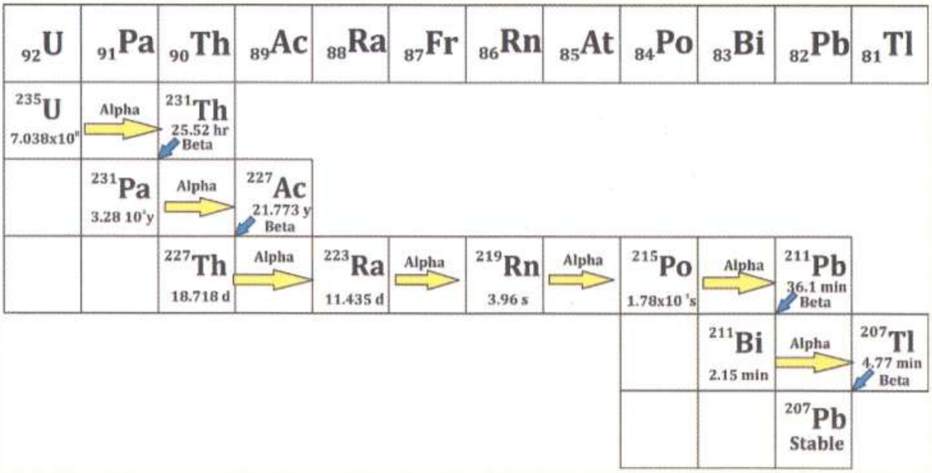


Fig. 3.1 Radioactive Decay of Uranium-235 and its Daughter Products.

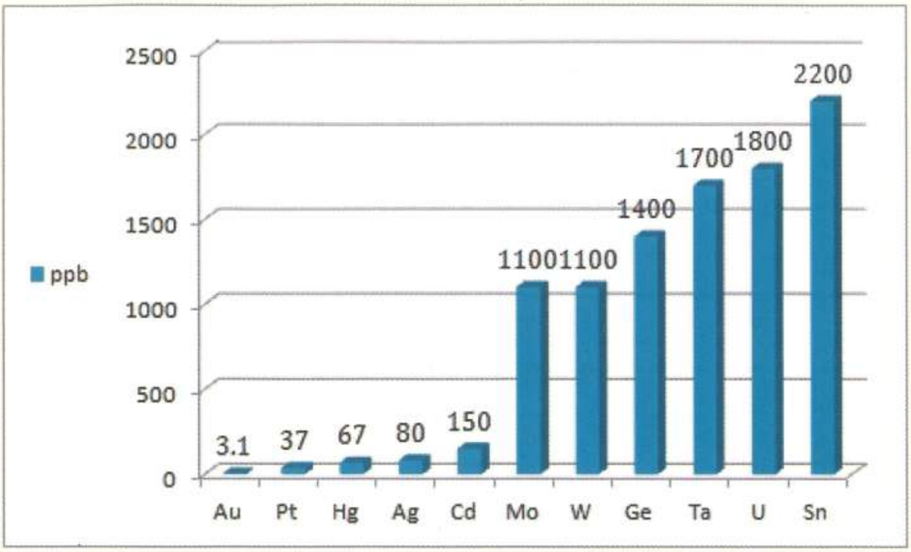


Fig. 3.2 Abundance of some Elements in Earth's Crust.

that when the earth was formed several billion years ago, ^{235}U content in natural uranium was about 14%. Over the years, there has been a steady decrease in ^{235}U content to the present level of 0.715%. This is adequate for the use of natural uranium in nuclear reactors. The change in this concentration in the next few thousand years would be insignificant.

Occurrence and Deposits

Uranium was discovered by Martin Heinrich Klaproth in 1789. During the next 107 years, its only application was to make coloured glass. Good quality glass having yellow, brown or green colour could be obtained by using different uranium compounds. Uranium is one of the more abundant elements in the earth's crust, its abundance being greater than that of gold, silver and mercury and similar to that of germanium, tantalum and tin. Abundance of uranium is shown with some other elements in Fig. 3.2. Uranium is much more abundant in rock formations than in water. Granite rock and coal contain 3 to 4 ppm of uranium, whereas, ocean water contains only two parts per billion of uranium. Like most metallic elements, uranium does not occur in nature as a free metal. It always exists as compounds of oxygen and other elements. The oxide minerals of uranium contain a mixture of uranium dioxide (UO_2) and uranium trioxide (UO_3), and these include pitchblende and uraninite. Coffinite is one of the

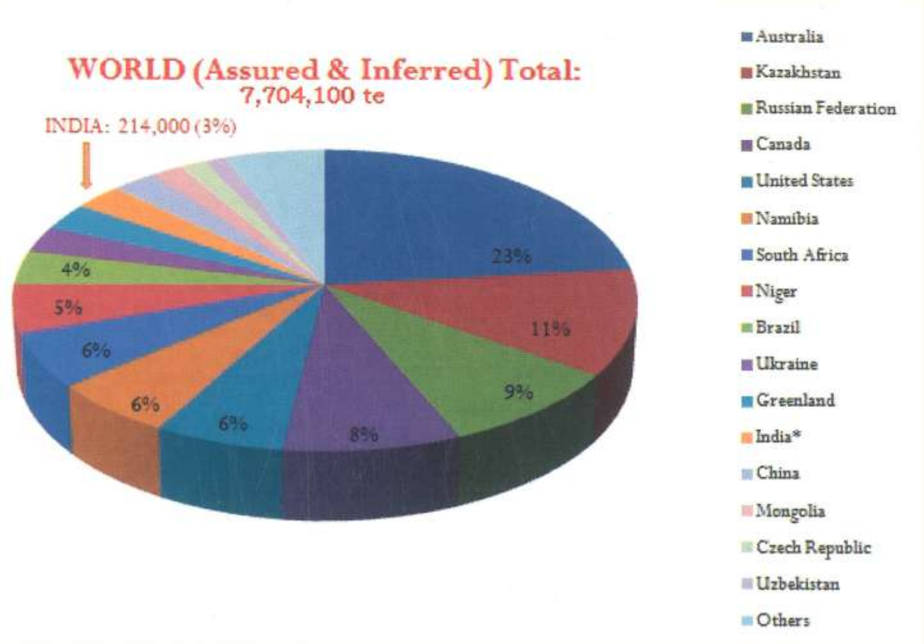


Fig. 3.3 Geographical Distribution of Uranium (te) in various Countries. Source: URANIUM 2014, Nuclear Energy Agency Publication NEA 7209, OECD Paris (2014)
**For India Source: Atomic Minerals Directorate News Letter Vol. 21 (Dec. 2014)*

silicate minerals $(U(SiO_4)1-x(OH)_4x)$ of uranium and carnotite $(K_2O.2UO_3.V_2O_3.2H_2O)$ is potassium uranium vanadate.

The discovery of radioactivity by Becquerel in 1896, which eventually led to the discovery of nuclear fission in 1939, and increased demand for uranium. In the initial phase of the development of nuclear reactor system in USA, local source of uranium was not known and uranium had to be imported from Belgian Congo. Soon after the secret of atomic energy was known to the world, many countries started extensive uranium exploration programmes and the present status of uranium resources in the world is given in Fig. 3.3. Most of the mineral deposits of uranium contain 0.1 to 1% of uranium. Some deposits have, however, been identified to contain 4 to 25% of uranium.

In India, zones having uranium minerals are identified all over the country, as shown in Fig 3.4. Most deposits identified so far are low grade (~ 0.05%), though some in Andhra Pradesh, Karnatka and Meghalya have uranium

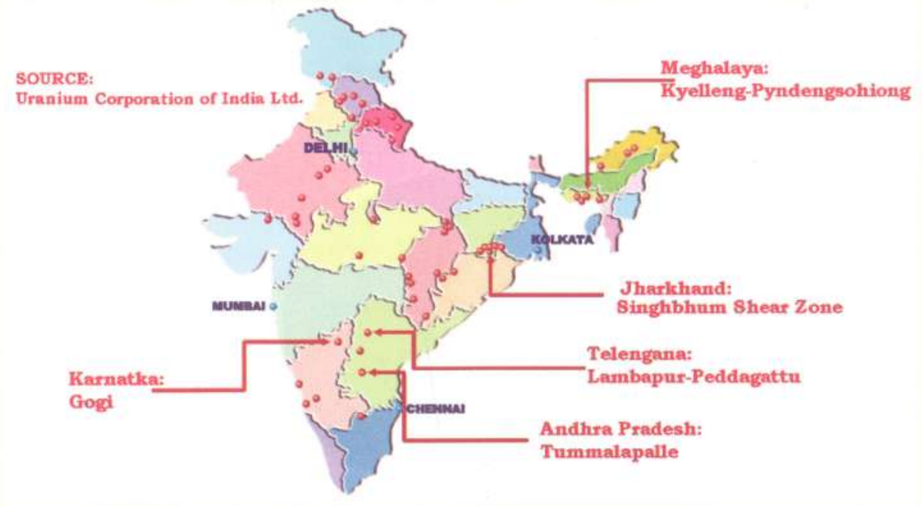

SOURCE:
Uranium Corporation of India Ltd.

Fig. 3.4 Zones of Uranium Mineralization in India.

concentration of 0.1 to 0.2%. Uranium deposits were first identified in Singhbhum district of Jharkhand. The first major site identified for the recovery of uranium was Jaduguda, and this continues to be one of the prominent sources of uranium in the country. Other sites include Bhatin, Narwapahar and Turamdih. Besides these areas in Bihar, deposits have been identified at Bodal and Jajawal in Madhya Pradesh, Gogi and Arbail in Karnataka, Asotatha in Himachal Pradesh, Domiasiat, Tyrnai and Gomaghat in Meghalaya, Lambapur in Telegana and Tummalapalle in Andhra Pradesh. The identified reserves of uranium currently stand at 214,000 tonnes of U_30_8.

Uranium Mining and Processing

Mining of Uranium

Recovery of uranium involves mining of the ore and its chemical treatment for the isolation of uranium. Mining can be underground or opencast depending on the nature of the deposit. In India, presently there are seven mines, all in the State of Jharkhand, six underground mines (Jaduguda, Bhatin, Narwapahar, Turamdih, Bagjata and Mohuldih) and one opencast mine (Banduhurang). All mining and milling operations for uranium are carried out by Uranium Corporation of India Ltd (UCIL). Ore produced from these mines are processed in two process plants located at Jaduguda and Turamdih. UCIL has taken up expansion of some of its operations in Jharkhand and started pre-project activities to set up new mines and plants in different parts of the country namely – Gogi in Karnatka, Lambapur in Telengana and KPM in Meghalaya.

Uranium Mines

Work on Jaduguda mine started in February 1963 and uranium ore production started in May 1968. Present production is about 1000 te of ore per day. The mine is accessed through a 5 metre diameter vertical shaft of depth of 640 meters. The shaft has two Friction Winders. One of the winders is fitted with a cage to accommodate 50 persons and other with a skip having a capacity of hoisting 5 tons of ore per trip. This shaft is also the main ventilation intake. The bottom most production level catering to this shaft is 555 metre level. Subsequently, a similar auxiliary vertical shaft with latest friction winders was sunk from 555 metre level to 905 meters to cater to ore hoisting requirement up to 880 metre level. The mining method followed for extraction of ore is Horizontal Cut and Fill with de-slimed mill tailings as back fill. Similar operations are carried out at Bhatin mine which produces about 370 te of ore per day.

Narwapahar mine is the first fully mechanized mine operating since April 1995. A new mine was commissioned at Turamdih in 2003. The entry into this mine is through an 8 degree decline which provides access to the ore up to a depth of 70 m. A 260 metre vertical shaft provides for mining the ore from deeper levels.

Bagjata mine is located in a remote area about 25 km east of Jaduguda. This mine was commissioned in 2008. The principal entry into the mine is through a 7 degree decline. A vertical shaft has been sunk to a depth of 375 metre to meet the requirements of ore hoisting and transportation of men and materials from the deeper levels. The ore of Bagjata mine is sent to Jaduguda by road for processing.

Mohuldih uranium deposit Mine in Gamharia block of Seraikella-Kharsawan district in state of Jharkhand and was commissioned in April 2012. Presently, the principal entry into Mohuldih mine is through an 8 degree decline of 5m width and 4.5 m height. A vertical shaft is being sunk for mining at deeper levels.

Uranium Mills

Jaduguda Mill

Ore from Jaduguda, Bhatin, Bagjata and Narwapahar mines is processed in the processing plant (Mill) at Jaduguda. It is located adjacent to Jaduguda mine. Uranium is extracted from ore by a hydro-metallurgical process. After three stages of crushing, and two stages of wet grinding, the slurry thus obtained is pumped to leaching pachucas for dissolution of Uranium. The leached slurry is filtered to obtain liquor containing uranium which is purified and concentrated by ion exchange method. Uranium is then precipitated from this concentrated liquor as magnesium di-uranate, generally known as "YELLOW CAKE" (see Fig. 3.5). This is thickened, washed, filtered and dried in the spray dryer and finally packed in drums and then sent to Nuclear Fuel Complex at Hyderabad for further processing into UO_2 pellets.

Turamdih Mill

A new plant at Turamdih has been set up to treat ore produced from mines at Turamdih, Banduhurang and Mohuldih. The flowsheet of this plant is similar to that of Jaduguda. However, taking into account of developments in hydrometallurgy / processing technology worldwide, suitable changes have been introduced in the mill. A view of the mill is shown in Fig. 3.6.

Fig. 3.5 Yellow cake.

Fig. 3.6 A view of the Turamdih Uranium Mill.

Chemistry of Uranium

Uranium is a member of 'actinides' series of fourteen elements in which the fifth, sixth and seventh electronic shells, and their associated sub-shells are incompletely filled. In the metallic state, uranium has 21 electrons ($5s^2$, $5p^6$, $5d^{10}$ $5f^3$) in the fifth shell, 9 electrons ($6s^2$, $6p^6$, $6d^1$) in the sixth and 2 electrons ($7s^2$) in the seventh shell. Electrons from all these shells take part in chemical bonding and uranium, therefore, displays variable valence ranging from +3 to +6. Uranium can combine with fluorine to from UF_3, UF_4, UF_5 and UF_6. Trivalent uranium can be prepared in solution, but it is unstable as it reacts with water with the evolution of hydrogen. Tetravalent uranium is also unstable with respect to oxidation under certain conditions. Pentavalent and hexavalent uranium exist as oxygenated species UO_2^+ and UO_2^{2+} in solution. Hexavalent uranium as UO_2^{2+} is the most stable species of uranium in aqueous solution. Uranium ions are electron acceptors and readily make coordinate bond to complex ions and compounds. For example, uranyl (UO_2^{2+}) ion can complex with sulphate (SO_4^{2-}) ion to form complexes of the type UO_2SO_4, $UO_2(SO_4)_2^{2-}$, $UO_2(SO_4)_3^{4-}$ etc. Similar complexes are formed with nitrate (NO_3^-), carbonate (CO_3^{2-}) and other anions. Uranium ions also form complexes with electron donating solvents like ethers, ketones and alkyl phosphates. Uranium ions hydrolyze under conditions of very low acidity.

Recovery of Uranium from Ore

The ore coming to the mill is in the form of small stones which contain about 0.07% of uranium. These stones are crushed to a very fine powder with particles of 0.1 mm dia or less. At some sites before treating the ground ore with acid for the recovery of uranium, it is possible to recover some copper (0.08%) and molybdenum (0.02%) which are also present in this ore. The sulphide ores of copper and molybdenum are readily floated on a froth and separated. The ore is also treated for the separation of magnetite (3%) which is an useful by-product. After this separation, the ore powder is treated with dilute sulphuric acid along with small amounts of MnO_2. This results in the following reactions:

$$UO_3 + H_2SO_4 \rightarrow UO_2(SO_4) + H_2O \tag{3.1}$$

$$UO_2 + O \text{ (from } MnO_2) + H_2SO_4 \rightarrow UO_2(SO_4) + H_2O \tag{3.2}$$

By proper control of leaching conditions, it is possible to have a fairly selective extraction of uranium from the ore powder because of the favourable dissolution properties of uranium oxides. Leaching is carried out in air agitated cylindrical vessels called 'pachucas'; and more than 96% of uranium from ore is leached out.

Most of the countries use acid leaching method for the recovery of uranium from the ore. At a few locations, which have ore with higher concentration of uranium, or alkaline nature of the ore, sodium carbonate (washing soda) solution is used for leaching. The concentration of uranium in the solution obtained after acid leaching is a few grammes per litre and it contains many impurities which must be removed for obtaining a uranium rich product. In fact, the concentration of uranium in the leach liquor is much less than that of many impurities as shown in Table 3.1. Fortunately, uranium forms anionic complexes and exists in the leach liquor as anoins $[UO_2(SO_4)_2^{2-}$ and $UO_2(SO_4)_3^{4-}]$. The first stage of purification is achieved by the use of anion exchange resin. Uranium retained on the resin is then eluted out by using a solution of common salt which also regenerates the resin for reuse. Uranium in the eluted solution is precipitated

Table 3.1: Typical Impurities in Uranium at Various Stages of Purification and their Concentration in ppm.

Impurity	Leach liquor	Yellow cake	UO_2 Product	Specifications for UO_2 Powder
U	10^6	10^6	10^6	10^6
Fe	5.9×10^6	6×10^3	30	50
SiO_2	2.0×10^6	5.4×10^4	25	30
SO_4	49.0×10^6	8.2×10^3	-	-
P_2O_3	$(0.6\text{-}1) \times 10^6$	1.7×10^3	-	-
Mn	$(4\text{-}1) \times 10^6$	-	2	5
R.E.	4×10^5	2×10^3	-	-
Cl-	-	4.3×10^3	-	-
Th	-	4.7×10^2	150	50
Ca+Mg	-	1.0×10^5	25 (Ca)+3(Mg)	50
Al	-	-	10	10
B	-	-	0.1- 0.3	0.3
Cd	-	-	0.1	0.2
Cu	-	-	6	10
Cr	-	-	10	15
Dy	-	-	0.1	-
F	-	-	5	-
Gd	-	-	0.04	-
Mo	-	-	5	2
	-	-		
	-	-		

with magnesium oxide or dolomite to obtain magnesium diuranate which is quite often called 'yellow cake' because of the yellow colour of this precipitate.

$$MgO + 2UO_2SO_4 + 2H_2O \rightarrow MgU_2O_7 + 2H_2SO_4 \qquad (3.3)$$

Uranium at this stage is still impure and is shipped to the Nuclear Fuel Complex, Hyderabad. The purification of this uranium to nuclear grade is achieved by selective extraction of uranium into well known solvent called tributyl phosphate (TBP). Uranyl nitrate solution when contacted with 30% TBP dissolved in kerosene, forms a complex $UO_2(NO_3)_2.2TBP$ which is extracted into the organic phase. The extracted uranium is then brought back into the aqueous solution by contacting with water and then precipitated with ammonia to get ammonium diuranate. This is heated in air to obtain UO_3 and then reduced with hydrogen gas at about 600°C to get UO_2.

$$(NH_4)_2U_2O_7 \xrightarrow{400^\circ C} 2UO_3 + 2NH_3 + H_2O \tag{3.4}$$

$$UO_3 + H_2 \xrightarrow{600^\circ C} UO_2 + H_2O \tag{3.5}$$

Uranium and its Compounds

Uranium Metal

Uranium metal is used as fuel in Gas Cooled Reactors and in a number of research reactors. Indian research reactor DHRUVA uses metallic uranium fuel. The metal is produced by reduction of uranium tetrafluoride with calcium or magnesium metals.

$$UF_4 + 2Mg \rightarrow U + 2MgF_2 \tag{3.6}$$

This reaction is exothermic in nature. Temperature during reduction is sufficiently high so that the salt and the metal formed, as products, are molten and readily separate from each other. In India, uranium metal is manufactured at Uranium Metal Plant in Bhabha Atomic research Centre (BARC) and about 150 kg of metal is produced per batch.

A typical uranium metal ingot is shown in Fig. 3.7. Metallic uranium is also expected to be useful, along with metallic plutonium, for making fast reactor fuels.

Uranium metal has a density of 19.07 g/cc and is 2.5 times heavier than steel and 1.5 times heavier than lead. Uranium is a white silvery metal but readily tarnishes and becomes black when exposed to air due to surface oxidation. Large chunks of uranium metal can be handled in air, as the oxidation takes place only on the surface. Uranium metal turnings or powder readily catch fire in air and need careful handling. Water also reacts with uranium metal but the oxide film prevents further reaction below 100°C. Uranium metal melts at 1132°C.

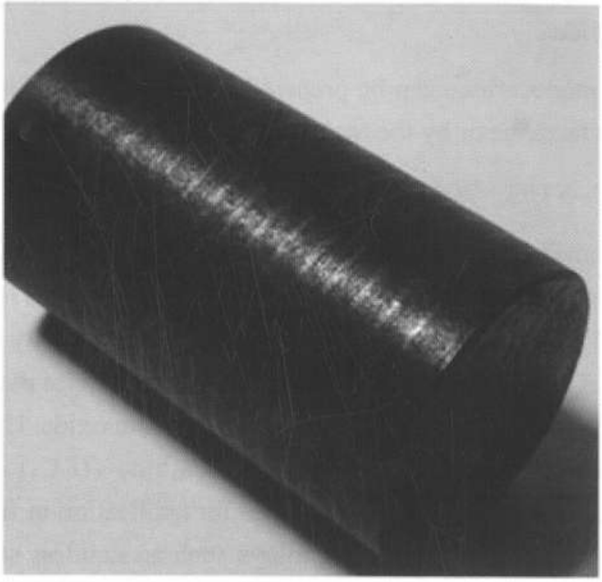


Fig. 3.7 Uranium Metal ingot.

However, even before melting, uranium metal undergoes changes in physical structure from alpha phase to beta phase at 662°C and from beta phase to gamma phase at 775°C. These phase changes are accompanied by sharp changes in the density of the metal.

Uranium Dioxide

In the process of recovery of uranium, we have come across two oxides; uranium trioxide (UO_3) in which the valence of uranium is 6 and uranium dioxide (UO_2) in which the valence of uranium is 4. Either of these oxides when heated in air above 800°C yields U_3O_8, wherein the valence is between 4 and 6. Out of these oxides, uranium dioxide is very important. It is brown in colour, has a density of 10.97 g/cc and a melting point of 2760°C. It has many favourable properties to be used as a reactor fuel, the prominent one being its stable structure right up to the melting point and excellent compatibility with cladding alloys. Even though the density is nearly half the density of uranium metal, which is not favourable from reactor physics point of view, the open structure of this material provides adequate space for accommodating the fission products formed during power generation. The UO_2 based fuel does not, therefore, swell as much as the higher density fuels.

Uranium Carbide

Uranium monocarbide can be prepared by the reaction of uranium metal with carbon or methane or by the reaction of uranium oxide with carbon.

$$UO_2 + 3C \rightarrow UC + 2CO \qquad (3.7)$$

It cannot be considered as a fuel for water cooled reactors, because it readily reacts with water. It is one of the advanced fuels being considered for fast breeder reactors which use liquid sodium as a coolant. With a density of 13.6 g/cc, melting point of 2500°C and thermal conductivity about twice that of UO_2, it is considered as a better fuel in comparison with uranium oxide. Uranium forms two other carbides namely; uranium sesquicarbide (U_2C_3) and uranium dicarbide (UC_2) but these are not considered for application in fast reactors in view of their reactivity with cladding alloys such as stainless steel. Uranium dicarbide is, however, a fuel for High Temperature Gas cooled Reactor (HTGR) which uses graphite as cladding material.

Uranium Nitride

Uranium mononitride can be prepared by the reaction of metal with nitrogen or ammonia or by the following reaction:

$$UO_2 + 2C + 1/2N_2 \rightarrow UN + 2CO \qquad (3.8)$$

With a density of 14.32 g/cc, melting point of 2630°C and thermal conductivity similar to that of carbide, mononitride is considered a promising fuel for fast reactors.

Uranium Tetrafluoride

Uranium tetrafluoride is an important intermediate in the preparation of uranium metal and uranium hexafluoride. It is prepared by the reaction of uranium dioxide with hydrogen fluoride at about 500°C.

$$UO_2 + 4HF \xrightarrow{500^\circ C} UF_4 + 2H_2O \qquad (3.9)$$

The fluoride which is green in colour is called green salt.

Uranium Hexafluoride

Uranium hexafluoride is prepared by the reaction of uranium tetrafluoride with fluorine at 400 to 500°C.

$$UF_4 + F_2 \xrightarrow{400\,^\circ C} UF_6 \qquad (3.10)$$

Uranium hexafluoride is a white solid, which sublimes when heated to 56°C (similar to ammonium chloride). Even at 20°C, the pressure of UF_6 vapour above solid UF_6 is 0.1 atm. Gaseous nature of the compound has been useful for enrichment of ^{235}U in natural uranium. The compound is highly reactive and moisture sensitive, and great care is required in its handling. Only nickel and aluminium alloy containers are useful for handling UF_6 because of its corrosive nature.

Uranium Enrichment

Uranium-235 is the only fissile isotope in natural uranium and its abundance is 0.715%. For many applications its concentration has to be increased. In reactors like Boiling Water Reactors and Pressurized Water Reactors, ^{235}U content ranging from 1.1% to 4.0% is required. For making nuclear explosives, the concentration of ^{235}U has to be above 10% (ideally >90%) since below this concentration, enriched metallic uranium metal cannot be made to explode. The quantity which must be assembled for explosion, the so called critical mass, is essentially infinite at these concentrations. Thousand kilograms of uranium metal would make one critical mass when the concentration of ^{235}U is 10%. The amounts of uranium metal required for one critical mass with ^{235}U concentrations of 20, 50 and 100% are, respectively, 250 kg, 50 kg and 15 kg.

Enrichment plants are used for enhancing the ^{235}U concentration. These plants take F kg of UF_6 feed material having enrichment N_F and split it into two streams: P kg of product stream with higher enrichment N_P and W kg of waste stream of lower enrichment N_W which is termed as 'tails'. This is schematically represented in Fig. 3.8.

The ratios R of the two isotopes of uranium ($^{235}U/^{238}U$) in these streams can be defined as:

$$R = N/(1-N) \qquad (3.11)$$

The separation factor q is defined as the ratio of R_P and R_W

$$q = R_P/R_W \qquad (3.12)$$

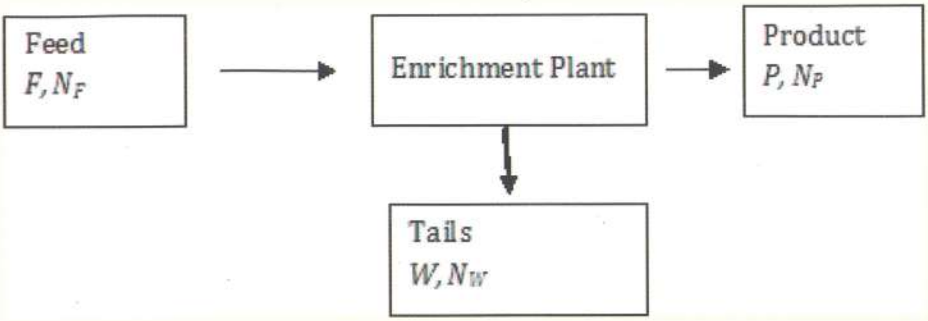


Fig. 3.8 A schematic of enrichment process.

All the enrichment processes which are in use, or have potential for use, are based on the use of uranium in the form of gas/vapour. The earliest process used for the enrichment of ^{235}U was based on the use of vapour of uranium tetrachloride which was ionized and isotope separation achieved by using large versions of mass spectrometers called calutrons. However, this method proved to be too expensive and all subsequent methods except one, are based on the use of uranium hexafluoride gas. One method is based on the use of metallic uranium vapour.

Because of very small differences in the properties of $^{238}UF_6$ and $^{235}UF_6$, the separation factor achieved in one stage is very small and a large number of stages are required to achieve desired enrichment. With UF_6 as feed, gaseous diffusion and gas centrifuge methods are being commercially used for enrichment of uranium isotopes. Enrichment capacity of a plant is measured in kilograms or tonnes of separative work units (SWU). In view of the complex nature of this term, it is merely illustrated by taking two examples of enrichment plants, each having capacity of 1000 te of separative work unit but one producing a product with 3% ^{235}U and another producing a product with 90% ^{235}U. The difference is illustrated in Fig. 3.9.

Gaseous Diffusion

On the average $^{235}UF_6$ molecules being lighter (approximately 349 amu) have a higher speed than the heavier $^{238}UF_6$ molecules (approximately 352 amu) at a given temperature. This forms the basis for enrichment by gaseous diffusion method. If UF_6 vapour are forced to diffuse through a porous barrier with tiny holes, the lighter $^{235}UF_6$ molecules diffuse faster than the $^{238}UF_6$ molecules and

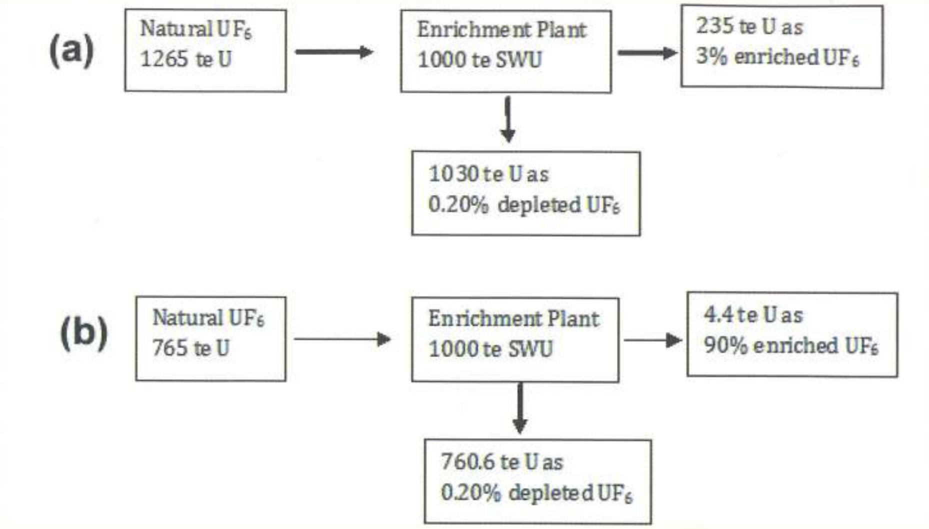


Fig. 3.9 Illustration of Separative Work Unit Concept of two cases of (a) 3% enrichment and (b) 90% enrichment

the gas coming out of the barrier is slightly richer in $^{235}UF_6$ (Fig. 3.10). Ideal separation factor in single stage of this process is about 1.0043, but in actual practice, it is only 1.0014. Because of this, an ideal gaseous diffusion plant would have about 1300 stages for producing 3% enriched uranium. Running of a plant based on gaseous diffusion requires tremendous quantities of electricity, about 3000 kWh/kg SWU.

Gas Centrifuge

We know that under the influence of gravity, the heavier bodies tend to settle at the bottom. If we fill a room with UF_6 gas, then the gas near the ceiling would be richer in $^{235}UF_6$. If the forces acting on the molecules are increased, then the separation factor can be increased. This can be achieved by putting the gas in a centrifuge rotating at a high speed of about 50,000 revolutions/minute. The molecules would then be subjected to a force of 250,000 times the force of gravity. Under these conditions, the ratio of isotopic abundance (q) between the centre of the centrifuge to the outer wall would be 1.147, though there would be very little gas near the centre of the centrifuge. The cylindrical centrifuge bowl can be designed to function as a multistage unit and a single centrifuge can produce separation factors as high as 1.5 (Fig. 3.11). However, because of extremely high speeds at which the centrifuge has to rotate, each of these units

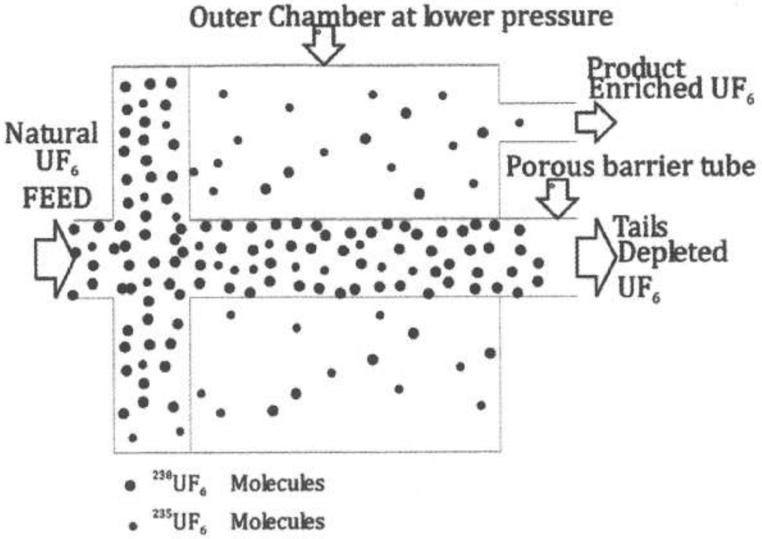


Fig. 3.10 Schematic of Enrichment by Gaseous Diffusion Method.

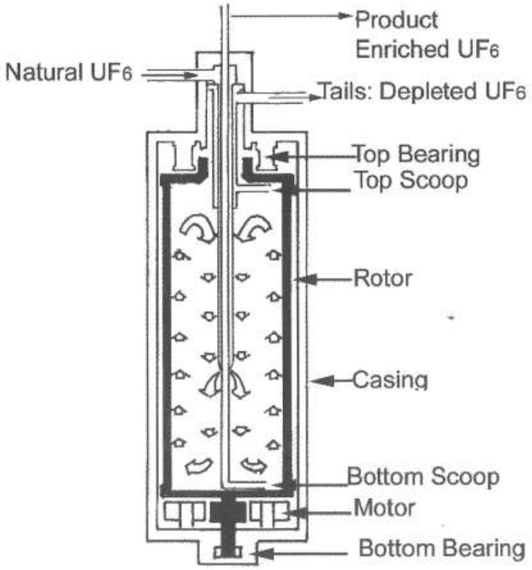


Fig. 3.11 Gaseous Centrifuge for $^{235}UF_6$ Enrichment.

has to be small (1.5 m long and 0.2 m dia) and a large number of centrifuges are required to produce quantities of enriched uranium required for reactors. A plant of 1000 te SWU per year capacity would require 66,000 centrifuges. Nevertheless, 3% enrichment can be achieved in about 13 stages. In spite of a large number of units required for the production, the electrical consumption for this process is only 1/10th of the gaseous diffusion process i.e. about 300 kWh/kg SWU.

Aerodynamic Methods

These methods are based on the pressure gradients which are generated due to high speed flow of gases along a streamlined curvature. Again, like in a centrifuge, the heavier $^{238}UF_6$ molecules tend to concentrate on the outer side of the curvature. There are two processes based on this principle; the jet nozzle process developed by the Germans and the Helikon process developed by the South Africans.

In the jet nozzle process, a mixture of uranium hexafluoride and hydrogen (96% of H_2) is allowed to expand through a narrow (0.05 mm wide) curved (0.1 mm radius) slit. The high speed gas experiences force equal to 160 million times the gravitational force in the curved nozzle. The stream coming out of the nozzle is divided into lighter and heavier fractions by a very sharp skimmer knife. A tube having about 80 such elements can achieve a separation factor of 1.0148. About 740 such stages would be required to produce 3% enriched uranium. The energy costs are more than 3,000 kWh/kg SWU.

In the Helikon process, or 'UCOR' process, a mixture of UF_6 and hydrogen (98 to 99% of H_2) is injected, at a very high speed, tangential to the inner wall of a tube. As the gas travels down the tube, the lighter component ($^{235}UF_6$) concentrates near the axis and this enriched uranium can be withdrawn from the central part of the other end of the tube. Stage separation factor of 1.03 has been reported for the process in a 3.5 m dia, 10 m long tube in which many streams, having different enrichments, flow simultaneously through the tube without mixing. About 100 modules are required to achieve uranium enrichment of 3%. Power consumption in this process is 3,000 - 3,500 kWh/kg SWU which is more than that for gaseous diffusion process.

Laser Isotope Separation

The position of electronic levels of uranium atoms, and vibrational levels of molecules, such as UF_6, differ marginally for the isotopes of uranium. The energy difference between two useful levels in uranium atoms is about 2.1 eV (red-orange coloured light) and the values for ^{235}U and ^{238}U differ by 4.2×10^{-5} eV. The availability of lasers which can be tuned very precisely so as to selectively excite only ^{235}U atoms without affecting the ^{238}U atoms has prompted the development of laser based process.

Atomic vapour laser isotope separation (AVLIS) technique is being investigated by many countries and has the potential for emerging as a new technology in this area. In this technique, selective ionization of ^{235}U atoms and their collection using electric and magnetic fields are used for isotope separation. Ionization of ^{235}U atoms requires approximately 6.2 eV of energy and this can be supplied by 3 laser photons of red-orange colour. Vapour of uranium atom is generated by heating uranium metal ingot with electron beam and ^{235}U atoms in vapour are ionized by precise tuning of energies of 3 laser photons. The ionized ^{235}U atoms are deflected onto collector plates for obtaining the product, whereas ^{238}U atoms which are not ionized are later collected on another plate above the source of the vapour. Ideal stage separation factors up to 15 are possible, but 5 to 10 appear practical. Enrichment to 3% ^{235}U in this process may require only a single stage. Further, power consumption is estimated to be only about 100 kWh/kg SWU.

In molecular laser isotope separation (MLIS), $^{235}UF_6$ molecules are first selectively excited with infra-red laser light and then irradiated with ultra-violet laser light to dissociate excited $^{235}UF_6$ to $^{235}UF_5$ and F. The pentafluoride is a solid and condenses out of the gas stream whereas $^{238}UF_6$ molecules are not affected. Complex spectrum of the UF_6 molecules makes selective excitation quite difficult. Many innovations like jet cooling of UF_6 vapour are under investigation for the development of the process. Currently, no data regarding separation factors have been reported for this process.

Uranium as Fuel

Characteristics of a Nuclear Fuel

Specific Power

Uranium metal rods or uranium dioxide pellets are always designed to have a fixed diameter depending upon the i) thermal conductivity of the material, ii) the maximum allowable centre line temperature and iii) the heat removal capacity of the cooling system. In the case of uranium metal, metallic rods of approximately 30 mm diameter are preferred because the central temperature has to be kept below 600°C to avoid any phase transition. The specific power is limited to 5 MWt/te. A reactor producing 1000 MWt (or approximately 300 MWe of electrical power) would require about 200 te of uranium metal. In the case of oxide fuel, for thermal reactors, uranium dioxide pellets having approximately 12 mm dia are used as fuel. Even though the thermal conductivity of oxide is lower than that of metal, the use of lower diameter and also because of the high melting temperature, specific power of 20 MWt/te is possible. A 300 MWe reactor would require only 50 tonnes of natural uranium oxide. When uranium dioxide is enriched, higher specific power of 25-35 MWt/te is possible and fuel requirement goes down even further. In fast reactors, the fuel has about 20% fissile content. By manufacturing fuel pins of about 5 mm diameter and using sodium as the coolant, the specific power can be increased to 200 MWt/te. Thus a 300 MWe fast reactor would require only 5 te of fuel. Fast reactors are thus very compact sources of energy.

Burn up

Another important characteristic of nuclear fuel is 'burn up' which is a measure of total energy produced by the nuclear fuel during its residence in the reactor. It is measured in terms of megawatt days of energy/te (MWd/te). Fission of 1 g of uranium produces approximately 1 MWd of heat energy which is the heat produced by 1,000 heaters of 1 kW capacity, each working for one day. About 2.5 te of coal would be required to produce the same quantity of heat. In a tonne of uranium if 0.1% of ^{235}U (i.e.~1 kg) undergoes fission, the burn up would be 1,000 MWd/te. The burn up which can be obtained from a fuel is thus very much dependent upon the concentration of fissile isotope in the fuel. In the case of natural uranium, consumption of all ^{235}U would correspond to 7,000 MWd/te. It is possible to achieve this burn up even when substantial fraction of ^{235}U is left over because energy is also produced by the fission of plutonium that is generated from ^{238}U. In practice, fuel is not kept in the reactor till all the fissile content undergoes fission because a minimum concentration of fissile material is essential to sustain the rated power level in the reactor. The burn up of fuel can also be limited if fuel swells due to accumulation of fission products. This is the case with metallic uranium fuel where a maximum burn up of 5,000 MWd/te is possible in spite of very strong cladding. Uranium metal swells during power generation due to the lack of space for fission products in the metal matrix. Uranium dioxide fuel is much more tolerant of fission products and when sufficient enrichment is provided, it can go to fairly high burn up. In this case,

Table 3.2: Special Features of Nuclear Fuel (1000 MWt (~300 MWe) Station).

Properties	PHWR	BWR/PWR	GCR	FBR
Fuel	UO_2	Enriched UO_2	U	UO_2-PuO_2
Specific Power MWt/te	20	30 ± 5	5	200
Total fuel (te)	50	33	200	5
Burnup (MWd/te)	7,000	30-40,000	5,000	>100,000
Annual Fuel Replacement	50	10	70	3.5

PHWR – Pressurized Heavy Water Reactor, BWR – Boiling Water Reactor, PWR – Pressurized Water Reactor, GCR – Gas Cooled Reactor, FBR – Fast Breeder Reactor

chemical corrosion of the cladding, by the fission products, combined with fuel swelling determine the upper limit of burn up. In Pressurized Water Reactors, burn up of the order of 33,000 MWd/te is possible. Annual requirement of fuel for a 1,000 MWt (300 MWe) PWR would, therefore, be only 10 tonnes. Efforts are in progress to increase this bum up to 50,000 MWd/te which would give better fuel economy. In the case of fast reactors, neutron damage to the clad material also comes into play. Burn up of the order of 100,000 MWd/te is routinely obtained and up to 200,000 MWd/te has been obtained in some cases. Annual requirement of fuel for fast reactors is thus very small. Some typical data on the fuel are summarised in Table 3.2.

Fuel Manufacture

Manufacture of metallic uranium fuel is a difficult technology in view of certain unfavourable characteristics of the metal. Uranium metal rods when repeatedly heated and cooled, as is likely to happen in a reactor, get elongated. As this type of behaviour cannot be tolerated in a reactor, special heat treatment is given, during fuel manufacture, to overcome this problem. Uranium metal also swells readily on irradiation and, therefore, either the clad has to be strong or the bum up has to be kept low.

As an example, the manufacture of a typical metallic fuel element is as follows. About 95 kg of uranium is taken, melted in a vacuum furnace and cast into a 75 mm dia, 900 mm long billet. This is then hot rolled to reduce the diameter to about 40 mm and given special heat treatment. This rod is machined to bring the diameter to 34.5 mm as required for a fuel element. The length of this rod is 3.1 m and it weighs about 55 kg. A tight fitting aluminium tube with fins is used to clad this uranium rod. A second aluminium tube covers the finned aluminium tube to make a channel for the flow of cooling water.

Oxide Fuel

Uranium oxide is a ceramic powder and cannot be made into a rod. Uranium oxide is, therefore, normally used in the form of pellets (tablets) about 12 mm diameter and 15 mm height. These are prepared by pressing UO_2 powder into pellets and heating them to about 1600°C for obtaining highly dense and hard material. It is necessary to control the diameter of each pellet within a few thousandth of an inch to ensure that it readily goes into the clad tube. Gap between the pellet and the clad tube should be small so that the heat is properly transferred from the pellet to the clad. Fuel pellets also have uniform density in order to prevent hot spots. Further, some of the fission products are gaseous and the pellet structure should ensure that most of the fission gases are retained within the pellet. The release of these gases can cause pressurization of the clad tube leading to fuel pin failure. Typical uranium oxide fuel pellets are shown in Fig. 3.12. The pellets are encased inside the clad tube made from zircaloy and welded. A number of such pins are held together to make a fuel bundle. For LWR fuel, the fuel pin is quite long and because of the high burn up achievable, some space is left to accommodate a fraction of fission gas released during power production. Typical characteristics of fuel bundles for Rajasthan and Tarapur Atomic Power Stations are given in Table 3.3.

Capabilities in Fuel Manufacture

Manufacturing of nuclear fuel is a demanding technology requiring very high purity materials fabricated to meet stringent specifications. The economics and safety aspects of nuclear reactor are strongly dependent upon the quality of fuel. In India, great attention has been paid to the development of this technology. Even for the first large research reactor CIRUS, half of the first charge of fuel was manufactured in India. Presently, the fuel requirements for

Fig. 3.12 Typical uranium dioxide fuel pellets.

Table 3.3: Particulars of Uranium Oxide Fuel for RAPS (PHWR) and TAPS (BWR) Reactors.

Item	RAPS	TAPS – 1 & 2
Enrichment %	Natural	1.1, 2.1, 2.66
Pellet dia x ht (mm)	14.26 x 22	12.24 x 20
Zircaloy tube O.D. (mm)	15.22	14.28
Wall thickness (mm)	0.38	0.89
Length of fuel element (mm)	495	3885
Fuel clad gap (pm)	50	100-150
Pellets per tube	24	200
Weight of Pellets per tube (g)	~800	4300-4500
Tubes per Bundle/Assembly	19	36
Weight of pellets/assembly (kg)	~ 15.2	150-160
Bundles per channel	12	
Total bundles/assemblies	3672	284
Weight of Fuel in reactor (te)	56	45

Fig. 3.13 Typical PHWR Fuel bundles manufactured at NFC.

research reactor DHRUVA are met by the fabrication facilities installed at BARC, Trombay. For the power reactors, which use oxide fuel, initial development and manufacturing activities were at BARC. But large commercial scale operations began at Nuclear Fuel Complex (NFC), Hyderabad in 1973. This plant gets its natural uranium supplies from Jaduguda or Turamdih as impure magnesium diuranate cake or from abroad as Uranium Ore Concentrate (UOC). Enriched uranium pellets required for TAPS (BWR) reactor are imported.

Natural uranium fuel fabrication plant had an initial capacity of 100 te/y. The plant covers all the steps from purification of uranium, preparation of high quality UO_2 powder, manufacture of pellets and encasement in clad tubes to fabrication of fuel bundles.

The current capacity of NFC is 1250 te/y and it can support PHWRs having an installed capacity of 4780 MWe and future PHWR reactors upto 8000 MWe. All requirements of fuel for reactors at Kota, Kalpakkam, Narora, Kaiga, Tarapur and Kakrapar are met by this plant. The capacity of this plant is being further expanded to 1500 te/y to meet the increased requirement of fuel. Typical PHWR fuel bundles are shown in Fig. 3.13. The manner of its positioning inside a pressure tube is shown in Fig. 3.14.

The fuel pellets with the enrichments of 1.1%, 2.1 % and 2.66% for boiling water reactors at Tarapur are being imported. The assembly and manufacture of BWR fuel assembly is being carried out in NFC. In a boiling water reactor, a few fuel rods have 1.5% of gadolinium oxide mixed with uranium oxide, which is used as burnable poison for enhancing the burn up of the fuel. The fuel bundles for TAPS have 36 elements in 6 x 6 array. A typical BWR fuel assembly and control blade, which sits in between four subassemblies, are shown in Fig. 3.15.

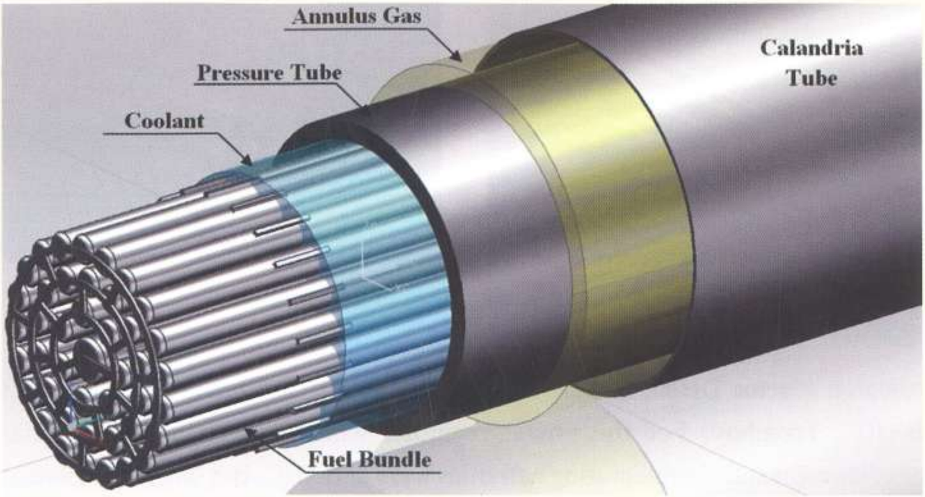


Fig. 3.14 Typical positioning of PHWR fuel bundle inside a pressure tube.

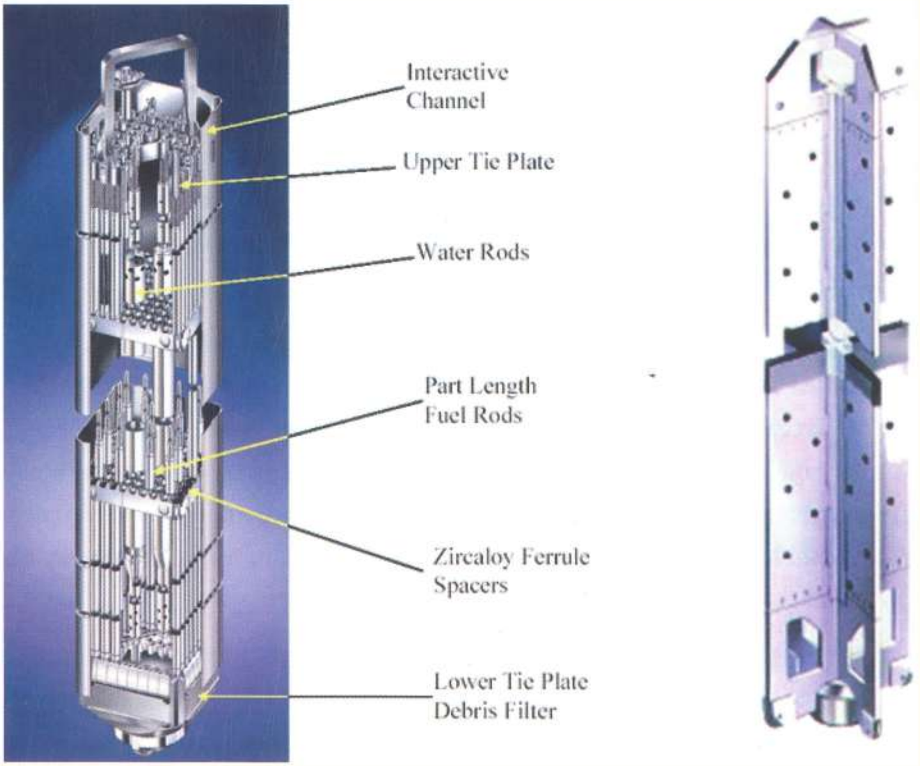


Fig. 3.15 BWR Fuel subassembly and control blade.

Zircaloy required for the manufacture of clad tubes as well as other components of the fuel assemblies is also produced at NFC, Hyderabad starting from zircon sand recovered from beach sands of Kerala/Orissa. This aspect is described in detail in Chapter 7.

Chapter 4

Plutonium

History

The discovery of nuclear fission in 1939 provided the impetus to the quest for the extension of periodic table. This opened a new branch of nuclear science and led to the discovery of transuranium elements. This lively and thriving field of research has resulted in the discovery of elements up to 118. Plutonium-238 was discovered in January 1941 by the efforts of the legend G. T. Seaborg and his coworkers. Plutonium was the first transuranium element that was isolated in weighable amounts. B. B. Cunningham and L. B. Werner isolated ^{239}Pu (weighing about one microgramme) on August 18, 1942. Five kilogrammes of uranyl nitrate hexahydrate was irradiated with neutrons produced by (α,n) reaction of ^{9}Be at 60 inch cyclotron of the University of California Radiation Laboratory, Berkeley. Five milligrammes each of Ce and La in 0.5 M H_2SO_4 were added to the solution which was concentrated by evaporation. Fluorides were precipitated by adding HF and KF solutions. Precipitated fluorides were converted to sulphates by fuming with H_2SO_4. At this stage, rare earths (La and Ce) were precipitated as fluorides and Pu remained in the solution. Repeated cycles were carried out to obtain pure Pu which was finally taken into dilute HNO_3 solution. However, plutonium content was too small to be weighable. Isolation procedure was, therefore, repeated with 90 kg of uranyl nitrate. On September 10, 1942, the first weighing of a pure compound of this artificially produced element Pu was made when an aliquot of the plutonium nitrate solution was delivered on to the previously weighed platinum weighing pan, dried and ignited. The deflection of the balance indicated 2.77 μg of PuO_2. This sample of PuO_2 is being preserved as an archival sample.

Conversion and Breeding

Plutonium is the key to the utilization of all the mined uranium for the production of nuclear power. It is the only artificial element which is produced in tonne quantities. The first globule of plutonium metal weighing about 3 microgrammes was produced in USA in November 1943. With the establishment of nuclear power reactors and conversion of fertile ^{238}U into plutonium, about, 100 te of plutonium is produced every year in the nuclear power reactors operating all over the world. The extent of the conversion of ^{238}U to plutonium varies from reactor to reactor. It depends upon the number of neutrons produced per fission in the reactor and the processes which absorb neutrons. At steady state, the number of neutrons present in a reactor is equal to the number of neutrons consumed by various nuclear reactions. As a typical illustration, neutron balance for 100 fissions in a light water reactor is given in Table 4.1.

Table 4.1: Neutron Balance in Light Water Reactors (100 Fissions, 259 Neutrons)

Neutrons Lost in		Neutrons Absorbed In U/Pu without Fission		Neutrons causing Fission in U/Pu	
Structural Materials	45	Pu	27	Pu	32
Fission Products	14	^{235}U	15	^{235}U	63
		^{238}U	58	^{238}U	5
TOTAL NEUTRONS	59	100		100	
End Product	Activation Products	Pu and higher Actinides		Energy and 259 Neutrons	

On an average, 100 fissions lead to the release of 259 neutrons in this type of reactor. Out of these, 100 neutrons are required to sustain the fission chain reaction and production of next generation of 259 neutrons. Out of the balance 159 neutrons about 100 are lost by absorption in plutonium and uranium without fission. Of these, 58 neutrons are absorbed by fertile isotopes ^{238}U which result in the production of fissile isotopes ^{239}Pu and similarly, absorption of neutrons in ^{240}Pu yields fissile ^{241}Pu. These absorptions partially replenish fissile material. However, about 42 neutrons are absorbed in ^{239}Pu, ^{235}U or ^{241}Pu without resulting in fission and this is wasteful in terms of neutron economics. Similarly about 59 neutrons are lost in structural materials and fission products. It is also seen from the Table 4.1 that a majority of fissions take place in ^{235}U, but a significant fraction of energy is produced by the fission of *in situ* produced plutonium (32%). Fast neutrons in the reactor cause fission of ^{238}U and this contributes about 5% to the energy production.

The ratio of fissile isotopes produced to the fissile isotopes consumed is called the conversion ratio. In light water reactors, the conversion ratio is approximately 0.55 meaning thereby that for every 100 atoms of ^{235}U lost, 55 atoms of fissile plutonium are generated. In the Pressurized Heavy Water Reactors (PHWR), the neutron economy is better, and the conversion ratio of 0.7 is possible. The annual production of plutonium from various reactors depends on the conversion ratio as well as the burn up of the fuel. Annual production of plutonium from different types of reactors of 1000 MWe capacity is as follows:

(i) Light Water Reactors: 220 kg
(ii) Pressurized Heavy Water Reactors: 500 kg
(iii) Gas Cooled Reactors: 700 kg

It is seen that the production of plutonium in a reactor is dependent upon the neutron balance and the energy produced by the fuel in the reactor. Energy produced by a nuclear fuel is measured in the units of MWd/te, which is defined as its burn up. If the neutrons produced from fission can be more, or if the loss in structural materials can be reduced, or the fuel burn up is low, then it should be possible to get better production of plutonium. This has been achieved in fast breeder reactors which make use of a very special nuclear property of plutonium. Fig. 4.1 shows the neutrons released per neutron absorbed (η) for various fissile isotopes as a function of neutron energy.

It is seen from this figure that when the neutrons have low energy (<1 eV), the fission of ^{233}U yields maximum number of neutrons. However, when neutron energies are of the order of 1 MeV, the neutrons released per fission of plutonium, starts increasing rapidly and approaches a figure of 3.4 at 10 MeV. In

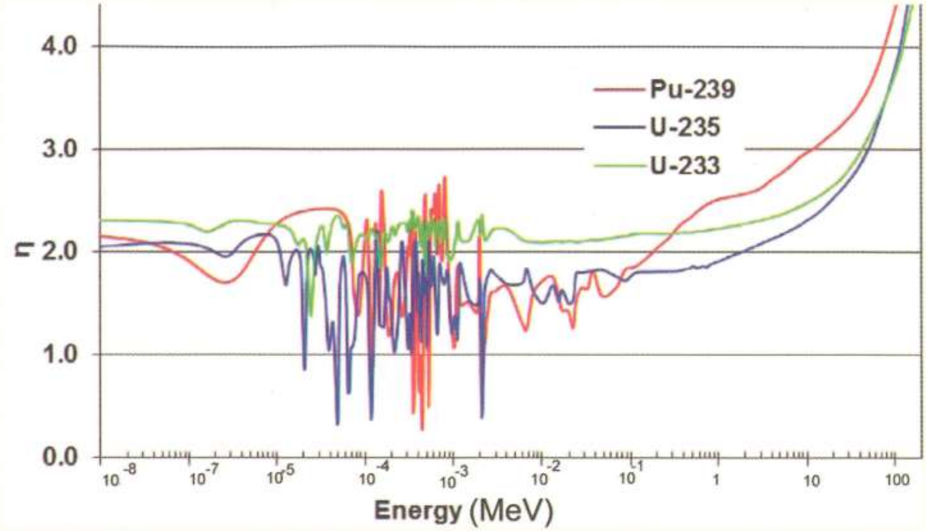


Fig. 4.1 Variation of neutrons released per neutron absorbed with Neutron Energy.

theory when the number of neutrons released per absorption of neutron is more than 2.0, it is possible to produce more fissile material. However, wasteful absorption and leakage of neutrons require substantially higher value of η. In fission reaction, average energy of neutrons released is about 1.1 MeV. Thus with the use of fast neutrons and plutonium fuel, it should be possible to have a large conversion ratio. In fact, this conversion ratio exceeds unity and therefore, such reactors are called breeder reactors. In practice, however, even when no moderators are used, neutrons do slow down due to interaction with structural materials and the components of the fuel. The breeding ratio would thus be dependent on various design parameters. A typical neutron balance in a fast reactor having mixed uranium plutonium oxide as fuel is given in Table 4.2.

At steady state, 100 fissions lead to the generation of 292 neutrons in an oxide fuelled fast reactor. The relative contributions to the total fission by various nuclides are: 84% by Pu (all isotopes), 13% by ^{238}U and 3% by ^{235}U. Out of these 292 neutrons, 100 neutrons are used to continue fission chain reaction. About 153 neutrons are absorbed by the fuel materials which lead to the production of fissile plutonium and 39 are lost by capture in structural materials and fission products. As the plutonium based fuel is expensive, and its recycle is also expensive, the fuel is allowed to stay in the reactor for longer periods and have high burn up to improve economics. This leads to loss of

Table 4.2: Neutron Balance in Oxide Fuelled Fast Reactors (100 fissions, 292 Neutrons)

Neutrons Lost in		Neutrons Absorbed In U/Pu without Fission		Neutrons causing Fission in U/Pu	
Structural Materials	33	Pu	32	Pu	84
Fission Products	6	^{238}U	121	^{235}U	3
				^{238}U	13
TOTAL NEUTRONS	39		153		100
End Products	Activation Products	Pu and higher Actinides		Energy and 292 Neutrons	

breeding. In France, demonstration fast reactors using oxide fuel have successfully achieved a breeding ratio of 1.25. Use of fuels which permit a faster spectrum of neutrons can lead to better breeding. Use of mixed carbide or nitride fuel is expected to give a breeding ratio of 1.3 to 1.4 and the use of metallic plutonium alloys could give a breeding ratio of 1.5. The concept of breeding is illustrated further in Fig. 4.2 by taking the case of an oxide fuelled 1000 MWe breeder reactor. This plant would have about 3 te of plutonium and 12 te of ^{238}U as oxides in the fresh fuel. Production of 1000 MWe power for one year in this plant would consume about one te of fissile material.

The spent fuel would then contain 3.25 te of plutonium, one te of fission products and 10.75 te of ^{238}U. Thus there is a net gain of plutonium by the conversion from ^{238}U and the energy is essentially produced by *in situ* produced plutonium from non-fissile ^{238}U. Out of the 3.25 te of Pu, 3 te should go back to the reactor for continuing energy production but 0.25 te can be used for setting up of new reactors. Thus the use of plutonium and fast breeders can lead to multiplication of the nuclear power capacity in a country. In India, the uranium resources of about 200,000 tonnes can be used to install

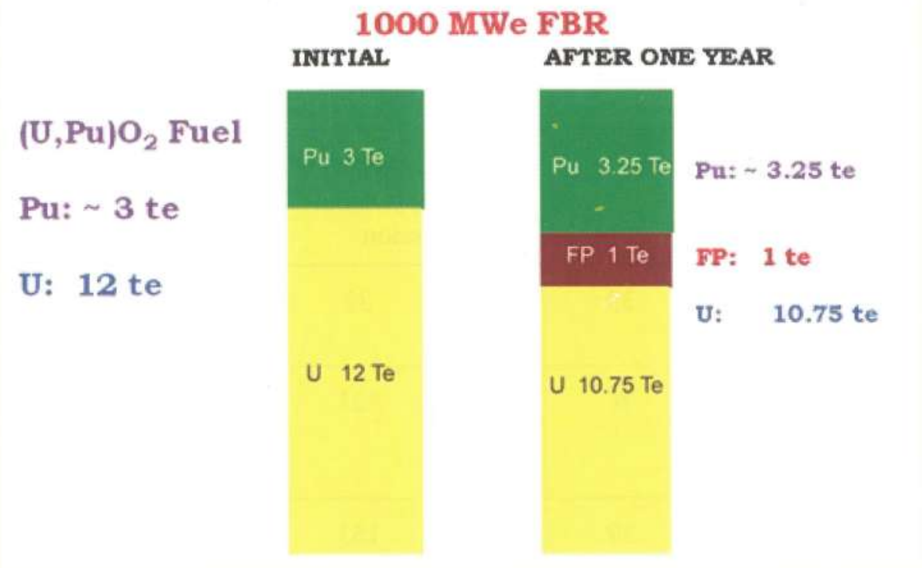


Fig. 4.2 Concept of Breeder in an (U,Pu)0_2 fuelled 1000 MWe FBR.

Pressurized Heavy Water Reactors of only 20,000 to 25,000 MWe capacity. However, the depleted uranium left and plutonium produced in these reactors, can be used in fast breeder reactors leading to a much higher installed capacity. Utilization of plutonium is thus a very important component of India's nuclear energy programme.

Properties of Plutonium

Nuclear Properties

During power production, uranium and plutonium undergo many nuclear reactions with neutrons which lead to the production of isotopes of plutonium. Prominent among these are - ^{238}Pu, ^{239}Pu, ^{240}Pu, ^{241}Pu and ^{242}Pu which are all radioactive. Except ^{241}Pu, they undergo alpha decay. Plutonium-241 decays by beta emission to the transuranium nuclide americium-241. Many alpha emitting isotopes of actinides also decay by spontaneous fission resulting in the production of fission products and neutrons. Some of the nuclear data for these plutonium isotopes are given in Table 4.3. The relative amounts of these isotopes in chemically separated plutonium depend upon the burn up of the fuel. When the burn up is low (1,000 MWd/te) as is the case in most research reactors like DHRUVA, ^{239}Pu

Table 4.3: Some Nuclear Decay Properties of Plutonium Isotopes.

Isotope	Half Life in Years			Radioactivity dps/g
	α	β	Spontaneous Fission	
^{238}Pu	87.74	-	4.77×10^{10}	6.34×10^{11}
^{239}Pu	2.41×10^{4}	-	-	2.30×10^{9}
^{240}Pu	6.57×10^{3}	-	1.34×10^{11}	8.39×10^{9}
^{241}Pu	-	14.4	-	3.81×10^{12}
^{242}Pu	3.76×10^{5}	-	6.75×10^{11}	1.45×10^{8}

content is about 95%. For Light Water Reactors, where the burn up approaches 35,000 MWd/te, ^{239}Pu content is about 60%. For fast reactors, the target for burn up is 100,000 MWd/te or higher. Typical data for some power reactors are given in Table 4.4.

Neutron induced fission is one of the most important nuclear reactions of Pu isotopes with large cross sections. Out of 5 isotopes mentioned, only ^{239}Pu and ^{241}Pu are fissile with thermal neutrons and the other isotopes of plutonium act as absorber materials. However, in fast reactors even the other isotopes of plutonium undergo fission and contribute to the production of energy. The fission cross sections with fast neutrons for ^{239}Pu, ^{240}Pu, ^{241}Pu and ^{242}Pu are, respectively, 1.9 b, 0.4 b, 2.6 b and 0.3 b.

Chemical Properties

Plutonium is one of the few elements in the periodic table which has very complex chemistry. Electronic configuration of Pu shows that shells 5, 6 and 7 of plutonium atom are partially filled and electrons from these shells can take part in chemical reactions. Plutonium can exist in trivalent, tetravalent, pentavalent and hexavalent oxidation states. In the case of pentavalent and hexavalent states, plutonium exists as Pu^{5+} and Pu^{6+} or in solution as PuO_2^+ and PuO_2^{2+}. In aqueous solution only PuO_2^+ and PuO_2^{2+} are stable. In alkaline solutions, plutonium can be oxidized to heptavalent state with strong oxidizing

Table 4.4: Average Isotopic Composition of Plutonium Produced in Uranium-Fuelled Thermal Reactors.

Reactor type	Mean Fuel Burn up MWd/te	Wt % of Pu Isotope at discharge				
		^{238}Pu	^{239}Pu	^{240}Pu	^{241}Pu	^{242}Pu
Magnox	3,000	0.1	80.0	16.9	2.7	0.3
PHWR	7,000	0.4	66.3	26.5	5.3	1.5
AGR	18,000	0.6	53.7	30.8	9.9	5.0
BWR	27,500	2.6	59.8	23.7	10.6	3.3
PWR	33,000	1.5	56.2	23.6	13.8	4.9

reagents like ozone to form tetraoxo species $PuO_4(OH)_2^{3-}$. Plutonium is the only element in which the stability of various valence states is quite comparable and all of them can coexist in solution simultaneously. By maintaining selective conditions, however, it is possible to stabilize one of the ionic species. For example, tetravalent plutonium is the most stable state in nitric acid solutions. Plutonium ions also readily form complexes with anions: for example, tetravalent Pu can form following species in nitric acid.

$Pu(NO_3)^{3+}$, $Pu(NO_3)_2^{2+}$, $Pu(NO_3)_3^{+}$, $Pu(NO_3)_4$ and $Pu(NO_3)_6^{2-}$

Understanding properties of oxidation, reduction, as well as complexation are very useful in designing separation and recovery procedures. Plutonium ions form complexes with many organic compounds like ethers, ketones and tributyl phosphate. Compounds like $Pu(NO_3)_4.2TBP$ are soluble in organic phase and, therefore, form the basis for many separation schemes.

Fuel Reprocessing

Fuel reprocessing is used for the separation of valuable plutonium as well as recovery of left over uranium from the spent fuel. This step also helps in the isolation of highly radioactive fission products which can be subsequently immobilized for safe storage and disposal. The fission products which were very carefully contained within the fuel up to this stage are now to be dealt with and, therefore, great precaution is required in all the steps of reprocessing. The spent fuel is highly radioactive, the level being of the order of a few million curies per tonne. All operations, with the spent fuel are, therefore, carried out remotely to minimize radiation exposure to the working personnel.

Fission products continue to accumulate in the fuel while the reactor is used for power production. The discharged fuel is stored in specially designed pools of water to allow the decay of short lived fission products. Water of the pool cools the fuel, which is essential, and also shields personnel from radiation. After about one year of cooling, the spent fuel is transported to a reprocessing plant in specially designed shielded containers. These containers are designed such that the radioactive products from the spent fuel are not released to the environment even in the worst imaginable accident. The spent fuel is then unloaded into the storage pool of the reprocessing plant. Reprocessing has to be carried out in specially designed buildings which ensure adequate radiation safety of operating personnel. The concrete walls of the process cells, in which the reprocessing equipment are installed, are several meters thick and lined with stainless steel. As these cells are likely to become contaminated with radioactivity, and virtually inaccessible for any repairs, the equipment design is such that it does not need replacement throughout its life period. Nevertheless, the design permits replacement by remote methods, in case it becomes essential. Most operations cannot be seen, but in areas where visual information is essential, special thick lead glass windows are installed. Closed circuit television is also used for monitoring some operations.

Many processes were used in the initial phase of spent fuel reprocessing but currently 'PUREX' (Plutonium Uranium Reduction EXtraction) process is almost universally used for the recovery of plutonium from spent fuel. The fission product elements present are noble gases, alkali metals, alkaline earth metals, rare earths, and many transition elements like Zr, Nb, Ru and Mo, and cover almost half of the periodic table. The process has, therefore, to achieve decontamination of uranium and plutonium from these fission products. Principles of some of the earlier processes and details with respect to various steps for Purex process are discussed.

Early Processes

In the earliest studies on the isolation of microgramme quantities of plutonium, G.T. Seaborg and his colleagues had developed a method for selective co-precipitation of plutonium with bismuth phosphate. Purification of plutonium in bismuth phosphate precipitate was carried out by repeated dissolution and precipitation. The process made use of the fact that tetravalent plutonium co-precipitates with bismuth and hexavalent plutonium does not. This process was used in USA for the isolation of plutonium required initially for nuclear weapons production. It was subsequently replaced by solvent extraction process. Methylisobutyl ketone (hexone) was one of the first extractants used for reprocessing of the spent fuel. This solvent readily extracts uranium and plutonium into the organic phase without appreciable extraction of fission product elements (Table 4.5). However, the flash point (60°C) of the solvent and reactivity with nitric acid were its drawbacks and it was soon replaced by other solvents. Ethyl ether had been known for a long time to extract uranium but it could not be used for reprocessing in view of its highly volatile and reactive nature. Another ether, dibutyl carbitol, which was less volatile and less reactive to nitric acid, was, therefore, successfully used in the United Kingdom for reprocessing the spent fuel.

Table 4.5: Distribution Coefficients of Uranium and Plutonium in Hexone and TBP.

Solution	U(VI)	Pu(VI)	Pu(IV)	Pu(III)	FP
Hexone	1.5	7.6	1.6×10^{-2}	4.5×10^{-4}	6×10^{-4}
TBP	8.0	0.6	1.5	2×10^{-2}	2×10^{-3}

Purex Process

The objective of the process is to recover uranium and plutonium quantitatively and with high decontamination factors from the fission product elements. High recoveries would ensure that the valuable fissile materials as well as fertile materials are recovered and prevent them from going into the waste streams which have to be subsequently treated for safe disposal. The reprocessing operations can be classified into the following major steps:

(i) Separation of fuel and cladding.
(ii) Dissolution of fuel
(iii) Extraction of uranium and plutonium
(iv) Partitioning of uranium and plutonium and their subsequent purification.
(v) Solvent recycling
(vi) Waste handling

A typical flow sheet is shown in Fig. 4.3.

Decladding and Dissolution

For the recovery of plutonium it is necessary to dissolve the irradiated fuel. During this step it is desirable to remove the cladding separately so that its constituents do not complicate the subsequent steps. One of the methods used for removing the cladding is by direct mechanical stripping and is practised for reprocessing fuels from Gas Cooled Reactors. Another method is to selectively leach the cladding without affecting the fuel constituents. Fuel elements from research reactors like DHRUVA, are clad with aluminium and are treated in this manner, where aluminium gets readily dissolved in sodium hydroxide solution and uranium metal or UO_2 is not affected. Zircaloy and stainless steel are highly corrosion resistant materials and their dissolution is quite difficult. Therefore, UO_2 and PuO_2 are selectively dissolved from stainless steel or zircaloy clad fuels and the cladding is left behind. The fuel elements in this process are cut into small pieces of about 5 cm long and treated for dissolution. This process is known as chop-leach process. The dissolution is carried out in nitric acid at about 100°C. The dissolution reactions for U metal and UO_2 are as follows:

$$U + 3/2O_2 + 2HNO_3 \rightarrow UO_2(NO_3)_2 + H_2O \qquad (4.1)$$

$$UO_2 + 2HNO_3 + 1/2O_2 \rightarrow UO_2(NO_3)_2 + H_2O \qquad (4.2)$$

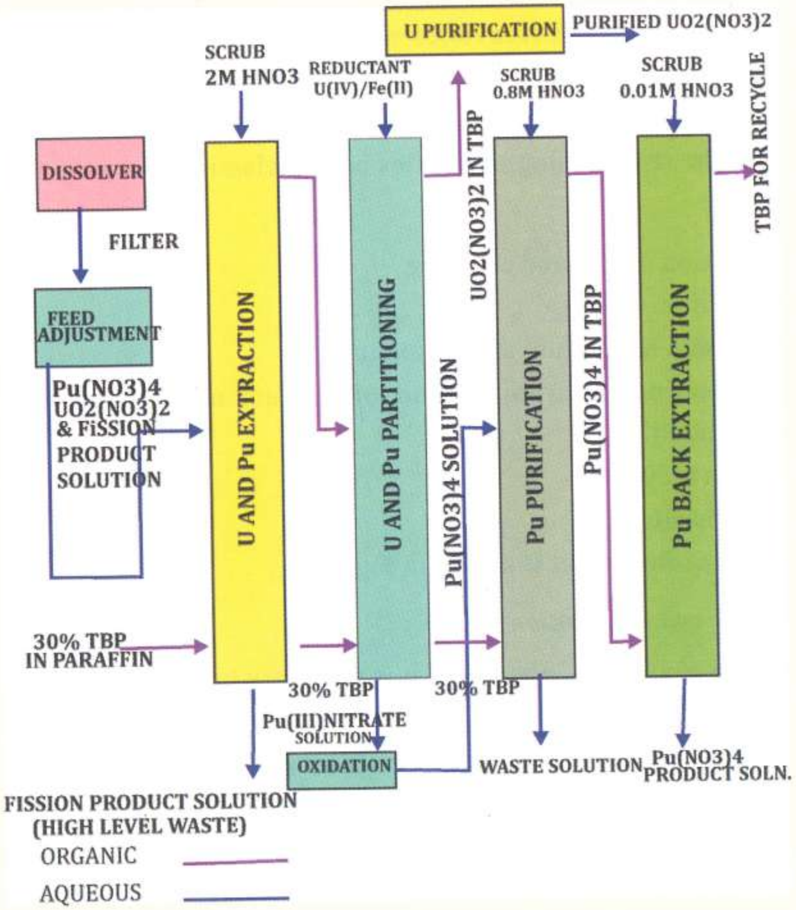


Fig. 4.3 Purex Process Flow Sheet for Plutonium Recovery.

The dissolution is carried out in the presence of air to minimize the loss of nitric acid as nitrogen oxide. Uranium metal and UO_2 dissolve readily. Plutonium oxide when present in larger quantities (>20%) causes some dissolution problems. In addition, at high burn up the fuel can contain noble metal fission product residues which do not dissolve. After dissolution of the fuel the cladding is separated. The solution is filtered to remove suspended particles and treated for the recovery of uranium and plutonium.

Extraction of Uranium and Plutonium

Uranium and plutonium ions combine with nitrate ions to form neutral salt species. Out of these, only the salt species having tetravalent plutonium ($Pu(NO_3)_4$) and hexavalent uranium ($UO_2(NO_3)_2$) are readily extractable in TBP (Table 4.5). Tributyl phosphate solution in long chain hydrocarbon diluent is used for extraction. Therefore, before starting the extraction, it is necessary to ensure that plutonium is present in the tetravalent state. This is achieved by treating the solution with oxides of nitrogen or sodium nitrite which stabilizes the tetravalent plutonium ion but does not affect uranium which continues to be present in the hexavalent state. The acid concentration of the solution, after dissolution is controlled to maximize the extraction of uranium and plutonium and minimize the extraction of fission products. The solution is fed to the extraction column in which 99.9% of uranium and 99.98% of plutonium get extracted into the organic phase with less than 0.5% of the fission products. An important precaution which is required to be taken when dealing with concentrated fissile materials like plutonium is regarding the criticality. Under certain conditions, less than 500 g of plutonium in solution is adequate to sustain a fission chain reaction. This can lead to local over heating of solution, disruption of plant and equipment and in worst cases, sufficient pressure generation leading to explosion. All plant handling fissile materials are, therefore, designed to ensure that condition favourable for criticality cannot be attained even unintentionally. In some equipment of the plant, for example the dissolver, neutron absorbers like boron or cadmium are incorporated in the design so that these poisons prevent the initiation of a chain reaction.

Partitioning of Uranium and Plutonium and their Subsequent Purification

Partitioning of uranium and plutonium is based on the non-extractability of trivalent plutonium into TBP. The organic solution is contacted with an aqueous solution having a reducing agent like ferrous sulphamate or tetravalent uranous nitrate. These reagents selectively reduce tetravalent plutonium to trivalent plutonium without affecting uranium. Reduction of plutonium causes its back extraction into the aqueous phase leaving uranium in the organic phase. Both uranium and plutonium streams at this stage have some amount of fission products and need further purification. The purification of uranium stream is always carried out by another cycle of solvent extraction. The purification of plutonium is carried out either by solvent extraction method or by anion exchange method. Reprocessing plant at Trombay uses the ion exchange method whereas the plant at Tarapur uses the solvent extraction method for plutonium purification. When the concentration of nitric acid is increased to 7 M, plutonium ion combines with 6 nitrate ions to form anionic species of the type $Pu(NO_3)_6^{2-}$. Very few metallic ions form this kind of anionic species and, therefore, separation of plutonium from a large number of impurities can be achieved by using anion exchange method. When the solution of tetravalent plutonium in 7 M nitric acid is passed through a column filled with anion exchange resin, plutonium is selectively retained on the resin. After washing the column, plutonium is eluted from the column by using dilute nitric acid (0.5 M).

Solvent Recycling

Tributyl phosphate as well as organic diluents are subjected to high radiation, emitted by the fission products, which results in their degradation and formation of degradation products. Some of them have detrimental effect on the extraction properties of the solvent. In view of the cost as well as the need for keeping the waste volumes low, it is customary to use the solvent many times before it is discarded. In order to recycle the solvent, it is essential to treat it for the removal of degradation products. The most common methods used for this purpose is to wash with sodium carbonate solution followed by a dilute nitric acid wash.

Waste Handling

The process of nuclear power production leads to the accumulation of fission products in the fuel and this comes into solution during the fuel dissolution. Reprocessing directs fission products to various waste streams. There are gaseous wastes, liquid wastes and solid wastes. None of these waste streams is allowed to be discharged into environment without extensive removal of the radioactivity. The streams containing high level waste and intermediate level wastes are never discharged but treated for immobilization and safe storage. Most of the gaseous products, tritium (as water), ^{14}C (as carbon dioxide), ^{85}Kr and ^{131}I, are fixed on charcoal or special absorbers. High level and intermediate level waste are sent separately to waste immobilization plant. In this plant, high level waste is evaporated and mixed with glass and melted to incorporate the radioactive materials into glass matrix. The glass is encased in stainless steel drums and stored safely in special facilities. In a similar manner, intermediate level waste is also immobilized and stored safely. Low level liquid effluents are treated for the removal of radioactive products below the prescribed permissible limits by Atomic Energy Regulatory Board (AERB) of India, and then discharged into large water bodies. All solid effluents like the cladding pieces and radioactive equipment are carefully treated for safe burial.

Capabilities in Fuel Reprocessing

The Government of India signed an agreement with Canada on Apri 28, 1956 for the construction and commissioning of the CIRUS reactor. In 1958, India decided to construct a reprocessing plant to treat the irradiated fuel from CIRUS reactor. The design, construction and commissioning of the reprocessing plant at Trombay was successfully accomplished by India by 1964, entirely with indigenous effort. At that stage, India was one of the seven countries in the world which possessed the complex technology of fuel reprocessing. When the construction of DHRUVA reactor was started, a decision was taken to refurbish and expand the Trombay reprocessing plant for reprocessing the fuel from CIRUS as well as DHRUVA reactors. This has been successfully achieved. The experience gained at Trombay plant was useful in setting up a 100 te per year capacity reprocessing plant at Tarapur. The plant is designed for reprocessing the fuel from the Tarapur and Kota reactors. This plant is currently reprocessing fuel from Kota reactors as well as from reactors at Kalpakkam. A new reprocessing plant of similar capacity, is in operation at Kalpakkam. More reprocessing plants are under construction/planning to cater to the requirement of additional reactors which are expected to be installed in our nuclear power programme.

Plutonium and its Compounds

Plutonium Metal

Plutonium metal is produced by the reaction of plutonium tetrafluoride with calcium metal.

$$PuF_4 + 2Ca \rightarrow Pu + 2CaF_2 \qquad (4.3)$$

Plutonium metal is one of the very dense metals with a density of 19.86 g/cc. It has a melting point of 640°C but between room temperature and its melting point, it undergoes many phase transitions with significant changes in density. Solid plutonium metal is, therefore, not directly suitable for making reactor fuel. This, however, is not a drawback, since pure plutonium metal is never required to be used in a reactor in view of its high fissile content. It is always diluted with uranium or other metals, for use in reactors.

Plutonium metal is highly reactive. It readily reacts with air and moisture. All operations involving plutonium metal are, therefore, carried out in inert atmosphere glove boxes.

Plutonium Oxide

Plutonium oxide is the starting material for fabrication of plutonium based fuels and is also used in the preparation of most of its compounds. The end product from the reprocessing plant is a solution of plutonium nitrate. Plutonium oxide is prepared, from this solution, by precipitation of oxalate and its calcination.

$$Pu(NO_3)_4 + 2H_2C_2O_4 \rightarrow Pu(C_2O_4)_2 + 4HNO_3 \qquad (4.4)$$

$$Pu(C_2O_4)_2 + O_2 \xrightarrow{500^\circ C} PuO_2 + 4CO_2 \qquad (4.5)$$

The colour of plutonium oxide depends upon its origin and varies from yellow black to green. Its theoretical density is 11.46 g/cc and melting point is 2400°C. It is stable under conditions of neutron irradiation and is a good candidate for nuclear fuel. Being a ceramic material, its thermal conductivity is low but it is more than compensated by its high melting point. Images of plutonium oxide and plutonium metal are given in Fig. 4.4.

Plutonium Carbide

Plutonium carbides are of interest in obtaining high breeding ratio in the fast breeder reactors. Plutonium monocarbide, which has only one carbon atom as against two oxygen atoms in oxides, moderates the neutron energy, in a fast reactor, to a lesser extent which is helpful in obtaining higher breeding ratios. Also the thermal conductivity of plutonium monocarbide is higher than that of the oxide which is useful in reducing the specific inventory of a fast reactor. Plutonium monocarbide can be obtained by direct reaction between plutonium metal and methane gas but it is more commonly prepared by carbothermic reduction of oxide.

$$PuO_2 + 2C \xrightarrow{1400^\circ C} PuC + CO_2 \qquad (4.6)$$

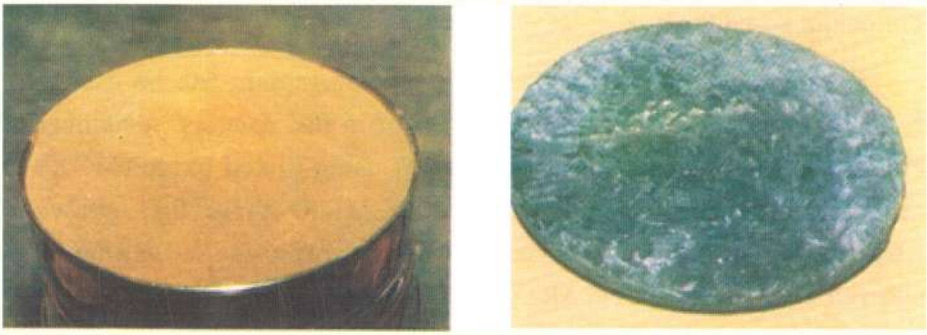


Fig. 4.4 Photographs of plutonium oxide and plutonium metal

Plutonium monocarbide has a theoretical density of 13.58 g/cc and its melting point is 1654°C. Presence of excess carbon can lead to the formation of plutonium sesquicarbide (Pu_2C_3) and plutonium dicarbide (PuC_2).

Plutonium Nitride

Plutonium nitride is also considered as an advanced fuel for fast reactors and is capable of high breeding ratios. It can be prepared by direct reaction between plutonium metal and nitrogen or by carbothermic reduction of plutonium oxide in nitrogen atmosphere.

$$PuO_2 + C + 1/2N_2 \xrightarrow{1400\,^{\circ}C} PuN + CO_2 \tag{4.7}$$

Plutonium nitride has a density of 14.22 g/cc and dissociates to plutonium and nitrogen at temperatures above 1600°C. Higher nitrides of plutonium are not formed.

Plutonium Tetrafluoride

Plutonium tetrafluoride is the starting material for the preparation of plutonium metal and is obtained from plutonium oxide by treatment with hydrogen fluoride.

$$PuO_2 + 4HF \xrightarrow{500\,^{\circ}C} PuF_4 + 2H_2O \tag{4.8}$$

It is pink in colour, has a theoretical density of 6.75 g/cc and its melting point is 1027°C.

Plutonium Based Fuels

Plutonium recovered from the reprocessing plant can be used as a fissile material either in thermal reactors or in fast reactors. A number of countries are exploring the possibility of using mixed oxide (MOX) of uranium and plutonium containing about 4% of PuO_2 as fuel for Light Water Reactors. For this purpose, enriched ^{235}U would not be required as plutonium substitutes for ^{235}U. Some MOX bundles were used to replace enriched uranium fuel bundles in TAPS BWR reactors. Plutonium, however, as mentioned earlier, is most beneficially used in fast breeder reactors. The nuclear properties of plutonium permit higher breeding when the neutrons of fast spectrum are used. Uranium-plutonium mixed oxide containing about 25% of PuO_2 is the most widely used fuel for fast reactors which include a 250 MWe reactor in UK (PFR), 1200 MWe reactor in France (Super Phoenix) and 600 MWe reactor in the former USSR (BN 600). Fuel for these reactors is manufactured by a process similar to that for uranium oxide. Uranium oxide powder is mixed with plutonium oxide powder and the blended powder is then used for making the fuel pellets of diameter ranging from 5 to 8 mm. They are encased inside a stainless steel tube to make a fuel pin. All the operations up to the manufacture of the fuel pin are carried out in special airtight glove boxes. Plutonium oxide powder is neither allowed to come into the laboratory air nor come in contact with any personnel. Handling in glove boxes complicates the operation of fuel manufacture to a certain extent. The external surfaces of the fuel pins are decontaminated and taken out of the glove box for making the fuel bundles.

Oxide fuels have demonstrated very successful performance up to a burn up of 150,000 MWd/te. The breeding ratio achievable with this type of fuel, however, is only 1.25 which limits the rate at which new reactors can be set up using plutonium generated by fast reactors. India which needs to have rapid multiplication of plutonium, to meet the large demands of electricity in the country, has to look for fuels which will permit higher breeding ratios. Nevertheless, based on the world wide experience at this stage, mixed oxide has been chosen as a fuel for the prototype fast breeder reactor of 500 MWe capacity at Kalpakkam, which is expected to start operation shortly.

Advanced fuels like mixed carbides and mixed nitrides are manufactured by carbothermic reduction process. The starting material in this case also is a uniform blend of uranium and plutonium oxides which are further mixed with carbon. The mixture is then heated in vacuum at approximately 1400°C for the manufacture of carbides and at about 1500°C in nitrogen atmosphere for the manufacture of nitrides. The materials so obtained are crushed to a fine powder and made into pellets of desired size and encapsulated in stainless steel tubes. All handling has to be done in glove boxes that have to be provided with high purity nitrogen or argon atmosphere. This is essential since carbides and nitrides of uranium and plutonium are highly reactive and can get deteriorated when exposed to moisture in the air. Fine powders can readily catch fire in presence of oxygen. Presently, there is very little experience on the use of carbide or nitride fuels in the fast reactors. In fact, India is the first country in the world to use a full core of mixed carbide fuel in its Fast Breeder Test Reactor (FBTR) at Kalpakkam. India is also investigating the possible use of metallic fuel in prototype fast breeds reactors at subsequent stages.

Metallic uranium and its alloys have been used as fuel in some of the early fast reactors installed for research in fast reactor technology. Plutonium based alloys have, however, not been used till recently. In USA, an alloy having 75% of U, 15% of Pu and 10% of Zr has been successfully irradiated in Experimental Breeder Reactor II.

Other Applications of Plutonium

Neutron Sources

Neutron sources in 1930s were made by combining radon or radium with beryllium powder. The alpha particles interact with beryllium to give neutrons as shown below:

$$^{9}_{4}\mathrm{Be} + ^{4}_{2}\mathrm{He} \rightarrow ^{12}_{6}\mathrm{C} + ^{1}_{0}\mathrm{n} \qquad (4.9)$$

However, because of the associated beta and gamma emitting nuclides in the decay chains of radium and radon, the use of these neutron sources is cumbersome. Replacement of radium/radon by plutonium has led to the development of very safe neutron sources which can be used in research laboratories. For this, either plutonium oxide is mixed thoroughly with beryllium metal powder or an alloy of Pu and beryllium is made. These are then encapsulated in suitable stainless steel capsules to ensure safety during handling.

Isotope Power Generators

Plutonium-238 is a short lived nuclide with a half life of 87.74 y and decays by alpha emission (Table 4.3). The energy of alpha particle emitted by ^{238}Pu gets converted to heat and the material becomes hot. A gramme of ^{238}Pu gives out 0.55 W of thermal power. This heat can be used for the generation of small amounts of electricity by incorporating a suitable thermoelectric device. Plutonium-238 can thus make a very reliable and compact battery useful for many critical applications. One of the most fascinating applications of ^{238}Pu based batteries has been for heart pace-makers. Plutonium-238 based batteries have also been used for providing power to many satellites. Systems ranging from 0.2 W to 30 W of power have been made with ^{238}Pu.

Safety Aspects of Plutonium

The name plutonium quite often strikes terror in many minds. Plutonium is radioactive and great care is always taken during its handling. All operations are carried out inside specially designed boxes and plutonium is not allowed to enter the laboratory air. A view of a typical plutonium laboratory is shown in Fig. 4.5. Health Physics personnel continuously monitor the air for any plutonium contamination and ensure the safety of persons working in the laboratory. Any release of plutonium is very easily detected as a microgramme of plutonium gives 140,000 alpha particles per minute. The occupational exposure of the staff members is controlled effectively to ensure that the body burden, defined as 0.6 microgrammes, is never exceeded. This is the amount that can be contained in the body without causing any known hazardous effects. The lethal dose of plutonium ranges from a fraction of a gramme to several gramme depending on the route by which it enters the body and its physical and chemical forms. This is well above the quantity for the conventional poisons. The air inside a plutonium laboratory is always monitored and the maximum allowable air concentration for plutonium is 0.00003 microgramme per cubic metre of air.

Fig. 4.5 A view of typical Plutonium Laboratory

Chapter 5

Thorium

Introduction

India's resources of thorium are almost four times its uranium resources. Thorium is a fertile material for the production of fissile uranium-233. There is great interest in the utilization of this important natural resource for the production of energy. The technology of thorium utilization is under development so that it would be available when required.

Baron Jones Jackob Berzelius, the famous chemist who started the use of symbols for chemical elements, discovered this new element in 1828. He named it thorium after the powerful Scandinavian God `Thor'. Thorium is much more abundant than uranium. The first practical application of thorium was made by Carl Auer von Welsbach who observed that a cloth dipped in a solution of thorium nitrate plus 1% cerium nitrate gave a brilliant white light when heated in a flame. Based on this observation, he perfected a gas mantle in 1891 which found immediate market and is still in use in many countries, including India. The discovery of gas mantle increased the demand for thorium and very soon thorite and monazite, recovered from beach sand of Brazil, were being used for producing thorium. In 1909, a German geologist, Schomberg was studying various beach sands as possible sources of monazite when he noticed that coir in a warehouse in Hamburg had a lot of heavy beach sand associated with it. He traced the coir back to its origin in Manavalakurichi in Travancore and found that the sand on this beach contains about 1% monazite. He started quietly carrying sand from this beach to Germany, as a ballast for ships, and process it there for the recovery of thorium. Subsequently, he came to India, settled here and married an Indian girl. He was separating monazite from sand and exporting it to Germany for recovery of thorium. Germany became a major centre for gas mantles during that period. The factory at Manavalakurichi was taken over by the British during the First World War. The discovery of electric bulb reduced the demand for thorium but beach sands became important for the recovery of illmenite, a mineral useful for making white paint. Presently, beach sands are mainly processed for the recovery of rare earth elements. The British company was taken over by the Indian Government and Indian Rare Earths (IRE) was established in August 1950. Subsequently, monazite has been found at many coastal beaches in Karnataka, Tamil Nadu and Orissa and the current reserves of thorium from these sands are estimated at 846,500 tonnes. Beach sands are being processed by IRE Limited and Kerala Minerals and Metals Ltd. Large plants exist at Manavalakurichi and Chavara in Kerala and Chatrapur in Orissa. At present, demand for thorium is small as it is mainly required for tungsten filaments, tungsten welding electrodes and special magnesium, alloys. Monazite sand is processed for the recovery of rare earths and thorium is a by-product.

Recovery of Thorium

Illmenite ($FeTiO_3$) is a major constituent (65 to 80%) of beach sands where monazite is only 0.5 to 1%. Other useful minerals in beach sand are zircon, rutile, garnet and silimanite. The beach sands are processed by gravity and magnetic separation methods to separate all these minerals. Thorium is recovered from the monazite fraction. Monazite is a complex phosphate mineral containing phosphates of thorium and rare earths. It has about 9% of ThO_2, 60% of rare earth oxides, 0.4% of UO_2 and 27% of phosphorous pentoxide. On treating it with concentrated sodium hydroxide, sodium phosphates and hydroxides of thorium, uranium and rare earths are formed.

$$Th_3(PO_4)_4 + 12NaOH \rightarrow 3Th\,(OH)_4 + 4Na_3PO_4 \tag{5.1}$$

$$R.E.(PO_4) + 3NaOH \rightarrow R.E.\,(OH)_3 + Na_3PO_4 \tag{5.2}$$

Sodium phosphate is water soluble and is recovered from the solution. It is used in textile industry for water softening. The residual cake called thorium concentrate, is dissolved in excess hydrochloric acid. From this solution, most of the thorium is precipitated as sulphate using 50% sulphuric acid. The solution is then treated with sodium fluoride and hydrofluoric acid to recover the remaining thorium, uranium and rare earths. Thorium sulphate is converted to thorium hydroxide by treating with sodium hydroxide, dissolved in hydrochloric acid and re-precipitated as sulphate to improve the purity. Thorium sulphate is then converted to hydro-carbonate by treatment with ammonium carbonate and then dissolved in nitric acid. The solution is evaporated to obtain crystalline thorium nitrate.

Thorium nitrate produced by the above process is commercially known as mantle grade. For use in nuclear reactors, thorium of high purity is required and many impurities, particularly boron and rare earths should be below parts per million. Purification of mantle grade thorium nitrate is achieved by solvent extraction with tributyl phosphate. A process has also been developed for direct solvent extraction of thorium and uranium constituents from the thorium concentrate obtained after treatment with sodium hydroxide. The thorium concentrate is washed with dilute sodium hydroxide solution and dissolved in nitric acid to obtain a solution having thorium, uranium and rare earth nitrates. Uranium from this solution is selectively extracted into an organic solvent having 5 to 10% tributyl phosphate in kerosene. In the second stage thorium is extracted into 40% tributyl phosphate in kerosene. Both thorium and uranium are separately back extracted into aqueous solution as nitrates, purified by more solvent extraction steps and then finally concentrated to obtain uranyl nitrate and thorium nitrate.

Thorium and its Compounds

Thorium Metal

Reduction of thorium tetrafluoride with calcium is one of the main methods for the production of bulk thorium. The procedure as practised for uranium and plutonium is not directly applicable to thorium since thorium metal has a melting point of 1750°C which is too high for its consolidation as an ingot during reduction. To overcome this problem, zinc chloride is added along with thorium fluoride, so that after reduction a thorium-zinc alloy containing about 20% of zinc is obtained. This alloy has a melting point of 1360°C and readily consolidates into a good ingot. Zinc is subsequently removed from thorium by distillation under vacuum at 1150°C. Thorium metal can then be melted by induction heating and cast into rods. Thorium is a white silvery metal but quickly tarnishes when exposed to air. It has a density of 11.7 g/cc. When heated in the absence of air at room temperature, alpha form of thorium becomes beta form above 1350°C and melts at 1750°C.

Thorium Oxide

Thorium oxide, suitable for fabrication of pellets required for use in nuclear reactors, is obtained by precipitation of thorium as oxalate from thorium nitrate solution.

$$Th(NO_3)_4\,(aq) + 2H_2C_2O_4 + 2H_2O \rightarrow Th(C_2O_4)_2.2H_2O + 4HNO_3 \quad (5.3)$$

Oxalate precipitate is filtered, washed and calcined to obtain ThO_2

$$Th(C_2O_4)_2\,.\,2H_2O + O_2 \rightarrow ThO_2 + 4CO_2 + 2H_2O \quad (5.4)$$

Thorium oxide is a white solid with a theoretical density of 10.00 g/cc. It is a very stable ceramic and can be heated up to its melting point of 3370°C without any deterioration. It has good compatibility with cladding materials and quite stable under conditions of neutron irradiation. It forms solid solution with fissile material oxides like UO_2 and PuO_2.

Thorium Fluoride

Thorium fluoride is an intermediate in the production of thorium metal and is produced by the reaction of thorium oxide with hydrogen fluoride.

$$ThO_2 + 4HF \xrightarrow{500-600\,^{\circ}C} ThF_4 + 2H_2O \quad (5.5)$$

Thorium tetrafluoride is a white solid with a theoretical density of 6.12 g/cc and its melting point is 1110°C.

Thorium Carbide

Thorium forms two carbides; thorium monocarbide (ThC) and thorium dicarbide (ThC_2). They can be prepared by reaction of Th metal with carbon or methane or by the reaction of ThO_2 with carbon at about 1500°C. ThC_2 with a density of 8.76 g/cc and a melting point of 2640°C is used as a fertile material in high temperature gas cooled reactors. It is also mixed with uranium dicarbide to make fuel for high temperature gas cooled reactors.

Thorium Breeders and Thorium Fuel Cycle

Thorium is a fertile material to produce ^{233}U. This can be done only with a large neutron source such as a reactor or spallation source. The reaction is as follows:

$$^{232}_{90}Th + ^{1}_{0}n \rightarrow ^{233}_{90}Th \xrightarrow[22.3\text{ min}]{\beta} ^{233}_{91}Pa \xrightarrow[26.967\text{ d}]{\beta} ^{233}_{92}U \qquad (5.6)$$

In the early stages, currently decommissioned Research Reactor CIRUS was used for ^{233}U production. Special elements containing ThO_2 pellets are arranged around the core of the reactor for this purpose. Currently, bundles containing ThO_2 are used in some PHWR reactors for initial flux flattening and are the main source of ^{233}U. A small experimental reactor (PURNIMA II) with ^{233}U as fuel was earlier installed at Trombay and another experimental reactor KAMINI is in operation at Kalpakkam.

In thorium fuel cycle, ^{233}U would be used as a fissile material and thorium as a fertile material. It is possible to set up a reactor which can be breeder or near breeder using this system. Some of the prominent concepts for this purpose are:

(i) Fast reactors
(ii) Thorium based pressurized heavy water reactors
(iii) Advanced heavy water reactors
(iv) Light water breeder reactors
(v) Molten Salt Reactors

Breeding ratio greater than one can theoretically be obtained only in fast reactors and molten salt reactors, but the gain is substantially smaller than that obtained in plutonium fuel cycle. The other concepts have potential for giving breeding ratio close to unity. In these systems a significant quantity of ^{233}U would be produced in the reactor for power generation and the external input of fissile material required would be small. However, such reactors cannot be used for expansion of nuclear power capacity. Another reactor concept which is based on thorium, but not a breeder, is the High Temperature Gas Cooled Reactor.

The two isotopes ^{233}Pa and ^{232}U which are produced in the irradiation of thorium make thorium fuel cycle more difficult as compared to the plutonium fuel cycle. The former is an intermediate in the production of ^{233}U from ^{232}Th. This isotope has a comparatively long half life of 26.967 d and high thermal neutron absorption cross section. Due to this, there will be loss of ^{233}Pa as well as neutrons resulting in lower breeding ratios. This problem could be overcome by using the concept of molten salt reactors in which the fuel is in the form of a molten mixture which could be circulated through a purification plant for the isolation of ^{233}Pa and removal of fission products. ^{232}U is produced in small quantities because of side reactions. ^{233}U, isolated after reprocessing of thorium fuel, contains a few parts per million of ^{232}U. The decay chain of ^{232}U has many short lived daughter products which emit highly penetrating gamma rays (Table 5.1). Handling of ^{233}U, therefore, is carried out remotely. The thorium fraction also contains ^{228}Th (a daughter product of ^{232}U) and cannot be handled like natural thorium for at least 10 to 12 years due to large α, γ activity of the products (Table 5.1). These factors combined with lower breeding ratios achievable in the thorium fuel cycle, have resulted in low emphasis on its development at present.

Table 5.1: Decay Products of Uranium-232 / Thorium-228.

Nuclide	Mode of decay	Half life	Prominent γ energy
Uranium-232	alpha	72 y	low energy
Thorium-228	alpha	1.9 y	low energy
Radium-224	alpha	3.6 d	0.24 MeV
Radon-220	alpha	55 s	0.54 MeV
Polonium-216	alpha	0.15 s	None
Lead-212	beta	10.6 h	0.3 MeV
Bismuth-212	alpha	60 min	0.78 MeV
Thallium-208	beta	3 min	2.6 MeV
Lead-208	-	stable	-

Thorium based Reactors and Fuels

Fast breeder reactors using thorium would be almost identical to the plutonium based systems except that the fuel would have ^{233}U in place of ^{239}Pu, and ^{232}Th in place of ^{238}U. Oxide, carbide or metallic fuel can be used for this purpose. Breeding ratio is expected to be substantially small as contribution of ^{232}Th direct fission to energy production is negligible as against ~15% for ^{238}U. Research efforts are currently pursued to develop thorium based nuclear fuels for fast reactors.

Light water breeder reactor is a pressurized water reactor with many changes in fuel design and control system. In order to improve neutron economy, a large fraction of the reactor control is achieved by using thorium as control material so that neutron absorption leads to production of ^{233}U. Mixed thorium uranium oxide fuel has a special design with central part having higher percentage of UO_2 called the seed and outer part having lower percentage of UO_2 as the blanket. With many such improvements, it is possible to obtain a breeding ratio approaching unity in this concept.

Thorium based pressurized heavy water reactors are similar to the conventional system with $(U,Th)O_2$ as fuel. This reactor is expected to have a better neutron economy and with a breeding ratio marginally exceeding one, if the bum up of the fuel is kept low.

India is currently developing an Advanced Heavy Water Reactor (AHWR) for the utilization of thorium. AHWR is designed as a tube type reactor (tubes being vertical), the tubes containing the fuel and separating the moderator and coolant. Heavy water and boiling light water are used as the moderator and the coolant respectively. Mixed oxide ($(U,Pu)O_2$ or $(Pu,Th)O_2$) is used as the main fuel which is surrounded by ThO_2. It is designed such that 75% of the power is due to the ^{233}U produced *in situ* from ThO_2. Hence the consumption of plutonium is small. Additionally the reactor has many enhanced safety features. AHWR concepts have been finalized and it is in advanced stages of implementation. Pilot scale reactor concept is demonstrated and Dummy fuel assemblies have been manufactured.

Only reactor concept which can give good breeding performance with thorium has been the Molten Salt Reactor. A prototype reactor of 8 MWt capacity was operated at Oak Ridge National Laboratory from June 1965 to December 1969. Based on this, a design for molten salt breeder reactor was evolved. In this reactor concept, the fuel is in the form of molten salt contained in a large pot. The salt contains fluorides of lithium, beryllium, thorium and uranium. Moderation is provided by graphite rods suspended in the molten salt. Coolant does not flow through the reactor but instead a stream of hot fuel is taken out and cooled in a heat exchanger and returned back to the reactor. A small stream of the molten fuel is taken through a purification system for the isolation of ^{233}Pa and removal of fission products. This type of reactor can give a breeding ratio of 1.05. Since the fuel requirement per MWe is 2 to 3 times less than that for fast breeders, the performance of molten salt reactors is comparable with plutonium based fast reactors.

Another reactor concept developed for thorium utilization is the Compact High Temperature Reactor (CHTR). This concept is receiving renewed attention because of some inherent safety features. Conversion ratio of 0.85 to 0.9 can be achieved in CHTRs with ^{233}U as fuel. CHTRs are based on a very different fuel concept and do not use metallic cladding due to fear of release of radioactive fission products in the event of failure due to loss of coolant. In CHTRs the metal is replaced by carbon and silicon carbide which have very high melting temperatures. As normal sized tubes of carbon or silicon carbide do not have adequate strength for application as clad tubes, the concept of coating small particles with layers of carbon and silicon carbide was evolved. The fuel $(U,Th)O_2$ is thus in the form of microspheres of approximately 0.2 mm dia (less than the mustard seed) which are coated by deposition of 3 successive layers of carbon, silicon carbide and carbon by chemical vapour deposition method. The coated particles are designed to have all the attributes of a fuel with special capability of withstanding high temperatures. As the reactor requires a fixed geometry as well as passages for flow of coolant and insertion of control rods, the fuel particles are mixed with high quality pitch and made into the shape of annular rods or balls and baked at high temperatures to have adequate mechanical strength. Graphite blocks with cylindrical holes or graphite balls are used as moderator depending upon the fuel form. Helium is used as a coolant with the typical inlet and outlet temperatures being 250°C and 750°C, respectively.

Thorium Fuel Reprocessing

In the thorium fuel cycle, the irradiated fuel is reprocessed for the recovery of fissile ^{233}U and left over ^{232}Th. Thorex process which is similar to the Purex process is used for the recovery of ^{233}U and ^{232}Th using tributyl phosphate for extraction. However, there are several differences as follows: A long cooling time is essential for thorium fuels since ^{233}Pa which decays to ^{233}U should be completely allowed to decay. This is achieved by cooling the fuel for 1-2 years. Even then the fuel is highly radioactive because of the fission products and all processing has to be carried out remotely in hot cells having several feet thick concrete walls. In the case of HTGR, the fuel has to be crushed and burnt to obtain a mixed oxide of uranium and thorium. Since thorium oxide is highly insoluble in acid media, dissolution of thorium based fuels in nitric acid is very slow. Hydrofluoric acid is essential for catalyzing the dissolution. This, however, leads to severe corrosion of stainless steel dissolver vessel which is partly overcome by the addition of aluminium nitrate during dissolution. After obtaining the solution, ^{233}U and thorium can be extracted into tributyl phosphate. Unlike uranium and plutonium, thorium is not readily extracted. Further, thorium nitrate solubility in the organic extractant is quite small and often the solvent splits into two organic phases, one rich and other poor in thorium. This limits the amount of thorium which can be extracted into the organic medium. As enough thorium cannot be extracted, there is adequate amount of free extractant available for reaction with fission products which results in contamination. After thorium and uranium have been extracted into the organic liquid, their partitioning cannot be achieved by change of valence as was done for plutonium since thorium exists in only one valence state. The partitioning has, therefore, to rely on poor extractability of thorium compared to uranium.

A typical Thorex flow sheet is shown in Fig. 5.1. Dissolver solution containing thorium, uranium and fission product nitrates in 1 M nitric acid is contacted with 30% tributyl phosphate in the first column resulting in the extraction of uranium as well as thorium. Any fission products extracted into the organic phase are scrubbed back by 1 M nitric acid. The organic solvent is then contacted with dilute nitric acid (0.2 M) such that only thorium is extracted back into the aqueous phase. As this thorium also contains ^{228}Th, it cannot be used for about 10 years and has to be stored. Uranium is stripped back from organic solvent by contacting with very dilute (0.01 M) nitric acid. This contains appreciable amounts of fission products and thorium and is, hence, further purified by ion exchange method.

Bulk of the recovery of ^{233}U has been from thorium metal/oxide blanket rods which have been used in various reactors for producing fissile ^{233}U.

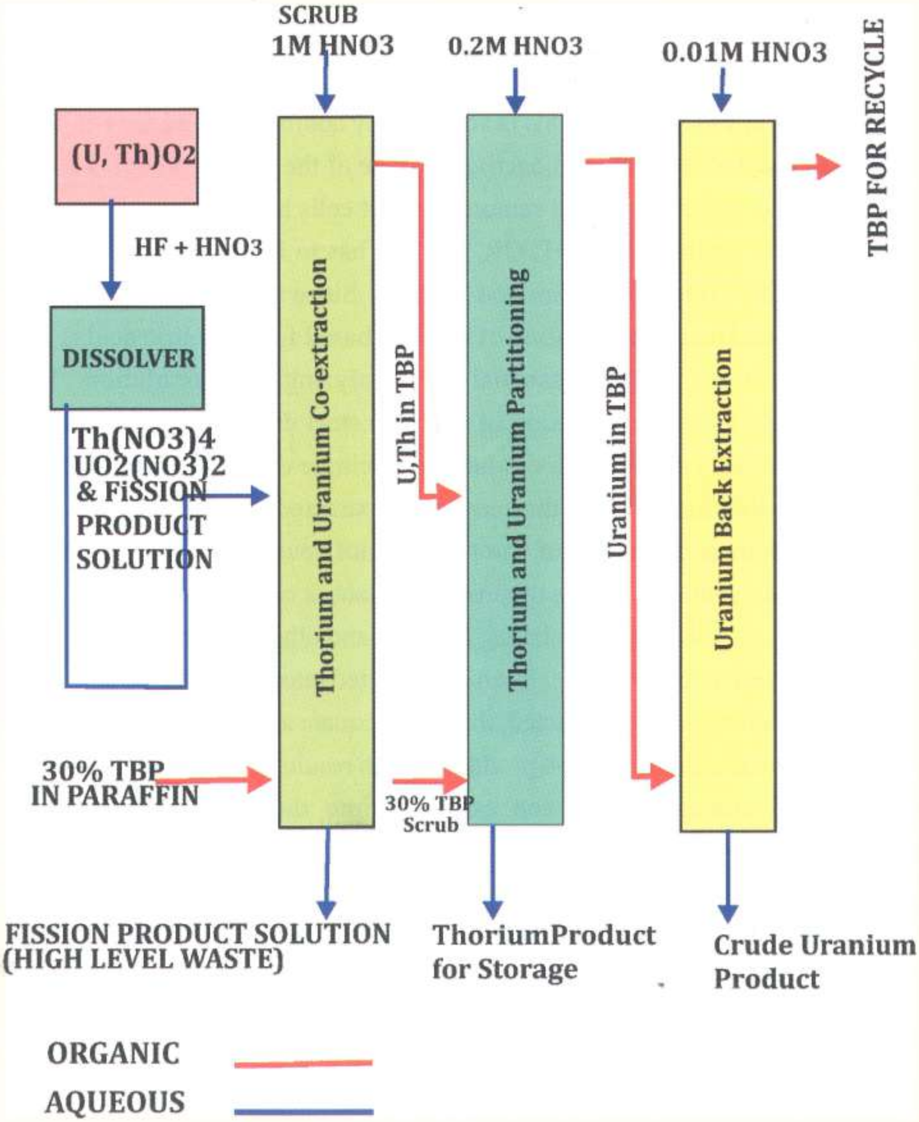


Fig. 5.1 Schematic of 'THOREX' Flow sheet for CHTR fuel.

Experience with processing actual thorium based fuels is limited to pilot plant level. In India, initially ^{233}U was recovered from thorium containing rods irradiated in now decommissioned Research Reactor CIRUS. These rods were made either by aluminium encapsulation of thorium metal rod (approximately 18.5 kg) or thorium oxide pellets (approximately 11.5 kg). About 10 to 15 g of ^{233}U is produced in each rod depending upon its residence time in the reactor. The recovery of uranium from these rods has been carried out both at BARC, Trombay and at IGCAR, Kalpakkam. In the process followed, only uranium is recovered and thorium is left behind along with the fission products. The rods are first treated with caustic soda solution to remove aluminium cladding. The exposed Th/ThO_2 is then dissolved in 8 M nitric acid having 0.05 M sodium fluoride and some aluminium nitrate. The solution containing about 200 g/L of thorium and about 0.2 g/L of uranium is treated with 5% TBP to selectively extract ^{233}U. Back extraction of uranium is achieved by dilute nitric acid to obtain uranium concentration of 5 to 10 g/L. This product has about 20 g/L of thorium and some fission products and is, therefore, treated by ion exchange procedure for purification.

Uranium-233 Based Research Reactors in India

Along with the development of technology for fabrication of thorium fuels, and their reprocessing, India has also initiated investigations on reactor physics aspects of ^{233}U based systems. A zero power research reactor PURNIMA II was commissioned at Trombay in 1978. This reactor used a solution of uranyl nitrate and operated with only 500 g of ^{233}U. A second reactor KAMINI is operating at Kalpakkam. This reactor has uranium-aluminium alloy fuel in the form of rectangular plates. This reactor has a power of 30 kW and is used as a source of neutrons for non-destructive examination of irradiated fuels.

Chapter 6

Heavy Water

Introduction

Hydrogen has three isotopes with atomic masses of 1, 2 and 3. The first two, ^{1}H and ^{2}H, are stable and ^{3}H is radioactive. Hydrogen isotope with mass number 2 is called deuterium and is represented by symbol D. Similarly isotope with mass number 3 is called tritium and is represented by symbol T. Natural water is a compound of ^{1}H and oxygen and is written as H_2O. If we were to make water with deuterium, then it would be written as D_2O and called heavy water as it is made with the heavier isotope of hydrogen. Heavy water is indeed heavier than natural water: one litre of heavy water weighs about 1.1 kg as against 1 kg for natural water. Other properties of heavy water such as freezing point (3.8°C) and boiling point (101.4°C) are also slightly different from light water but indistinguishable by appearance due to very similar physical properties. Natural water contains only 145 parts per million (ppm) of heavy water i.e. a million litres of natural water contains about 145 litres of heavy water. Hydrogen in other natural compounds like natural gas and petroleum also contains 100 to 120 ppm of deuterium. As discussed in Chapter 2, heavy water is important for nuclear industry because it is used for moderation of neutrons. Heavy water with deuterium content of better than 99.8% is used as moderator in reactors with natural uranium fuel. Production of heavy water thus requires enrichment of deuterium content from 145 ppm to 99.8 % i.e. by a factor of about 7000. The difference in the mass of hydrogen and deuterium is sufficient to cause subtle chemical changes in their compounds which could be exploited for the production of heavy water. Even though, in principle, a number of chemical equilibria may be exploited for the production of heavy water, in practice, most of them are not adopted for economic or technological reasons. Heavy water production is a highly complex technology, with added handicap of being strategic, which makes it a challenging task for our scientists and engineers.

The first plant to produce heavy water in India started operating at Nangal in 1962 and was stopped in 2002 after 40 years of operation. It was based on a hybrid process of electrolysis and liquid hydrogen distillation. Plants based on ammonia and hydrogen exchange process are operating at Thal (Maharashtra) and Hazira (Gujarat). Two plants based on hydrogen sulphide and water exchange process are operating at Kota (Rajasthan) and Manuguru (Telangana).

Deuterium Enrichment Processes

The differences in physico-chemical properties of hydrogen compounds having hydrogen and deuterium as their constituents, form the basis of all the enrichment processes. Chemical exchange of deuterium between gas/vapour and liquid phases are used for enrichment and important features of some of the processes are given below. The primary source of deuterium is either water or hydrogen available from synthesis gas used in fertilizer plants for the manufacture of ammonia.

Distillation of Water

Deuterium in water can exist as HDO or D_2O. When deuterium content of water is low, it mainly exists as HDO with boiling point of 100.7°C. The vapour of water, therefore, contains slightly less deuterium than the liquid. Water of tropical oceans contains 0.0156 atom % (156 ppm) of deuterium whereas water vapour in air above the sea contains 7% less deuterium i.e. 0.0146 atom %. Similarly, when vapour of water partially condenses, the liquid is richer in deuterium. The separation factor for deuterium in the distillation of water is 1.05 at 50°C and 1.026 at 100°C. Production of 99.8% D_2O would, therefore, require about 700 equilibrium stages involving evaporation and condensation. Also because of low deuterium content of water, about 200,000 litres of water would be required to produce one litre of heavy water. Even though the process is highly expensive, it is relatively simple and was hence adopted by the USA for production of heavy water during World War II. Three plants with a combined capacity of 13.8 te/y produced about 20.7 te of 99.8% D_2O before being shut down. No plant of this type has been built subsequently.

Though distillation is one of the most expensive processes for heavy water production, it is economical for upgrading water having a few percent of D_2O and is, therefore, preferred at many plants. Many heavy water production plants, based on other processes, produce heavy water having 2 to 40% of D_2O and then up-grade this to 99.8% of D_2O by distillation. Distillation is used for final enrichment of heavy water at all the plants in India and at many plants all over the world. Distillation is also used for upgrading heavy water which leaks out of the reactor system, as per design intent, and gets degraded by mixing with normal water. For example, Rajasthan Atomic Power Station and all other Pressurised Heavy Water Reactors in India use distillation process for upgradation of degraded heavy water.

Electrolysis

E.W. Washburn and H.C. Urey proposed electrolysis of water as the first method for the production of heavy water in 1932. The first plant in the world was set up by Norsk Hydro, Norway in the year 1934. The plant was set up primarily to produce about 90,000 te of ammonia per year from electrolytic hydrogen but also produced 1.5 te of D_2O/y. During World War II, the plant was captured by the German army. German scientists were planning to increase the capacity of the plant for D_2O production to 5 te/y by incorporating steam hydrogen exchange stages to recover more deuterium from hydrogen. This could not be achieved. The plant was recommissioned after the World War and was improved by having more efficient recovery of deuterium and by incorporating water distillation for final enrichment. The present capacity of this plant is 6.5 te/y. The only other heavy water plant to use electrolysis as one of the process steps for the production of heavy water was at Nangal in India.

Separation of hydrogen and deuterium is achieved in electrolysis by many chemical steps. Principal among them are the higher mobility of hydrogen ion, slower discharge of deuterium at the cathode and the following chemical equilibrium:

$$H_2O(l) + HD(g) \rightarrow HDO(l) + H_2(g) \qquad (6.1)$$

This reaction has an equilibrium constant of 3.8 at 25°C. All these chemical steps tend to concentrate deuterium in the liquid phase. As both kinetic and thermodynamic equilibrium phenomena are involved, a number of variables, such as electrode material and cell design, play important roles and the separation factor is, therefore, variable. Highest separation factor of 13.2 has been reported at 15°C with iron as cathode. The separation factor decreases with increasing temperature e.g., 10.6 at 25°C and 7.1 at 75°C. In spite of the high separation factor, the electrolysis process requires about 220 kWh of energy to produce one gramme of D_2O and is, therefore, practical only where cheap electricity is available. Only Norway and India were using this process. At Nangal plant which has a capacity of 14 te D_2O/y, electrolysis was used to produce hydrogen having 450 ppm of deuterium.

Electrolysis, like distillation, is highly energy consuming for primary production of heavy water. It is, however, quite economic and reliable for concentration of heavy water having a few per cent deuterium or for upgradation of heavy water at reactor sites. Electrolysis was used for upgrading heavy water at Madras and Narora Atomic Power Stations. At Madras, a separation factor of 8 was achieved at 40°C. This plant had 14 banks of 14 electrolytic cells each and had a capacity of upgrading 526 te of heavy water from 30% of D_2O to 99.8% of D_2O ever year. The reject water contains about 0.2% of D_2O. The performance of plants has been very satisfactory.

Distillation of Hydrogen

Hydrogen gas is converted into liquid by cooling to 20.3K. During distillation of this liquid, deuterium gets enriched in the liquid phase and the separation factor is 1.5. In view of this high separation factor, this process is attractive but has not been used widely because of the complexities involved in attaining and maintaining low temperatures and also ensuring reliability of the equipment at these temperatures. In 1958, the then USSR announced the operation of a plant based on distillation of electrolytic hydrogen for the production of heavy water and the capacity of the plant was 4 te/y. In the same year, two companies specializing in cryogenic engineering, one in France and the other in Germany, set up plants to recover deuterium from hydrogen produced by reforming of natural gas. These plants with respective capacities of 2 te/y and 6 te/y were shut down in 1960 because of high cost and technical problems. When a large fertilizer plant, based on electrolytic hydrogen, was being set up at Nangal, it was decided to set up a heavy water plant at the same site. The plant was installed by a German company viz Gessellschaft Fur Lindes

Eismaschinen. This plant, with a capacity of 14 te D_2O/y, was commissioned in 1962. In earlier years this plant used electrolytic hydrogen in which deuterium content has been enriched to thrice the natural level i.e. 450 ppm. Hydrogen from electrolytic plant is compressed and cooled to 28K by cooled hydrogen, which is depleted in D_2 content and is being returned to the fertilizer plant. Further cooling and liquefaction are achieved by rapid expansion. Distillation is carried out in specially designed columns to obtain pure deuterium which is reacted with oxygen to form D_2O.

Ammonia-Hydrogen Exchange Process

NH_3-H_2 exchange process is designed to extract deuterium from hydrogen used for fertilizer production. Both ammonia and hydrogen required are obtained from the fertilizer plant and, therefore, this type of plants are located at fertilizer plant sites. The extraction of deuterium from hydrogen is achieved by the following chemical reaction:

$$HD(g) + NH_3(l) \rightarrow H_2(g) + NH_2D(l) \qquad (6.2)$$

The separation factor in this process increases with decreasing temperature. Separation factor is 5.2 at 25°C and hydrogen pressure of 350 atm. The exchange reaction does not take place unless an efficient catalyst is present. Potassium amide (KNH_2-produced by dissolving K metal in liquid ammonia) is used as a catalyst. About 1 to 2 mole % i.e. 35 to 70 g of KNH_2/kg of ammonia is required for efficient exchange. The process technology was developed in France and a pilot plant of 26 te of D_2O/y capacity started functioning at Mazingarbe in 1968. This plant used two exchange towers to concentrate deuterium to 1.32% in ammonia. Further concentration of deuterium was achieved by distillation of ammonia. However, this plant was permanently shut down in 1972. In 1969, Dr. Vikram Sarabhai, Chairman, Atomic Energy Commission explored the possibility of setting up heavy water plants based on the French technology in India and a contract to set up two plants of about 45 te/y capacity was signed. The plants at Baroda and Tuticorin were set up by a consortium of European companies having expertise in this area. The group was called GELPRA i.e. Groupement Eau Lourde Procede Ammoniac. A schematic flow sheet of the process used in these plants is shown in Fig. 6.1. Baroda plant was the first large plant to be designed by GELPRA. Shutting down of Mazingarbe plant was a handicap. A number of modifications were, therefore, necessary at Baroda. All

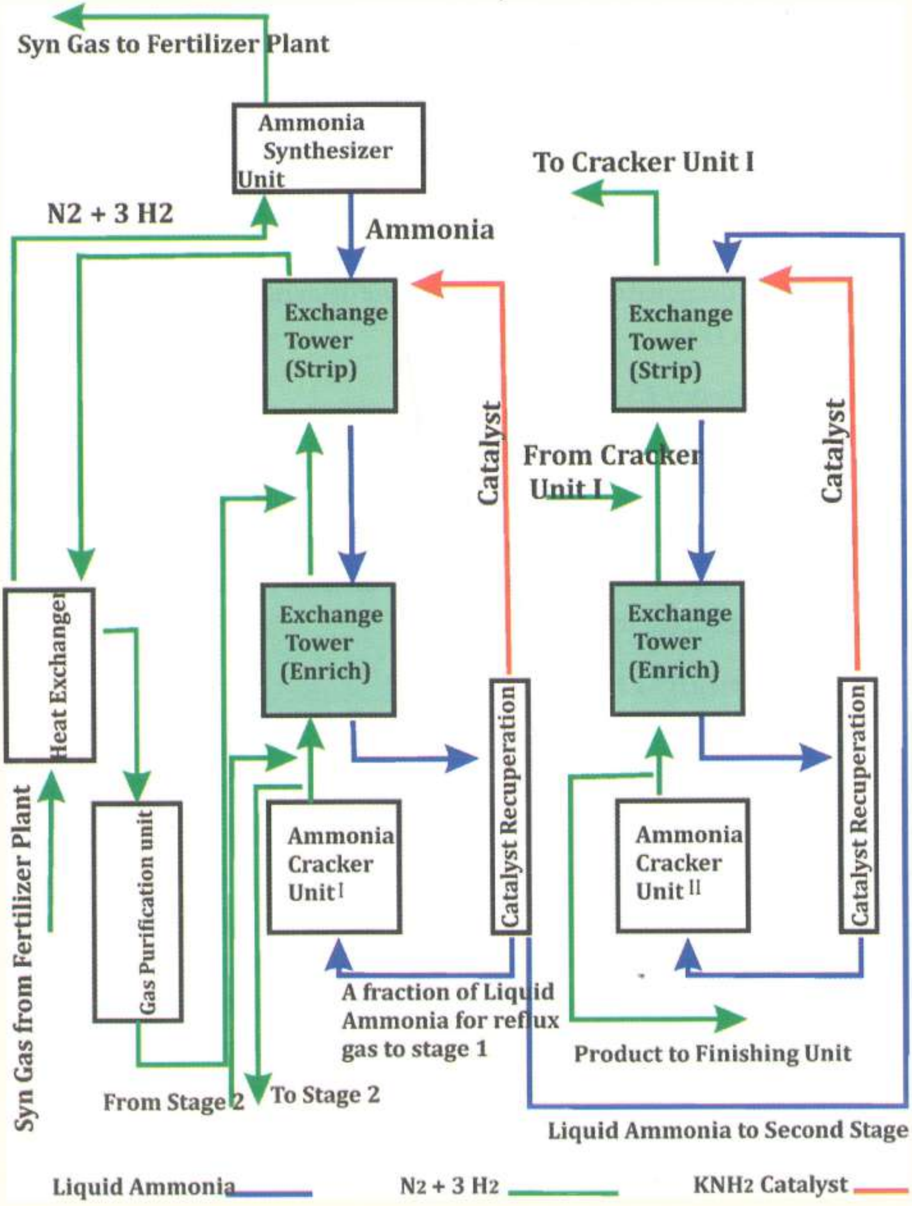


Fig. 6.1 Schematic Flow Diagram of Ammonia - Hydrogen Exchange Process.

the modifications carried out at Baroda were incorporated at Tuticorin plant but GELPRA withdrew its technical support. Therefore, the solutions to many problems had to be worked out indigenously. Though considerable delay had taken place in the commissioning of plants, the experience generated was useful for assimilation of this technology and the next plant of 110 te/y capacity were set up at Thal-Vaishet & Hazira. These plants are indigenously designed.

Fig. 6.2 A view of the Hazira Heavy Water Plant.

Typical flow sheet is shown in Fig. 6.1. A vew of the Hazira plant is given in Fig. 6.2.

Hydrogen required for fertilizer production is obtained by reforming of natural gas with excess steam when the following equilibria are established.

$$CH_4(g) + H_2O(g) \rightarrow CO(g) + 3H_2(g) \qquad (6.3)$$

$$CO(g) + H_2O(g) \rightarrow CO_2(g) + H_2(g) \qquad (6.4)$$

Deuterium in hydrogen thus generated exists as HD. Presence of KNH_2 is essential for proper deuterium exchange. But, impurities like H_2O, CO_2, CO and O_2 react with KNH_2 and are, therefore, removed before sending hydrogen to the exchange tower. After enriching ammonia with deuterium, potassium amide is recovered and recycled. Before recycling, deuterium present in the amide as KNHD is recovered by exchange with hydrogen. Even though the process has high separation factor, the kinetics are very slow. Specially designed columns permit more intimate mixing of gas and liquid but this requires pumping of liquid ammonia from one stage in the column to the next with pumps immersed in liquid ammonia. The exchange towers are about 40 meters tall and the wall thickness of the towers is more than 32.5 cm to withstand high pressure. For getting better performance, the exchange columns have to be provided with optimal liquid to gas ratio. Besides, the required vapour and liquid phases at appropriate deuterium concentration levels in the above streams, are provided by a suitable cracker for NH_3 at one end and a synthesizer for $N_2 + H_2$ at the other end of the column.

One problem with using natural gas as a source of hydrogen is related to the loss of deuterium to the water phase as per the following reaction:

$$HD(g) + H_2O(l) \rightarrow H_2(g) + HDO(l) \qquad (6.5)$$

This reduces the deuterium content significantly. For example, at Baroda and Tuticorin the deuterium content decreases from 126 ppm in the natural gas to less than 115 ppm in hydrogen. This reduces the production of heavy water from the plant. Synthesis gas supplied to the heavy water plant is normally at a pressure of more than 250 atm. Under these conditions, it is expected that the spent hydrogen would be having less than 15 ppm deuterium. However, when the pressure is low, the recovery is also low and spent hydrogen could contain 25 to 45 ppm of deuterium.

Sudden stoppage of power or synthesis gas supply results in mixing of enriched and depleted fractions and loss of production. Enrichment to 99.8% level requires about 20 days of continuous operation and any stoppage is highly detrimental. It was seen that enrichment to 40% of deuterium level requires only 2-3 days. Accordingly, the plants at Thal and Hazira now produce 40% enriched D_2O by NH_3-H_2 exchange and further enrichment to 99.9 % is achieved by distillation.

India is the only country in the world currently having the technology to set up large plants based on this process.

Girdler Sulphide Process

Girdler sulphide (GS) process is based on exchange of deuterium between water and hydrogen sulphide gas.

$$H_2O(l) + HDS(g) \rightarrow HDO(l) + H_2(g) \qquad (6.6)$$

This reaction has equilibrium constants of 2.32 at 32°C and 1.80 at 138°C. The technology for this process was developed in the USA by J. S. Spevack in 1942 and based on that Girdler Corporation designed and built a plant of 490 te/y capacity at Dana in 1952. Another plant of 480 te/y capacity was also built in 1952 by du Pont at Savannah River. Due to reduced demand, Dana plant was shut down in 1957 and the capacity of Savannah River plant was decreased to 69 te/y. Canada set up its first heavy water plant of 250 te/y capacity at Glacebay. This plant came on stream in 1976, 14 years after the start of construction. Subsequently, however, Canada successfully operated one plant of 400 te/y capacity and 4 plants of 800 te/y capacity each. The process is very attractive as the exchange reaction can take place without any catalyst and also the strong dependence of the equilibrium constant on temperature permits the use of a bithermal process which eliminates the need for chemical steps required for providing reflux in the exchange towers. The process uses two towers, a cold tower maintained at 32°C and a hot tower maintained at 138°C. Fresh water enters the cold tower and comes in contact with deuterium enriched hydrogen sulphide entering from hot tower. This results in the transfer of deuterium from the gas to water. Enriched water coming out of the cold tower is partly withdrawn as a product and partly used as a feed to the hot tower for deuterium enrichment of hydrogen sulphide. In the hot tower, partially enriched water is contacted with depleted hydrogen sulphide coming from the top of the cold tower and deuterium gets transferred from water to the gas phase. By proper adjustment of flow ratios of gas and water in the two towers, it is possible to obtain water with about 15% of D_2O as product. In this process, hydrogen sulphide gas essentially acts as a medium for splitting the natural water into two streams: (i) product stream containing about 15% of D_2O and (ii) waste stream containing about 120 ppm of D_2O. Further enrichment is carried out by distillation of water. A schematic flow sheet of the process is given in Fig. 6.3. The plant is normally operated at a pressure of about 20 atm. High toxicity of H_2S gas and its highly corrosive nature are the main problems in this process.

In India, the proposal to setup a plant based on this process was made in 1966, just a few days prior to the tragic death of Dr. Homi J. Bhabha, the founder of the Atomic Energy Programme in India. Two plants, based on this process, one of 85 te/y capacity at Kota and the other of 185 te/y capacity at Manuguru are successfully operating. A view of the Manuguru Heavy Water Plant is given in Fig. 6.4.

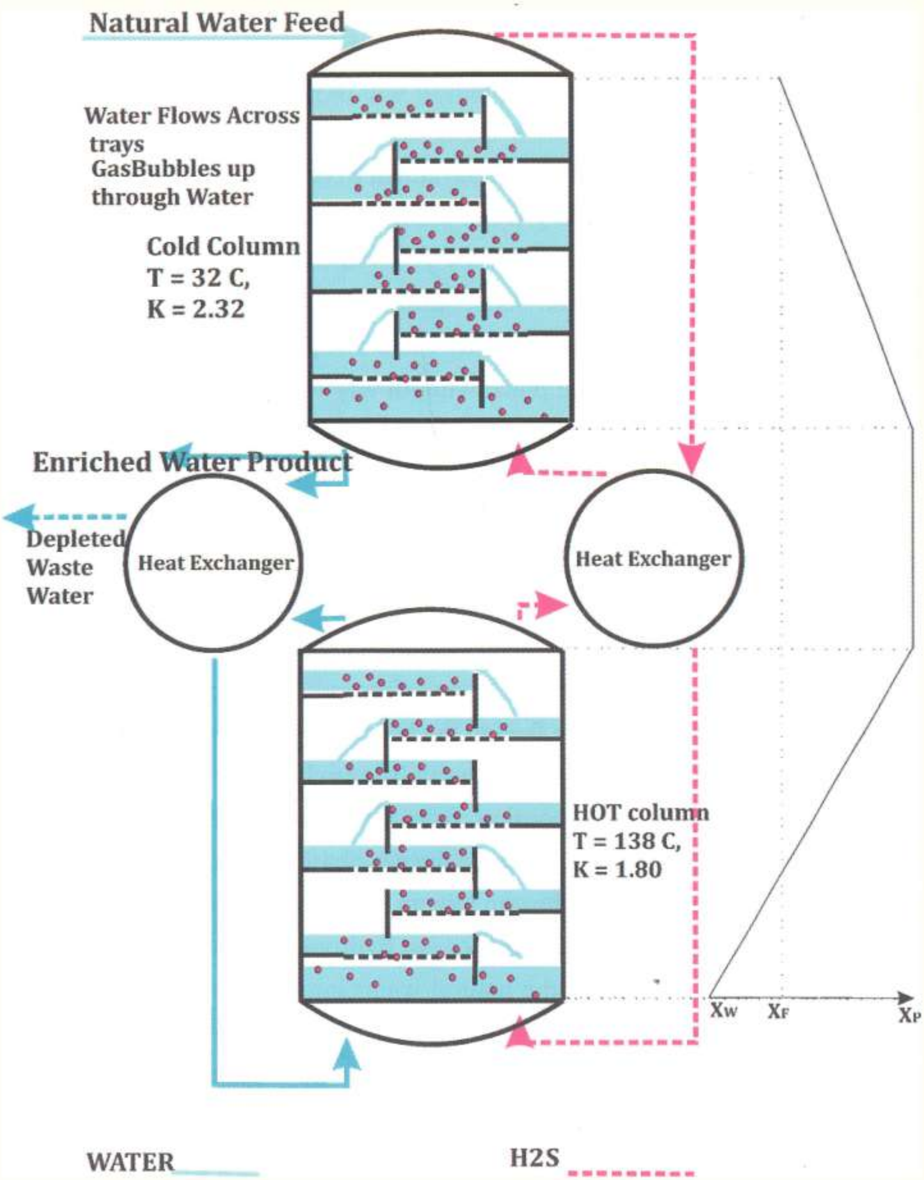


Fig. 6.3 The Water-Hydrogen Sulphide Dual-Temperature Exchange Process for Production of Heavy Water.

Other Processes

Many other processes have been proposed for heavy water production but they have not been used for setting up heavy water plants. With interest in heavy water technology, India has been exploring some of these processes and two of these are discussed below:

Fig. 6.4 A view of the Heavy Water Plant at Manuguru

Ammonia Water Exchange Process

Production capacity of heavy water plants based on NH_3-H_2 exchange process is limited by the availability of synthesis gas. Ammonia plant having a capacity of 1000 te/y can support D_2O plant having capacity to produce 65 te/y. Further, the D_2 content of synthesis gas is 110 ppm which is substantially lower than 145 ppm available in natural water. These problems can be overcome if suitable process is developed for ammonia water exchange for the enrichment of ammonia with deuterium as per the following reaction:

$$HDO + NH_3 \rightarrow H_2O + NH_2D \qquad (6.7)$$

The separation factor is very close to unity and efficient exchange towers are, therefore, required for enrichment. The process has been studied on an engineering scale using an exchange tower operating at 150°C and 20 atm pressure. Studies indicate the possibility of enriching deuterium content of ammonia from about 40 ppm to more than 100 ppm. This enriched ammonia could easily be the input to NH_3-H_2 exchange process. Incorporation of this step at head end of the plant would eliminate the dependence on the fertilizer plant for hydrogen as a source of deuterium. A pilot plant to establish the feasibility of this step was setup at heavy water plant at Baroda and Engineering data have been collected with a view to design a larger assembly based on this process.

Water Hydrogen Exchange Process

It was mentioned earlier that deuterium from hydrogen can be preferentially transferred to water as shown in equation 6.5 :

$$HD(g) + H_2O(l) \rightarrow H_2(g) + HDO(l) \qquad (6.5)$$

The equilibrium constants for this reaction are 2.58 at 100°C and 1.99 at 200°C. This process could also form the basis for heavy water production, but for the fact that a very efficient catalyst is required. Platinum supported on charcoal and nickel supported on chromium oxide have been reported to be good catalysts for this purpose. However, these catalysts are wetted by water to prevent hydrogen from reaching the catalyst site. The catalysts are, therefore, useful only if steam is used instead of water. However, since this would be quite energy intensive, the possibility of making hydrophobic catalyst has been under investigation in many laboratories. At BARC, good results have been obtained during laboratory studies on platinum catalyst made hydrophobic by teflon and for nickel catalyst made hydrophobic with silicones. The process has a potential to produce heavy water in combination with electrolysis or by getting hydrogen from a fertilizer plant. The development of a new catalyst is being explored now by Heavy Water Board and Raja Ramanna Centre for Advanced Technology jointly.

In reactors using heavy water as coolant/moderator, small quantities of tritium, which is radioactive, are produced due to neutron absorption by deuterium. Any leakage of heavy water thus entails release of tritium in that area of the reactor building. In order to protect operating personnel, bulk of the tritium has to be removed. Water-hydrogen exchange processes is being investigated for removal of tritium from heavy water as per the following reaction:

$$DTO(l) + D_2(g) \rightarrow D_2O(l) + DT(g) \qquad (6.8)$$

In feasibility experiments, 90% of tritium could be transferred to gas phase even when tritium was present at ppm levels.

Chapter 7

Zirconium

Introduction

Zirconium occurs widely in nature with an abundance of 0.028%. It is eleventh most abundant metal with its abundance is greater than that of common metals like copper, lead, nickel, and zinc. Two main minerals of zirconium are silicate mineral zircon $(Zr,Hf)SiO_4$ and oxide mineral baddleyite $(Zr,Hf)O_2$. Most countries use zircon for zirconium production. Zirconium attracted the attention of engineers when they were looking for a light metal with high strength and high corrosion resistance. Zirconium produced in the early stages was hard and brittle mainly because of the presence of impurities of oxygen, nitrogen and carbon. Zirconium, free from these impurities, was prepared by Van Arkel and de Boer in which they grew crystal bars of high purity zirconium. In 1949, it was decided by USA to use it as a material of construction for the first Submarine Thermal Reactor (STR). One problem encountered was that this material had a high thermal neutron cross section (approximately 2 barns). It was soon discovered that hafnium present at the level of 0.5 to 2% was responsible for this. A process for the separation of these two chemically similar elements was developed by the Oak Ridge National Laboratory, USA. Zirconium fraction (a mixture of zirconium isotopes ^{90}Zr, ^{91}Zr, ^{92}Zr, ^{94}Zr and ^{96}Zr) was observed to have thermal neutron cross section of 0.18 barns. Hafnium (a mixture of ^{176}Hf, ^{177}Hf, ^{178}Hf, ^{179}Hf and ^{180}Hf) had thermal neutron cross section of 102 barns. Crystal bar quality zirconium having less than 100 ppm Hf was used in the first STR. Subsequently, however, National Bureau of Standards, USA developed an easier process for making zirconium metal based on metallothermic reduction of halides. Several zirconium alloys with improved strength and corrosion resistance were prepared by 1953. Zirconium was initially developed for reactor applications, which required the removal of hafnium. The use of zirconium in chemical plants and refractory alloys now far exceeds the reactor applications and this does not require hafnium separation. Only a few countries in the world have the technology for producing zirconium and India is one of them. The separated hafnium is also a very valuable material for use in control rods of reactors.

Recovery of Zirconium and its Separation from Hafnium

Zircon which is recovered from beach sands by various physical separation techniques is the main source of zirconium. Zircon contains 63 to 65% of ZrO_2 with 0.5 to 2% of HfO_2. Zircon is a refractory mineral and it requires special treatment for the recovery of metal. In fact, zircon itself is very useful in foundry sands, abrasives and ceramics. Three prominent methods are used for treatment of zircon, to separate silica. These are; (i) high temperature conversion to zirconium tetrachloride, (ii) sodium hydroxide fusion, and (iii) fusion with potassium silicofluoride. Each of these methods forms the head-end step for zirconium-hafnium separation processes which are, (i) hexone extraction, (ii) TBP extraction, (iii) extractive distillation of zirconium and hafnium chlorides and (iv) fractional crystallization of complex fluorides. Some details of these processes are discussed in the following sections.

Hexone Extraction Process

This is the most widely used process for zirconium hafnium separation. Chlorination of zircon is primarily used for recovering zirconium, though alkali fusion can also be used. For the chlorination, zircon is mixed with carbon and reacted with chlorine in quartz lined furnaces at 1200°C to obtain zirconium tetrachloride by the reaction,

$$ZrSiO_4 + 4C + 4Cl_2 \rightarrow ZrCl_4 + SiCl_4 + 4CO \qquad (7.1)$$

Many other impurity elements present along with zircon also get converted into chlorides. Zirconium chloride is volatile and leaves the reaction chamber along with chlorides of aluminum, titanium, silicon and iron. Out of these, $ZrCl_4$ and $FeCl_3$ are less volatile and are separated from the other chlorides by condensation at 100°C. Separation from $FeCl_3$ is achieved by reducing it to less volatile $FeCl_2$ and subliming $ZrCl_4$. Hafnium accompanies zirconium quantitatively up to this stage. Separation of zirconium and hafnium is achieved by selective extraction of thiocyanate complex of hafnium. Zirconium/hafnium tetrachloride is dissolved in dilute hydrochloric acid. Ammonium thiocyanate is added to make thiocyanate complexes which are extracted into methyl isobutyl ketone (hexone) containing thiocyanic acid. Zirconium-hafnium separation factor of 80 is achieved with hafnium concentrating in the organic phase. Thus, there is preferential extraction of hafnium into the organic phase and any zirconium extracted into this phase is scrubbed back by hydrochloric acid solution. The aqueous product contains zirconium. Hafnium is back extracted by using dilute sulphuric acid. Zirconium is recovered by precipitation as hydroxide under carefully controlled conditions. Hydroxide is then dried at 350 to 400°C to obtain zirconium oxide (ZrO_2). Thiocyanic acid in the aqueous streams is extracted into pure hexone for reuse.

Tributyl Phosphate Extraction Process

This process is currently used in India for the separation of zirconium from hafnium. The head-end step for this process is the fusion of zirconium with sodium hydroxide at 565°C.

$$ZrSiO_4 + 4NaOH \rightarrow Na_2ZrO_3 + Na_2SiO_3 + 2H_2O \qquad (7.2)$$

Sodium hydroxide melts at 313°C and readily reacts with zircon. Sodium silicate (Na_2SiO_3) is soluble in water and is leached out. The residue is then dissolved in nitric acid to obtain zirconium nitrate solution containing hafnium. A 33% TBP solution in kerosene is used for the preferential extraction of zirconium. Under optimum conditions the Zr/Hf separation factor is 10, with zirconium concentrating in the organic phase. Any Hf extracted into organic phase is scrubbed back with dilute nitric acid. Zirconium is then back extracted from the organic phase by using de-mineralized water. The flow sheet of the process is shown in Fig. 7.1.

Extractive Distillation Process

This process utilizes extractive distillation for the separation of zirconium and hafnium using potassium chloroaluminate ($AlCl_3$ / KCl) as the solvent. The main advantages of this process are decrease in the number of processing steps, reduced specific energy consumption and reduction in the amount of liquid effluent generation during the separation of Zr and Hf from the zircon ore material. In this process, $Zr(Hf)Cl_4$ vapor entering the column at 350°C, flow in a

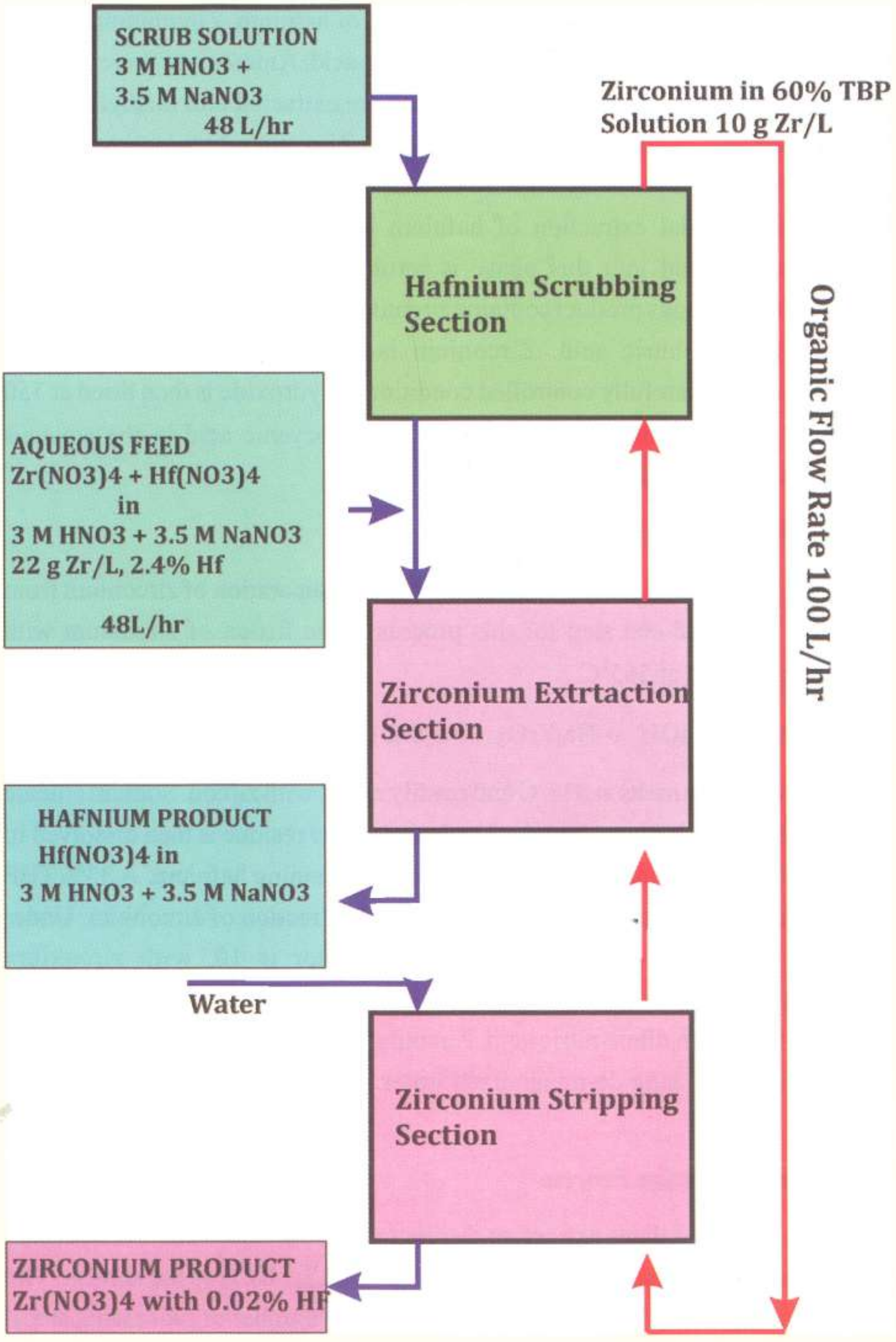


Fig. 7.1 Zirconium-Hafnium Separation by TBP Process.

counter direction against the $AlCl_3/KCl$ molten salt solution for preferential absorption of $ZrCl_4$ leaving $HfCl_4$ as the top product. Further, the $ZrCl_4$ absorbed in the solvent is separated by stripping with nitrogen followed by condensation. Typical separation factor achieved in this process is around 2. Presently, this process is being followed at M/s CEZUS, France.

Fractional Crystallization Process

In this process, zircon is first fused with potassium silicofluoride to obtain potassium zirconium fluoride.

$$ZrSiO_4 + K_2SiF_6 \rightarrow K_2ZrF_6 + 2SiO_2 \qquad (7.3)$$

Fusion is carried out at 650 to 700°C and the product leached with dilute HCl to solubilise zirconium salt leaving behind insoluble silica. Fractional crystallization of double fluorides was one of the first processes developed for the separation of zirconium and hafnium. The solubility of potassium zirconium fluoride is much less than that of corresponding hafnium salt and therefore, crystallizes more readily. Separation factor of 1.5 is achieved in a single stage at room temperature. Repeated dissolution and crystallization can be used for obtaining hafnium free zirconium product. This process is not in use currently.

Production of Zirconium Metal

Zirconium is a highly reactive metal and its strength goes down in the presence of oxygen, nitrogen, carbon and other impurities. Preparation of high purity zirconium requires use of high temperature and high vacuum techniques. Kroll process is mainly used for production of zirconium throughout the world. Crystal bar zirconium is also produced for some special applications requiring very high purity zirconium.

Crystal Bar Zirconium

This process is based on the principle that above 200°C iodine reacts with zirconium to form zirconium tetra iodide and at higher temperature; (> 1000°C) zirconium tetra iodide decomposes to form zirconium metal and iodine as shown below:

$$Zr(s,impure) + 2I_2(g) \xrightarrow{200\,^{\circ}C} ZrI_4(g) \xrightarrow{1300\,^{\circ}C} Zr(s,pure) + 2I_2(g) \qquad (7.4)$$

In this process, crude zirconium metal and iodine are sealed in a vacuum container in which a tungsten filament is kept. The vessel is heated to produce zirconium iodide which migrates to the hot filament and deposits zirconium metal. Iodine released reacts with more impure zirconium and zirconium iodide produced is again decomposed at tungsten filament. In this manner, large amounts of impure zirconium are converted into high purity zirconium. Crystal bars of zirconium having diameter of 1.7" and length upto 50 feet have been produced. Similar process is used for the production of high purity hafnium required for control rods.

Kroll Process

In USA, W.J. Kroll developed this process for the production of titanium and this has been adopted for the production of zirconium. The principal steps in the process are:

(i) Production of zirconium tetrachloride
(ii) Reduction of zirconium tetrachloride with magnesium metal
(iii) Vacuum distillation of reduced mass (consisting of zirconium, $MgCl_2$ and residual Mg)
(iv) Consolidation by arc-melting of metal

For the production of zirconium tetrachloride, zirconium oxide is mixed with carbon and binder to make into small briquettes. These are heated at 800 to 1000°C in a stream of chlorine gas when $ZrCl_4$ is volatilized out as vapor.

$$ZrO_2 + 2C/CO + 2Cl_2 \rightarrow ZrCl_4 + 2CO/CO_2 \qquad (7.5)$$

Zirconium tetrachloride is reduced with magnesium in vacuum tight stainless steel vessels. In this vessel, $ZrCl_4$ vapor is reacted with liquid magnesium at 850°C to obtain zirconium metal.

$$ZrCl_4 + 2Mg \rightarrow Zr + 2MgCl_2 \qquad (7.6)$$

Magnesium chloride and zirconium are present at the bottom of the crucible and their separation is achieved by vacuum distillation. The crucible containing Zr and $MgCl_2$ is taken to a vacuum distillation unit and heated to about 900°C at a vacuum of 100 micron Hg for removal of $MgCl_2$ and residual Mg. Zirconium sponge left behind is taken out and consolidated as an ingot. For the preparation of alloys, suitable alloying elements are also mixed with the sponge at this stage.

Zirconium Sponge

Zircaloy-4 Calandria Tubes

Zircaloy-4 Square Channels for BWRs

Fig. 7.2 Zirconium sponge and zircaloy products.

The ingot made from the sponge is melted in a vacuum arc furnace to obtain high purity zirconium alloy rod. This rod is subsequently used for the fabrication of tubes, pipes and other materials required for reactor applications. Presently, about 250 te of zirconium sponge is produced annually at Nuclear Fuel Complex, Hyderabad and converted in to zircaloy products for nuclear reactors installed in the country. Fig 7.2 gives a view of zirconium sponge and some zircaloy products.

Zirconium Alloys

Zirconium forms alloys with many metals such as Sn, Nb, Ni, Fe, Cr and Al. Alloying elements are added to zirconium to improve its mechanical properties and resistance to corrosion by water at high temperatures (>300°C). Zircaloy 2 and zircaloy 4 are most widely used. The nominal composition of these two alloys is given below:

Zircaloy 2:1.5 % Sn, 0.14 % Fe, 0.09 % Cr, 0.05 % Ni and balance Zr
Zircaloy 4: 1.3 % Sn, 0.22 % Fe, 0.1 % Cr, 0.002 % Ni and balance Zr

These alloys have very good strength and corrosion resistance to water and steam up to 400°C. Tubes made from zircaloy are, therefore, used as fuel clad for all water reactors and as calandria tubes for heavy water reactors. Many other structural components of nuclear reactors are also made by using zircaloy. Zircaloy 2 is used in light water reactors and zircaloy 4 is preferred in heavy water reactors. Zircaloy corrosion is prevented by a very thick and adherent black oxide layer which is formed by exposure of alloy to high temperature water. Another important alloy of zirconium is obtained by adding 2.5% of Nb. This Zr-Nb alloy has been used for making pressure tubes for heavy water reactors. Zirconium alloy having 1% of Nb is used extensively in the Russian reactors for fuel cladding and also in a few Pressurised water reactors. For high burn up fuel in light water reactors, double clad material is being used with inner layer having low tin zircaloy and outer layer having zircaloy 2. Zirconium alloy inner liner is also being tried in fast breeder reactors where the fuel clad is mainly special stainless steel.

Chapter 8

Beryllium

Introduction

Dark green emeralds, greenish blue aquamarines, bright pink morganites and golden heliodors are gem stones of exquisite beauty. These are well crystallized forms of beryl, silicate ore of beryllium, with general formula $3BeO.Al_2O_3.6SiO_2$. Beryl crystals are colourless but minor additions of impurity elements make them coloured. Beryl is the main source of beryllium and normally occurs as prismatic crystals in pegmatites. Sometimes, these crystals can be quite large and a gigantic crystal of 28 feet long weighing 61 tonnes was found once. In India, beryl is found along with columbite - tantalite and mica ores. Beryl of gem quality is mainly found in Brazil. The abundance of beryllium on earth is only 0.005%, which is very small for a light element. India has fairly large deposits of beryl in Bihar, Rajasthan, Andhra Pradesh and Tamil Nadu. Other producers of beryl include; Brazil, former USSR states, Argentina, South Africa, Uganda and Rwanda.

R.J. Hary in 1798 observed that optical properties of emerald were identical with those of commercial beryl. Chemical analysis by Louis Nicolas Vauquelin proved that both materials are identical and contained a new element which was called `Glucinium'. The name beryllium was given in 1828 by F. Wohler who simultaneously with W. Bussy in France succeeded in isolating beryllium metal by reduction of beryllium chloride with potassium. Beryl is recovered from surface mines by hand picking and several hundred tonnes of rock would contain one tonne of beryl crystals. Till 1930s, beryllium was only a laboratory curiosity. The discovery of neutrons by bombardment of alpha particles on beryllium rendered this metal important in the field of nuclear science. Subsequently, its properties as a moderator made it a valuable material in nuclear industry.

Extraction of Beryllium

Beryl is a very stable mineral and the first step in its extraction is to open up this ore for the recovery of beryllium. The two main methods employed for this purpose are the fluoride process and the sulphate process. Fluoride process is used in India. Beryl is reacted with sodium silicoflouride and sodium carbonate at 750°C and the following reaction (eq. 8.1) takes place:

$$3BeO.Al_2O_3.6SiO_2 + 2Na_2SiF_6 + Na_2CO_3 \xrightarrow{750^\circ C} 3Na_2BeF_4 + 8SiO_2 + Al_2O_3 + CO_2 \quad (8.1)$$

Fluoride selectively attacks beryllium present in the ore and converts it into sodium beryllium fluoride. Out of the reaction products, only sodium beryllium fluoride is water soluble and is, therefore, recovered by leaching. The solution is then treated with sodium hydroxide to precipitate beryllium hydroxide. Sodium fluoride left behind in the solution is then reacted with ferric chloride or sulphate to generate sodium fluoroferrate which is subsequently used for beryllium recovery as per the following (Eq 8.2) reaction:

$$3BeO.Al_2O_3.6SiO_2 + 2Na_3FeF_6 \xrightarrow{750^\circ C} 6SiO_2 + Fe_2O_3 + Al_2O_3 + 3Na_2BeF_4 \quad (8.2)$$

Beryllium hydroxide is heated to about 800°C for conversion to beryllium oxide.

In the sulphate process beryl is heated to 1625°C to obtain molten glassy material. This is quenched in water to obtain fine frit of beryl which is leached with sulphuric acid at 200 to 300°C. Aluminium and beryllium form soluble sulphates and are, therefore, dissolved from the ore. Aluminium is separated by adding ammonium hydroxide and crystallizing out ammonium aluminium sulphate. Sodium hydroxide is then added for conversion of beryllium to sodium beryllate which is hydrolyzed to obtain beryllium hydroxide. During hydroxide precipitation step, chelating agents are added to the solution to prevent the precipitation of nickel and iron along with beryllium.

Beryllium obtained by the above process is not very pure and further purification is carried out by fractional crystallization, controlled precipitation as carbonates or by solvent extraction methods.

Preparation of Beryllium Metal and Alloys

Beryllium is a highly reactive metal and reduction of its compounds requires the use of strong reducing metals under inert atmospheric conditions. Reduction of beryllium fluoride with magnesium is the most commonly practised route for this purpose. Beryllium fluoride is obtained by the reaction of beryllium hydroxide with ammonium bifluoride

$$Be(OH)_2 + 2NH_4HF_2 \rightarrow (NH_4)_2\,BeF_4 + 2H_2O \qquad (8.3)$$

$$(NH_4)_2\,BeF_4 \xrightarrow{900\,^{\circ}C} BeF_2 + 2NH_4F \qquad (8.4)$$

The hydroxide cake is treated with ammonium bifluoride solution to obtain ammonium beryllium fluoride which is crystallized out from the solution. Anhydrous beryllium fluoride is obtained by thermal decomposition of this bifluoride. Reduction of beryllium fluoride with magnesium is carried out in a graphite crucible at 1100 to 1400°C. The quantity of magnesium added along with beryllium fluoride is only 75% of that required for complete reduction. The reaction is first carried out at 900°C and then temperature is increased to 1400°C to allow collection of beryllium metal. Magnesium fluoride and beryllium fluoride combine to form a low melting slag and facilitate good separation of the metal. Subsequently, flux is leached out and beryllium pebbles are separated and consolidated.

Beryllium is also prepared by electrolysis of beryllium chloride. Beryllium oxide is mixed with carbon and chlorinated at 1000°C to obtain beryllium chloride. High vapour pressure of beryllium chloride allows its evaporation from reaction zone and the sublimate condenses in a condenser kept at temperatures below 400°C.

$$BeO + C + Cl_2 \xrightarrow{1000\,^{\circ}C} BeCl_2 + CO \qquad (8.5)$$

Electrolysis is carried out in a nickel/stainless steel pot which also acts as the cathode. Graphite is used as the anode. Beryllium chloride is mixed with sodium chloride to obtain an electrolyte which melts at 370°C. Electrolysis yields beryllium flakes which are subsequently purified by vacuum melting.

Beryllium is a steel grey metal with a melting point of 1285°C. It is the only stable light metal with high melting point. Beryllium metal is fabricated into various shapes only by powder metallurgical methods. Melting and casting techniques often yield metal with large grains and anisotropic structure which do not give good metallic properties. Beryllium ingots obtained after melting are, therefore, machined into chips and ground to fine powder suitable for powder metallurgical operations.

One of the major uses of beryllium is in the form of beryllium copper alloys. Beryllium fluoride is reduced with magnesium in the presence of copper metal and the reaction is given below.

$$BeF_2 + Cu + Mg \rightarrow Cu\text{-}Be + MgF_2 \qquad (8.6)$$

Copper-8% beryllium master alloy is usually prepared by this method. This process is also used for obtaining alloys having desired beryllium content. Direct reduction of beryllium oxide with carbon in the presence of copper has also been reported to be useful for making beryllium copper alloys. This reaction has to be carried out at temperatures of the order of 2000°C.

Uses of Beryllium and Beryllium Alloys

Use in Nuclear Systems

Beryllium metal has the lowest thermal neutron absorption cross section (0.0095 b) among all metals. This property combined with its large scattering cross section, good moderating properties, high melting point and good strength make it an excellent moderator and reflector material. Its use has, however, been restricted to only special reactors because of the high cost. Beryllium metal or beryllium oxide has been used as structural and reflector materials in Material Testing Reactor, Engineering Test Reactor, Advanced Test Reactor and Experimental Breeder Reactor-II in USA. In India, beryllium oxide is used as moderator for ^{233}U based neutron source reactor KAMINI. Many components in neutron research are made from beryllium or beryllium oxide. Beryllium is also used for making neutron sources required for starting the nuclear reactors as well as for research applications. In addition to making (α,n) neutron sources, (γ,n) neutron sources can also be made. Most prominent sources of this type are $^{239}Pu\text{-}^{9}Be$ and $^{124}Sb\text{-}^{9}Be$.

When used as moderator or reflector in a reactor, beryllium undergoes the following nuclear reactions :

$$^{9}Be + n \rightarrow {}^{6}He + \alpha \qquad (8.7)$$

$$^{6}\mathrm{He} \rightarrow {}^{6}\mathrm{Li} + \beta \qquad (8.8)$$

$$^{6}\mathrm{Li} + \mathrm{n} \rightarrow {}^{4}\mathrm{He} + {}^{3}\mathrm{H} \qquad (8.9)$$

$$^{9}\mathrm{Be} + \gamma \rightarrow {}^{8}\mathrm{Be} + \mathrm{n} \qquad (8.10)$$

$$^{8}\mathrm{Be} \rightarrow 2\alpha \qquad (8.11)$$

$$^{9}\mathrm{Be} + \mathrm{n} \rightarrow {}^{8}\mathrm{Be} + 2\mathrm{n} \qquad (8.12)$$

Applications in Other Industries

Beryllium is the lightest structural material having density one third that of aluminium. It is the only stable light metal with high melting point. Even red hot beryllium does not react with air or steam since highly protective layer of beryllium oxide prevents further reaction. It has excellent electrical conductivity, high heat absorption and conductivity, and good mechanical properties at elevated temperatures. Its modulus of elasticity is one third greater than that of steel. Beryllium metal finds extensive applications in space science. The possibility of machining beryllium to very close tolerances coupled with dimensional stability, has led to its nearly exclusive use in inertial guidance systems, and navigational control devices such as gyroscopes and accelerometers. In aerospace applications, beryllium provides 60% weight savings over the corresponding materials and, therefore, is used for making many parts for missiles, space vehicles and military aircrafts. It has excellent thermal properties which make it a good material for heavy duty brake drums in military aircraft. Being a light metal, it transmits X-rays 17 times as effectively as aluminium. It is almost exclusively used as X-ray tube window for the transmission of the X-rays and stopping of electrons. Highly polished surface of beryllium retains brilliance for years and it is, therefore, used for making special mirrors for space applications. Beryllium has also been used as heat shield in Mercury space flights and in many space craft cabin sections.

In conventional industry, beryllium is most often used in the form of alloys and among various alloys, beryllium copper alloys are the most prominent. Addition of a small quantity of beryllium to copper produces significant hardening. High beryllium alloys like alloy-25 have about 2% of beryllium and 0.3% of cobalt. This alloy has high strength and is used in many applications particularly precision springs. Hardness of beryllium-copper alloys has also resulted in its use for tools in refineries and explosive factories where sparking can be dangerous since tools made from beryllium-copper alloys are non-sparking. Beryllium alloys of type 50C contain about 0.6% of Be and 1.6% of Co. These alloys have very good electrical and thermal conductivity and are used in electronics, automation applications and instrumentation. Beryllium can also be used to alloy magnesium to reduce its inflammability. Tarnishing of silver can also be prevented by alloying with beryllium. India has a pilot plant for making 10 te/y of copper-beryllium alloy for various applications.

Beryllium oxide has excellent properties as a refractory material and is used in critical applications like spark plugs for aircrafts and in radar installations. Beryllium oxide is very inert, refractory and can be used as a crucible material for containing highly reactive metals.

Health and Safety Aspects

Many compounds of beryllium like beryllium oxide and beryllium fluoride are highly toxic and great care is required during handling. Contact with these compounds can result in dermatitis. Inhalation of beryllium causes symptoms similar to the inhalation of poison gas 'phosgene'. All operations involving beryllium are, therefore, carried out in specially ventilated areas and a close control is kept over the amount of beryllium in the work space. An upper limit of 2 microgramme per meter cube of air and 10 nanogramme per meter square on surface has been specified for this purpose.

Bibliography

1. The nature of matter, G. Amaldi, The Univ. of Chicago Press, Chicago (1961).
2. The atom and its nucleus, G. Gamow, Jaico Publishing House, Bombay (1961).
3. Introduction to nuclear physics and chemistry, B.G. Harvey, Prentice Hall of India Pvt. Ltd, New Delhi (1965).
4. The world of the atom, H.A. Boorse, L. Motz., Vols. 1 and 2, Basic Book Inc. New York (1966).
5. Nuclear physics, Y.M. Shirokov, N.P. Yudin, Vols.1 and 2, Mir Publishers, Moscow (1982).
6. Nuclear chemistry - theory and applications, G.R. Choppin, J. Rydberg, Pergamon Press, Oxford (1980).
7. Perspectives of modem physics, A. Beiser, McGraw Hill Kogakusha Ltd., Tokyo (1969).
8. Source book of atomic energy, S. Glasstone, Van Nostrand Reinhold Co., New York (1967)
9. A guide to nuclear reactors, A.V. Nero Jr., University of California Press, Berkley (1979).
10. A Guide to nuclear power technology, F.J. Rahn, A.G. Adamantiades, J.E. Kenton, C. Braun, John Wiley & Sons, New York (1984).
11. Nuclear energy : a sensible alternative, K.O. Olt, B.I. Spinard, Plenum Press, New York (1985).
12. The necessity of nuclear power, G. Greenhalgh, Graham and Totman Ltd., London (1980).
13. Nuclear power in perspective, E. Addinal, H. Ellington, Kogan Press, London (1982).
14. Energy or extinction? The case for nuclear energy, Fred Hoyle, Heinmen, London (1979).
15. Health hazards of not going nuclear, R. Beckman, The Golden Press, Boulder (1976).

16. Man and atom, G.T. Seaborg, W.R. Corliss, E.P. Dutton and Co, New York (1971).
17. Nuclear energy technology, R.A. Knief, Hemisphere Pub. Co, Washington (1981).
18. Nuclear power technology: W. Marshall, 3 Volumes, Clarendon Press, Oxford (1983).
19. Energy handbook, R.L. Loftness, Van Nostrand Reinhold Co., New York (1978).
20. Energy technology handbook, D.M. Considine, McGraw Hill Book Co, New York (1977).
21. McGraw Hill encyclopedia of energy, D.N. Lapedes, McGraw Hill Book Co, New York (1971).
22. Energy in a finite world, W. Hafele, Ballinger Pub. Co., Cambridge (1981).
23. Nuclear power policy and prospects, P.M.S. Jones (Ed.), John Wiley & Sons, Chichester (1987).
24. The nuclear age, Jacques Leclercq, Sodel (1986).
25. The chemistry of actinide elements. J.J. Katz, G.T. Seaborg, L.R. Morss, Chapman Hill, London (1986).
26. Handbook of Physics and Chemistry of Actinides, Vols. 1 & 2: A.J. Freeman, O.H. Lander (Ed.), Vol. 3: A.J. Freeman, C. Keller (Ed.), North Holland, Amsterdam (1984).
27. Chemistry in Nuclear Technology, S. Peterson, R. Wymer, Addison Wesley Pub. Co. Inc. Reading (1963).
28. Nuclear Materials by H.N. Sethna, R.K. Garg in Chem Tech. I, Indian Institute of Technology, Madras (1975).
29. Materials in nuclear energy applications, Vols. I & II, C.K. Gupta, CRC Press Inc., USA (1989)
30. Nuclear reactor materials, C.O. Smith, Addison Wesley & Co., Reading (1967).
31. Materials for nuclear reactors, B. Kopelman, McGraw Hill Book Co. Inc., New York (1959).

32. Metallurgy in nuclear power technology, J.C. Wright, ILIFFE Book Ltd., London (1962).
33. Nuclear engineering materials, V. Gerasimov, A. Monokhov, Mir Publishers, Moscow (1983).
34. Physics and technology of nuclear materials, loan Ursu, Pergamon Press, Oxford (1985).
35. The chemistry of uranium, E.H.P. Cordfunke, Elsevier Pub. Co., Amsterdam (1969).
36. Uranium ore processing, J.W. Clegg, D.D. Foley, Addison Wesley & Co., Reading (1958).
37. Uranium, J.H. Gittus, Butterworth, London (1963).
38. Extractive metallurgy of uranium, R.C. Merrit, United States Atomic Energy Commision (1971).
39. Uranium and thorium, L. Grainger, George Newness Ltd., London (1958).
40. Thorium production technology, F.L. Cuthbert, Addison Wesley & Co., Massachusetts (1958).
41. Thorium production and properties, J.F. Smith, Iowa State Univ. Press, Ames (1975).
42. Extraction and metallurgy of uranium, thorium and beryllium, R.G. Bellamy, N.A. Hill, Macmillan, New York (1963).
43. Nuclear chemical engineering, M. Benedict, T.H. Pigford, H.W. Levi, McGraw Hill Book Co., New York (1981).
44. Engineering for nuclear fuel reprocessing, J.R. Long, Gordon and Breach, New York (1967).
45. Reactor Handbook, Vol.1: Materials, C.R. Tipton Jr. (Ed.), Interscience Publishers Inc., New York (1960).
46. Reactor Handbook Vo. II: Fuel Reprocessing, S.M. Stoller, R.B. Richards (Ed.) Interscience Publishing Inc., N.Y. (1960).
47. Nuclear reactor materials and applications, Benjamin M. Ma., Van Nostrand Reinhold Co., New York (1983).
48. Nuclear fuel elements, B.R.T. Frost, Pergamon Press, Oxford (1982).

49. Nuclear fuel elements, H.H. Hausner, J.F. Schumar, Reinhold Pub Co., New York (1959).
50. Nuclear fuel elements - metallurgy and fabrication, A.R. Kaufman (Ed.), Interscience Publishers, New York (1962).
51. Metallurgy of nuclear fuel: Properties and principles of technology of uranium, thorium and plutonium, V.S. Yemelyanov, A.I. Yevstyukhin, Pergamon Press, Oxford (1969).
52. Fundamental aspects of nuclear reactor fuel elements, D.R. Olander: TID 26711 (1976).
53. The metal plutonium, A.S. Coffinberry, W.N. Miner, University of Chicago Press, Chicago (1961).
54. The chemistry of plutonium, J.M. Cleveland, Gordon Breach, New York (1967).
55. Plutonium : A general survey, M. Taube, Verlag Chemie, Weinheim (1974)
56. Plutonium Handbook A guide to technology Vol: 1 and 2, O.J. Wick (Ed.), Gordon Breach, New York (1967)
57. The metallurgy of plutonium, A.N. Vol'skiv, Ya M. Sterlin, Israel Programme for scientific translation, Jeruslam, (1970).
58. The chemistry of transuranium elements, C. Keller, Verlag Chemie, Weinheim (1971).
59. Transplutonium elements - Production and recovery, J.D. Navratil, W.W. Schulz, ACS Symposium series 161, American chemical Society, Washington (1981).
60. The theory of isotope separation, K. Cohen, McGraw Hill, New York (1951).
61. Separation of isotopes, H. London, Newness, London (1963).
62. Isotope separation, S. Villani, American Nuclear Society, La Grange Park (1976).
63. Uranium enrichment, S. Villani (Ed.) Topics in applied physics, Vol. 35, Springer Verlag, New York (1979).
64. Uranium enrichment by gas centrifuges, D.G. Avery, E. Davies, Mills and Boon, London (1973).

65. Isotopes in the atomic age, H.J. Arnikar, Wiley Eastern Ltd., New Delhi (1989).

66. Production of heavy water, G.M. Murphy (Ed.), McGraw Hill, New York (1955).

67. Production of heavy water, E.W. Becker, .International Atomic Energy Agency, Vienna (1961).

68. The metallurgy of zirconium, B. Lustman, F. Kerze Jr., McGraw Hill, New York (1955).

69. Zirconium in nuclear industry, A.L. Lowe, G.W. Perry (Ed.), Special technical publication 633. American society for testing of materials, Philadelphia (1977).

70. The metallurgy of zirconium D.L. Douglas, International Atomic Energy Agency, Vienna (1971).

71. History of the development of zirconium alloys for use in nuclear reactors, H.Rickover, L.D. Geiger, B. Lustman, USERDA report TID-26740 (1975).

72. Zirconium in nuclear industry, D.G. Franklin (Ed.), American Society for testing of materials, Philadelphia (1982).

73. The chemistry of beryllium, D.A. Everest, Topics in inorganic and general chemistry Volume VI, Elsevier, Amsterdam (1964).