Energy resources and mineral exploration

Radioactive minerals

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***Keywords*: Radioactivity, Detection and Measurement, Geochemistry, inerals, Prospecting, Distribution in India, Nuclear Waste Disposal**

1. RADIOACTIVITY

Radioactivity was discovered in 1896 by A. Henri Becquerel (Fig.1) and Pierro and Marie Curies (Fig. 2). It is the property of *spontaneous emission of radiations* of alpha (α: $^{4}_{2}He^{2+}$) particles, beta (β: high energy electrons, accompanied by neutrinos) particles and gamma (γ: high energy, short wavelength x-rays) rays due to the disintegration of the nuclei of certain elements of high atomic weight, like Radium (Ra), Actinium (Ac), Thorium (Th) and Uranium (U). These radiations can penetrate opaque bodies and affect a photographic plate, even when separated by a thin sheet of metal. Alpha particles have lower velocity and smaller penetrating power than the other radiations, and their direction can be slightly changed by magnetic field. Beta particles are faster than alphas and their direction is changed markedly by magnetic field. Gamma rays have the greatest penetrating power with their velocity almost that of light and their direction is not changed by magnetic field. As the atoms of the radioactive elements are not stable, they disintegrate at a definite rate, measured by their half-life. The *half-life of an element is the time required for radioactive decay of one half of its mass*. Each radioactive element has a characteristic half-life, a constant that cannot be changed by any known means. By disintegration, elements of lower atomic weight are produced from those of higher atomic weight, which constitutes a *disintegration series*. The final element of such series is a non-radioactive element, e.g., $^{238}U \rightarrow {}^{206}Pb$. Radioactivity

may be induced in certain elements (that are not normally radioactive) by exposure to the bombarding particles, such as protons, neutrons or deuterons. When this happens, a new species of radioactive atom, usually of short half-life, is formed, e.g., ^{90}Sr and ^{137}Cs.

Fig.1. Henri Becquerel (1852-1908), the discoverer of 'Radioactivity'. (Source: 'The Nuclear Age', by Jacques Leclercq; Publisher: Le Chene, p. 16, 1986).

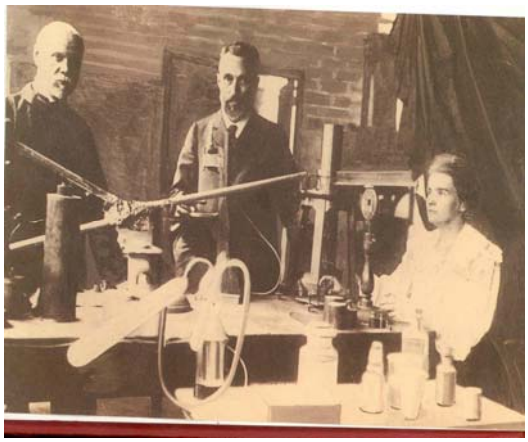


Fig. 2. Pierre and Marie Curies at work in their Laboratory. (Source: 'The Nuclear Age' , by Jacques Leclercq; Publisher: Le Chene, p. 16, 1986).

2. DETECTION AND MEASUREMENT OF RADIOACTIVITY

2.1. Detection of Radioactivity: The average abundance of uranium, thorium and potassium in the earth's crust (upper part) is, respectively, about 2 ppm (parts per million, x 10^{-6}), 8 ppm and 1.2%, with the value for Th/U being between 3 and 4. Their average abundance in the deeper parts of the earth, viz., mantle and core, is much less, since they have concentrated progressively with time in the crustal part. As U and Th occur usually in such low contents in the Earthy materials, like rocks, soil and water, their presence needs to be detected. For their detection, the phenomenon of radioactivity is taken advantage of. In the early period, the instruments used for their detection were the photographic plate, electroscope, electrometer, ionization chamber and spinthariscope. In 1908, H. Geiger developed the Geiger tube. This

was modified in 1928 by W. Müller as the Geiger-Müller (GM) tube that was adapted to use in the field in 1932. The first radioactivity surveys using a GM counter were carried out in Canada in 1939. Electronic scintillation counters, based on the principle of the spinthariscope, but employing sensitive photomultiplier tubes, were developed in 1944 by S.C. Curran and W.R. Baker. This was followed by much research on large volume crystals for counting beta particles and gamma radiation. This culminated in the development by R. Hofstadter in 1948 of sodium iodide (NaI)-thallium (Tl)-activated crystals for the detection of gamma radiation. Since then, these crystals have remained the most important detector medium for gamma-ray scintillation spectrometry. Presently, many scintillation spectrometers have reached a high degree of sophistication employing as many as 1000 channels for total gamma counting and specific quantitative analyses of elements, such as U (as ^{214}Bi), thorium (as ^{208}Tl) and K (^{40}K). Early radiometric surveys were conducted on-foot, using either a GM counter or scintillometer; presently, many of the surveys are jeepborne, airborne or shipborne, using multichannel gamma-ray spectrometers.

Other methods to detect radioactivity, utilizing the radiation feature, are radioactivation analysis, autoradiography, radiation track analysis, radioactive tracers and fluorescence. Radioactive analysis is based on certain nuclear properties of the isotopes (nuclides with same atomic number but different mass number, e.g., ^{238}U and ^{235}U) of the elements sought in the sample. This utilizes thermal neutrons as the bombarding particles (neutron activation analysis). This method has an extremely high sensitivity to detect elements in the parts per billion (ppb, $x10^{-9}$) range for elements, like gold, platinum group of elements, U, etc., Autoradiography of polished and thin sections of rocks and ores has been in use for decades mainly to detect the location, and to some extent qualitative to semi-quantitative estimation, of U and Th in samples. The method records alpha particle events in a photographic emulsion on films or plates in contact with the sample for long exposures over a few days; on development of the emulsion, an estimate of this activity can be made based on the intensity of darkening of the film or plate. An advancement of this method is the 'Solid State Nuclear Track Detection' that does not require a dark room. In this, alpha-sensitive cellulose nitrate film, instead of photographic film or plate, is placed in contact with the sample. After such an exposure for a few days, the tracks are developed on the film, due to alpha-bombardment from U and Th in the sample. These tracks can be seen by etching the film with 10% Na- or K-hydroxide solution at about 30-40˚C. The density of alpha tracks in the unit area is directly proportional to the contents of U and Th or intensity of radioactivity. Similar to this is radiation track analysis using induced fission processes in a nuclear reactor. The fourth method uses radiotracers, like tritium and other suitable isotopes. This method has been employed for many years to trace various processes in living and in dynamic geologic systems, such as diffusion processes in soils and rocks, and metal adsorption on stream sediments and peat. As many U-salts fluoresce under ultraviolet light of suitable wavelengths (2537 Å, 3660 Å), this provides a suitable method for detection of some U-minerals that might otherwise escape detection by GM counter or scintillometer.

Ground radiation surveys, with GM and scintillation counters, have been employed extensively since 1950. These are mainly instrumental in locating at least 80% of the U and Th deposits mined. Airborne radiation surveys, employing scintillation spectrometers, came into general use in the 1960s. These are instrumental in locating a number of U-Th belts and a few deposits. The main advantage of these surveys is rapid, low-cost coverage of large regions with poor ground access and trafficability. Radiation surveys can be carried out with gross (total) count instruments or with discriminating spectrometers.

2.2. Measurement of Radioactivity: This is done in terms of the contents of radio elements in a sample. It is carried out either by radiometric analysis, using gamma-ray spectrometry, or chemical analysis. In the gamma-ray spectrometry, the intensity of peaks of 1.46 MeV (energy) from K (^{40}K), 1.76 MeV from U (actually of the daughter-product of U, ^{214}Bi), 2.62 MeV from Th (actually of the daughter-product of Th, ^{208}Tl) and >0.1 MeV from the total (i.e., all the three) is counted as counts per second (cps). The 'cps' of each are then compared with those of standards containing known quantity of K, U, Th and total of all the three. As both U and Th are alpha-emitters, and since the measurement is based on the gamma or beta radiation from their daughter products in the decay series of Th (Table 1) and U (Tables 2 and 3), accuracy of such estimates depends on 'radioactive equilibrium' in the radioactive series. The decay series is said to be in radioactive equilibrium, when the various daughter nuclei of the family become constant, and each bears a fixed proportion to the parent. Thus, by counting the beta or gamma rays emitted by some of the daughter products of U or Th, the quantity of the parent in the sample is inferred. Since it is not known whether the total radioactivity measured in a sample originates from U or Th or both or from any other radio element and whether U in the sample is in radioactive equilibrium, it is expressed as 'equivalent (e) U_3O_8'. This means that the radioactivity of the analyzed sample is equivalent to the radioactivity of a sample that contains the amount of U inferred by the analysis. In other words, the sample in question should have contained that much actual U_3O_8 had the U present been in radioactive equilibrium with its daughters and no Th is present. Thus, the value of eU_3O_8 could be less than, equal to or greater than the actual U_3O_8 content, depending upon the state of equilibrium of the U-series and/or presence of Th. As daughters of Th have short half-lives, Th is almost always found in equilibrium, and the disequilibrium, if any, in a sample is due to U. This radioactive disequilibrium is of two kinds, viz., one in favor of daughter-products of U and the other in favor of parent U. For example, if U gets leached away from an old deposit, the gamma-activity shows practically no change and the eU_3O_8 content will be much higher than the actual uranium content. On the other hand, if U were deposited recently in a locale, the gamma-activity will be very low and the eU_3O_8 content of a sample from this will give a value much lower than the actual content of U. In view of these possibilities, it is desirable to chemically analyze the uranium content. It may be noted that U_3O_8 is a stoichiometeric material of $U^{4+}O_2 + 2\ U^{6+}O_3$, and not a compound.

Chemical analysis for U is carried out by various techniques like gravimetry, volumetry, colorometry and fluorometry. Of these, fluorometry, in the form of laser pellet, is versatile. Hence, it is usually adopted for even very low concentrations at ppb level.

3. GEOCHEMISTRY

Of the nearly 100 elements in the Periodic Table, only 3, viz., Uranium [U - Atomic Number (Z) – 92], Thorium (Th, Z – 90) and Potassium (K, only the isotope with mass no. 40) are the naturally occurring `Radio Elements'. Among these, the first two, being highly radioactive, are more important. Their contents in the Earth and in different major rock types are very low, being in the range of a few ppm or gram/ton (g/t). They generally occur together with `Rare Metals' [Niobium (Nb), Tantalum (Ta), Beryllium (Be), Lithium (Li), etc.] and `Rare Earth Elements' [REE: Lanthanum (La) to Lutetium (Lu) plus Yttrium (Y) and Scandium (Sc)] due to comparable geochemical properties.

3.1. Naturally-occurring Radio Elements: The three naturally occurring radio elements - Uranium, Thorium and Potassium [(K), only the isotope, ^{40}K, constituting 0.012% of K], respectively, generate 0.73, 0.20 and 27 x 10^{-6} (^{40}K: 0.22) calories/gm/year radioactive heat.

This heat is mainly responsible for the convection process in the interior of the Earth. It accounts for much of the internal dynamic activity of the Earth. Of the three elements, U and Th due to their notable contribution to the radiogenic heat are more important radio elements. Uranium and thorium are members of the actinide (Ac) series. In the Periodic Table, U is the first element of Group VI B and Th is the last element in Group IV B. Although both Th and U are markedly oxyphile (affinity to oxygen), they have biophile tendency. Due to this, they are found in various organisms and concentrate in organic compounds, like humus, coal, petroleum, bitumen and thucolite (a mixture Th, U and C).

Thorium (Th), with atomic number 90, has 6 isotopes. Of these, the most abundant and longest lived (with half-life of 1.39×10^9 years) is ^{232}Th. This decays in a series of stages to yield ultimately ^{208}Pb (Table 1). The isotope, ^{232}Th absorbs slow neutrons and is converted to ^{233}U that, in turn, is fissionable. Hence, Th is utilizable as a nuclear fuel in breeder reactors. This indeed is the third stage of the India's 3–stage nuclear power programmme. Only one principal oxidation state of throium, viz., Th^{4+}, is of importance. Chemically, Th resembles Zirconium (Zr), Hafnium (Hf) and certain of the rare earth elements, especially Cerium (Ce), besides U, at higher temperatures. Hence in minerals, there is extensive replacement of Zr, Y, Ce (and other lanthanides, La - Lu) and U. Th^{4+} undergoes extensive interaction with water (hydrolysis) at pH >3.

Table 1. The Thorium – 232 (4n) decay series

Element	Isotope	Half-life	Decay Constant (s^{-1})	Radiation
Thorium	$_{90}Th^{232}$	1.39×10^{10} y	1.58×10^{-18}	α, SF, γ
Radium	$_{88}Ra^{228}$	6.7 y	3.30×10^{-9}	β, γ
Actinium	$_{89}Ac^{228}$	6.13 h	3.10×10^{-4}	β, γ
Thorium	$_{90}Th^{228}$	1.91 y	1.15×10^{-8}	α, γ
Radium	$_{88}Ra^{224}$	3.64 d	2.20×10^{-6}	α, γ
Radon	$_{86}Rn^{220}$	55.3 s	1.30×10^{-2}	α, γ
Polonium	$_{84}Po^{216}$	0.158 s	4.30	α
Lead	$_{82}Pb^{212}$	10.64 h	1.80×10^{-5}	β, γ
Bismuth	$_{83}Bi^{212}$	60.5 m	1.90×10^{-4}	β, α, γ
Polonium	$_{84}Po^{212}$	3.04×10^{-7} s	2.30×10^{6}	α
Thallium	$_{81}Tl^{208}$	3.1 m	3.70×10^{-3}	β, γ
Lead	$_{82}Pb^{208}$	stable		

SF: spontaneous fission

Uranium (U), with atomic number 92, is composed of three principal isotopes, viz., ^{234}U (0.0054%), ^{235}U (0.720%) and ^{238}U (99.275%). ^{235}U, with a half–life of 0.713×10^9 years, and ^{238}U, with a half–life of 4.51×10^9 years, decay in a series of steps to yield ultimately ^{207}Pb and ^{206}Pb, respectively (Tables 2 and 3). ^{235}U undergoes fission (Fig. 3)

with slow neutrons and can sustain a fission or chain reaction (Fig. 4) with release of enormous amount of energy. ^{235}U, on increased content from 0.72% to about 2.5–3%, constitutes the enriched fuel for light water nuclear power reactors, as at Tarapur. ^{238}U, like ^{232}Th, absorbs slow neutrons to form ^{239}U. This, in turn, decays to ^{239}Pu (Plutonium) that can sustain a fission reaction. Hence, U can be used as nuclear fuel, like the one used in many heavy water-moderated nuclear power reactors at Kota, Narora, Kakrapar, Kaiga etc. Of the oxidation states of U, U^{4+} and U^{6+} are of interest, whereas U^{5+} as $(UO_2)^+$ may be present in some natural waters and environments with a low oxidation potential. The hexavalent state, as the uranyl ion $(UO_2)^{2+}$ (Fig. 5), is the most stable oxidation state. In nature, it is commonly reduced to the U^{4+} state and precipitated as the oxide, UO_2, or precipitated in U^{6+} state. Depending upon the availability of various ligands, U^{6+} forms complex hydrated oxides, hydroxides, silicates, phosphates, arsenates, vanadates, molybdates, sulphates, selenites, tellurites and carbonates. Due to certain chemical similarities of ionic size, ionic charge, electronegativity etc., U replaces Y, REE, Zr, Th, Ca and Ba.

Table 2. The Uranium – 235 (4n+3) decay series

Element	Isotope	Half-life	Decay constant(s^{-1})	Radiation
Uranium	$_{92}U^{235}$	0.71×10^{9} y	3.10×10^{-17}	α, SF, γ
Thorium	$_{90}Th^{231}$	25.6 h	7.40×10^{-6}	β, γ
Protactinium	$_{91}Pa^{231}$	3.4×10^{4} y	6.50×10^{-13}	α, γ
Actinium	$_{89}Ac^{227}$	21.6 y	10^{-9}	β, α, γ
Thorium	$_{90}Th^{227}$	18.7 d	4.35×10^{-7}	α, γ
Francium	$_{87}Fr^{223}$	22.0 m	5.20×10^{-4}	β, α, γ
Radium	$_{88}Ra^{223}$	11.4 d	7.04×10^{-7}	α, γ
Radon	$_{86}Rn^{219}$	4.0 s	0.17	α, γ
Astatine	$_{85}At^{219}$	54.0 s	1.28×10^{-2}	α, β
Polonium	$_{84}Po^{215}$	1.8×10^{-3} s	3.80×10^{2}	α, β
Astatine	$_{85}At^{215}$	10^{-4} s	6.90×10^{3}	α
Bismuth	$_{83}Bi^{215}$	8.0 m	1.44×10^{-3}	β
Bismuth	$_{83}Bi^{211}$	2.15 m	5.35×10^{-3}	α, β, γ
Polonium	$_{84}Po^{211}$	0.52 s	1.32	α, γ
Lead	$_{82}Pb^{211}$	36.0 m	3.20×10^{-4}	β, γ
Thallium	$_{81}Tl^{207}$	4.8 m	2.40×10^{-3}	β, γ
Lead	$_{82}Pb^{207}$	stable		

SF: spontaneous fission.

Table 3. The Uranium –238 (4n+2) decay series

Element	Isotope	Half-life	Decay constant(s^{-1})	Radiation
Uranium	$_{92}U^{238}$	$4.51x10^{9}$ y	$4.9x10^{-10}$	α, SF, γ
Thorium	$_{90}Th^{234}$	24.1 d	$3.3x10_{-7}$	β, γ
Protactinium	$_{91}Pa^{234}$	6.7 h	$2.84x10^{-5}$	β, γ
Uranium	$_{92}U^{234}$	$2.48x10^{5}$ y	$8.9x10^{-14}$	α, SF, γ
Thorium	$_{90}Th^{230}$	$8x10^{4}$ y	$2.75x10^{-10}$	α, γ
Radium	$_{88}Ra^{226}$	1622 y	$1.35x10^{-11}$	α, γ
Radon	$_{86}Rn^{222}$	3.82 d	$2.07x10^{-6}$	α, γ
Polonium	$_{84}Po^{218}$	3.05 m	$3.8x10^{-3}$	α, β
Astatine	$_{85}At^{218}$	1.35 s	0.51	α
Bismuth	$_{83}Bi^{214}$	19.7 m	$5.85x10^{-4}$	α, β, γ
Polonium	$_{84}Po^{214}$	$1.64x10^{-4}$ s	$4.25x10^{3}$	α
Lead	$_{82}Pb^{214}$	26.8 m	$4.3x10^{-4}$	β, γ
Lead	$_{82}Pb^{210}$	21 y	$1.05x10^{-9}$	β, γ
Bismuth	$_{83}Bi^{210}$	5 d	$1.58x10^{-6}$	β
Polonium	$_{84}Po^{210}$	138.4 d	$5.7x10^{-2}$	α, γ
Thallium	$_{81}Tl^{210}$	1.3 m	$8.85x10^{-2}$	β, γ
Thallium	$_{81}Tl^{206}$	4.2 m		β
Lead	$_{82}Pb^{206}$	stable		

SF: spontaneous fission.

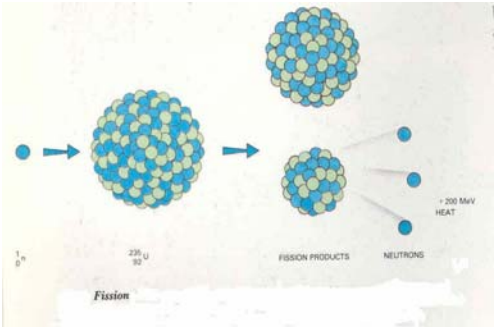


Fig. 3. Fission of ^{235}U. (Source: 'The Nuclear Age', by Jacques Leclercq; Publisher: Le Chene, p. 18, 1986).

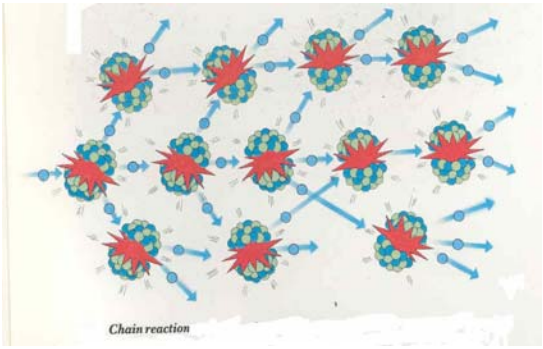


Fig. 4. Chain reaction of U. (Source: 'The Nuclear Age', by Jacques Leclercq; Publisher: Le Chene, p. 18, 1986).

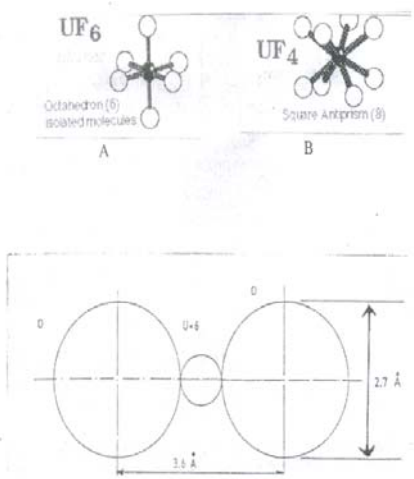


Fig. 5A, B & C: A: Uranium in six-fold coordination with central cation (filled circle, U) surrounded by six anions (open circles, F); B: Uranium in eight-fold coordination with central cation (filled circle, F), surrounded by eight anions(open circles, F); C: Dumb-bell shaped uranyl $[(UO2)^{2+}]$ ion.

3.2. Why U, Th and Related Elements concentrate in the Crust? : The occurrence and concentration of different elements in the Earth depend mainly upon their geochemical coherence, i.e., elements with similar or comparable chemical properties of ionic radius, ionic charge, electronegativity etc., occur and concentrate together, just like birds of the same feather flock together. Thus, U with its charge of 4^+ and 6^+, and corresponding ionic radii of 0.89 and 0.73 Å (1 Å = 10^{-10} meter), and Th with its charge of 4^+ and ionic radius of 0.99 Å go together with elements of same or nearly same charge and/or similar ionic radii. Such elements include Rare Metals (RM: Zr –

Hf, Nb – Ta, Be, Li and Sn) as well as Rare Earths (RE : La to Lu, Y). During the evolution of the earth, much of all these elements was expelled from the mantle and core, and concentrated in the shallower crust. Accordingly, the crustal acid magmatic rocks and their derived products of sedimentary and metamorphic rocks house the radioactive minerals containing the above elements.

3.3. U and Th contents in the Earth and in Common Rock Types: The average abundance of uranium and thorium in the Earth's crust (upper part) is, respectively, about 2 and 8 ppm, with the value for Th/U being between 3 and 4; their average abundance in the deeper parts of the earth, viz., mantle and core, is much less, since all the three radio-elements concentrate progressively in the crustal part. In the common rock types, both U and Th prefer (i) acidic (with high silica content of >62%), especially alkali (K and Na) – rich magmatic rocks; (ii) carbonaceous and phosphatic sedimentary rocks and (iii) pyritiferous (FeS_2) quartz-pebble conglomerate and low–grade (Temp. ~<350^oC) metamorphic rocks such as, phyllite and schist, with Th/U value ranging from <1 to 5 (Table 4). Like U and Th, potassium also is relatively more in the crust (av. 1.2%), with recent investigations indicating 0.12% K in the Earth's core as an alloy with Fe and, thus, contributes to some radiogenic heat from core, besides much higher heat from the crust.

Table 4. Average Uranium(U) and Thorium (Th) contents (in ppm) of Common Rock-types*

Rock-type	U	Th	Th/U
A. Igneous Rocks			
Ultrabasic rocks (SiO_2 <45%)	0.02	0.1	5
Basic rocks (SiO_2 45-52%)	0.6	3	5
Intermediate (SiO_2 52-~62%)	2	5	2.5
Acidic rocks (SiO_2 >~62%)	4.5	15	3.3
Kimberlites	4.5	12	2.6
Lamprophyres	5	15	3
Alkali-granites & -syenites	up to 100	up to 100	1
B. Sedimentary Rocks			
Arenites (sandstone etc.)	1.5	5	3.3
Argillites (shale etc.)	3.5	12	3.4
Precipitates (Limestone etc.)	1.5-2	1-3	0.6-1.5
Evaporites (anhydrite etc.)	0.1	0.2	2
Phosphorites (Oceanic)	up to 300	up to 12	-
Sapropelites(C-pyritic shales)	up to 1200	up to 20	-

C. Metamorphic Rocks

Quartzite,Meta-conglomerate	1.5	5	3.3
Quartz-pebble conglomerate (py)	up to 2000+	up to 435	-
Marble	0.5	1	2
Phyllite	2.5	10	4
Schist	2-2.5	6-10	3-5
Amphibolite	0.5-2	2-8	4
Greenstones	0.5	2	4
Gneiss, Granulite	3	10	3.3
Skarn, Hornfels	2-3	10-15	5

*Source: Geochemical prospecting for Th and U deposits – R.W. Boyle, Elsevier, 1982.

4. MINERALOGY

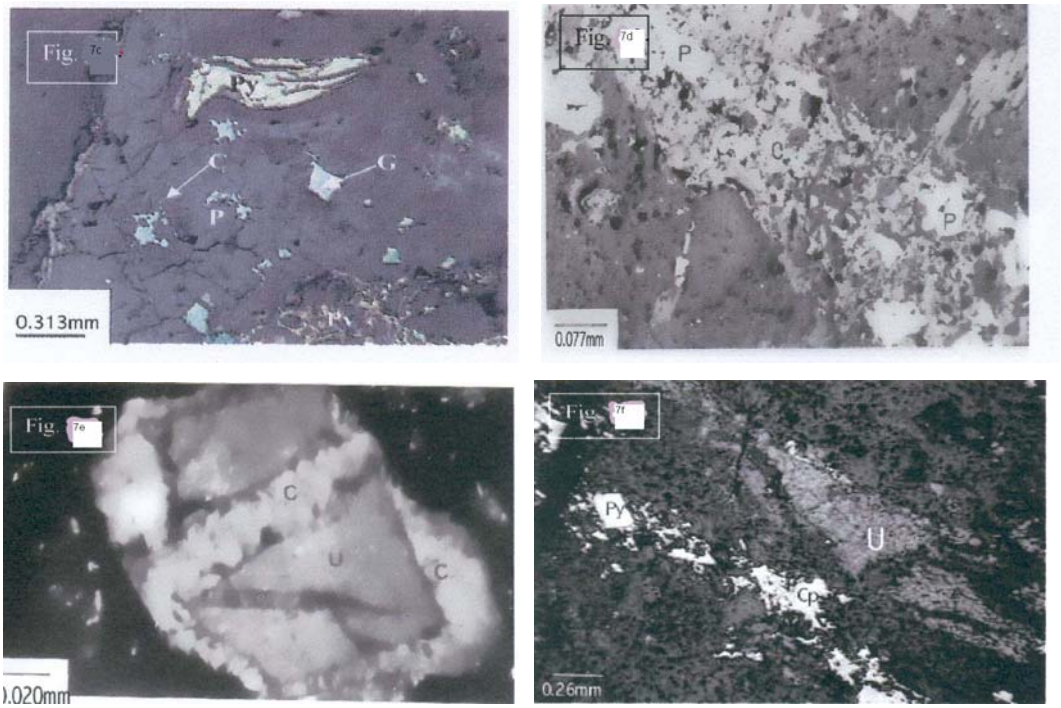
Radioactive minerals are the discrete minerals of uranium and/or thorium as well as those of other elements, like rare metals (Nb – Ta, Li, Be, Sn, W etc.) and Rare Earths (REE: La to Lu, Y) in which either U or Th or both occur in notable quantity. These minerals occur in very low content (usually <1%) in different rock types, viz., in (i) magmatic or igneous rocks (rocks formed from a molten rock material, called magma) mainly acidic (silica content, ~ >65 wt%) type, (ii) sedimentary rocks (rocks formed by consolidation of detrital material like sands, silt, clay or chemical/biological precipitation like lime, iron, sulphate etc.,), mainly in sandstone and rarely in limestone; and (iii) metamorphic rocks (formed by transformation of magmatic and sedimentary rocks) of low–grade (low temperature and pressure) like phyllite and schist (Figs. 6 a to h).

4.1. Occurrence of Radioactive Minerals: Radioactive minerals that contain U, Th and RMRE (Rare Metals and Rare Earths) occur in diverse magmatic, sedimentary and metamorphic rocks. In the magmatic rocks, they usually concentrate in acidic plutonic (deep–seated) and volcanic rocks, which include granitoids – pegmatites and rhyolites, respectively; besides, in placers (resistant material) derived from and occurring close to these magmatic rocks. Amongst the sedimentary rocks, sandstones, quartz–pebble pyrite-bearing conglomerates and phosphatic and carbonaceous rocks are good hosts for these minerals. Low–grade (low temperature, <350^{o}C) metamorphic rocks like phyllite and schist, infested with metasomatic alterations involving addition of volatiles (H_2O, OH, F, Cl, CO_2 etc.) within structurally weak zones are the loci for these minerals. Accordingly, terrains with these rocks are usually explored for radioactive minerals.

4.2. Primary and Secondary Radioactive Minerals: Radioactive minerals are broadly divided into primary and secondary discrete minerals of U and Th. Nearly 200 such minerals are known. The primary minerals are those formed directly from magmas, hydrothermal solutions and ground water. Secondary minerals are those formed due to remobilization of elements from primary minerals, their transportation in solution as

complexes and later precipitation due to over-saturation in oxidizing or supergene environment. The most common primary minerals of uranium are uraninite (Fig. 7) (pitchblende, if microcrystalline) (oxide), coffinite (silicate) and brannerite (complex oxide) (Fig. 8); in these, U occurs mostly in U^{4+} (uranous) state, besides some U^{6+} (uranyl) in pitchblende. Secondary minerals of uranium (Fig. 9) occurring in supergene (in surface or in shallow surface) conditions are many (~180) in which U occurs entirely in the U^{6+} state and, hence, all these are uranyl. These include various oxides and hydrated oxides, silicates (Fig. 10), vanadates, carbonates, sulphates, molybdates, phosphates and arsenates, and their complex derivatives. The most common primary minerals of throium are thorianite, thorouraninite (oxides) and thorite/uranothorite (silicates). A few secondary (supergene) minerals of Th are known, the most common being thorogummite.

4.3. U- and Th-bearing Accessory Minerals: Uranium and thorium in notable amounts (≥ 1%) occur in a large number of rock-constituting accessory minerals, like zircon, apatite, monazite, xenotime, allanite and sphene. Alpha emission of uranium may render some of these minerals metamict by destruction of the internal order of the original crystalline structure, mostly to a limited degree and rarely completely. U, as a substitutional ion, occurs in about 20 uranium niobates, tantalates and titanates. The important ones of these are betafite, davidite, euxenite, samarskite (Fig. 11), brannerite (Fig. 12), columbite–tantalite and pyrochlore. Important properties of radioactive minerals, including their maximum contents of U and Th, are given in Table 5.



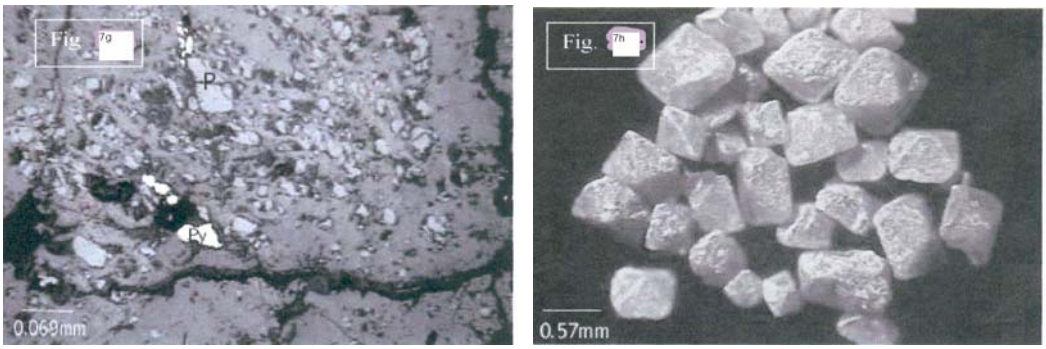


Fig. 6. Some important atomic (radioactive) minerals in different magmatic, sedimentary and metamorphic rocks. (a):Th-bearing uraninite (U), rimmed by pyrite (P) in the biotite granite from Binda-Nagnaha, Bihar; (b): Th-poor uraninite (medium grey with fractures) associated with pyrite (white) in the basement granite at Lambapur, Andhra Pradesh; (c): Pitchblende(P), associated coffinite (C), pyrite (Py) and galena (G), in the biotite granite from Gogi, Karnataka; (d): Coffinite (C) as veins, associated with pyrite (P) in the fluorite-bearing biotite granitoid from Jajawal, Chhattisgarh; (e): Thucholite [Th-bearing uraninite (U) with fractures and borders occupied by carbonaceous matter (C)] in mica-quartz schist from Arbail-Dabguli, Karnataka; (f): Uraninite (U) and sulphides [pyrite (P) and chalcopyrite (Cp)] as veins in the biotite-chlorite-quartz schist from Bagjatha, Jharkhand; (g): Pitchblende (P) with pyrite (Py) in sandstone from Domiasiat, Meghalaya: and (h): Xenotime grains, separated from the riverine placers along the Siri river, Chhattisgarh. (all in reflected light with 1 Nicol) (Source: 'Radioactive Minerals', by R. Dhana Raju; published by Geol. Soc. India, Aug. 2005, 65p.).

Table 5. Some important properties of the common Radioactive Minerals

Sl. No.	Mineral (Formula)	*Up to %U	%Th	Colour	H	Specific Gravity	Crystal System	Opaque Tsp-Tslc	Remarks
A. Oxides									
1.	Uraninite	88	45	Brown	5.5	9-9.7	Isometric	Opaque	Contains Pb,Zr,REE,N,He,Ar,Ca
	Pitchblende $(U^{4+}U^{6+})O_{2+x}$	88	-	Black	≤ 4	< 6.5	Cryptocry-stalline, Amorphous	Opaque	Th &REE absent;Ca,H_2O present (both with Pb,Ag,Co,Ni,Cu,Fe, Zn sulfides)
2.	Thorianite $(Th,U)O_2$	44.6	88	Black	6.5	9.3	Isometric	Nearly opaque	High temperature formation
3.	Brannerite (UCaCeTh) $(TiFe)_2$ $(O,OH)_6$	43.6	47.5	Black	4.5	4.5-5.4	Monoclinic	Opaque	Refractory
4.	Fergusonite $(NbTaTi)O_4$	7.2	6.0	Brownish black	5.5-6	5.8	Tetragonal sluscent to Opaque	Sub-tran-refractory	High temperature, (YCeFeU)
5.	Samarskite (YCeUCaPb)$(NbTaTi)_2O_6$	16.6	3.7	Velvet black	5-6	5.6-5.8	Orthorho-mbic	Nearly opaque	Sn,W in small amounts; high temperature, refractory

6. Betafite $(CaNaU)_2 (NbTaTi)_2 O_6(OH)$	24.5	1.1	Greenish black	5	4	Isometric	Opaque	Refractory
7. Pyrochlore-Microlite $[(NaCaCeU)_2 (NbTaTi)_2 (O,OH,F)_7]$	17.1	5.5	Brown (reddish/	5-5.5 5.5(Micr)	4.2-4.36(py) -do-	-do-	Sub-transluscent to opaque	Refractory -do-

B. Silicates, Phosphates, Carbonates, Vanadates

8. Coffinite $(USiO_4)_{1-x} (OH)_{4x}$	60.2	-	Black	~3.5	~4.5	Tetragonal	Opaque	Low temperature
9. Thorite $(ThSiO_4)$	10.1	64.1	Black	4.5-5	4.5-5	Tetragonal	Isotropic	
10. Zircon $(ZrSiO_4)$	2.7	13.1	Colorless,	7.5	4.2-4.86	Tetragonal	Transparent,sub-translu-scent, opaque	Contains HfO2(up to 4%), REE, produces pleochroic haloes in host minerals
11. Allanite $(CeCaYTh)_2(AlFeMg)_3 (SiO_4)_3(OH)$	2.95	4.35	Brown to black	5.5-6	3-4.2	Monoclinic	Sub-transluscent to opaque	Produces pleochroic haloes in biotite
12. Uranophane $[Ca (UO_2)_2 Si_2O_7. 6 H_2O]$	55.6	-	Yellow	2-3	3.81-3.90	Orthorhombic	Transsparent	Massive, fibrous (in granite)
13. Xenotime (YPO_4)	3.6	2.2	Yellowish brown,flesh red, yellow	4-5	4.45-4.56	Tetragonal	Opaque	HREE,especially Er, in large amount; U,Th & Si present
14. Monazite $(PO_4,,SiO_4)$	0.1	26.4	Hyacinth-red,Yellowish brown	5-5.5	4.9-5.3	Monoclinic	Sub-transparent-translu-scent	LREE,Th,Si (Th-silicate in solid solution with Ce-phosphate) (CeLaNdTh)
15. Torbernite $Cu(UO_2)_2 (PO_4)_2. 8\text{-}12 H_2O$	47	-	Emerald-& Grass-Green	2-2.5	3.2	Orthorhom-Pseudo-tetra-gonal	Transpa-rent-Sub-translu-scent	As may replace P; forms in air at <100°C; dehydrates to meta-variety

…contd.

16. Autunite $Ca(UO_2)_2(PO_4)_2. 10\text{-}12 H_2O$	50	-	Lemon- to Sulphur-Yellow	2-2.5	3.1	Orthorhombic, nearly tetra-gonal	Transpa-rent to translu-scent	Secondary in origin; some-times with ores of Ag, Sn, Fe
17.Meta-uranocircite $Ba(UO_2)_2 (PO_4)_2. 8 H_2O$	47	-	Yellow-green	2	3.5	-do-	-do-	-do-
18. Carnotite $K_2(UO_2)_2 (VO_4)_2. 3 H_2O$	55	-	Yellow	~2	~ 4	Orthorhombic		As yellow crystalline masses/ powder in quartzose rocks
19.Tyuyamunite $Ca(UO_2)_2(VO_4)_2. 5\text{-}8 H_2O$	54.1	-	Yellow	Soft	3.7-4.3	-do-		As scales, crystalline or earthy masses

*Data from Boyle, R.W.: Geochemical Prospecting for Thorium and Uranium, Elsevier, 1982.
Hardness (in Moh's scale); Tsp: transparent; Tslc: transluscent.

4.4. Location and Identification of Radioactive Minerals: Radioactive Minerals (RM) occur usually in very low content (<1%) in rocks. Hence, they are difficult to locate and identify by normal megascopic and microscopic techniques, which are used in identification of rock–forming minerals that occur in major to minor quantities (>1%). However, the intrinsic property of radioactivity resulting in spontaneous emission of alpha – beta particles and gamma rays of RM is taken advantage of for their location as well as estimation of the contents of eU, U and Th. Thus, location of RM in a rock sample is done by the technique of `radioluxography (RLX)' or `solid state nuclear detection (SSNTD)'; the latter is a modified, easy version of the former. In

RLX, either an even surface or a thin (polished – thin) section of a rock specimen is exposed in a dark room for about 3 days to a high – speed (usually 400ASA) photographic film. In this, the film is put over the specimen, with silver-activated zinc sulfide phosphor screen (phosphor sprinkled as a thin layer on the sticky side of transparent adhesive) in between the two, using rubber bands to hold them together tight. Before exposing, an indicator (U^{6+}- bearing solution prepared from uranyl or secondary U–minerals) is put as small differently shaped spots in different corners of specimen so as to get back the original position of the two during exposure; this facilitates easy matching. After exposure, the film is developed and dried, when black spots (formed due to bombardment of alpha particles from radioactive minerals in the specimen) appear. By matching these spots with the help of indicator, the exact location of radioactive minerals in the specimen is noted. As the yield of alphas is directly dependent on the contents of U and Th that produce the black spots on the film, the intensity of blackness of spots is a measure of amount of radioactivity of RM (Figs. 16 a and b). In the SSNTD technique, instead of photographic film, an alpha–sensitive cellulose nitrate film (Kodak CA 850) or coating on a plastic film (Kodak LR 115 Film) is used and exposed in a laboratory without the necessity of a dark room. After exposure, the film is etched in 10% Na-/ or K-hydroxide solution at about 30 – 40^{o}C on a hot plate for about 30 minutes, when tracks formed due to bombardment of alphas from RM are recorded. The density of these alpha tracks in unit area is directly proportional to the contents of U and Th or intensity of radioactivity. Hence, these tracks help in both locating the RM with its shape and indicating, at least qualitatively, the intensity of radioactivity in them. After locating the RMs, their identification is carried out under a microscope (Fig. 13), based on their optical properties like colour, relief, pleochroism, internal reflections, reflectivity and micro-hardness. Generally, the above methods are used for identification of primary minerals. For secondary and metamict (crystal-structure damaged due to bombardment of radiation from RM) minerals as well as primary minerals, the technique of X-ray Diffraction (XRD) is used, after pre-concentration of RMs by heavy liquid and magnetic methods.

5. PROSPECTING (OR EXPLORATION) FOR RADIOACTIVE MINERALS

Prospecting or exploration for radioactive minerals is a multi-disciplined, -stage, -technique and wide-spectrum programme. It encompasses both field- and laboratory-based investigations. These are simultaneously undertaken, starting from regional level and ending with establishment of a cost-effective deposit. The investigative methodology adopted in exploration for RM is given in Fig. 14. Important aspects of each of these field and laboratory investigations during different stages of exploration are mentioned below.

5.1. Regional Stage: At the very outset, fertile terrains that are favourable for mineralisation of radioactive minerals are to be identified for taking up exploration. Selection of such terrains is based on geological favourability, as indicated by major deposits worldwide, . This selection is done by a scrutiny of geological literature for broad features of RM mineralisation *vis–a-vis* regional geology. Thus, (i) Proterozoic (2500 – 570 Million years or aeons, My or Ma) – Phanerozoic (<570 Ma) terrains of acidic igneous rocks (granite – pegmatite, rhyolite), (ii) sedimentary basins of similar age comprising sandstone/limestone-shale sequences and (iii) low-grade (greenschist –

amphibolite facies) metamorphic rocks, with all these three containing reductants and affected by major structural disturbances (shears, thrusts, faults, folds etc.) are fertile for U. For Th, high-grade (granulite facies) metamorphic rocks and acidic igneous rocks, and more so their derived sands, like coastal and inland placers are fertile. Similarly for RMRE, granite – pegmatites, syenites, carbonatites and their derived gravels are fertile. Apart from literature search, remote sensing technqiues are utilised to identify such fertile and favourable terrains.

5.2. Sub-Regional Stage: In this stage, aerial photos of diverse types, like black and white, colour, infra-red, multi-band maps and imageries are examined. Simultaneously in the field, geophysical and geochemical surveys are carried out in the favourable terrains to identify target-areas and local anomalies for further exploration. These surveys vastly reduce the areas of interest from regional to sub–regional level of exploration. Of the geophysical surveys, important at the sub-regional stage are airborne ones. These use small aircraft or helicopter, fitted with instruments of gamma–ray spectrometer, magnetometer and a probe; they fly at altitudes of about 100-150 m, above ground. Airborne geophysical surveys cover large areas rapidly with low-cost for line km and record radio – elemental (U, Th, K and total) and magnetic data. After necessary corrections like altitude etc., the data are converted into suitable maps of radio–element concentration and their ratios. Such maps provide critical information on the concentration level of radio–elements and their regional trends. Aeromagnetic data are used to know about structural aspects in the flown areas. Likewise, jeep-borne radiometric surveys are carried out in areas having good network of roads. Similarly, regional to sub–regional scale geochemical surveys of low- to high-density sampling are carried out over vast areas in a favourable/fertile region. Depending upon the nature of samples, these geochemical surveys are designated as litho (rock)-, hydro (water)-, pedo (soil)-, bio (plants)- and atmo (atmospheric gases)-chemical. Of these, hydrogeochemical surveys, subject to availability of water sources in the area, provide lot of information on the (i) concentration levels of radio-elements and their associated critical elements and radicals, like Na, K, Ca, Mg, F, Cl, sulphate, carbonate, bicarbonate, phosphate etc., and (ii) electrical conductivity (EC), pH and Eh. The chemical data of these surveys are converted into suitable geochemical maps. Such data are also used for geostatistical analyses. like correlation matrix and factor analysis. A critical examination of the resultant maps of airborne and jeepborne geophysical and geochemical surveys leads to identify (i) potential areas for further exploration and (ii) the physico–chemical systems, operating in the surveyed areas, and their bearing on mineralisation.

5.3. Local Anomalies to Deposit Stage: This part is a critical one in exploration. In this, comprehensive and combined geological, geophysical and geochemical surveys, together with simultaneous petro-mineralogical and physical–chemical analytical work, are undertaken so as to finally establish a cost-effective deposit of radioactive minerals

5.4. Uranium: In the geological front, first on-foot reconnoitory radiometric survey is carried out in the potential areas, identified by investigations done up to sub-regional stage. The reconnoitory radiometric survey is usually done using portable GM counter or preferably more sensitive scintillometer survey on the outcrops to identify anomalous areas of radioactivity. Such areas are marked by higher radioactivity, qualitatively by many times than the normal background ($\sim\geq$ x 5 bg; bg is measured on a nearby water-body), or in terms of absolute unit of $\sim\geq$0.1 mR (milli-Rontgen)/hour.

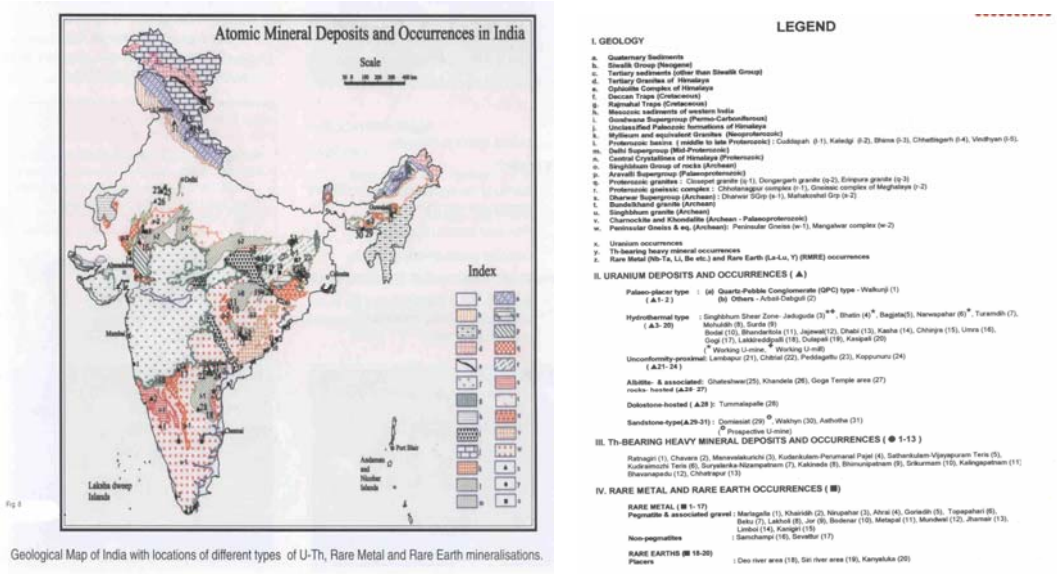
When once a radioactive anomaly is located, its areal extent is delineated by semi-detailed studies like trenching, test-pitting and channel-sampling. Specimens of the outcrops representing the entire anomalous area, thus, established, are collected. These are then analysed in the laboratory by physical (for eU_3O_8, U_3O_8 and ThO_2 contents) and chemical (U and related elements/radicals) analysis. Generally, specimens analysing more than 0.01% eU_3O_8 are given importance for further laboratory studies of petro-mineralogy, X-ray diffraction (XRD), detailed geochemical analysis involving wet chemistry, emission spectrography, X-ray Fluorescence Spectrometry (XRFS), Electron Probe Micro-Analysis (EPMA) and mineral processing. Such studies are also done on non-radioactive specimens, closeby to the radioactive specimens, so as to understand the major differences between the two and their causes. All these help to understand the physico-chemical system operating in the anomalous areas of radioactivity. In the petro-mineralogical or ore petrological investigations, various studies are carried out from megascopic to microscopic level, using ore microscope. These result in establishment of : (a) proper rock nomenclature and its mineralogy; (b) mineralogical alterations and structural-textural-weathering phenomenon having bearing on radioactivity; (c) identification of discrete radioactive and associated non-radioactive minerals, and their textural (including paragenetic) aspects; and (d) petro-mineralogical aspects, including mineralogical guides, for radioactivity in the area of radioactive-anomaly. These studies are followed by those of (i) XRD for identification of discrete radioactive phases, like primary, secondary and metamict U-minerals and associated ore minerals and (ii) geochemistry (wet chemistry, emission spectrography, X-ray fluorescence spectrometry, Electron Microprobe, Neutron Activation analysis etc.) for quantification of radio–elements and their associated elements/radicals, including high–value metals like gold and silver; these may be recovered as co-/by-products during mineral processing. After detailed ore petrology and geochemical analyses, the suite of radioactive samples are investigated by techniques of ore dressing or mineral processing. These help to (i) establish the process of recovery (acid or alkali routes), (ii) its percentage for radio-elements like U under different physicochemical conditions, and (iii) the flow-sheet for its recovery as well as its co-/by-products; all these decide the cost-effectiveness of a deposit. It should be noted that what is important in mineral exploitation is not simply the grade of the ore (e.g., percentage of U_3O_8) but how much of the metal(s) is economically recovered so as to make the venture cost-effective. When once the area of radioactive anomaly is established to be promising, its continuity is probed by geophysical (adopting magnetic, electromagnetic, resistivity etc., techniques) and geochemical surveys, while the third dimension or depth-wise extension of the mineralisation is investigated by drilling. Drilling is done at 3 levels, viz., reconnoitory, exploratory and evaluation, by core/non-core drilling. The coring type is slow (a few metres per working day) and costly (~Rs. 3,000/- per meter); it can be vertical or inclined. It gives the following sub-surface information: (i) lithological variation, (ii) provides radioactive and associated non-radioactive core for detailed laboratory studies mentioned above, (iii) correlation of lithology with radioactivity, (iv) nature and degree of alterations, (v) content and nature of reductants (like organic matter/sulphides) and clays, and (vi) their bearing on U-mineralisation. The non-coring type is vertical, fast (tens of meters per working day) and is of less cost (~ Rs. 300/meter). It enables (i) to scan the area rapidly for its radioactivity and (ii) delineation of different radioactive bands at different depths and their grade, which is done by radiometric logging along the drill-hole. A judicious mix of core and non-core drilling is followed to obtain maximum subsurface data on U-mineralisation.

5.5. Thorium: For establishing mineralization of Th, in the form of monazite, and its associated placer minerals, like ilmenite, rutile, zircon, garnet, and sillimanite, drilling of a sand deposit (like the ones along the coast) is done in both the dry zone (i.e., above water table) and wet zone (below water table), down to bed rock. Following a methodology for field-based exploration of placer heavy minerals, sand samples are collected at regular intervals for subsequent laboratory study to estimate heavy mineral resources. For this, representative sand sample is subjected to mechanical analysis by sieving, followed by magnetic and heavy media (bromoform) separation of each sieved fraction, and estimating the wt.% of different heavy minerals, including Th-bearing monazite, by microscopic , XRD and XRF studies.

5.6. Reserve Estimation, Flow-sheet and Mining: Using the sub-surface data on mineralisation like its areal extent and grade, combined with the bulk density of the ore, the ore reserve in different blocks of a deposit are estimated under different categories of proved (or measured), indicated and inferred, in the decreasing order of confidence. Simultaneously, a suitable flow-sheet is established by repetitive ore dressing operations on the run-of-the mine (ROM) ore. These operations range from laboratory to industrial scale, through pilot–plant. Sometimes, as in the case of RMRE deposits, mobile ore dressing plants are operated in the field to pre-concentrate rare metals like Nb-Ta, and Y and heavy REE-bearing xenotime in the gravel, before final recovery at industrial-scale. After establishing a deposit, it is mined. This is done first on an exploratory scale and then on industrial scale, either by open-cast or underground methods. Selection of methods depends upon various factors, like depth of mineralisation, grade, tonnage, characteristics of rock and environmental/ ecological-considerations. The ore obtained, thus, is treated on an industrial-scale in a mill for recovery of metals like U. The mill can be located close to the mining area as in the case of the uranium deposits at Jaduguda and nearby areas in the State of Jharkhand or at a farther distance, depending upon environmental, ecological, infrastructural, socioeconomic and related factors.

6. DISTRIBUTION OF RADIOACTIVE MINERAL DEPOSITS IN INDIA

6.1. Indian Uranium deposits: Uranium deposits of different types, with variable tonnage and usually of low grade (<0.1% U_3O_8), occur in different states of India (Fig. 15). Their notable features are given in the following.



Geological Map of India with locations of different types of U-Th, Rare Metal and Rare Earth mineralisations.

Fig. 15. Geological map of India showing Atomic (Radioactive) Mineral Deposits* and important occurrences, with legend of Geology (I) and Deposits/occurrences of U (II), Th (III) and Rare Metal-Rare Earths (IV).

6.1.1. Hydrothermal (Vein and Disseminated) type: This type accounts for much of the uranium resources in the country. It mainly occurs in the Singhbhum Shear Zone (SSZ), in the State of Jharkhand and to a limited extent at Gogi in the State of Karnataka. The hydrothermal type in SSZ is both of vein and disseminated type. It is hosted mostly by low-grade metamorphic (schistose) rocks containing major rock-forming silicates of chlorite, sericite, biotite, quartz and rarely tourmaline. Other host rocks include apatite-magnetite rock and quartzite. The major uranium mineral is uraninite with minor pitchblende and brannerite, associated mainly with sulphides like pyrite, chalcopyrite, bornite, molybdenite etc., and Fe (-Ti) oxides like magnetite and ilmenite. The mineralisation is accompanied by wall-rock alterations of chloritisation, sericitisation and epidotisation. It is controlled mainly by structure (shear zone, cross-folds etc.), lithology and metamorphism-metasomatism. The average grade of U varies from ~0.035 to 0.065% U_3O_8 with a total tonnage of ~60,800 U_3O_8 in various deposits within SSZ. These include the deposits of Jaduguda, Narwapahar, Turamdih, Bhatin, Mohuldih and Bagjatha, with each containing a few hundreds to thousands of tonnes of U. Besides, U is recovered as a by-product of copper from the tailings of the copper deposit at Ghatsila in the southeastern part of SSZ.

At Gogi, the hydrothermal vein type deposit is of low-tonnage (~3000 t) but of the highest grade (~0.2% U_3O_8) so far identified in India. It occurs in both the basement biotite granite and its overlying limestone, respectively, below and above the unconformity, in the late Proterozoic (~1000-600 Ma) intracratonic Bhima basin in Karnataka. The major U-minerals are pitchblende and coffinite, intimately associated with organic matter and sulphides like pyrite, chalcopyrite, galena and arsenopyrite. It is controlled mainly by structure (fault zone). In this deposit, there is a possibility of recovery of Ag as a by-product of U. Similar hydrothermal vein type uranium mineralisation along the fractures of Gulcheru quartzite in the Cuddapah basin of Andhra Pradesh is under detailed exploration; in this, gold in association with U is reported.

6.1.2. Sandstone type: The sandstone type uranium mineralisation occurs in the (i) Upper Cretaceous (~100 Ma) Mahadek sandstone in the Domiasiat-Wahkyn area in the State of Meghalaya and (ii) in the Neogene ((~<35 Ma) Siwalik sandstones along the foothills of Himalaya in the States of Himachal Pradesh, Uttar Pradesh, Uttaranchal and Jammu & Kashmir. The former is established as a medium-tonnage deposit with an average grade of ~0.1% U_3O_8. Its major primary uranium minerals are coffinite and pitchblende, associated with organic matter and sulphides like pyrite and chalcopyrite.

6.1.3. Unconformity-proximal type: This occurs in the Lambapur-Peddagattu-Chitrial area in Andhra Pradesh. It occurs in the northeastern part of the intra-cratonic middle Proterozoic (~1700-1100 Ma) Cuddapah basin, on either side of the unconformity between the basement biotite granite and its overlying Srisailam/Banganapalle quartzite. The uranium mineralisation is hosted by both the granite (~80%) and quartzite (~20%) along their structurally weak zones. It is in the form of uraninite and lesser coffinite, associated with sulphides. This deposit is of medium-tonnage with reserves of ~18,200t U_3O_8 and grade of 0.05-0.1% U_3O_8.

6.1.4. Stratabound, Carbonate-hosted type: This deposit is hosted by phosphatic siliceous dolostone of the Vempalle Formation along the southwestern margin of the intracratonic Cuddapah basin in the State of Andhra Pradesh. It is rather a rare deposit, since carbonate-rocks are considered as unfavorable hosts for U due to the soluble nature of uranyl bi-/tri-carbonate complex in which form U is normally transported. This deposit extends for ~160 km in length with a width of ~100-150 m. It is a low-grade (~0.045% U_3O_8) but large-tonnage (>15,000 t) deposit. The major uranium minerals are pitchblende and coffinite, associated with collophane and silicate minerals like quartz and feldspars. During extraction of U from this deposit, molybdenum and vanadium, each of ~200 ppm, may be recovered as by-products.

6.1.5. Albitite type: This appears to be a potential type. It occurs in the Rohil-Ghateswar-Khandela area in the State of Rajasthan. The uranium mineralisation occurs in diverse rock types that are albitised along structurally weak zones. The primary uranium minerals like uraninite are intimately associated with notable content of a host of sulphides. There is a possibility of recovering Ag as a by-product of U from this deposit that is still under detailed exploration.

6.1.6. Other types: These include (i) the pyriteferous quartz-pebble conglomerate type at the base of the Dharwar Supergroup and overlying the Archaean basement at Walkunji and Chickmagalur, and similar type but hosted by meta-arenite at Arbail and Dabguli in the State of Karnataka, with U-mineralisation in both as mainly detrital Th-bearing uraninite, thucolite, brannerite and thorite, associated with sulphide and oxide ore minerals; and (ii) the phosphorite type in the Mussorie area in the State of Uttaranchal and Mardeora in the State of Uttar Pradesh, from which U can possibly be recovered as a by-product.

Since the Proterozoic intra-cratonic basins like the Cuddapah and Bhima host diverse types of U-deposits with notable tonnage and grade, detailed exploration by AMD is being carried out in other similar basins like the Chhattisgarh, Gwalior, Vindhyan, Kaladgi-Badami, Pranhita-Godavari and Abujhmar.

6.2. Indian Thorium Deposits: Thorium deposits, in the form of the mineral, monazite (associated with other placer minerals like ilmenite, rutile, garnet, sillimanite and zircon),

occur at many places along the East and West Coasts of India (Fig. 15). Notable ones of these are at Chhatrapur-Gopalpur in Orissa, Bhavanapadu-Kalingapatnam-Srikurmam-Bhimunipatnam in Andhra Pradesh, Manvalakurichi, besides Teri inland placers, in Tamil Nadu, Chavara in Kerala and Ratnagiri in Maharashtra.

6.3. Indian Rare Metal - Rare Earth Deposits: Deposits of rare metal minerals, viz., columbite-tantalite (for Nb-Ta), cassiterite (Sn), spodumene-lepidolite (Li), and beryl (Be), occur mainly in the pegmatite belts of Bastar (Chhattisgarh)-Malkangiri (Orissa), Marlagalla (Karnataka) and in parts of Bihar, Jharkhand and Rajasthan (Fig. 15). Besides, Nb-Ta prospects in the form of pyrochlore-microlite occur in the carbonatites of the Sung Valley (Meghalaya) and Sevattur (Tamil Nadu).

Deposits of Rare Earths, in the form of the minerals, xenotime and monazite, occur in the riverine placers of the Siri River in the Jashpur district (Chhattisgarh) and Deo River in the Gumla district (Jharkhand), besides in the apatite (RE-bearing)-magnetite veins at Kanyaluka, Singhbhum dist. (Jharkhand).

6.4. Radioactive Mineral Resources in India: AMD, with its multi-disciplinary, -faceted and -dimensional exploration activities spread over all parts of our country, has established during the last 58 years the following resources of radioactive, rare metal and rare earth minerals and placer heavy minerals.

6.4.1. Uranium: As noted earlier, almost all the uranium deposits, barring possibly the Gogi deposit, established so far are of low-grade [(<0.1% U_3O_8), as per the International standard]. Nearly 1,00,000 tonnes of U_3O_8 (Chaki, 2007) under measured (proved, with ~90% confidence), indicated (~70% confidence) and inferred (~50% confidence) categories are identified so far. Uranium mineralisataion in these deposits is mostly in the form of uraninite, pitchblende, coffinite and brannerite/U-Ti oxide. It is associated primarily with many sulphides, organic matter and Fe-Ti oxides. There is a possibility of recovering some high-value metals like silver, gold, molybdenum and vanadium as by-products during processing of these ores for extraction of uranium.

6.4.2. Thorium: About 0.9-1.0 Million tonnes (Mt) of ThO_2 contained in 10.21 Mt of monazite (light REE and Th phosphate) are established so far, mainly in the coastal and to a lesser degree in the inland placer mineral sands. This resource constitutes nearly 36% of the world resource. Along with monazite, notable resources of the following placer heavy minerals (having many hi-tech industrial applications) are established in the coastal and inland mineral sand deposits:

Ilmenite ($FeO.TiO_2$): 461 Mt (~16 % of the world resource)

Rutile (TiO_2): 27 Mt (~15 % of the world resource)

Zircon ($ZrO_2.SiO_2$): 28 Mt (~5% of the world resource)

Garnet (Fe-Mg-Ca-Mn, Al Silicate): 150 Mt

Sillimanite ($Al_2O3.SiO_2$): 190 Mt

Of the total resources identified in India (by Sept. 2005), the State of Andhra Pradesh hosts 35%, Orissa 25%, Tamil Nadu 21% and Kerala 18%.

[Source: Chandrasekharan, 2007]

7. NUCLEAR OR RADIOACTIVE WASTE (RAW) AND ITS DISPOSAL

India's radioactive mineral resources proved so far, as mentioned above, are limited uranium and abundant thorium. These are intended for use by the Country's nuclear industry. This is involved (i) mostly for generation of nuclear power for civilian purpose to supplement the energy from fossil fuels of coal and oil-natural gas, and (ii) to a lesser extent to meet strategic and defense requirements. The 'Indian Nuclear Power Programme', as envisaged by the visionary, the late Dr. Homi J. Bhabha, comprises 3-stages. The *first stage* is setting up of 'Pressurized Heavy Water Reactors' (PHWR), using natural uranium as fuel and heavy water (H_2O with heavy isotope of H) as moderator; thirteen of this are already operating at places like Kalpakkam, Narora and Kaiga, besides the first two 'Light Water Reactors' (LWR) at Tarapore that use enriched uranium (U with 3-4% fissile ^{235}U) as fuel. The *second stage* envisages setting up of 'Fast Breeder Reactors' (FBR), backed by reprocessing plants and plutonium-based fuel from the reactors of first stage; already operation of the 'Fast Breeder Test Reactor' (FBTR) and 'Prototype FBR' (PFBR) has been successfully demonstrated at the Indira Gandhi Centre for Atomic Reasearch (IGCAR), Kalpakkam. The *third stage* is to be based upon Thorium-^{233}U cycle, with ^{233}U (fissile) obtained by irradiation of thorium in PHWRs and FBRs; for this an 'Advanced Heavy Water Reactor' (AHWR) is being developed at the Bhabha Atomic Research Center (BARC), Mumbai. As the Indian U-resources so far established are of low-grade (mostly <0.1% U_3O_8) and insufficient to meet the ever growing demands of the U-based nuclear power plants in the Country, the Govt. of India has entered in July, 2005 with USA into the 'Indo-US civilian nuclear deal', subject to the final approval, for supply of U-fuel to the civilian nuclear power reactors from the countries of Nuclear Suppliers Group. If this were approved, the import of U-fuel plus the indigenous production of U currently from a few operating mines and the mill at Jaduguda in the State of Jharkhand, together with those being planned in the States of Meghalaya and Andhra Pradesh, will increase substantially the present ~3% contribution of nuclear power (~3000 Mwe) to the Country's total power generation. Thus, operation of (a) the nuclear power plants, (b) units of fuel-mining, -milling and –fabrication, (c) proposed units in the near future, (d) reprocessing of the spent fuel, (e) recycling of fissile material and (f) R & D programmes in nuclear sciences, leads to accumulation of notable amount of nuclear or radioactive waste that needs to be safely disposed. Important aspects of the 'Radio-Active Waste' (RAW), such as its general characteristics, kinds, classification and different stages of its disposal are presented below, in brief.

7.1. General Characteristics of RAW: Of various types of industrial wastes, the RAW from nuclear industry has two important characteristics, viz., (i) very little space-requirement for its storage and (ii) reduction of intensity of its harmful effects with time. Thus, the operation of a large nuclear power station for one complete year results in only 4 cubic meters (cu. m.) of high-level RAW and ~100 cu. m. of other long-lived waste materials, even after conditioning by incorporation into a solid host material. It was estimated that in India by the year ~2000, there will be ~3.3 billion curies of radioactivity contained in high-level RAW, with a volume of ~11,700 cu. m. in liquid form that on solidification reduces to ~600 cu. m. (Raja Ramanna: *Safety of nuclear installations*, Nuclear India, v. 14, no. 8 & 9, 1976, DAE, Mumbai). Furthermore, the intensity of radioactivity at the end of one year reduces nearly to 1/10 of the level existing at the initial stage, and after 100 years, the level of radioactivity remaining in the used fuel is only 1% of what it was after one year of discharge from the reactor (*Management and Disposal of Used Nuclear Fuel and Reprocessing Wastes,* Uranium Institute, London, 68 p., 1983). Contrary to the general belief, the components of the used

nuclear fuel are not unique amongst industrial wastes in the sense that they are neither the only toxic nor the only carcinogenic/mutagenic wastes generated. Several of the hazardous wastes produced routinely by many industries, like lead, mercury and dioxin are stable, which means they never decay. In contrast, the radioactivity of nuclear wastes decays progressively and quite predictably over time, thereby resulting in the marked reduction of both toxicity and handling problems.

7.2. Kinds and Classification of RAW: The RAW, arising from production of nuclear power, is mainly of four kinds. These are: (i) residue left from the processing of U or low-level but long-lived naturally occurring elements mined with U, and chemicals used in the separation processes; (ii) materials and equipment, like protective clothing, cleaning materials, filters, etc., which got contaminated during different stages of nuclear fuel cycle; (iii) wastes resulting from the eventful dismantling of nuclear reactors; and (iv) wastes arising from the nuclear fuel after it has been used in a nuclear reactor, which contains both used fuel and the wastes formed due to its reprocessing. Of these 4 kinds, the (iv) accounts for nearly 99% of the radioactivity produced during the generation of nuclear power; it also includes the only high-level and some long-lived, intermediate- and low-level RAW, produced during reprocessing of the fuel.

Based on the intensity of radioactivity, the RAW is broadly classified as low-level (within the range of ~1 micro-curie per gallon of cu. m. or so), high-level (with 100s to 1000s of curies per gallon or cu. m.) and intermediate-level (with intermediate activity, and which after 100 y still contains significant amounts of radio-nuclides but with negligible release of thermal energy) wastes. The half-life (years) and radioactivity (Curie, Ci) of main high-level and long-lived radio-nuclides in solid RAW are as follows:

^{3}H: 12.3 & 300; ^{14}C: 5.6 x 10^{3} & 2; ^{60}Co: 5.27 & 20,000; ^{59}Ni: 8.0 x 10^{4} & 50; ^{63}Ni: 125 & 500; ^{90}Sr: 28 & 10,000; ^{129}I: 1.7 x 10^{7} & 0.5; ^{135}Cs: 3 x 10^{6} & 0.5; ^{137}Cs: 30 & 100,000; and ^{239}Pu: 2.4 x 10^{4} & 0.5.

The low- and intermediate-level RAW is usually disposed of by (i) shallow land burial, (ii) emplacement in suitable abandoned mines or (iii) by deep well injection and hydraulic fracturing; it does not pose major environmental problems. On the other hand, the high-level and long-lived trans-U-bearing RAW (with appreciable to high radiation hazards and toxicity) requires complete isolation and safe disposal/storing in a medium of high integrity.

7.3. Stages in the Disposal of RAW: There are three main stages in the disposal of RAW, the first involving initial storage, followed by reprocessing and conditioning of the reprocessed wastes. The second stage involves the storage of the solidified high-level and long-lived wastes in a monitored place for ~20 years. The third stage comprises transport of the packed RAW and final disposal in a medium of high integrity.

7.3.1. Initial Storage: When the used fuel is taken out from the reactor, about 96-98% of it is still U, but with the fissile content significantly reduced; this makes it inefficient for generating electricity. The balance, 2-4% contains the elements that result from the processes in the reactor, with about ¾ being fission products. These contain high-level but relatively short-lived (with half-life of 30 y or less) elements of intermediate atomic weight. Their radioactivity virtually disappears in ~1000 years and after that period, they will no longer be a problem. In contrast, the ‘trans-uranium (TRU) elements’ are generally of low-level but long-lived, and are radiogenically and carcinogenically very toxic. If stored, they will last or

cause concern for 500,000 to 1,000,000 years. On removal from the reactor, the used fuel is highly radioactive and contains 'residual heat' due to continued radioactive disintegration; hence, it requires special handling. As the initial rate of reduction of radioactivity and the associated output is quite rapid (1/10 of radioactivity in the first year), the fuel is invariably stored for an initial period, using either 'wet storage' or 'dry storage' technique. In the widely used wet storage, fuel bundles are stored in water pools. Water in these serves both as a coolant and as a simple optically transparent radiation-barrier. In the dry storage method used for some heavy-water reactor fuel (CANDU type) and for gas-cooled reactor fuel, the used fuel is stored in a cask, vault or dry well with cooling achieved by natural or forced air circulation. At the Tarapur nuclear power plant, air-cooled vault with connective air circulation system is used.

7.3.2. Reprocessing and Conditioning of Reprocessed Wastes: After initial storage, radioactive wastes, constituting nearly 2-4% of the original fuel element, are in some cases reprocessed to extract uranium and plutonium by chemical processes. In the reprocessed or non-reprocessed RAW, more than 93% of radioactivity is concentrated in one high-level stream that is temporarily stored in cooled tanks as a liquid. Although it is proved feasible to store this high-level waste as a liquid in stainless steel tanks, the waste is generally 'solidified' or 'immobilized' in a host material for easy handling and later disposal. Generally, the host-materials used are borosilicate- and aluminosilicate-glasses. The 'vitrification' process, by which highly radioactive, reprocessed liquid waste is immobilized in glass, has been in commercial operation in France since 1978. In India, high-level RAW is immobilized by incorporating it in the matrix of alkali borosilicate glass. The remainder of RAW from reprocessing plants comprises a number of different liquids and solids in much greater dilution than in the high-level waste stream. From these, the long-lived RAW is also incorporated in a suitable stable solid.

7.3.3. Storage in Monitored Place for ~20 years: Following solidification, the high-level and long-lived RAW is kept for ~20 years in a monitored surface or near surface storage facility. In the case of the vitrification, the glass blocks, encapsulated in steel containers, are stored in specially designed concrete pits that are provided with water- cooling or forced air-cooling. The RAW is then packed in various corrosion-resistant metallic and ceramic materials. It is transported to a disposal site, using heavy transport casks of steel, with a neutron-absorbing layer and external cooling fans.

7.3.4. Transport and Final Disposal: This third and final stage involves the disposal of the conditioned and packaged RAW in a suitable place. This is the most critical and crucial stage in the treatment of RAW, as the protection of man and the environment solely depends upon the efficacy of the disposal system. Therefore in almost all the major nuclear countries, active research is being carried out on several aspects involved in the selection of proper disposal sites as well as in developing suitable barriers to ensure maximum safety to man and the environment from hazards of radioactivity. These barriers are mainly two types, viz., man-made or the engineering barriers and geological barriers. The first category includes (a) selection of proper solidifying material, incorporating RAW and packing material immediately around the waste, (b) various layers of encasing material, (c) buffer and backfill materials around the waste-package in the repository and (d) the material to be used to seal repository. While man-made barriers provide additional safety factor, it is the geological barrier that ultimately constitutes the basic protection against possible radiotoxic effects from the low-level but long-lived TRU elements. Three types of such barriers to dispose of high-level and long-lived RAW are suggested, viz., (i) ice sheets, (ii) sea bed and (iii) geological

formation. Due to many unfavorable factors, like extended transport, mobility of sea water resulting in dispersal of RAW, poor retrievability and monitorability, and ecological problems, the first two are not favored. Hence, storage of RAW in a geological formation is the best mode of disposal available. Selection of a suitable rock formation and the site within that rock formation for a possible repository of high integrity needs extensive in-depth studies. These involve geological, geophysical, hydrological and chemical aspects. Research on these aspects is going on since many years in the terrain of Columbia basalts in USA and Granitic batholith in Canada. In India, active investigation is going on for identification of final disposal-site in both the granitic and basaltic terrains [A.V. Phadke, R. Dhana Raju and T.N. Parthasarathy: *Petromineralogical considerations in Selection of Rock Candidates as High-level and Long-lived Radioactive Waste Repository in India*, Geological Society of India (Bangalore) Memoir 5, pp.89-106, 1986].

Suggested Bibliography

1. Chaki, A. (2007). Exploration Strategy for Atomic Minerals in India. Indian Nuclear Sciety Annual Conference (INSAC)-2007, Nov. 21-24, Nuclear Fuel Complex (NFC), Hyderabad, Abst.: I-1.
2. Chandrasekharan, S. (2007). Mineral Sand Resources in India – Some Constraints in Exploitation. INSAC-2007, Nov. 21-24, NFC, Hyderabad, Abst. : E-5.
3. Dhana Raju, R. (2005). *Radioactive Minerals.* Geological Society of India, P.B. No. 1922, Gavipuram P.O., Bangalore – 560 019, 65 p.
4. Dhana Raju, R. (2007). Nuclear Fuel Resources in India. Proceedings of the 'Foundation-Day Lecture' of Prof. C. Mahadevan's Students and Admirers Association, Belson Tajmahal Hotel, Secunderabad, Dec. 29, 2007, pp. 3-19.
5. Frondel, C. (1958). *Systematic Mineralogy of Uranium and Thorium.* US Geological Survey Bulletin 1064, Washington D.C., 400p.
6. Frondel, J.W., Fleischer, M. and Jones, R.S. (1967). *Glossary of Uranium- and Thorium-bearing Minerals.* US Geological Survey Bulleting1250, Washington D.C.
7. George D'Arcy, R. (1950). *Mineralogy of Uranium and Thorium Bearing Minerals.* RMO-563, USAEC Technical Information Service, Oak Ridge, Tennessee.
8. Heinrich, E.W. (1958). *Mineralogy and Geology of Radioactive Raw Materials.* McGraw-Hill, New York, 654p.
9. Nininger, R.D. (1954). *Minerals for Atomic Energy.* D. Van Nostrand Co. Inc., New York, 367p.