CHAPTER 1

INTRODUCTION

1.1. General considerations:

Production of the high specific activity radioisotopes (especially carrier-free ones) from materials irradiated in nuclear reactors presents an important field of radiochemistry. The high rate of production of various carrier-free materials is paced by the increasingly broad applications of radioisotopes to problems of science and industry **(Veljković and Milenković, 1958)**. For example, the availability of radioisotopes of the highest possible specific activity is necessary for nuclear medicine applications (e.g., radiolabeling of tumor-specific antibodies for both diagnostic and therapeutic applications and the use of receptor mediated radiopharmaceuticals that are potentially very important for the clinical evaluation of neurological diseases), so that they will not cause either a toxic or pharmacological response in the patient **(Mirzadeh et al., 1992)**.

Carrier-free radionuclides can be produced either by (i) direct irradiation of special target materials, only if the product is chemically different from the target material, (ii) Szilard-Chalmers method which utilizes the changes in the atom stage at the moment when the (n,γ) reaction is taking place to separate the produced isotope from the bulk of unreacted target, which results in obtaining a high specific activity radioisotope **(Nath et al., 1958; Svoboda, 1958)**, or (iii) the fission reaction itself (e g., fission reaction of ^{235}U). For the case in which the product is not chemically different from the target material (e.g., the production of ^{99}Mo by ^{98}Mo (n,γ) ^{99}Mo reaction), the product radioactivity is usually diluted with the great fraction of the unreacted target **(Ayers et al., 1985)**.

Currently, fission products of ^{235}U are considered excellent potential sources of high specific activity radioisotopes. The processes used to fragments and emits two or three free neutrons, along with about 200 MeV of energy per nucleus fissioned **(Bodansky, 1996)**. A helpful insight into some of the characteristics of the fission process is obtained by the use of the liquid-drop model of the atomic nucleus **(Glasstone, 1955)**. Uranium-235 is the only naturally occurring nuclide that can be fissioned with thermal neutrons. There are other nuclides, such as ^{233}U and ^{239}Pu, that can also be fissioned by thermal neutrons but they are not naturally occurring **(Arora and Singh, 1994)**.

The probability that fission, or another reaction, will occur is described by the "cross-section" for that reaction. For neutron induced reactions, the cross-section is conceptually an area surrounding the target nucleus and within which the incoming neutron must pass for the capture to take place. The cross-section for fission increases greatly as the neutron velocity, v, reduces (the so-called $1/v$ effect). In odd-numbered nuclei such as ^{235}U, the cross-section for fission becomes very large at thermal energies, i.e. when the neutron has slowed down to be in thermal equilibrium with the surroundings. Hence the main application of uranium-235 fission is in thermal reactors incorporating a moderator to slow the neutrons down, such as the common "Light Water Reactors" **(Marks, 1999)**. Cross-section of ^{235}U for fission induced by thermal neutrons is 585 barn, i.e., 585×10^{-24} cm^2 **(Ehman and Vance, 1991)**.

The fission reaction of ^{235}U can be written in the following general form:

$$n + {}^{235}\mathrm{U} \longrightarrow {}^{236}\mathrm{U}^* \longrightarrow (A_1, Z_1) + (A_2, Z_2) + N\mathrm{n} + \gamma\text{'s}$$

In this form, additional particles, most notably α particles, were ignored. This expression represents the formation of ^{236}U* and split of it into two fragments (with atomic mass numbers A_1 and A_2) and N neutrons

($N = 2$ or 3). From conservation of charge and of numbers of nucleons, $Z_1 + Z_2 = 92$ and $A_1 + A_2 + N = 236$. If $A_1 = A_2$, or nearly so, the fission process is called "symmetric fission". Otherwise it is called "asymmetric fission" **(Bodansky, 1996)**. At low neutron energies, asymmetric fission predominates. At high energies, neutrons and charged particles will produce a single-humped fission yield curve indicating that symmetric fission is favored.

For the binary fission of ^{235}U by thermal neutrons, the fission products are a mixture of nuclides of 37 elements; from zinc (atomic number 30) to dysprosium (atomic number 66), and their atomic masses are distributed between 72 and 161 **(Lee and Bang, 1983)**. Actually, some 200 different isotopes have been detected, most of them are radioactive.

1.2.2. Radioactive decay of the initial fission fragments:

Decay of fission fragments proceeds via **(Glasstone, 1955; Arnikar, 1994; Bodansky, 1996)**:

1. *Gamma-ray emission from excited nuclei.* Since the initial fission fragments are usually formed in excited states, they decay by gamma-ray emission to the ground state before beginning a β^--decay chain. Gamma decay usually occurs within about 10^{-14} s of the fission event.

2. *Alpha decay.* Alpha-particle emission, with energies up to 20 MeV, occurs in 0.2 % of fission events.

3. *Beta emission.* In fission, aside from the few emitted neutrons, the average value of Z/A of the initial fragments must be the same as that of the fissioning nucleus. Thus for their mass region, the fission fragments will be proton-poor or, equivalently, neutron-rich. For this reason, fission fragments undergo β^- decays to reach the stable nuclei.

4. Delayed neutrons. Most of the neutrons produced in fission are emitted promptly, essentially simultaneously with the fission itself. However, some neutrons are emitted from nuclei produced in β^- decay of the original fission fragments, these are called "delayed neutrons". This delay has a time scale determined by the β^--decay half-life of the precursor to the neutron emitter. The neutron emission itself follows virtually immediately after the β^- decay. For ^{235}U, delayed neutrons form about 0.65 % of fission neutrons. The precursors for these neutrons have half-lives ranging from 0.2 to 56 s, with the largest group having a half-life of about 2 s. The existence of these delayed neutrons is crucial for the stable operation of nuclear reactors.

1.2.3. Specific activities of ^{235}U-fission isotopes:

The maximal in time (irradiation to saturation) specific activity, $A_{s(max)}$, of any isotope born in fission of ^{235}U can be calculated by the following equation **(Knoll, 1961)**:

$$A_{s(max)} = \frac{A_v a}{3.7\times10^4\, M}\,\sigma\,\phi\,Y_f \qquad (\mu\text{Ci/g}) \qquad (1.1)$$

Where,

A_v = Avogadro's number ($A_v = 6.023 \times 10^{23}$).

a = isotopic abundance of ^{235}U in the uranium target (a = 0.72 % by weight in natural uranium).

M = mass number of ^{235}U (235).

σ = cross-section of ^{235}U for fission induced by thermal neutrons (585 barn, i.e., 585×10^{-24} cm^2).

ϕ = the thermal neutron flux, n cm^{-2} s^{-1}

Y_f = fission yield of the considered isotope.

Specific activity, $A_{s(0)}$, at end of irradiation for time t_R for any isotope produced from ^{235}U-fission can be calculated as follows:

$$A_{s(0)} = A_{s(max)}(1 - e^{-\lambda t_R}) \qquad (\mu Ci/g) \qquad (1.2)$$

Radioactivity, A_0, at end of irradiation for any isotope produced from ^{235}U-fission reaction can be calculated as follows:

$$A_0 = A_{s(0)} W \qquad (\mu Ci) \qquad (1.3)$$

Where,

W = weight of the irradiated uranium target (g).

1.2.4. Relative importance and uses of fission products:

From the chemical standpoint, it is the nature of the elements present in the fission products that is important. The existence of these elements in several different isotopic forms is not significant, since the isotopes of a given element have essentially the same chemical properties. Thus any separation process, except isotopic separation processes, that separates one isotope will separate all the other isotopes of the same element **(Glasstone, 1955)**. In chemical processing, there are four factors that determine the relative importance of fission products; these are given below.

1. Mode and energy of decay. The isotopes which emit only beta radiations of fairly low energy are mostly ignored.

2. Chemical behavior. The isotopes which exist in various species and those which show abnormal behavior in very dilute solutions have special importance in separations processes.

3. *Half-life.* Generally, fission products of very short or very long half-lives are not taken in consideration.

4. *Fission yield.* Relative importance of a radioisotope increases as its fission yield increases.

The utilization of fission products is in a sense an aspect of the waste disposal problem. Fission products have important applications in many fields. These applications are mostly dependent upon the ionization and/or radiation effects produced by the beta and gamma radiations. Some of the possible uses of fission products are summarized in Table 1.1.

1.3. Uranium targets:

1.3.1. Irradiation behavior of uranium:

When uranium is irradiated with neutrons, it tends to distort and to swell due to (i) the crystallographic modifications (which occur at different temperature ranges), and (ii) the fission process. Crystallographic properties of uranium are shown in Table 1.2. Much effort has been devoted to evolving carefully controlled methods for the casting and heat treatment of the metal to ensure the metallurgical properties needed to minimize these effects.

Irradiation of unalloyed uranium in the temperature range (400-670°C) is accompanied by significant and variable volume increase. This swelling is a major concern in reactor design and operation since in some cases it may contribute to fuel failure. A further cause of trouble is that solid fission atoms occupy more volume than did the fissioned uranium atoms. The swelling thus occasioned is independent of the irradiation temperature and is 3% per atom percentage burn-up of uranium. When the irradiation temperature has been over 300°C, the fission product gases xenon and krypton agglomerate and form small bubbles visible in replicas taken from irradiated metal as voids of 0.01 to 1.0 μ in diameter. A volume

Table 1.1. Possible uses of fission products **(Glasstone, 1955).**

Application	Remarks
Activation of phosphors	For luminescent pigments for use in signs visible in the dark. Very pure isotopes necessary.
Static eliminators	Ionization of air allows static charge to leak away. May also prevent agglomeration of fine particles in grinding processes. This is useful in printing, textile, plastic, and rubber industries.
Fluorescent light tubes	Permanent ionization of the gas will permit faster starting and lower starting voltages.
Instruments	Thickness and level-indicating gauges based on penetration of beta- or gamma-rays. Marking of interface between products in pipelines.
Radiography	Gamma-ray sources of high activity and low energy give sharp definition. This is useful in nuclear medicine and in industry, e.g., well logging in petroleum industry.
Cold sterilization of foods and drugs	Beta- and gamma-rays destroy microorganisms. Especially advantageous for heat-sensitive products, e.g., antibodies. Prevent off-taste flavors in canned foods; increase shelf life.
Power source	Direct conversion of beta-particle energy into electricity, e.g., in a battery. Pure beta-emitter of relatively long half-life desirable, e.g., strontium-90.
Heat source	Because of self-absorption of beta and gamma rays, radioactive material has higher temperature than surroundings.
Chemical reactions	Facilitation of flame propagation in internal-combustion and jet engines; polymerization, etc

Table 1.2. Crystallographic properties of uranium at atmospheric pressure **(Peehs et al. 1996).**

Allotropic modifications	**Geometry**	**Lattice parameters**	**Temperature**
α-uranium	Orthorhombic	$a = 2.858$ Å $b = 5.876$ Å $c = 4.955$ Å (at 25.15 °C)	< 669 °C
β-uranium	Tetragonal	$a = 10.759$ Å $c = 5.656$ Å (669)	669-776 °C
γ-uranium	Body-centered cubic	$a = 3.524$ Å (at 776 °C)	776-1135 °C

increase of several percent may be caused by the gas bubbles, the increase becoming greater as irradiation temperature and burn-up is increased. The effects of swelling may be minimized by the use of alloying elements, such as Nb, Cr, Mo, Zr, or Al, and by employing high strength cladding over the target element **(Cordfunke, 1969)**.

1.3.2. Cooling of irradiated uranium targets:

Cooling of the irradiated uranium targets after removal from the reactor is necessary to allow a drop in the dose level and in the heat level resulting from β/γ-ray emissions by short-lived fission products. The cooling time differs from one case to another according, mainly, to: (i) the half-life of isotope(s) to be separated and (ii) time needed for separation process(es).

Major contributions to the total radioactivity of fission products (in curies) made by a number of radioisotopes after various cooling times are shown in Figure 1.1. The results are based on the supposition that the targets have been in a reactor for an extended period so that at the time of target removal from the reactor an approximate condition of equilibrium has been attained. It is evident from Figure 1.1 that the isotopes of some twelve or thirteen elements are responsible for nearly all of the activity after 100 days or so of cooling **(Glasstone, 1955)**.

1.3.3. Dissolution of irradiated uranium targets:

The irradiated uranium targets are either submitted to acidic dissolution (e.g., dissolution in HNO_3, HCl, or H_2SO_4 acid solutions), or to alkali digestion (e.g., digestion in NaOH or KOH solutions). The choice of dissolution (or digestion) method depends on many factors such as: (i) the chemical composition of the irradiated target, (ii) the processing technique

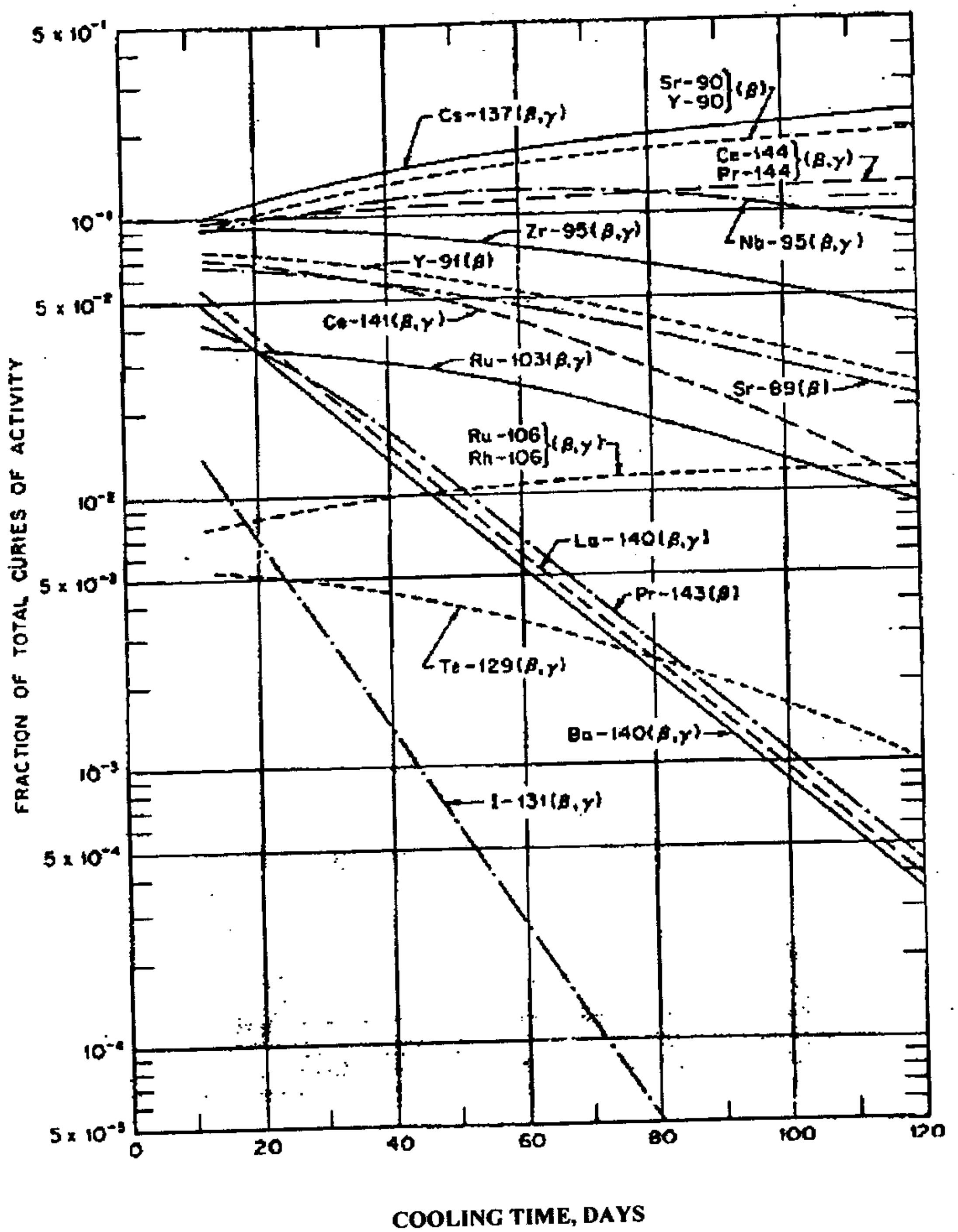


Figure 1.1. Isotopes of major contributions to radioactivity of fission products (**Glasstone, 1955**).

and the separation method used (precipitation, ion exchange, etc.), and (iii) the isotope(s) to be separated and recovered. According to the same previous factors, catalysts (oxidants and/ or other chemical reagents) may be added during dissolution (or digestion).

Generally, the equipment used for dissolution (or digestion) includes the following three major units: (i) a charger of the irradiated target, (ii) dissolution (or digestion) vessel, and (iii) off-gas system. The off-gas system is concerned with the disposal or recovery of the gaseous radioactive fission products (krypton, xenon, and iodine), and other gases obtained during dissolution (or digestion) process.

Foster et al. (1955) described an off-gas processing equipment for a typical batch uranium fuel dissolution in nitric acid. In nitric acid dissolution, the heat generates is usually so great that 90-95 % of the gas that leaves the dissolver is steam. The gases remaining after the steam has been condensed are principally oxides of nitrogen, with radioactive (and other) gases present as minor constituents. The first piece of this equipment is a condenser. If the condenser is connected so that the gases enter the top and leave the bottom, much better absorption of NO_2 by the condensed water vapor will be accomplished. This is because the condensate drains down the condenser tubes, rendering the entire tube area available for NO_2 sorption. The resulting acid can be returned to the dissolver, reducing the acid required for the metal dissolution, to remove iodine from the off-gas stream, the gas is heated to about 200°C and then passed through a packed tower where the packing is coated with silver nitrate. The iodine in the gas reacts with the silver nitrate to form silver iodide. After iodine removal, the remaining gases may be vented to the stack.

Oak Ridge National Laboratory (ORNL) in U.S.A. developed what is called "the low-temperature adsorption process" used for rare-gas isolation. In this process, after dissolution in nitric acid and removal of nitric oxide, nitrogen dioxide, nitrous oxide, and hydrogen, the process gases are cooled before entring the liquid-nitrogen-cooled charged adsorption beds. The latter, which contain activated charcoal in a parallel tube arrangement, are maintained at about – 180°C to adsorb krypton and xenon. The rare gases are removed from the charcoal by warming the charcoal bed and venting it to a cold trap maintained at about – 210°C. When desorption is completed, the trap is heated to transfer the collected crude rare gases under moderate pressure to lead shielded gas cylinders for shipment **(Ayers et al., 1958)**.

Nesmeyanov (1974) mentioned methods for separation and purification of fission iodine. In one method, the irradiated uranium is dissolved in concentrated HNO_3, the major part of iodine being evaporated and collected in a condenser maintained at a temperature of 3 °C. The iodine left in the nitric acid solution is distilled off by a stream of water vapor together with oxygen. Oxygen oxidizes nitrogen oxide to nitrogen dioxide. Thus, in the condenser, along with iodine, a mixture of nitric and nitrous acids is collected. The nitrous acid is oxidized by H_2O_2 to nitric acid and the iodine is distilled off on a fractionating column into sodium hydroxide. Then, for the solution to be completely freed from the impurities present, sulfuric acid is added and the solution is again distilled on the fractionating column into a dilute solution of sulfurous acid. The hydroiodic acid formed is neutralized with sodium bicarbonate to pH 9. The yield of iodine is about 85 % and its specific activity reaches 10^4 Ci/g of NaI. Another method of purifying radioactive iodine consists in oxidizing after the removal of the major portion of nitric acid and H_2O_2, with a solution of $KMnO_4$ in 20 % H_2SO_4 solution. After traces of HNO_3 are removed, to the solution are added concentrated H_2SO_4 and a solution of H_3PO_4 with a small amount of H_2O_2 as a catalyst. The elemental iodine formed is distilled into a receiver containing a solution of sulfurous acid and then the HI is neutralized by sodium bicarbonate. A third method provides for the oxidation of iodine, after the target is dissolved in nitric acid, by a solution of 50 % chromium trioxide in sulfuric acid to iodate ion. After this, the nitric acid is distilled off and the solution treated with oxalic acid to reduce the iodine to the elemental state and the chromium to Cr_2O_3. Then the iodine is distilled off just as in the methods described above.

Henrich and Schlich (1984) invented a method for desorbing fission iodine from a solution containing nitric acid and nuclear fuel, in a dissolver. In this process, at least a part of the solution is distilled by boiling creating an iodine-containing vapor, and the condensate vapor is conducted in an ascending condenser in countercurrent with its condensate. The resulting condensate is returned to the dissolver. The desorption of the iodine in the condenser is affected by means of a gas, where at least in the course of one to several hours towards and after the end of the dissolution, nitrogen oxides selected from the group consisting of NO_2 and mixtures of NO and NO_2 are introduced into the solution in order to reduce "hard to distill" or "non-distillable" oxidized iodine species. Towards the end of the desorption process, after the fission iodine content has dropped to several parts per thousand to several percent, inactive iodine carrier is added to the solution in order to accelerate the desorption of the remaining iodine.

In a process invented by **Koehly and Madic (1987)** for the recovery of ^{99}Mo, 10 roll-bonded ^{235}U/Al-irradiated targets (each is formed from ~4 g ^{235}U and ~35 g Al) are dissolved in sulfuric acid (0.1 to 8 M). During dissolution, advantageous use is made of a tantalum apparatus for the purpose of limiting corrosion. In order to prevent explosion risks and radioactive releases, dissolution is preferably carried out in a vacuum and with the circulation of an inert gas, such as nitrogen or argon. The gaseous flux that is charged with hydrogen, which given off by dissolving reaction, and also xenon passes successively into a gas washing or scrubbing means, on to silver zeolite-charged cartridges for trapping any iodine which may be have given off, and on activated carbon-charged cartridges in order to retaining xenon isotopes.

In a technique used for the triple production of ^{99}Mo, ^{131}I, and ^{133}Xe from a single irradiation, which is used in the Institut National des Radioéléments (I.R.E) in Belgium **(Salacz, 1989)**, recovery of xenon-133 is achieved during digestion of the targets. When the targets (each is essentially composed of 30 g Al and 4.2 g of 89 to 93 % enriched U) are digested in 3 M NaOH-4 M $NaNO_3$ solution. Xenon is liberated and is carried by helium towards the condensation traps, where it is condensed on copper clippings cooled down to –196°C by means of liquid nitrogen. Further down from this first trap, there is an active carbon trap installed which is also cooled, preventing discharge of xenon towards the ventilation system. The trapped xenon is subsequently transferred in a container and shipped to a purification plant.

Hladic et al. (1989) described a process for the production of fission ^{99}Mo in which natural uranium as uranium oxide is used as target material. According to a representative example, 400 g UO_2 in three irradiation cans of 20 mm diameter and 150 mm length are irradiated for 100 h at 5×10^{13} n/cm^{2}s. Radioiodine and xenon, which escape during the decanning operation, are removed by suction through an iodine-absorption filter and a xenon-delay line. The iodine filters consist of alumina impregnated with silver nitrate. Decontamination factors of $> 10^3$ for radioiodine have been observed under process conditions. The rare-gas-delay line consists of molecular sieve and charcoal-filled absorbers at 30°C. Under process conditions, the stay period is $>$ 50 days for xenon. The irradiated uranium oxide is transferred into the dissolver and 700 ml of HNO_3, resulting in a final concentration of 500 mg/ml of uranium, are added. During the dissolution process, air is continuously fed in the dissolver by an air lift in order to oxidize lower nitrous oxides to NO_2 and on the other hand to establish nitric acid circulation. In this process the main part of NO is washed out by the condensate in the reflux condenser. Addition of $Hg(NO)_2$ to the feeding acid in a concentration of 1.1 mol/l allows the retention of the main part of radioiodine in the uranium-fission product solution. The reaction gases from the dissolution process pass a sodium hydroxide absorber before feeding in the iodine and xenon line. It is possible to establish a ^{133}Xe-production line by a bypass containing a charcoal-filled absorber unit at 80°C which retains the necessary xenon radioactivity. Finally, the gas is fed into the cell ventilation after passing the xenon-delay line. After passing usual radioiodine safety and particle filters these cell effluents are fed into the ventilation duct.

In Japan Atomic Energy Research Institute (JAERI), UO_2 pellets (2.6 % enrichment) were chosen as a target material for the production of fission ^{99}Mo **(Kudo et al., 1989)**. UO_2 pellets were enclosed into two capsules. The primary capsule was made of 304-stainless steel and the secondary one of aluminum. The gaps between the pellets, primary and secondary containers were 0.05 mm. Helium was filled in the plenum inside the capsule. The secondary capsule was provided with fins to enhance the cooling efficiency with water. When capsules are opened, after irradiation and cooling, radioactive iodine and rare gases stored in the plenum inside are released. These gases are removed in an evacuated reservoir and stored there. The UO_2 pellets are transferred into a dissolution vessel containing 10 M HNO_3. During the dissolution process, some portions of radioactive gases are evolved. These gases are introduced to alkali scrubbers connected to the dissolution vessel to collect ^{131}I and then transferred through pipings into molecular sieve columns, cooled with liquid nitrogen to collect ^{133}Xe.

In the process of fission ^{99}Mo production developed in the Argentine Atomic Energy Commission, the target consists of an Al/U alloy core (UAl_x) with 1 g uranium enriched to 90 %, which is aluminum-wrapped as a sandwich **(Marqués et al., 1989)**. The methodology employed involves depressure conditions during almost all the process in order to keep the fission gases in a closed system. The irradiated targets, in the first chemical step, are dissolved in hot alkaline medium with a continuous flow of N_2. The solution, after cooling, is filtered through a fritted plate, built in stainless steel. The H_2 produced during dissolution of Al/U plates in alkaline medium is driven into an oxidation system with CuO at 400 °C and the formed water is condensed. The remaining gases (a nitrogen stream permanently carries the fission gases through the system) are collected in pre-evacuated stainless steel tanks (total volume = 400 l). After a week of storage, the gases are transferred to four tanks (100 l each) filled with activated charcoal. After another week of storage, the gases are carried into five tanks (89 l each) filled with activated charcoal. These off-gases are delivered to the ventilation system of the hot cells, which involves fourteen 200-l towers, located in the cellar-containing activated charcoal, which can work in series connection or in parallel. After passing these columns, the air is forced through a battery of absolute filters.

At Chalk River Nuclear Laboratories (CRNL) in Canada, highly enriched uranium (HEU) is used for ^{99}Mo production **(Burrill and Harrison, 1989)**. The target is made from U/Al-fuel core, its outer coat is made of Al with fins. The target is mechanically stripped ready for dissolution. After irradiation and a short cooling period, eight targets are stripped and dissolved initially in dilute HNO_3 which contains $Hg(NO_3)_2$ to assist aluminum dissolution. The dissolver diameter has been limited to less than 15 cm for criticality concerns. Concentrated HNO_3 is added part way into the dissolution to achieve a maximum dissolution rate. The dissolution is rapid and violent. Foaming into the reflux condenser is typically observed in glass equipment in the laboratory. About one hour is reserved for dissolution. Water is added to the solution for pH adjustment at the end of the dissolution. Dissolving more than eight targets per batch using this dissolution recipe causes foaming past the condenser into off-gas scrubbers.

In the process developed by Commissariat à l'Energie Atomique (CEA) in France in the 1980's for a weekly production of ^{99}Mo **(Bourges et al., 1996)**, the targets (consist of an aluminum-clad uranium plate, UAl_X) are dissolved in H_2SO_4 and Hg_2SO_4 at 95°C, with a gas pressure drop of 4 to 10 cm H_2O. This operation causes the liberation of hydrogen and xenon. The hydrogen is diluted to 4 % by volume in a nitrogen stream at a flow rate 25 times that of the hydrogen flow rate (0.386 m^3/dissolution). The released radioxenon is then driven by the nitrogen stream towards the condensation traps (soda cartridges and loaded silver zeolite) to prevent accidental release of iodine, and then it is trapped on two activated charcoal columns at room temperature.

In molybdenum production cycle from uranium silicide, U_3Si_2, targets which is carried out in Karlsruhe Nuclear Research Center (KFK), the irradiated targets (which are mixed with aluminum powder and covered with an aluminum-magnesium alloy called AlMg1) are digested in 6 M KOH solution. The off gas of this alkaline digestion contains the hydrogen generated from the aluminum dissolution and the magnesium conversion to the hydroxide together with the equivalent amount of the fission noble gases. The major radioactivity of this gas stream is caused by Xe-133. The noble gases leave the dissolver at its upper end driven by nitrogen, which is constantly metered into the dissolver together with the hydrogen. The hydrogen is oxidized via a copper oxide oven and the resulting water vapor is then condensed. Xenon is collected together with the nitrogen in pre-evacuated stainless steel tanks and later pumped to the xenon delay section passing deep bed carbon filters **(Sameh and Bertram-Berg, 1992)**.

Buchholz and Vandegrift (1995) described a procedure in which low-enriched uranium silicide targets, designed to recover fission-^{99}Mo, were dissolved in alkaline hydrogen peroxide (H_2O_2 + NaOH) at about 90 °C. Sintering of matrix aluminum powder during irradiation and heat treatment retarded aluminum dissolution and prevented silicide particle dispersion. Gas evolved during dissolution is suspected to adhere to particles and block hydroxide ion contact with aluminum. Reduction of base concentrations from 5 M to 0.1 M NaOH yielded similar silicide dissolution and peroxide destruction rates, simplifying later processing.

Srinivasan et al. (1995) described a closed stainless-steel dissolver that was designed, built, and tested for dissolving up to 18 g of uranium foil. The results were quite successful, with the uranium foil being dissolved within one hour as desired. To do this, the dissolver temperature must be in the range from 97 to 102 °C, and the dissolver solution (cocktail) must have a composition of 3 M nitric acid and 2 M sulfuric acid. The final dissolver solution is subsequently processed to separate ^{99}Mo from uranium fission products and other elements.

In a process developed by **Aly (1997)** for the separation of fission ^{99}Mo, individual target samples of uranyl nitrate of natural enrichment (30 mg of each, 0.07 % ^{235}U) wrapped in small pieces of thin aluminum foil and irradiated jointly in a thermal neutron flux of approximately 10^{13} n/cm^2.s for 48 h. The irradiated targets are left to cool for a suitable period, and then are digested in 2M NaOH solution. The radioactive gases escaping during digestion are sucked through a charcoal filter.

In Radioisotope Production Center in Indonesia **(Soenarjo et al., 1999)** target capsules containing highly enriched uranium (92 % ^{235}U) are used to produce ^{99}Mo. The irradiated target capsule is connected to a stainless-steel column filled with copper wool to trap the radioiodine and a cold finger tube to collect the noble gas. The attachment units are vacuumed and stopcocks separating each unit are closed. 85 ml of a mixture of 0.1 M H_2SO_4-concentrated HNO_3 (80:5, v/v) is injected to the target capsule for dissolving the irradiated target. The radioiodine and radioxenon are vacuum distilled into the copper wool column (radioiodine trap) and the cold finger (noble gas trap) by heating the target capsule at 95 °C for 30 min, immersing the cold finger in the liquid nitrogen, and opening the stopcocks. The column containing trapped radioiodine is detached from the system and repeatedly washed with water. The washing is collected In a waste bottle containing 25 ml of 7 M NaOH. The column is then eluted with 3 × 20 ml of 0.2 M NaOH. The basic eluate is transferred into a distillation bottle containing 1 ml of ammonium hexachloro ruthenate (IV) (5 mg Ru / ml, as a carrier to inhibit the volatility of radioruthenium) and acidified by the addition of 40 ml of 8 M HNO_3. The distillation bottle is then connected to a set of two charcoal columns and vacuum system. The solution is vacuum distilled in a boiling water-bath until a little wetness of charcoal in the second column is observed (for 4-5 h). the system is then kept to ambient temperature. The radioiodine is mostly trapped in the first charcoal column (more than 95 %). Finally, the first charcoal column is detached and fractionally eluted with 3 × 20 ml of 0.2 M NaOH solution. However, for safety reason, the second charcoal column is installed all the time as a second trap of the purified radioiodine, but if radiation exposure of the second column cannot be ignored as compared to that of the first column, radioiodine in the second column should be eluted.

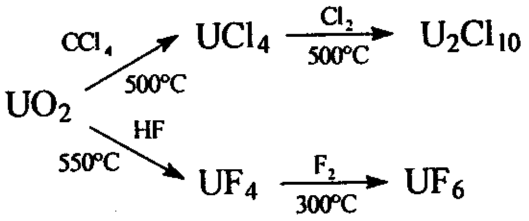
1.4. Chemistry of uranium and fission products:

1.4.1. Chemistry of uranium:

Uranium is a radioactive element. As found in nature, it contains three radioactive isotopes ^{234}U (0.0055 %), ^{235}U (0.72 %), and ^{238}U (99.27 %) with half-life periods of 2.47×10^5 y, 7.04×10^8 y, and 4.47×10^9 y, respectively.

Uranium is a member of actinide series and it shows oxidation states of +3, +4, +5, and +6. The most stable state of these is +6. In the +3 and +4 states, the compounds of uranium are similar to lanthanides. The ions formed in the oxidation states of +3, +4, +5, and +6 are U^{3+}, U^{4+}, UO_2^{+} and UO_2^{2+}, respectively. Oxidation-reduction reactions are rapid between U^{3+} and U^{4+}, or UO_2^{+} and UO_2^{2+}, as these only involve the transfer of an electron. Oxidation of U^{4+} to UO_2^{2+} is slow because it involves transfer of oxygen **(Lee, 1991)**.

There are three oxides of uranium; UO_2 (brown-black), U_3O_8 (greenish black), and UO_3 (orange-yellow). The oxide UO_3 is soluble in most acids, forming solutions which contain the yellow linear $[O=U=O]^{2+}$ ion or its complexes. Reduction of U_3O_8 with hydrogen at 600°C yields UO_2, which is the key compound for the preparation of many other uranium compounds **(Sharpe, 1984)**:



The more common uranyl compounds are the halides, nitrate, sulfate and acetate. These are soluble in water. The uranyl ion exhibits a green-yellow fluorescence, weak in an aqueous solution, but strong in the crystalline state **(Etherington, 1958)**. Hydrolysis of the uranyl ion, UO_2^{2+}, leads to the formation of polymeric ions such as $U_2O_5^{2+}$, $U_3O_8^{2+}$, and $U_3O_8(OH)^+$. In dilute solutions the existence of the ions $UO_2(OH)^+$ and $(UO_2)_2(OH)^{3+}$ has been suggested. For later stages of hydrolysis even trimeric species such as $(UO_2)_3(OH)_4^{2+}$, $(UO_2)_3(OH)_5^+$,... $(UO_2)_3(OH)_8^{2-}$ have been described . Uranyl nitrate can exist in anhydrous from, $UO_2(NO_3)_2$, monohydrated form $UO_2(NO_3)_2.H_2O$, dihydrated form $UO_2(NO_3)_2.2H_2O$, trihydrated form $UO_2(NO_3)_2.3H_2O$, or hexahydrated form $UO_2(NO_3)_2.6H_2O$.

1.4.2. Chemistry of fission products:

Since elements in the same group of the periodic table have similar chemical properties, it is convenient to consider the fission products according to the groups in which they appear.

Group 0:

The gaseous fission products, krypton and xenon, belong to this group **(Glasstone, 1955)**.

As the other noble gases, krypton and xenon have electron affinity near to zero and have ionization energies higher than any other element in periodic table so that they are chemically inactive.

Noble gases can form compounds by using excitation conditions and by dipole/induced dipole attractions. They can also form clathrate compounds **(Cotton and Wilkinson, 1979)**.

Group I:

This group is represented by rubidium and cesium in the A subgroup and by silver in the B subgroup. Because of their short half-lives or low yields, all of the isotopes of rubidium and silver are not important

(Glasstone, 1955). Cesium is by far the most important having a high fission yield and long-lived isotopes **(Etherington, 1958)**.

Cesium is an alkali metal and it has, invariably, an oxidation number of +1 in its compounds. Most of salts of this metal are soluble. They react violently with water to form the metal hydroxide with the ignition of hydrogen which is liberated. In aqueous solutions, cesium ion is surrounded octahedrally by six water molecules **(Sharpe, 1984)**. Cesium has low tendency to form complexes.

Group II:

Among the fission products there are strontium and barium in Group IIA and zinc and cadmium in Group IIB. Here again the members of Group IIB are of no importance because of the small yields or short half-lives of their isotopes **(Glasstone, 1955)**. The alkaline-earth metals strontium and barium are highly metallic, highly electropositive metals with a valence of +2. These metals combine with oxygen, nitrogen, sulfur, halogens, and hydrogen when heated. Both metals dissolve readily in acids **(Etherington, 1958)**.

Strontium peroxide may be obtained from strontium oxide at 350 °C under 200 atm pressure of oxygen, whereas barium oxide reacts with oxygen at 600 °C to form the peroxide.

Strontium and barium form only a few complexes in aqueous solution, notably with various polyphosphate anions and other chelating agents such as the ethylenediamine tetraacetate anion $EDTA^{4-}$ **(Sharpe, 1984)**.

Strontium and barium sulfates are the principle sources of these elements; they are reduced to sulfides by heating them with carbon; treatment with hydrochloric acid then produces the chlorides, from which other salts are readily obtained **(Sharpe, 1984)**.

Group III:

Group IIIA is represented by gallium and indium, which have low fission yields, and Group IIIB by yttrium. Since the latter behaves chemically very much like the rare-earth elements, it is convenient to include the lanthanides, which are produced in fission reactions of ^{235}U, with Group III, especially since lanthanum, at least, may regarded as a member of Group IIIB that need to be considered. Eight rare-earth elements, namely, lanthanum, cerium, praseodymium, neodymium, promethium, samarium, europium, and gadolinium are found among the fission products, but the last five need no further mention because of their low fission yields or their very short or very long half-lives **(Glasstone, 1955)**.

Yttrium and lanthanum always exist in the oxidation state of +3. They are quite reactive; they tarnish in air and burn in oxygen, giving the oxides M_2O_3. Yttrium forms a protective oxide coating in air, which makes it unreactive:

$$2La + 3O_2 \longrightarrow 2La_2O_3$$

These metals react slowly with cold water, but more readily with hot water, liberating hydrogen and forming either the basic oxide or hydroxide:

$$2La + 6H_2O \longrightarrow 2La(OH)_3 + 3H_2$$

$$La(OH)_3 \longrightarrow \underset{\text{Basic oxide}}{LaO.OH} + H_2O$$

When the chlorides are prepared in solutions, they crystallized as hydrated salts. Heating these hydrated salts yields oxohalides according to:

$$MCl_3.(H_2O)_7 \xrightarrow{heat} MOCl + 2HCl + 6H_2O$$

Despite the charge of +3, Y^{3+} and La^{3+} do not have a strong tendency to form complexes. This is because of their fairly large size. Thus complexes are formed with strong complexing agents such as oxalic acid, citric acid, acetylacetone (acac), and EDTA. The complexes $[Y(acac)_3(H_2O)]$, $[Y(NO_3)_5]^{2-}$, $[La(acac)_3(H_2O)_2]$, and $[La(EDTA)(H_2O)_4].3H_2O$ are common **(Cotton and Wilkinson, 1979)**.

Both of cerium and praseodymium have oxidation numbers of +3 and +4. The only binary solid compounds of Ce^{4+} are the oxide CeO_2, the hydrous oxide $CeO_2.nH_2O$, and the fluoride CeF_4 **(Cotton and Wilkonson, 1979)**. CeO_2 is insoluble in acids and alkalis, but dissolves if reduced giving Ce^{3+} solutions **(Lee, 1991)**. Ce^{4+} in solution is obtained by treatment of Ce^{3+} solutions with very powerful oxidizing agents such as peroxodisulfate or bismuthate in nitric acid. The aqueous chemistry of Ce^{4+} is similar to that of Zr and, particularly, tetravalent actinides. Thus Ce^{4+} gives phosphates insoluble in 4 M HNO_3 and iodates insoluble in 6 M HNO_3, as well as insoluble oxalate. The phosphate and iodate precipitations can be used to separate Ce^{4+} from the trivalent lanthanides. Cerium(IV) is used as an oxidant, not only in analysis, but also in organic chemistry where it is commonly used in acetic acid **(Cotton and Wilkinson, 1979)**. It is used in volumetric analysis instead of $KMnO_4$ and $K_2Cr_2O_7$ **(Lee, 1991)**. There are, however, several stable complexes containing Ce(IV), among them ceric ammonium nitrate, $(NH_4)_2[Ce(NO_3)_6]$ **(Cotton and Wilkinson, 1979)**. The sulfates $Ce(SO_4)_2.nH_2O$ (n = 0,4,8,12) and $(NH_4)_2Ce(SO_4)_3$, and the iodate are also known **(Greenwood and Earnshaw, 1984)**. Only a few solid compounds of praseodymium are known, the commonest being the black non-stoichiometric oxide formed on heating Pr(III) salts or oxide in air. The oxide system that is often formulated as Pr_6O_{11} is actually very complicated with five stable phases each containing Pr^{3+} and Pr^{4+} between Pr_2O_3 and the true dioxide PrO_2. There is some evidence that $Pr(NO_3)_4$ is partially formed by action of N_2O_5 and O_3 on PrO_2. Pr^{4+} is a very powerful oxidizing agent, the Pr^{3+}/Pr^{4+} couple being estimated as +2.9 V. This potential is such that Pr^{4+} would oxidize water itself, so that its non-existence in solution is not surprising. Pr_6O_{11} dissolves in acids to give aqueous Pr^{3+} and liberate oxygen, chlorine, etc., depending on the acid used **(Cotton and Wilkinson, 1979).**

Group IV:

Of the elements of Group IV, namely, germanium and tin in subgroup A and zirconium in subgroup B, only the latter is important in process chemistry.

Like the other members of Group IV, ziconium has a characteristic oxidation number of +4, it has also oxidation numbers of +1, +2, and +3. Zirconium has an extensive aqueous chemistry because of its lower tendency toward complete hydrolysis. Nevertheless hydrolysis does occur and it is very doubtful indeed if Zr^{4+} aquo ions exist even in strongly acid solutions. The hydrolyzed ion is often referred to as the "zirconyl" ion, ZrO^{2+}. The most important zirconyl salt is $ZrOCl_2.8H_2O$ which crystallizes from dilute hydrochloric acid solutions and contains the ion $[Zr_4(OH)_8(H_2O)_{16}]^{8+}$. In 2.8 M HCl, the main species appears to be trinuclear, perhaps $[Zr_3(OH)_6Cl_3]^{3+}$, and the stable phase that crystallizes from HCl solutions, $ZrOCl_2.8H_2O$, contains tetramers. Chelating agents such as EDTA and nitrilotriacetate (NTA) form complexes with Zr^{4+}; an example is the complex $\{Zr[N(CH_2COO)_3]_2\}^{2-}$. The chemistry of lower oxidation states of zirconium is limited to non-aqueous chemistry of lower halides and some complexes thereof. The three trihalides $ZrCl_3$, $ZrBr_3$, and ZrI_3 are well-established compounds which can be prepared in several ways. Zr^{4+} gives an insoluble iodate which can be crystallized from nitric acid solution **(Cotton and Wilkinson, 1979).** Normal salts of Zr^{4+} such as

$Zr(NO_3)_4.5H_2O$ and $Zr(SO_4)_2.4H_2O$ can only be isolated if the solution is sufficiently acidic **(Greenwood and Earnshaw, 1984)**.

Group V:

Two members of Group VA, namely, arsenic and antimony, appear among the fission products, but neither of these is important; in Group VB, however, there is niobium-95, the decay product of zirconium-95 **(Glasstone, 1955)**.

The oxidation state of +5 is the most common one for Niobium in its compounds, lower oxidation states are less stable. There are four oxides of niobium; these are NbO, Nb_2O_3, NbO_2, and Nb_2O_5 **(Etherington, 1958)**. Nb_2O_5 is rather unreactive but is amphoteric. It has only very weak acidic properties. It reacts with HF, and form niobates when fused with NaOH **(Lee, 1991)**. When the pentoxide is hydrated, it gives the metaniobic acid ($HNbO_3$) which is an insoluble white amorphous precipitate **(Etherington, 1958)**. Niobium produces a variety of complicated and ill-defined, but probably polymeric, species which include the nitrate $NbO(NO_3)_3$, sulfate $Nb_2O(SO_4)$, and double sulfates such as $(NH_4)_6Nb_2O(SO_4)_7$, all of which are extremely readily hydrolyzed. Niobium also produces peroxo-compounds, e.g., the pale yellow $K_3[Nb(O_2)_4]$ **(Greenwood and Earnshaw, 1984)**.

Zirconium and niobium tend to form radioactive colloids in solution. These colloids tend to be adsorbed on surfaces (container walls, dust particles, etc.), and they also contribute to erratic behavior of zirconium and niobium in aqueous separations processes **(Etherington, 1958)**.

Group VI:

This group is represented by selenium and tellurium in subgroup A and by molybdenum in subgroup B. Because of their very long or very short half-lives and their low yields, none of isotopes of selenium is significant **(Glasstone, 1955)**.

Tellurium dissolves in oleums to give red solution, which is unstable and changes in color when kept or warmed **(Cotton and Wilkinson, 1979)**. Tellurium have oxidation numbers of –2, +2, +4, and +6, the last is the most important **(Etherington, 1958)**. It forms the volatile bivalent hydride H_2Te which dissociates in water according to:

$$H_2Te_{(hydrated)} + H_2O \rightleftharpoons H_3O^+ + HTe^-_{(hydrated)}$$

There are three oxides of tellurium; these are TeO, TeO_2, and TeO_3. TeO_2 is almost insoluble in water, so that tellurius acid has not been characterized. The dioxide reacts with strong bases and form tellurites, acid tellurites, and various polytellurites. Telluric acid, H_6TeO_6, is prepared by the action of powerful oxidizing agents such as $KMnO_4$ on Te or TeO_2. Telluric acid is a fairly strong oxidizing agent, but a weak dibasic acid and forms two species of salts, for example $NaTeO(OH)_5$ and $Li_2TeO_2(OH)_4$ **(Cotton and Wilkinson, 1979)**. Te^{4+} ion forms a white basic nitrate, $2TeO_2.HNO_3$, which can be obtained by treating the metal with hot nitric acid **(Greenwood and Earnshaw, 1984)**.

Molybdenum shows a wide range of oxidation numbers; -2, 0, +1, +2, +3, +4, +5, and +6. Of these oxidation numbers, +6 is the most important, +2 and +4 are not stable in water, whereas the oxidation numbers –2, -1, and 0 are rare **(Etherington, 1958)**. Molybdenum is inert towards most acids but is rapidly attacked by fused alkalis in the presence of oxidizing agents, by oxygen at high temperatures, and by halogens; fluorine yields the volatile hexafluoride MoF_6 even at room temperature **(Sharpe, 1984)**.

Many molybdenum oxides are known. The simple ones are MoO_3, Mo_2O_5, and MoO_2. White solid MoO_3 is the anhydride of molybdic acid, but it does not form hydrates directly, although these are known. Violet solid Mo_2O_5 is soluble in warm acids. Brown-violet solid MoO_2 is obtained by reducing MoO_3 with hydrogen or NH_3 below 470°C (above this temperature reduction proceeds to the metal) and by reaction of molybdenum with steam at 800°C. MoO_2 is insoluble in non-oxidizing mineral acids but soluble in concentrated nitric acid with oxidation of the molybdenum to Mo(VI).

On fusion of MoO_3 with alkali or alkaline-earth oxides, mixed oxide systems are obtained that are not related to the molybdates made in aqueous solution. These usually have chain structures with linked MoO_6 polyhedra but the stability of a particular type of structure depends on the cation size, e.g., $K_2Mo_4O_{13}$. The so-called "blue oxides" of molybdenum or "molybdenum blue" are obtained by mild reduction, for example, by Sn(II), SO_2, N_2H_4, H_2S, etc., of acidified solutions of molybdates or of suspensions of MoO_3 in water. The blue oxides of molybdenum contain both oxide and hydroxide. In blue oxides, the mean oxidation state of Mo is between 5 and 6, e.g., $MoO_{2.0}(OH)$ and $MoO_{2.5}(OH)_{0.5}$.

MoO_3 dissolves in aqueous alkali-metal hydroxides, and from these solutions the simple or normal molybdates can be crystallized. They have the general formula M_2MoO_4 and contain the discrete tetrahedral ions MoO_4^{2-}. When solutions of molybdates are made weakly acid, polymeric anions are formed, but from more strongly acid solutions substances often called "molybdic" acid are obtained. At room temperature, the yellow $MoO_3.2H_2O$ crystallizes. From hot solutions, monohydrate is obtained rapidly **(Cotton and Wilkinson, 1979)**. In aqueous solution, equilibrium of the molybdenum species is complete within a matter of minutes. The first major polyanion formed when the pH of an aqueous molybdate solution is reduced below about 6 is the heptamolybdate $[Mo_7O_{24}]^{6-}$, traditionally known as the paramolybdate. Anions with 8 and 36 Mo atoms are also formed before the increasing acidity suffices to precipitate the hydrous oxide. The formation of these isopolyanions may be represented by the net equations:

$$7[MoO_4]^{2-} + 8H^+ \rightleftharpoons [Mo_7O_{24}]^{6-} + 4H_2O$$

$$8[MoO_4]^{2-} + 12H^+ \rightleftharpoons [Mo_8O_{26}]^{4-} + 6H_2O$$

$$36[MoO_4]^{2-} + 64H^+ \rightleftharpoons [Mo_{36}O_{112}]^{8-} + 32H_2O$$

of course many intermediate reactions occur: in particular, hydration (which raises the coordination number of the molybdenum from 4 to 6) and protonation (which reduces the high charges on some of the ions). Of the ions mentioned, $[MoO_4]^{2-}$, $[Mo_7O_{24}]^{6-}$, and $[Mo_{36}O_{112}]^{8-}$ are known to have the same structures in solids and in solution, whereas $[Mo_8O_{26}]^{4-}$ forms two different isomers in solids and its structure in solution is uncertain. Careful adjustment of acidity, concentration, and temperature, often coupled with slow crystallization, can produce solids containing many other ions which are apparently not present in solution. Amongst the distinct species which have been characterized are: the dimolybdate, $[Mo_2O_7]^{2-}$; the hexamolybdate, $[Mo_6O_{19}]^{2-}$; and the decamolybdate, $[Mo_{10}O_{34}]^{8-}$ **(Greenwood and Earnshaw, 1984).**

Group VII:

Bromine and iodine from Group VIIA and Technetium from Group VIIB appear among fission products, but bromine has no long-lived radioisotopes.

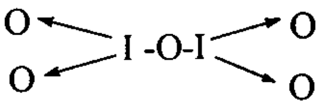
Iodine is a black solid with slight metallic luster. Like the other members of Group VIIA (halogens), iodine has an oxidation number of −1. It sublimes (violet vapor) at atmospheric pressure. Its solubility in water is slight ($0.33 gl^{-1}$ at 25 °C). It is readily soluble in non-polar solvents such as CS_2 and CCl_4 to give violet solutions, spectroscopic studies indicate that "dimerization" occurs in solutions to some extent:

$$2I_2 \rightleftharpoons I_4$$

Iodine pentoxide, I_2O_5, is a white solid and is the most stable of all the oxides and it can be used as oxidizing agent. Pentoxide is formed by dehydrating iodic acid by heating to 170 °C:

$$2HIO_3 \xrightarrow{170\,°C} I_2O_5 + H_2O$$

Heating to 300 °C decomposes I_2O_5 to the elements. Structure of I_2O_5 can be shown as:



The compounds I_2O_4 and I_4O_9 are ionic and are probably iodates $IO^+.IO_3^-$ and $I_3^+.(IO_3^-)_3$, respectively.

Iodic acid HIO_3 exists as a white solid. HIO_3 can be made by oxidizing iodine with fuming nitric acid. The common form of periodic acid is $HIO_4.2H_2O$ or H_5IO_6. This is obtained by passing chlorine into a solution of iodine in NaOH. The salt $Na_2H_3IO_6$ so formed is treated with $AgNO_3$ giving Ag_3IO_5, which on treatment with chlorine and water and evaporating with concentrated H_2SO_4 gives H_5IO_6. When heated, the acid first loses water, polymerizes, and forms an isopolyacid. More water is lost on further heating, and eventually oxygen is lost giving iodic acid:

$$\underset{\text{paraperiodic acid}}{2H_5IO_6} \xrightarrow[-\,3H_2O]{80\ ^\circ C} H_4I_2O_9 \xrightarrow[-\,H_2O]{100\ ^\circ C} \underset{\text{metaperiodic acid}}{2HIO_4} \xrightarrow{140\ ^\circ C} \underset{\text{iodic acid}}{2HIO_3} + O_2$$

Interhalogen compounds can be prepared by direct combination, or by the action of a halogen on a lower interhalogen. ICl, ICl_3, IF_5, IF_7 are examples of interhalogen compounds of iodine.

The solubility of iodine in water is greatly increased by the addition of iodide ions, due to the formation of the triiodide ion I_3^-:

$$I_2 + I^- \longrightarrow I_3^-$$

More complex ions such as pentaiodide I_5^-, hepta iodide I_7^-, and enneaiodide I_9^- have also been prepared. The direct addition of iodine to the iodide, either with or without a solvent, results in polyhalides such as $KI_3.H_2O$, RbI_3, and NH_4I_5. A number of polyhalides are known which contain two or three different halogens, for example $K[ICl_2]$, $K[ICl_4]$, Cs[IBrF], and K[IBrCl]. These are formed by the reaction of metals and interhalogens. Polyhalides are typically ionic compounds, though they tend to decomposition by heating **(Cotton and Wilkinson, 1979)**:

$$Cs[I_3] \xrightarrow{\text{heat}} CsI + I_2$$
$$Rb[ICl_2] \xrightarrow{\text{heat}} RbCl + ICl$$
$$K[BrICl] \xrightarrow{\text{heat}} KCl + IBr$$

In iodide solutions, silver nitrate gives a yellow precipitate of AgI insoluble in nitric acid and also in ammonium hydroxide. Silver iodide dissolves in $Na_2S_2O_3$ and KCN solutions which form with Ag^+ the complexes

$[AgS_2O_3]^-$, $[Ag(S_2O_3)_3]^{5-}$, and $[Ag(CN)_2]^-$. The reaction with $Na_2S_2O_3$ requires a large excess of this reagent:

$$AgI\downarrow + 3S_2O_3^{2-} \longrightarrow [Ag(S_2O_3)_3]^{5-} + I^-$$

Silver iodide is decomposed by the reaction of zinc dust in the presence of water or 4 M H_2SO_4:

$$2AgI\downarrow + Zn\downarrow \longrightarrow Zn^{2+} + 2I^- + 2Ag\downarrow$$

Solutions of I_2^+ and I_3^+ can be obtained by oxidation in oleum:

$$2I_2 + 6H_2S_2O_7 \longrightarrow 2I_2^+ + 2HS_3O_{10}^- + 5H_2SO_4 + SO_2$$
$$3I_2 + 6H_2S_2O_7 \longrightarrow 2I_3^+ + 2HS_3O_{10}^- + 5H_2SO_4 + SO_2$$

The natural abundance of technetium is, as just indicated, negligibly small **(Greenwood and Earnshaw, 1984)**. Much is not known about the chemistry of technetium, however, it lies between those of manganese and rhenium. Technetium has different oxidation states from −1 to +7 and forms compounds in all oxidation states. The most stable being those from +4 to +7. It has practically no cationic chemistry, form practically no compounds in the oxidation state of +2 and has extensive chemistry in the oxidation state of +4 and, specially, in the oxidation state of +5 **(Cotton and Wilkinson, 1979)**. Oxidation states lower than + 4 could definitely be realized only through complex stabilization **(Schwochau and Pleger, 1993)**.

The halides $TcCl_4$, TcF_5, and TcF_6 are reported for this metal **(Sharpe 1984)**. The tetrahedral pertechnetate, TcO_4^-, ion is quite stable in alkaline solution and it is reduced by HCl, HBr, or HI. The pertechnetates are among the most important compounds formed by technetium.

The aqueous acids or their salts are formed on oxidation of all technetium compounds by nitric acid, hydrogen peroxide, or other strong oxidizing agents **(Cotton and Wilkinson, 1979)**.

The known technetium oxides are TcO_2, TcO_3, and Tc_2O_7. TcO_2 is formed as the final product when any Tc/O_2 system is heated to high temperatures (500°C) **(Boyd, 1952)**. TcO_2 can also be obtained by reduction of aqueous solutions of TcO_4^- with zinc and HCl. TcO_3 can be obtained by either thermal decomposition of NH_4TcO_4 or by heating the heptaoxide and the metal. Tc_2O_7 is the most important oxide of technetium which is formed when technetium metal is burned in an excess of oxygen **(Smith et al., 1953)**. It readily dissolves in water giving $HTcO_4$ which is a strong acid in aqueous solution.

Group VIII:

Three of the platinum metal group result from fission reactions of ^{235}U; these are ruthenium, rhodium, and palladium **(Etherington, 1958)**. Because of its multiple valence states and its complex chemistry, ruthenium is the most important of these metals in separations chemistry **(Lee and Bang, 1983)**. Ruthenium shows the oxidation numbers -2, 0, +1, +2, +3, +4, +5, +6, +7, and +8. It is basic in the lower oxidation states, while it tends to be acidic in the higher oxidation states **(Etherington, 1958)**. In the presence of strong oxidizing agents, ruthenium exists as the volatile RuO_4 **(Lee and Bang, 1983)**. RuO_4 is a volatile yellow compound which explodes above 180 °C, forming the dioxide and oxygen. It is a very powerful oxidant which reacts violently with organic compounds **(Sharpe, 1984)**.

The highest chloride of ruthenium is $RuCl_3$, but the complex $[Ru_2OCl_{10}]^{4-}$ is formed, together with $[RuCl_5(H_2O)]^{2-}$ and $[RuCl_6]^{3-}$, by the action of hydrochloric acid on RuO_4; the $[RuCl_6]^{2-}$ ion is best obtained by oxidation of $[RuCl_6]^{3-}$ with chlorine.

Substitution in Ru(III) complexes is generally very slow, and large numbers of aquo halo complexes have been characterized; they form the chief constituents of the material commonly described as '$RuCl_3.3H_2O$' and obtained by the action of concentrated hydrochloric acid on RuO_4. By prolonged aquation, the aquo complex $[Ru(H_2O)_6]^{3+}$ can eventually be obtained in solution; it can be reduced to $[Ru(H_2O)_6]^{2+}$ electrolytically:

$$[Ru(H_2O)_6]^{3+} + e^- \rightleftharpoons [Ru(H_2O)_6]^{2+} \quad E° = +0.23\ V.$$

By treatment of '$RuCl_3.3H_2O$' with zinc dust in strongly ammoniacal solution, $[Ru(NH_3)_6]^{2+}$ is obtained, and may be oxidized to $[Ru(NH_3)_6]^{3+}$ by air **(Sharpe, 1984).**

A trivalent cation of ruthenium species was found in a certain proportion in nitric acid solution of some of the nitrosyl ruthenium compounds such as nitrosyl ruthenium trinitrate, $RuNO(NO_3)_3$, and nitrosyl ruthenium hydroxide, $RuNO(OH)_3$ **(Sato, 1989).**

The spontaneous oxidation of Ru^{3+} to Ru^{4+} can be proceeded as follows **(Fletcher, 1965):**

$$4Ru^{3+} + 4H^+ + NO_3^- \longrightarrow [RuNO]^{3+} + 3[Ru]^{4+} + 2H_2O.$$

Photolysis of nitrosylruthenium in nitric acid with UV light results in the formation of Ru^{3+} according to **(Maya, 1979):**

$$[RuNO]^{3+} \xrightarrow{hv} Ru^{3+} + NO.$$

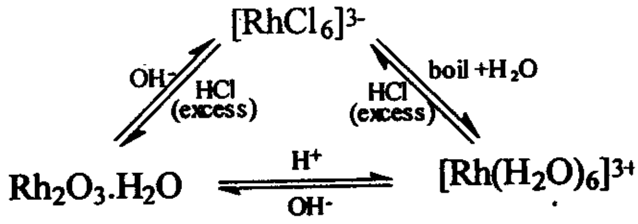
In the closed system, Ru^{3+}, which is generated by photolysis, may react with the produced NO and regenerate $[RuNO]^{3+}$ or be oxidized to Ru^{4+}.

Rhodium shows oxidation states of +1, +2, +3, +4, and +6. Of these oxidation states, +3 and +4 are the most important **(Etherington, 1958).** Heating rhodium metal or the trichloride in oxygen at 600 °C, or simply heating the trinitrate, produces dark-gray Rh_2O_3; it is the only stable oxide formed by this metal **(Greenwood and Earnshaw, 1984).** $Rh_2O_3.nH_2O$ is formed as a yellow precipitate from Rh^{3+} solutions. In base solution, powerful oxidants convert it into $RhO_2.nH_2O$, and loses oxygen on dehydration.

On the dissolution of $Rh_2O_3(aq)$ in cold mineral acids, the stable yellow aquo ion, $[Rh(H_2O)_6]^{3+}$ is formed. This aquo ion also occurs in alums, $MRh(SO_4)_2.12H_2O$, and in the yellow sulfate, $Rh_2(SO_4)_3.14H_2O$, obtained by vacuum-evaporation at 0 °C of solutions of $Rh_2O_3(aq)$ in H_2SO_4. A red sulfate, $Rh_2(SO_4)_3.6H_2O$, obtained by the evaporation of the yellow solutions at 100 °C, gives no precipitate with Ba^{2+} ion and is presumably a sulfato complex.

When $RhCl_3.3H_2O$ is dehydrated in dry HCl at 180 °C, the red product is much more reactive and dissolves in water or tetrahydrofuran; this property is lost on heating at 300 °C **(Cotton and Wilkinson, 1979).**

The reactions of the $[RhCl_6]^{3-}$ ion with alkali and water are indicated below **(Sharpe, 1984):**



Palladium shows the oxidation states +2 and +4 **(Etherington, 1958)**, but +2 is the most stable oxidation state **(Sharpe, 1984)**. Palladium is oxidized by O_2, F_2, and Cl_2 at red heat and dissolves slowly in oxidizing acids. It also dissolves in fused alkali metal oxides and peroxides. The aquo ion $[Pd(H_2O)_4]^{2+}$ occurs in aqueous solutions from which potential ligands are excluded. Addition of alkali to aqueous solutions of $Pd(NO_3)_2$ produces a gelatinous dark-yellow precipitate of the hydrous oxide which is soluble in acids. The addition of alkali to aqueous solutions of Pd^{4+} produces a strong oxidizing, dark-red precipitate which slowly loses oxygen and, at 200 °C, forms PdO.

1.5. Chemical separation concepts:

1.5.1. Criteria for selection of the separation process:

When a suitable separation process is to be selected, the following criteria are considered **(Nicholls, 1955)**:

1. Chemical selectivity.
2. Radiation and chemical stability.
3. Low-corrosion characteristics.
4. Short reaction times and process continuity.
5. Minimum volume of fission-product effluents.
6. Safe operation.

Generally, the effectiveness of any separation method can be expressed in terms of separation or removal change in concentration of a specific material. This is often expressed with respect to the substance not separated.

1.5.2. Topics of important separation processes:

1.5.2.1. Precipitation methods:

Precipitation methods have long been used by chemists, both in the laboratory and on the large scale, for the separation of elements or for the removal of impurities from a desired product.

1.5.2.1.1. Conditions affecting precipitation:

In case of radioactive precipitations, many factors are to be controlled because they are responsible for the purity and completeness of precipitation. These factors are (i) type and excess of precipitating reagent, (ii) temperature, (iii) concentrations of the trace, carrier, and precipitating ions, (iv) order of addition of the reagents, (v) the rate of precipitation, agitation, etc.

Generally, the precipitate obtained in radioactive chemical methods is separated by centrifugal means rather than by filtration. In filtration the precipitate has to be taken repeatedly to the filter cone and the container, i.e., the yield is lost (**Etherington, 1958; Srivastava and Jain, 1989; Glasstone, 1955**).

In traces, particularly, the concentration in solution is so small that the precipitation is prevented, even if this concentration exceeds the solubility of the insoluble material. In this case, the presence of what is called "carrier", which is a substance added in substantial amounts to enable a trace element to be precipitated more or less quantitatively, is necessary. There are two main types of carrying illustrated by:

1. Isotopic carrying. A salt, which has the element to be carried, is added to the radioactive substance, which is then precipitated. For example, ^{140}Ba can be carried from a solution by adding $BaCl_2$, and any soluble sulfate is further added to precipitate $BaSO_4$. The isotopic ion is homogeneously mixed in the crystals of $BaSO_4$. In this type of carrying, it is necessary that the isotopic carrier is chemically analogous to the radioactive substance, i.e., they must have the same oxidation number and their species must have one form before precipitation **(Glasstone, 1955; Srivastava and Jain, 1989)**.

2. *Non-isotopic carrying.* This type of carrying is necessary when the high specific activity of the desired substance is to be maintained. There are four types of non-isotopic carrying; these are (i) isomorphous replacement, (ii) formation of anomalous mixed crystals, (iii) surface adsorption, and (iv) internal adsorption **(Srivastava and Jain, 1989)**.

1.5.2.1.2. Practical limitations of precipitation methods:

Usually, but not in all cases, there are two significant disadvantages which should be mentioned relative to precipitation-type separation processes; these are: (i) radionuclidic purity of the isotope(s) separated by precipitation is not high as in other separation processes, and (ii) yields of recovery are not high as some of the other methods **(Lawroski, 1955)**.

1.5.2.2. Solvent extraction methods:

1.5.2.2.1. Solvent extraction system and techniques:

The solvent extraction method for separating components of an aqueous solution can be used when one of the components is not only appreciably soluble, but is more stable than the other components, in an organic liquid, which is essentially immiscible with water. The two liquids, aqueous solution and organic solvent, are brought into contact.

For the extraction of an inorganic substance into organic solvent, it is necessary that the substance is present in a suitable chemical form (usually as a complex species) **(Srivastava and Jain, 1989)**. Morrison and Frazer **(Morrison and Frazer, 1957)** have classified the extraction systems of metal ions into two types of uncharged molecules; (i) chelates, and (ii) ion-association complexes. Chelate is a coordination compound in which a ligand molecule contains more than one donor atom. In the ion-association type of complexes, metal ion (which is attached to water molecules in aqueous phase) combines with organic solvent molecule and forms an uncharged complex **(Diamond, 1957)**.

Solvent extraction can be improved by (i) scrubbing (by decreasing the concentration of an impurity that is extracted simultaneously with the desired component into the organic solvent), (ii) Successive and re-extractions, and (iii) Prevention of emulsion formation (by adding surface active reagents, mixing an inert diluent, filtration for removing the base material, and centrifugation) **(Glasstone, 1955; Srivastava and Jain, 1989)**.

For operation with highly radioactive solutions, the contacting devices used in different techniques of solvent extraction must have the following characteristics: (i) long operation life with low maintenance requirements, (ii) small size in order to minimize shielding, (iii) simplicity of operation and control, (iv) easy replacement of parts, (v) adaptability to changes in process conditions. These devices are: (i) separatory funnel (for batch extraction), (ii) continuous extractor (for continuous extraction), and (iii) backed columns, pulse columns, and mixer-settlers (for counter current extraction) **(Glasstone, 1955)**.

1.5.2.2.2. Practical limitations of solvent extraction processes:

Some processing problems may be encountered in the operation of solvent extraction facilities such as: (i) the coexistence of two or more chemical compounds of a given element with widely different solvent extraction characteristics, (ii) the process abnormalities obtained by the presence of hydrolysis products of process chemicals, and (iii) the presence of solid impurities which absorb certain fission products and contaminate product solutions by entrainment.

Generally, the problems mentioned above are not necessarily observed in laboratory-scale investigations, but prove to be serious impediments to the successful operation of a production facility. In many cases, the problem becomes apparent only after a process is in operation for many hours or days. When encountered, the definition and resolution of the problem may require extensive and continued experimentation that may be very costly **(Tomlinson, 1955)**.

1.5.2.3. Ion-exchange separations:

1.5.2.3.1. Theory and technique of ion exchange:

"Ion exchange" is a process in which reversible stoichiometric interchange of ions of the same sign takes place between an electrolyte solution or molten salt and ion-exchange sites of a solid material called "ion exchanger". These sites are ionic groupings capable of forming an electrostatic bond with an ion of opposite charge. "Total ion-exchange capacity" of an exchanger may be defined as the total number of ion-active groups per unit weight of exchanger, it is expressed in units of milli-equivalent per gram of exchanger.

There are three important explanations proposed for the ion-exchange process; these are (i) the crystal-lattice exchange theory, (ii) the double-layer theory, and (iii) the Donnan membrane theory **(Etherington, 1958)**.

Generally, There are three types of exchangers; these are organic exchangers, inorganic exchangers, and composite exchangers. The first two types are more common. Synthetic organic exchangers can be classified according to (i) exchangeable species (cation, anion, ampholyte, and multifunctional types), (ii) functional group (strong and weak acid or base types), (iii) skeleton types (polymers, copolymers, and polycondencates).

While the ion-exchange process for some inorganic materials fulfills the definition conditions for the classical concept of ion exchange, although often for only a limited range of experimental conditions, there are many materials where one or more of the definition conditions for exchange are not fulfilled. Therefore, The term ion exchangers is inaccurate for this group of materials and the more general term "ion-exchange sorbents" would be preferable, as it describes more closely this group of materials **(Qureshi and Varshney, 1991)**.

A composite ion exchanger can be formed by the implantation of an inorganic sorbent during the formation of an organic resin. For example, the composite ion exchanger with nickel hexacyanoferrate(II) (NCF) was obtained by direct implantation of this inorganic sorbent into a resin formed by formaldehyde cross-linked sulfonated phenols **(Szeglovski et al., 1994)**.

The varying affinities of different ions for a given ion exchanger can be used as the basis of a technique for the separation of such ions from each other **(Glasstone, 1955)**. Ion-exchange separation is done either by "batch" or "column" operation. Although the second operation is generally practiced, the combination of both is advantageous **(Srivastava and Jain, 1989)**.

Electrochemical ion exchange **(Turner et al., 1991)** is a new separation technique in which the absorption and elution behavior of ion exchangers incorporated into an electrode is controlled by an external potential. A negative potential applied to a weak acid cation exchanger electrode causes cations to be absorbed progressively to low concentrations as the feed passes up through the cell. On polarity reversal, the absorbed ions can be eluted into a limited volume to give a concentrated product.

1.5.2.3.2. Practical limitations of ion-exchange processes:

From the practical point of view, some of the conditions of rapid-equilibrium attainment are undesirable. For example, if the exchanger particles are too small, the pressure drop through the column will be too great; slow flow rates and low ion-to-exchanger mean low yields per unit time. The number of theoretical plates can be increased, of course, by increasing the length of the exchanger column, but this means that larger volumes of eluent have to be used and that the elution time is increased.

The actual conditions employed in any particular case must thus represent a balance between the separation efficiency of the column, on the one hand, and the desire for high yields, on the other **(Glasstone, 1955)**.

1.5.2.4. Distillation:

1.5.2.4.1. Definition and theory of distillation:

"Distillation" is the process in which a liquid mixture of two or more substances is separated into its component fractions of different boiling points, by the application and removal of heat **(Tham, 2001)**. Thus, if two or more substances possess at any temperature a marked difference in vapor pressure, it is possible to use this fact as the basis of a separation between them by using distillation. The basic requirement for separation of components by distillation is that the composition of vapor be different from that of the liquid form which it is formed. If all or part of the vapor is condensed, there will have been an enrichment of the more volatile component in the overhead and of the less volatile component in the undistilled liquid **(Etherington, 1958)**. If the boiling points of the constituents of a mixture differ only slightly, complete separation cannot be achieved in a single distillation and, in this case, redistillation for one or more times is necessary.

One of basic data needed in a distillation problem is the liquid-vapor equilibria of the components over the composition range of interest. Quantitative equilibrium relationships are often complex and frequently must be determined experimentally. However, two generations can be made that hold in certain ideal cases and are approached, practically over narrow ranges, in many others; these are the well-known Raoult's law and Henry's law **(Etherington, 1958; Stichlmair et al., 1998)**.

Distillation can be demonstrated in the laboratory using relatively simple apparatus consists mainly of a round-bottom flask (boiler), water-cooled condenser (Leibig condenser), and a receiver. Technically, the term "still" is applied only to the vessel in which liquids are boiled during distillation (the boiler), but the term is sometimes applied to the entire apparatus.

1.5.2.4.2. Types of distillation:

Generally, there are three main types of distillation processes **(Etherington, 1958; Walker and O' Mahony, 2000)**;

1. Simple distillation. This type of distillation includes (i) equilibrium distillation (which involves vaporizing a definite fraction of a batch liquid maintaining liquid and vapor in contact with one another until the end of the process, at which the vapor is removed and condensed), (ii) differential distillation (wherein the vapor from a batch liquid is continuously removed as fast as it forms, the volume of liquid in the still decreasing continuously), (iii) steam distillation (in which steam is introduced into the still in excess so that advantage is taken of the fact that when liquids are immiscible each exerts its full vapor pressure and, thus, the introduced steam reduces the partial pressure of the high-boiling component necessary for distillation), (iv) vacuum distillation (in which the still is partially evacuated to get a lower distillation temperature), and (v) molecular

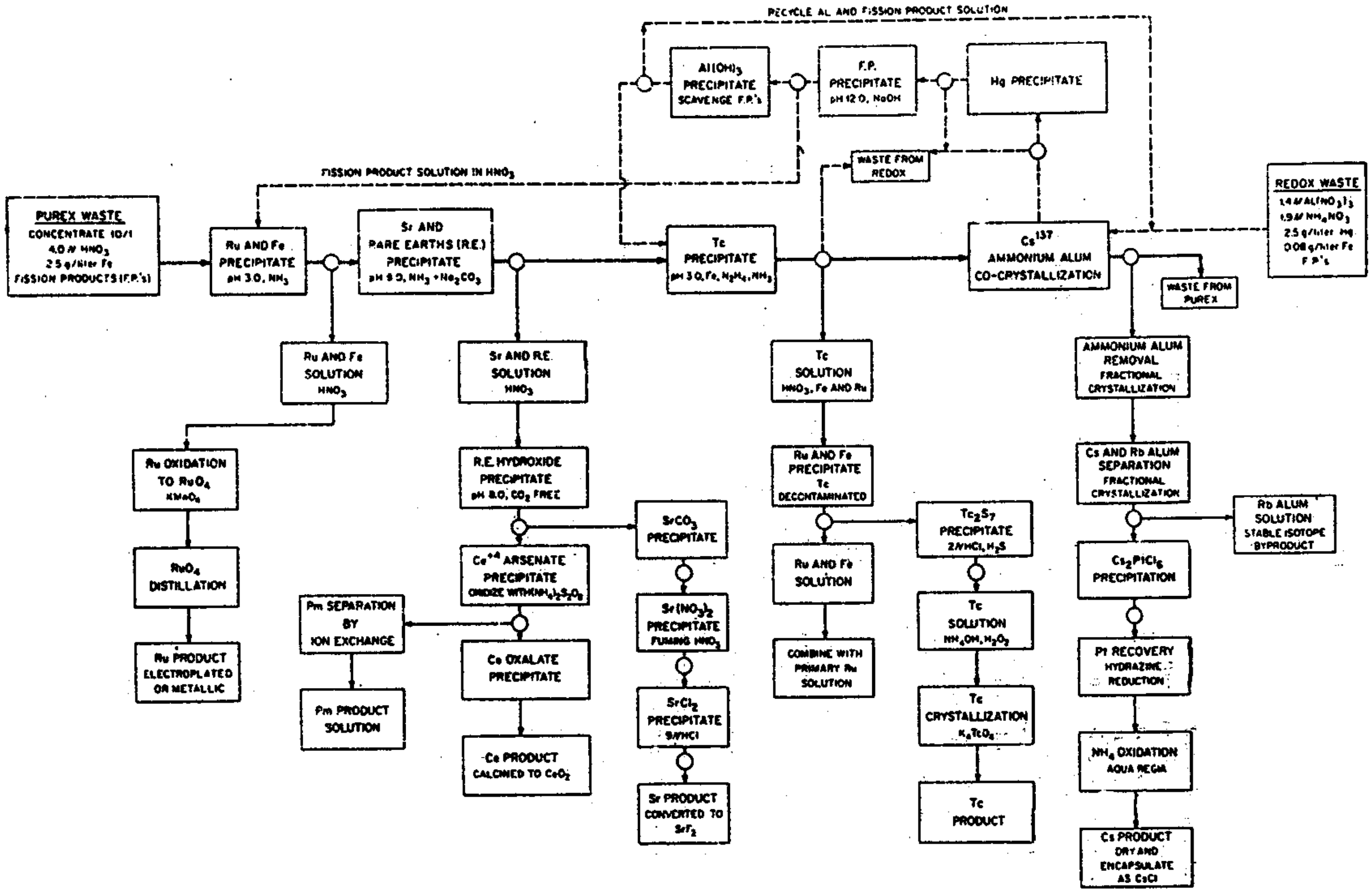


Figure 1.2. Processes of fission-products separation from reactor waste at ORNL (Lamb et al., 1958).

1.6.1. Separation of iodine:

Some of the separation procedures of iodine are already mentioned during the elucidation of the dissolution of irradiated uranium targets (Section 1.4.4). Two other separation procedures of iodine are briefly mentioned below.

Kimura et al. (1957) conducted some experiments in order to find out the best condition for conveniently separating carrier-free radioactive iodine from gross fission products by extraction. A solution of carrier-free ^{131}I in 5 % Na_2SO_3 was diluted with water to a suitable concentration. Then, the distribution ratios of ^{131}I between two liquid phases were determined for the carbon tetrachloride extraction from HNO_3 solution of various concentrations with or without iodine carrier. In this extraction process, 50 ml of HNO_3, of known concentration, and 1 ml of radioactive carrier-free iodine solution were placed into a separatory funnel. When iodine-carrier was needed, two drops of KI solution (10 mg iodine per ml) were added. 1 ml of 30 % H_2O_2 was added and the solution was allowed to stand for 5 min. 5 ml of carbon tetrachloride were added and, then, the funnel was shaken well for 2 min. After settling, the organic layer was drained off into another separatory funnel. The extraction was repeated two times with the residual aqueous phase in the original funnel. The three organic fractions obtained were combined in another separatory funnel and, then, the funnel was shaken for 2 min with 10 ml of water containing 1 ml of 5 % Na_2SO_3 solution. Thus, the iodine in the organic phase was stripped into the aqueous solution after its precipitation as AgI. To the aqueous solution, 1 ml of the KI solution and five drops of aqueous ammonia were added, and then all the iodide was precipitated as AgI with 5 % $AgNO_3$ solution. The precipitate was filtrated rapidly, through a filter paper, and dried at 110 °C. finally the radioactivity of the precipitate was measured. The extraction procedure was then applied to a sample of the gross fission products (radioactive debris), which was so aged that iodine activities in it had completely decayed, where the sample was dissolved in HNO_3 and diluted with water so that 1 ml of the solution had the radioactivity of ~ 10,000 cpm. The extraction with carbon tetrachloride was carried out with solutions containing 1 ml of the sample solution in the presence of H_2O_2 and HNO_3 of various concentrations. The organic phase separated after each run was dried in a sampling pan, and its radioactivity was measured. In this extraction procedure, the addition of iodine carrier is unnecessary. However, extraction without iodine carrier recovers only 30 to 50 % of the iodine, with poor reproducibility. This may be caused not only by an anomalous behavior of iodine in tracer-scale concentration, but by other factors such as the valency state of the radioactive iodine in solution, as **Glendenin et al. (1951)** pointed out. In practice, the chemical forms of iodine should be taken into account whenever extraction with carbon tetrachloride is carried out, either with or without iodine carrier.

Itawi (1993) developed a method for the separation of iodine-131 as iodide ion. The method is based on the solvent extraction of iodide with 2-mercaptobenzothiazole (2-MBT) in chloroform. Iodine-131 was found to be fully extracted with 1 % 2-MBT solution in chloroform at the HCl normality range of 8.0-11.0. It was also separated from irradiated uranium nitrate (fission fragments) and irradiated tellurium oxide by this method.

1.6.2. Separation of ruthenium:

Gandon et al. (1993) studied a coprecipitation method to separate ruthenium during the processing of spent nuclear fuel using PUREX process. This method is based on the addition of ferrocyanide ions to the solution to form a ruthenocyanide complex which is subsequently coprecipitated as copper ferrocyanide by the addition of copper(II) nitrate. The highest yields were obtained with 5×10^{-4} M sodium ferrocyanide and

1×10^{-3} M copper(II) nitrate. The optimal pH is 5 ± 1. The method is also efficient at lower pH values, but above pH 8 the ferrocyanides are partly soluble, thus preventing good coprecipitation yields.

Mutojima (1990) invented a process for removing radioactive ruthenium from an aqueous solution, comprising oxidizing ruthenium in the aqueous solution of ruthenium tetroxide, extracting the resulting ruthenium tetroxide with a halogen-free aliphatic, or alicyclic hydrocarbon solvent, and separating the precipitated solid ruthenium dioxide. At the step of oxidation and extracting ruthenium, a lower acidity of nitric acid is more effective. At a nitric acid concentration of about 3 M, commonly used in the reprocessing operation, it was found that cerium(IV), which is not influenced by the acidity and is considered in a considerable amount in the fission products, is acceptable as an oxidant for ruthenium and that use of a solution of its nitrate is simpler and most preferred. It is preferred that the extraction temperature be 50 to 60 °C, though the reaction is advanced at room temperature. In the case where ruthenium in the aqueous phase is present in the form of a stable nitrosyl complex, it is necessary that the aqueous solution be heated (up to 60 °C, to 80 °C) in advance to be converted to a form which is easily extracted. In this case, if 30 % hydrogen peroxide is added in an amount of about 1 % by volume, the effect of degradation becomes higher. Where the removal of ruthenium through extraction is not satisfactory, the procedure should repeated. Liquid paraffin is preferably used as the solvent for extracting ruthenium tetroxide. From the practical point of view, use of n-dodecane actually used at the reprocessing step is acceptable. It is considered that ruthenium tertroxide undergoes reduction by the hydrocarbon solvent at first. In order to agglomerate ruthenium dioxide formed in the solvent and facilitate the decomposition, it is preferred that after the operation, the hydrocarbon solvent be heated or allowed to stand still for a certain time. In the case where the temperature of the extraction vessel is elevated, this operation is not necessary, and even if treating or the like is not performed agglomeration, ruthenium dioxide can be separated. It is preferred that the heating temperature be 80 to 90 °C. if the heating temperature is higher than 100 °C, there is a risk of bumping when a droplet of the aqueous phase carries into the system. The black precipitates are amorphous ruthenium dioxide and are chemically stable and hardly soluble in nitric acid. However, they are gradually dissolved in nitric acid containing an oxidizing agent such as Ce(IV) or in sodium hybochlorite (NaOCl) solution.

Motoki et al. (1985) developed a novel method for the separation of radioactive ruthenium from liquid wastes, during the production of ^{99}Mo by the reaction of ^{235}U(n,f), using a column packed with adsorbents composed of zinc and activated charcoal. The optimum condition of the adsorption of ^{106}Ru by this method was to use zinc-charcoal column or zinc-electrodeposited charcoal column of 30~80 % of zinc content for the treatment of liquid waste within the acidic region of $pH < 3$, at the flow rate of ~2 cm^3/min. The adsorbed ^{106}Ru can be recovered by washing the column with water or dilute nitric acid after use. The column could, therefore, repeatedly be used for the treatment of a large amount of waste. High adsorption efficiency of zinc-charcoal mixed column for ruthenium was described to that combination of zinc and chemically inert conductors of electricity which transforms anionic, neutral, and cationic ruthenium species in the solution into eight kinds of highly adsorbable ruthenium species, and adsorption of the species on the charcoal surface with large surface area simultaneously.

The separation of ruthenium from other fission products can be performed by a distillation method in which ruthenium is oxidized to tetroxide prior to the distillation. Some oxidizing agents, such as $HClO_4$ and $KMnO_4$, have been recommended by **Glendenin et al. (1957)** and by **Hume (1951)** to oxidize fission-ruthenium to ruthenium tetroxide.

Shiokawa et al. (1956) Conducted a series of experiments on the distillation of ruthenium, using a variety of oxidizing agents, and came to a conclusion that a few oxidizing agents, such as $K_2Cr_2O_7$, $Ce(SO_4)_2$, $(NH_4)_2S_2O_8$ and PbO_2, are superior. The optimum conditions for the distillation using these oxidants are briefly described below:

1. *$K_2Cr_2O_7$ method.* ^{106}Ru is distilled from a solution containing 1 g of the oxidant and 44 % H_2SO_4 by volume.
2. *$Ce(SO_4)_2$ method.* The starting solution in a distilling apparatus contains ^{106}Ru, 1.5 g of the oxidant and 40 % H_2SO_4 by volume.
3. *$(NH_4)_2S_2O_8$ method.* The distillation is made with 45 ml of the starting solution containing 10 g of the oxidant, 1 ml of 1 M $AgNO_3$ and 5-10 ml of concentrated HNO_3.
4. *PbO_2 method.* The distillation is best affected by 45-50 ml of a solution containing 2 g of PbO_2 and 44 % H_2SO_4 by volume.

Some experiments were performed by **Koda (1957)** on the distillation of carrier-free ^{106}Ru by using $KMnO_4$ as an oxidizing agent. The yield of ^{106}Ru fluctuates from one run to another, and approximately 20-40 % of the ruthenium in the original solution is found neither in the starting solution nor in the distillate. It was confirmed that this is due to the deposition of ruthenium on the inside walls of both the distilling flask and the condenser.

1.6.3. Separation of barium and strontium:

Ayers et al. (1958) mentioned a precipitation method for the recovery of barium and strontium. In this method, carrier barium is added to 6 M HNO_3 solution which contains uranium, barium, strontium, and other fission products. After the addition of carrier barium, evaporation is made to initiate the precipitation of barium and strontium as nitrate salts. Addition of fuming nitric acid to the concentrate completes the precipitation. This mixture is centrifuged to remove dissolved uranium and fission products from barium and strontium nitrate precipitates. The barium and strontium nitrate precipitates are first dissolved in water and then converted to the chromates by the addition of sodium dichromate. 4 M sodium acetate is added to buffer the solution to pH 4.25±0.25, where barium chromate is selectively precipitated. The chromate solution is centrifuged to remove dissolved strontium from precipitated barium chromate. The barium chromate is then dissolved in 0.2 M HNO_3 and another separation of barium and strontium is made after inactive strontium carrier has been added to enhance the removal of radioactive strontium from the barium. The precipitated barium chromate is converted to barium nitrate by fuming nitric acid and excess acid is removed by centrifugation. Barium nitrate is dissolved in water and re-precipitated upon addition of fuming nitric acid. From this point, the lanthanum growth from radioactive barium decay is retained in the final product. The nitrate solution is washed and centrifuged to remove final impurities from the barium nitrate precipitate. The precipitate is dissolved in water and transferred to a product-cup where evaporation reduces barium nitrate to a dry crystalline form.

1.6.4. Separation of zirconium and niobium:

Dash et al. (1993) finalized a new method for the separation of ^{95}Zr-^{95}Nb from irradiated uranium using the ion exchanger hydrous tin(IV) oxide. In this method, the irradiated sample is dissolved in concentrated HNO_3, evaporated to near dryness and taken up in 0.5 M HNO_3. The solution is then passed through a pre-conditioned tin(IV) oxide column.

The column is profusely washed with water and the absorbed ^{95}Zr-^{95}Nb eluted with 10 M HNO_3 subsequently. An overall yield greater than 80 % has been obtained. The product is obtained in a pure nitrate form, which is generally preferred for different applications.

1.6.5. Separation of rare-earth metals:

Heckman and Strand (1991) presented a method for the separation of actinides as anionic complexes by precipitation with cationic surfactants. In this method, tetravalent cations, specially those of actinides can be precipitated with alkyl pyridinium salts from acid nitrate solutions as hexanitrato complexes, and from alkaline carbonate solutions as carbonato complexes. Because only tetravalent cations form anionic hexanitrato complexes, it is possible to separate them from cations in other oxidation states. From carbonate solutions both tetra- and hexavalent cations precipitate with organic cations, which means that, e.g., Pu(IV) and U(VI) are precipitated simultaneously. Due to the simultaneous precipitation, both metals are mixed very intimately, and therefore, after thermal decomposition and reduction in CO mixed oxides of the type $U(Me)O_2$ are formed.

Faubel (1991) studied separation of the trivalent actinides and lanthanides from concentrated nitric acid-intermediate level-waste (ILW) solutions with octyl(phenyl)-N,N-diisobutyl carbamoyl methyl phosphine oxide (CMPO) by the use of extraction chromatography. The influence of numerous elements occurring in the ILW solutions on the loading capacity of the resins have been investigated. A very interesting result is revealed by the fact that molybdenum causes large losses on the capacity of the resin, which can be avoided either by complexing the Mo species with citric or oxalic acid or by removing it by sorption on manganese dioxide. The

CMPO resin was produced by fixing CMPO, liquified at 50 °C, directly to the organic Bio Beads SM7 or silica gel by stirring both components in a beaker up to saturation of the SM7 at 55 wt % CMPO or in the conventional method, where the CMPO resin was produced using a solvent (TBP / kerosene). The loading capacity was more than 20 g / kg, and the performance of the loading and the elution can be significantly improved at higher temperatures up to 75 °C.

Horwitz et al. (1979) invented a process for partitioning and recovering actinide values from acidic waste solutions resulting from reprocessing of irradiated nuclear fuels. In this process, hydroxyl ammonium nitrate and hydrazine are added to the waste solution to adjust the valence of the neptunium and plutonium values in the solution to the +4 oxidation state, thus forming a feed solution and contacting the feed solution with an extractant of dihexoxyethyl phosphoric acid in an organic diluent whereby the actinide values, most of the rare-earth values and some fission product values are taken up by the extractant. Separation is achieved by contacting the loaded extractant with two aqueous strip solutions, a nitric acid solution to selectively strip the americium, curium and rare-earth values, and an oxalate solution of tetramethyl ammonium hydrogen oxalate to selectively strip the neptunium, plutonium, and fission product values. Uranium values remain in the extractant and may be recovered with a phosphoric acid strip. The neptunium and plutonium values are recovered from the oxalate by adding sufficient nitric acid to destroy the complexing ability of the oxalate, forming a second feed and contacting the second feed with a second extractant of tricapryl methyl ammonium nitrate in an inert diluent whereby the neptunium and plutonium values are selectively extracted. The values are recovered from the extractant with formic acid.

Mathur et al. (1995) studied an extraction chromatographic technique using CMPO adsorbed on chromosorb-102 (CAC). In this technique, CMPO has been used as the extracting agent to recover minor actinides from HLW solutions originated from PUREX process. The batchwise uptake behavior of U(VI), Pu(IV), Am(III), Eu(III), Zr(IV), Fe(III), Ru(III), and TcO_4^- from a nitric acid medium by CAC has been studied. The uptake of actinides and lanthanides are higher than those of other fission products and inert materials. The batchwise loading experiments in the presence of Nd(III) / U(VI) have shown that at lower concentrations of these metal ions, the uptake of Pu(IV), U(VI), and Am(III) are reasonably high. Studies on loading of Nd(III), U(VI), and Pu(IV) on a column containing 1.7 g of CAC have shown that Nd(III) (30 mg) and U(VI) (90 mg) could be loaded, while Pu(IV) (~0.6 mg) was loaded on a small column containing 100 mg of CAC without any breakthrough. Further, a synthetic HLW solution, after depleting the uranium content by a 30 % tributyl phosphate contact, were loaded on a CAC column. The effluents did not contain only alpha radioactivity above the background level. The radioactivities could subsequently be eluted with 0.04 M HNO_3 (americium and rare earths), 0.01 M oxalic acid (plutonium), and 0.25 M Na_2CO_3 [U(VI)]. The recoveries of these metal ions were found to be > 99 %.

Koma et al. (1998) provided a method for separating trivalent actinides and rare-earth elements in the TRUEX method using a CMPO-TBP mixed solvent. Examples of trivalent actinides obtained by this method are Am, Cm, Bk, and Cf. Examples of rare-earth elements obtained by this method are Y and the lanthanides from La, Ce and Nd to Lu, but particular Y, and the lanthanides from La to Gd. This method comprises three steps; (i) the extraction step, wherein trivalent actinides and rare-earth elements are extracted by the mixed solvent from highly acidic waste generated by reprocessing of spent nuclear fuel, (ii) nitric acid removal step, wherein the nitric acid concentration of the solvent used for extraction is reduced to 0.1 M or less, and (iii) separation step, in which the trivalent actinides and rare-earth elements combined in the solvent of low nitric acid concentration are separated from each other. In the third step, CMPO-TBP mixed solvent containing trivalent actinides and rare-earth elements is brought into contact with an aqueous solution comprising a nitrate salt ($NaNO_3$) of 1-5 M concentration, and a complexing agent (DTPA) of 0.01-0.1 M concentration. Thus, trivalent actinides are stripped into the aqueous phase and, thereby, separated from rare-earth elements. It is preferable that pH is adjusted to be within the range 1.8-2.2 in the separation step.

1.6.6. Separation of cesium:

Shiokawa et al. (1956) studied the use of phosphotungstic acid as a precipitating agent for ^{137}Cs. Among other fission products, only ^{137}Cs is precipitated with this reagent and its precipitation is best effected in HCl stronger than 1.8 M in the presence of ammonium ion, which can be precipitated as phosphotungstate carrying ^{137}Cs with it. The precipitate is dissolved in 0.1 M NaOH and scavenged with $La(OH)_3$. The filtrate is neutralized with HCl to phenolphthalein and treated with 10 mg of ammonium ion, and 1 ml of 5 % H_2PtCl_6 solution. The precipitate is washed with absolute ethanol, heated to 600 °C and the residue extracted with HCl to give pure ^{137}Cs solution. The average yield is of the order of 80 % and the time required for separation is 2 h. Contamination with other fission products was checked and found to be insignificant. Contamination with ^{95}Zr is eliminated either by repetition of the precipitation of $(NH_4)_2PtCl_6$ or by scavenging with CuS, which simultaneously minimizes the contamination with tellurium and ruthenium.

Yamageta et al. (1957) used univalent thallium as a carrier, which was subsequently oxidized to the trivalent state and separated from ^{137}Cs with ease. Various precipitating agents were tested, including dipicrylamine, sodium cobaltinitrite, chloroplatinic acid, phosphotungstic acid, copper ferrocyanide, silicotungstic acid, and iodide. The first five reagents revealed themselves useful for this purpose; among these, dipicrylamine appears to be the most suitable. When this method is applied to the separation of ^{137}Cs from other fission products, satisfactory results are obtained. Removal of thalium from the precipitate was attempted by the oxidation of Tl(I) to Tl(III), which is either (i) precipitated together with $Fe(OH)_3$, (ii) submitted to ion-exchange separation, or (iii) extracted with hexone. It was found that the last method is the best. In the last method, the precipitate is dissolved in 5 to 10 ml of hexone and shaken with an equal volume of 2 M HCl containing 1 ml of saturated chlorine water. The aqueous layer is washed with the ketone to provide a carrier-free solution of ^{137}Cs.

The use of sodium tetraphenylborate ($Naph_4B$) was studied by **Murakami (1958)** and also by **Sugawara and Tanaka (1958)** for the separation of ^{137}Cs. Murakami studied the co-precipitation of ^{137}Cs with ammonium or potassium tetraphenylborate and also the solubility of ammonium tetraphenylborate. The solubility of ammonium tetraphenylborate at 20°C was found to be 5×10^{-5} M by colorimetric determination of the dissolved ammonium ion. When the precipitate is made with 0.1 % $Naph_4B$ solution (in 0.01 M NaOH) at pH 9 in the presence of 5 mg of ammonia or potassium, more than 90 % of the ^{137}Cs is carried down with the salt. The optimum pH for the co-precipitation was found to be 9. To obtain ^{137}Cs which is free from the contamination of other fission products, scavenging with $Fe(OH)_3$ is effective. The scavenging is more effective when the precipitate is formed with sodium hydroxide than with ammonia because of less adsorption of ^{137}Cs. Aluminum hydroxide is of no use as a scavenger. Also the precipitation of this salt in the solution containing EDTA and some hold-back carriers under the same conditions mentioned above is very successful method for carrier-free separation of ^{137}Cs (from fission products) because of its speed and because there is no necessity for filtration of $Fe(OH)_3$.

Rahman et al. (1997) studied a chemical precipitation method for the co-precipitation of cesium from LLW and ILW with nickel ferrocyanide. High amounts of precipitated cesium were observed in the pH range of 9 to ~ 11. The removal percentages of ^{137}Cs from 37 kBq, 370 kBq, and 3.4 MBq per liter of simulated effluents were approx. 90 %, 99.7 %, and 99.8 %, respectively.

Deodhar et al. (1997) used tetraphenyl boron (TPB) for the extraction of Cs^+ from nitric acid medium. Quantitative extraction of ^{137}Cs was found possible at 0.01 M HNO_3 employing 0.05 M TPB in nitrobenzene. Selective nature of the extractant was demonstrated by the fact that other fission products like ^{95}Zr, ^{95}Nb, ^{133}Ba, ^{85}Sr, ^{89}Sr, ^{103}Ru, and ^{152}Eu do not extract under these conditions.

In case of separation of cesium from fission products using ion-exchange processes, most of the work has been carried out on inorganic absorbers. Cesium can be taken up by a variety of inorganic sorbents, e.g., ammonium phosphomolybdate, ammonium phosphotungstate, titanium phosphate, and zirconium antimonate **(Jenkins, 1984)**.

Ammonium phosphomolybdate has been used by **Murthy (1978)** to separate Cs from other fission products. In Murthy's studies, cesium was absorbed onto ammonium phosphomolybdate or phosphotungstate from about 2 M HNO_3 and it was eluted with 3 M NH_4NO_3 at 40-50 °C after washing the column; high-purity cesium was produced by this method.

The absorption of cesium from alkaline waste (spent fuel handling pond water) has been described by **Bradbury and Swan (1981)** who used a sequential ion-exchange technique. Cesium was adsorbed onto a cation exchanger (Lewatit DN) and eluted with 2 M $(NH_4)_2CO_3$. Because of the alkalinity of the pond water, the main ion adsorbed by the resin was sodium and only 10^{-2} % of the ion exchange sites were occupied by Cs when the column was fully loaded. After elution of the Cs, it was necessary to regenerate the column with ammonium carbonate solution rather than dilute H_2SO_4 since the hydrogen form of Lewatit DN does not show good selectivity for cesium. A further column of Lewatit DN was then used to concentrate the cesium.

Satayanarayana et al. (1994) prepared the synthetic inorganic exchanger ammonium molybdophosphate with alumina as binder AMP-Al_2O_3 and suggested a method to isolate pure cesium from the mixture of fission-products solution. Selective removal and recovery of ^{137}Cs from the fission-products solution (after the removal of uranium and plutonium) may be obtained by passing through the AMP-Al_2O_3 at an overall acidity adjusted to 2 mol dm^{-3} HNO_3, and washing the column with the same molarity of acid. The absorbed cesium can be eluted with 8 mol dm^{-3} NH_4NO_3 solution which can be used for various uses.

Reddy et al. (1994) prepared the new inorganic exchanger zirconium phosphate-ammonium phosphotungstate (Zr-P-APW) and developed a selective method for the removal of cesium from other radioactive fission products. Distribution ratios of various elements, which are likely to be present in the gross fission-products waste solution were studied on Zr-P-APW in the acid concentration range from 0.1 M to 10 M nitric acid. It was observed that the cesium is preferentially taken up by this exchanger when compared with other elements though Rb, Zr, and Ce compete to some extent. It was also observed that, values of distribution ratio of cesium decrease with increasing acid concentration but this trend is predominant in the case of other elements resulting in a wide difference (when compared to cesium) as the acid concentration increases. The elution studies showed that, 90 % of cesium was eluted in 15 bed volumes with

6 M NH_4NO_3 as eluent. Further increase in NH_4NO_3 has little effect on elution pattern.

Zirconium molybdoantimonate (ZrMA) is suitable for column operation. From the detailed investigations carried out on this exchanger, it has been seen that the fission-cesium can be effectively separated from the other accompanying fission products by passing the solution of the gross fission products at an overall acidity adjusted to 2 M HNO_3. The absorbed cesium can be eluted with 8 M NH_4NO_3 as the eluting agent (**Satayanarayana et al., 1995**).

1.6.7. Separation of molybdenum:

Blagojevic et al. (1985) developed a method for the preliminary separation of fission-^{99}Mo from irradiated UO_2. This method uses toluene-3,4-dithiol to precipitate carrier-free molybdenum from fission products dissolved in nitric acid. The recommended procedure is to add 0.5 ml of n-butanol to 25 ml of fission product solution. The solution should be stirred vigorously until the alcohol dissolves. Then, 7 ml of dithiol reagent is added. The resulting green molybdenum complex is filtered through a fast glass fiber filter in which 2 to 3 mm of filter aid is deposited. The precipitate is washed with 1.5 M HNO_3 to remove fission product traces and a small amount of air then should be drawn through to remove excess liquid. Finally, the molybdenum dithiol can be recovered by dissolving it in approximately 20 ml of acetone. This procedure has the following advantages: (i) it is fast and efficient (the efficiency is greater than 90 %), (ii) the precipitate is stable even if the acid concentration is increased above 6 M, (iii) separation of ^{99}Mo from other fission products and uranium is achieved in a single precipitation step, (iv) liquid waste is reduced to a minimum, and (v) the radionuclidic purity of the product is approximately 97 %.

The basic extraction study on the separation of the fission-molybdenum-99 and uranium in sulfuric acid solution by tri-n-octylamine (TOA) in kerosene has been investigated by **Lee et al. (1984)**. Coextraction of 99.9 % U and 99.9 % ^{99}Mo was carried out by using 30 % TOA-10 % octanol-60 % kerosene in two steps. Based on the complex stability difference between UO_2(VI) and MO_2(VI) with TOA, 99 % uranium in the organic phase can be back-extracted by 1.5 M NaCl in six steps. On the other hand, 90 % ^{99}Mo can be stripped from the organic phase by 1 M Na_2CO_3 in two steps.

In JAERI, after dissolution of the irradiated UO_2 pellets in HNO_3, UO_2-dissolved solution (to which iodine carrier is added) is distilled to remove ^{131}I. Then, ^{99}Mo is extracted in the organic phase by stirring with D2EHPA solution. Almost all of the fission products are retained in the aqueous phase and stored in a tank for high-level wastes. The ^{99}Mo is back-extracted in aqueous solution with 0.5 M HNO_3 solution containing H_2O_2. The organic solution containing trace amounts of uranium and fission products is stored in a tank for organic wastes. After decomposition of H_2O_2 with $NaNO_2$, the volume of the aqueous solution is reduced by evaporation and then the solution is passed through a column filled with alumina on which ^{99}Mo is adsorbed. The column being washed with 0.1 M HNO_3 and water, ^{99}Mo is eventually eluted with 1 M NH_4OH solution **(Kudo et al., 1989)**.

In the French project developed in the 1980s for the production of ^{99}Mo from the fission of ^{235}U, three chromatographic extraction cycles using the extractant tri-n-butyl acetohydroxamic acid (TBAH), in a 0.05 mol/l solution in xylene adsorbed on hydrophobic (SiO_2 at a level of 30 % by weight are used to recover and purify ^{99}Mo from the dissolution liquor stripped of tellurium and iodine). The first chromatographic cycle is conducted in a sulfuric acid medium, and the remaining two are conducted in a nitric acid. For the quantitative extraction of molybdenum, it is only necessary to guarantee that this element is present in the dissolution liquor in the Mo(VI) oxidation state. This condition is satisfied under radiolysis in the first chromatographic cycle simply by aging the dissolution liquor. No molybdenum oxidation state adjustment is required for the second and third chromatographic extraction cycles **(Bourges et al., 1996)**.

In the process invented by **Kohly and Madic (1987)** for the recovery of molybdenum-99 from irradiated targets of an U/Al alloy, after dissolution in sulfuric acid, the iodine and tellurium present in solution are separated. Inactive sodium or potassium iodide and inactive tellurium (in the form of tellurous acid) are added to the solution as well as metallic aluminum. Thus, the tellurite is reduced to elemental tellurium. Then, silver nitrate is added which leads to the precipitation of silver iodide. The solution is then filtered and the filtered residue containing the iodine and tellurium is recovered for conditioning in tight containers, which are stored for three months before being dispatched to the waste processing plant. After precipitation of iodine and tellurium, ^{99}Mo(III) is oxidized to ^{99}Mo(VI) by using H_2O_2. Following this oxidation, extraction of ^{99}Mo(VI) by hydroxamic acid is performed using extraction chromatography technique. In this technique, a column with a diameter of 3 cm and a height of 30 cm is lined with silica gel charged with 30 % of a mass of a solution containing 5×10^{-2} mol/l of tributylacto hydroxamic acid in mesitylene. The solution containing ^{99}Mo(VI) (~ 2 M-acidity solution) is passed through the column, the latter is washed with approximately 1 liter of 0.2 M sulfuric acid solution. The molybdenum extracted on the column can then be recovered by elution with 10 g / l ammonium carbonate solution. Acidity of the eluate is then adjusted to 2 M by adding sulfuric or nitric acid. This is followed by repeating the same previous extraction process but with the use of a second chromatographic column having smaller dimensions. This repeating is made in order to increase the degree of ^{99}Mo purity. The eluate from the second column is purified from the traces of organic products by passing through a silica gel-filled column charged with dodecane.

Hadi et al. (1978) developed a process for recovering ^{99}Mo from a matrix which has been irradiated with neutrons and contains fissionable materials and fission products, wherein the matrix is decomposed in an aqueous alkali hydroxide solution. In this process, the alkali solution containing molybdenum, in the form of MoO_4^{2-}, is conditioned with an iodine reducing agent. Mineral acid is added to the alkali solution. The molybdenum contained in the acidified solution is reduced to form Mo(III). The Mo(III) is complexed with SCN^- ions to form $[Mo(SCN)_6]^{3-}$-containing solution is treated with a previously-contained organic ion exchanger to selectively sorb the molybdenum. The ion exchanger, which is now charged with molybdenum, is separated from the solution which is now free of molybdenum. The separated molybdenum charged ion exchanger is washed with a wash solution in order to remove residual quantities of the molybdenum-free solution. The molybdenum from the washed ion exchanger is eluted with a liquor at an elution temperature in the range from about 20 °C to about 70 °C.

In I.R.E, after digestion of the irradiated uranium targets in NaOH-$NaNO_2$ solution and filtration, the filtrate is diluted with 1.8 ml H_2O, 1.46 ml concentrated HNO_3. The solution is shaken by means of air bubbles and heated. The released iodine is trapped on platinum asbestos. The 1 M HNO_3 acid solution is passed through an alumina column. The Mo-99 is adsorbed on Al_2O_3 while 90 % of the fission products are eliminated to the waste in the fixation effluents and in the subsequent phases 1 M HNO_3, H_2O, and 10^{-2} M NH_4OH. Mo-99 is then desorbed by concentrated NH_4OH. The column is submitted to further washing with

H_2O and 3 M NaOH in view of its generation and reutilization in the following cycles. The Mo-99 of the NH_4OH (2 ml) eluate is fixed on 1×8 Dowex resin (200-400 mesh) which is next washed with water, then eluted with 1 M $(NH_4)_2CO_3$. The eluate is acidified with 12 M H_2SO_4 and passed through a column of activated carbon. After fixation, washing is done with H_2O and finally elution is carried out with 100 ml of 0.3 M NaOH. The molybdenum yield in this operation is about 85 to 90 %. the final solution is sampled to measure volume activity and radionuclidic purity **(Salacz, 1989)**.

At CRNL, after dissolution of targets in HNO_3 and $Hg(NO_3)_2$, the solution is drawn through a glass column containing preconditioned Al_2O_3. The flow rate is monitored closely to prevent channeling of load solution through the bed. The column is rinsed with dilute HNO_3, water, then dilute NH_4OH before recovery of the ^{99}Mo by elution with 1 M NH_4OH **(Burrill and Harrison, 1989)**.

El-Absy (1991) described a radiochemical procedure to separate mCi quantities of carrier-free ^{99}Mo from irradiated uranium targets. In this procedure, Mo(VI) was quantitatively adsorbed onto small columns of charcoal impregnated with tin (IV) chloride from fission-products solution in 0.25 M HCl. From a single adsorption-desorption cycle, > 99.6 % radionuclidic-pure ^{99}Mo was obtained. A product purity of > 99.98 % ^{99}Mo was obtained by recycling on a new column.

In the process developed by **Aly (1997)** for the separation of fission-^{99}Mo, after uranyl nitrate targets are digested in NaOH solution, the supernatant withdrawn and centrifuged to separate traces of the residue. One drop of H_2O_2 is added to the solution which is then heated for 5 min to expel excess H_2O_2. After heating, the solution is acidified with HNO_3 solution till pH 1. The solution of pH 1 is loaded onto a column packed with 1.1 g of 12-molybdocerate(IV). The column is washed with appropriate volumes of HCl or HNO_3 containing $NaNO_3$ or NH_4NO_3 mixture solutions. The column is then conditioned for ^{99m}Tc elution by passing 25-30 ml of 0.9 % saline solution through the column matrix. The generated ^{99m}Tc radionuclide is eluted after a growth time of 24 h with 0.9 % NaCl solution.

In the process for the production of fission-^{99}Mo described by **Hladic et al. (1989)**, after the irradiated uranium oxide targets were dissolved in HNO_3, the process solution is diluted to a uranium concentration of 170-180 mg/ml by adding washing solutions of the dissolver up to a total volume of two liters and then poured through an alumina column which contains 150-200 g alumnia with a flow rate of about 10 ml/min. by this procedure, > 95 % of the ^{99}Mo radioactivity is retained on the column. After washing with 150 ml 0.1 M HNO_3, 150 ml H_2O, and 0.01 M NH_3 solution, the ^{99}Mo radioactivity is obtained in this way. The depleted dissolver solution containing uranium and the residual fission products are stored together until waste treatment. Purification of the Mo-99 is accomplished by an additional chromatographic step followed by sublimation of the evaporated eluate. For this, the eluate is adjusted to 0.1 M HNO_3 and poured through a second small column filled with about 30 g of alumina. After washing and elution, the ^{99}Mo radioactivity is in a volume of about 100 ml to which 10 ml of concentrated HNO_3 is added. This mixture is evaporated to dryness in three quartz ampoules. After heating the dry residue at 1000°C, the purified ^{99}Mo is dissolved in 50 ml of 1 M NaOH and is ready for loading ^{99}Mo/^{99m}Tc generators.

Ali and Ache (1989) developed a new procedure for the final purification of ^{99}Mo, generated for medical use by the reaction ^{235}U (n,f) ^{99}Mo. It consists in the sorption of molybdate species on metal oxide ion exchangers from nitric acid medium followed by a thermal desorption of the volatile molybdenum(VI) oxide from the adsorber matrix by applying temperatures up to 1250 °C. This method could efficiently substitute the existing final purification of ^{99}Mo, which is currently performed by sublimation of MoO_3 from the residue of an evaporated ^{99}Mo, so that it concentrates a labor intensive and time consuming operation. The investigations presented describe the thermal desorption of molybdenum(VI) oxide species from Mo-loaded Al_2O_3 and SnO_2 ion exchangers. The influence of temperature, sublimation time, Mo-loading, carrier gas, atmosphere, and grain size of the oxide particles on the sublimation yields has been determined. The assumption that water vapor present in the carrier gas applied during the volatilization would lead to a drastic increase in the sublimation yields was confirmed for both oxides. SnO_2 exchanger demonstrated a distinct superiority for practical applications. When heated up to 1250 °C in presence of an O_2/H_2O-carrier gas, porous oxide permits quantitative Mo-yields within 30 minutes.

In KFK-molybdenum production cycle from uranium silicide targets, after digestion in KOH, the alkaline solution containing molybdenum enters a column filled with the strong basic exchanger AG1X8 (200-400 mesh), which had been converted into the OH^- -form prior to use. The molybdenum is retained quantitatively on the stationary phase. After washing the column subsequently with 3 M KOH and water, the molybdenum is eluted quantitatively with HNO_3 or $HNO_3/NaNO_3$ solution. The choice of eluent concentration depends on the process conception. In case that iodine shall be separated, the acid concentration has to be lowered and the salt content has to be increased. To separate iodine, the eluate from the AG1 column is collected in a stainless-steel off-gas controlled vessel. After adding a solution of $NaNO_2$ in water, the matrix is passed through a column of a non-polar macroporous matrix of polystyrene divinylbenzene (such as Lewatit 1023, the Bio-Beads Adsorbents SM-2, SM-4, SM-16, or the slightly polar macroporous matrix of a cyclic ester SM-7). Iodine is retained on these stationary phases quantitatively in form of the element. The Mo-containing solution, which is now free from iodine, is directly passed through a chromatographic column of manganese dioxide. Molybdenum is adsorbed quantitatively on the stationary phase together with the main bulk of the accompanying fission products. Iodine impurities in every oxidation stage as well as anionic species, and the alkaline and alkaline-earth cations are not retained on the oxide. After washing the oxide with HNO_3 and subsequently with water, the dry column is treated with 10 column volumes of a mixture of ammonium thiocyanate, potassium iodide, and sodium sulfite in 2 M sulfuric acid. Suitable concentrations for the added compounds are 0.02 mol/l for SCN^-, 0.04 mol/l for SO_3^{2-}, and 0.001 mol/l for the I^-. The feeding of this solution through the column has to be carried out from the bottom to the top. Under these conditions, the whole stationary phase including the adsorbed radioactivity is being dissolved. The solution containing molybdenum, dissolved manganese, and the accompanying fission-product impurities are passed through a chelex-100 column which is pretreated, just before the molybdenum loading, with 2 M sulfuric acid containing approximately the same SCN^-, SO_3^{2-}, and I^- amounts as in the feed. The molybdenum is retained quantitatively on the exchanger as $[Mo(SCN)_6]^{3-}$, while the manganese ions and the fission-product species are not adsorbed on the column. The column is subsequently washed with sulfuric acid containing thiocyanate, pure sulfuric acid, and water. The molybdenum elution from the column is carried out with 1 M NaOH. To guarantee a product of highest purity, the procedure is repeated on a second smaller chelex-100 column of a particle size range between 100-200 mesh. A significant difference presents the molybdenum elution from this column. It has to be carried out with 6 M ammonium hydroxide. The ammonium molybdate eluate is transferred to a sublimation cell. The molybdenum solution is evaporated to a volume of few milliliters and then placed into a platinum crucible. The solution is evaporated on an electric hot plate and the crucible with the completely dry residue slowly heated up to about 700 °C in a quartz glass apparatus. At this temperature, all organic impurities possibly introduced from the ion exchangers into the product are removed. A quartz glass condensation device is placed over the quartz vessel in the furnace and the temperature is increased to about 1150 °C. The molybdenum volatilization is completed in about 30 minutes. Molybdenum trioxide is condensed between the upper part of the quartz apparatus located in the furnace and the quartz condensation device. After removal of the platinum crucible with the residue out of the quartz device, the oxide on the quartz glass is dissolved with ammonia vapor. The molybdenum solution is mixed with sodium hydroxide and ammonia is removed by boiling. The solution obtained represents the final product **(Sameh and Bertram-Berg, 1992)**.

1.7. Radiochemical processing plants:

1.7.1. Processing stages of irradiated uranium targets:

Design of a radiochemical processing plant for the treatment of irradiated uranium targets to produce different isotopes that are born during fission may be based on the following stages **(Glasstone, 1955)**:

1. Storage (or cooling) of the irradiated uranium targets.
2. Dissolution of targets and preparation of the feed solution.
3. Storage of feed solution prior to introduction into the separation process.
4. Separation of desired isotope(s) from unfissioned uranium and other fission products.
5. Collection and disposal of waste streams.
6. Collection of product(s) streams and preparation for shipment.
7. Preparation, distribution, and recycling of process reagents.

1.7.2. Maintenance of the equipments used during processing:

Equipments used for processing must be properly designed and manufactured so as to require the absolute minimum of repair or replacement. Special precautions must be taken to ensure good workmanship, and the materials of construction should be resistant to the process solutions. All piping must be absolutely leaktight. The use of complicated equipment with moving parts requiring lubrication should be avoided if possible. The same stipulation applies to valves and pumps with packing. If equipment that might need fairly frequent maintenance must be used, then it should be installed in separate shielded compartments.

In spite of all precautions taken to prevent equipment failure, it is inevitable that some maintenance will be required. In the design of radiochemical processing plants, two basically different approaches have been used; these are (i) remote maintenance and (ii) direct maintenance.

1.7.2.1. Remote maintenance:

The equipments and piping are so designed that when repair is necessary any item can be removed and replaced by a duplicate using remotely operated mechanical devices. The faulty equipment can then either be discarded or decontaminated and repaired elsewhere. In the case of remote maintenance, a considerable amount of space is required, since every piece of equipment must be located in such a manner that it can be reached by a crane without displacing any other piece. Remote-maintenance plants seem to be more desirable where large volumes of solution must be treated and where continuity of production is important. The main advantage of remote maintenance is that it permits operation with the minimum interruption. Even a major break can be rectified in a short time by removal and replacement of the equipment. One of the disadvantages of remote maintenance is that greater effort is demanded in the design of the plant so that every piece of equipment can be readily removed by remote control. In addition, the remote-maintenance type of design means low flexibility and that process changes are difficult to incorporate **(Glasstone, 1955)**.

1.7.2.2. Direct maintenance:

The equipment is designed so that its parts can be decontaminated, by flowing suitable solutions through them, to an extent that will permit maintenance personnel to effect direct repair in place. In the case of direct maintenance, cells with concrete walls are used to segregate process equipment according to function and activity. Isolation of blocks of equipment makes possible the decontamination and repair of a section of the plant while other sections remain in operation. The installation is determined largely by process and engineering requirements, so that the plant is more compact than in the case of the remote maintenance. The lower construction and operating costs of a direct-maintenance plant may be the determining factors when smaller volumes are to be processed.

On contrast with remote-maintenance type of design, direct-maintenance type of design allows high flexibility during operation and permits process changes to be incorporated easily. Direct maintenance, on the other hand, may mean in an emergency that the plant will be shut down for a period of time sufficient to accomplish both decontamination and repair. However, where duplicate plant units have been installed, maintenance can be carried out without shutdown **(Glasstone, 1955)**.

1.7.3. Radiation shielding:

When it comes in contact with, and attempts to pass through, any type of mass, nuclear radiation is attenuated or weakened by the ionization process. Each time an alpha or beta particle or a gamma photon comes in contact with an atom, the radiation causes an electron to leave the atom's orbit, either through attraction, repulsion or propulsion. Each time this electron interaction process occurs, the radiation loses a little energy. The amount of radiation attenuation that occurs depends on: (i) the type and thickness of the mass and (ii) the particular type of radiation that is attempting to penetrate the mass.

Alpha and beta particles are easily attenuated and, in most cases, are not a major concern when it comes to shielding, but gamma radiation is not readily attenuated and is biologically destructive **(Hoag, 1998)**. The commonest three ways in which gamma radiation is attenuated are photoelectric absorption, Compton scattering, and pair production **(Kaplan, 1958; Arnikar, 1994)**.

The so-called "transmission calculations" and "shielding calculations" must be taken into consideration during the selection of any shielding material **(Evans, 1955; Garth and Turinetti, 1997; Knoll, 1979)**.

Lead shielding represents a practical approach to the need for protection from X-rays and gamma radiations. Its uniform density, high atomic number, level of stability, ease of fabrication, high degree of flexibility in application, and its availability at reasonable cost are principal factors. Lead brick is available in different thicknesses and it is designed to interlock at all surfaces; each brick plugs into the adjacent one, thereby assuring no straight-line leakage is possible. At the edges of the brick areas, the outside surface of the brick is cut at 90 degrees to the face, thereby assuring a tight fit where the contaminant occurs.

It should be mentioned that, the absorption of high-energy beta radiation (e.g., from Sr-90) in high-Z materials such as lead and tungsten may result in the production of electromagnetic radiation called "bremsstrahlung" **(Choppin and Rydberg, 1980; Kaplan, 1958)** which is more penetrating than the beta radiation that produced it. Low-*Z* materials such as plastics and glass minimize the production of bremsstrahlung **(NCRP, 1971).**

1.7.4. Radioactive waste disposal:

Radioactive waste is measured in terms of its volume (cubic meters) and its radioactivity content (curies). According to the level of radioactivity, radioactive waste can be classified to (i) high-level waste (HLW), (ii) intermediate-level waste (ILW), and (iii) low-level waste (LLW). High-level waste is the residue left when the irradiated uranium targets are chemically processed to separate the required isotopes. Disposal of HLW type of waste includes the following principal steps **(Bodansky, 1996; Krauskopf, 1988)**:

1. Vitrification into appropriate matrix, e.g., borosilicate (Pyrex) glass.
2. Sealing into corrosion-resistant container, such as stainless-steel cylinders, surrounded with an impermeable backfill, such as bentonite clay.
3. Burying about one kilometer deep at suitable and preferably dry repository with long-term geological stability.

ILW consists of radioactive resin and sludge, spent filter cartridges and scrap pieces from normal maintenance of the processing equipment. ILW may be solidified by combining it with a sand/cement mix or bitumen, and then placed into concrete drums, which are transported to the radioactive waste disposal for burial.

Low-level waste consists of day-today refuse such as gloves, glassware, plastic containers, and disposable overalls and overshoes. LLW is compressed into steel drums, sealed and transported for disposal **(Krauskopf, 1988).**

Placement of radioactive wastes in deep geologic repositories has been favored for many decades worldwide. A good repository site is one for which the location and type of rock (i) prevent or limit the entry of water into the repository; (ii) in the event of entry of water, slow the outward migration of water to the biosphere; (iii) provide geochemical conditions favorable to low solubility of radionuclides and low rate of corrosion of the waste package; (iv) retard the motion of major radionuclides so that they move more slowly than the water; and (v) are at low risk of future disruption by earthquake, erosion, or other natural phenomena **(Bodansky, 1996)**.

1.7.5. Transportation of radioactive materials:

In case of transportation of the irradiated targets or any other radioactive material (desired isotope or waste) during the production process, the following principals must be considered:

1. Radioactive material must be moved in such a manner that material cannot be released from the package.
2. A liquid, gas, or dispersible solid must be transported in a suitable vessel with an outer container that has been passed several tests against leakage, dropping, pressure, fire etc.
3. A liquid must be packaged with sufficient absorbent material to completely absorb twice the volume of liquid, e.g., approximately a 4.5:1 ratio by volume for fine grade vermiculite.
4. The inner container must be clearly marked with a "Radioactive Materials" label listing the amount and identify of the radioisotope(s).
5. Adequate shielding must be provided.
6. The inner container must be placed within a closed, strong outer package known to be free of contamination.