Chapter 1
INTRODUCTION

1.1. General Statement

Man has been consciously modifying his environment and using its resources to improve the quality of his life since the earliest civilizations. The industrial revolution, however, arose a new problem of pollution. Growing exploitation and processing of environmental resources of all kinds, the presence of biological effects of many chemical residues, such as those of pesticides, industrial solvents, fossil-fuel combustion products besides the radioactive wastes which are at low concentrations and quite undetectable by the senses. During their lifetimes, human and other animal as well as plant organisms are exposed not to one but to several contaminants, either simultaneously or consecutively.

For environmental safety, different operations are required to control side effects of human activities that produce several hundreds of contaminants. The radioactive pollution is indeed greatly harmful and represents one of the most dangerous hazards that would seriously affect the living environment. This is due to the fact that waste effluents from nuclear activities generally contain trace to minor quantities of radionuclides and would represent variable radiation levels. Release of these effluents to environment represents radiation hazards for man and his environment. Decontamination of these waste effluents from radioactive materials to acceptable levels is thus of major importance. Such decontamination is indeed of vital importance as some of these substances eventually enter the body either by inhalation (via the air that is breathed), or by ingestion of contaminated foodstuffs and drinks, or direct adsorption through skin.

During the last decades, radioactive materials and radiation sources have been widely used in various fields such as energy production, industry,

medicine, research, and agriculture. Various incidents and accidents could happen during these multifield applications and would thus result in relatively large amounts of radioactive wastes and contaminated objects. Therefore, increasing attention has been made to removal and recovery of metal ions that result from industrial and radioactive activities that generate large amounts of liquid waste. This task is of multi purpose; namely pollution control, raw material recovery, reuse of treated waste water as well as protection of public health. Therefore, various physicochemical and biological methods were studied for metal ions removal from solutions.

Concerning the nuclear activities, many efficient separation techniques of radioactive metal ions have been studied and actively developed in a manner that new advanced processes with superior properties have been set up [1].

The recovery of metals from waste aqueous solutions may be achieved by applying a variety of methods such as chemical precipitation, complexation, reverse osmosis, adsorption, evaporation, ion exchange, solvent extraction, electrochemical methods, and others. Such processes should be of small space requirement, inexpensive, and can be applied in small and large scales.

1.2. Nuclear Fuel Cycle

It is interesting to mention that among the radioactive contaminants, uranium which is still considered as the primary element used in commercial nuclear reactors. Besides, it is one of the important actinides in irradiated uranium fuel. Uranium is found in various radioactive wastes [2-4], its concentration in intermediate level active wastes attains 0.08mol/l [5].

The nuclear fuel cycle comprises a wide range of various processes associated with the production of fuel for nuclear reactors and reprocessing for recycling or direct disposal. From these processes, different types of wastes are produced. The front-end of fuel cycle includes mining of uranium ores, processing, enrichment, fuel fabrication, and reactor operation. The back-end of

fuel cycle deals with spent fuel or reprocessing for recycling purposes. A schematic simplified diagram for the nuclear fuel cycle is given in figure (1.1). The extent of fuel cycle depends on reactor type i.e. natural or enriched uranium fuelled, extent of uranium utilization, indigenous nuclear raw materials resources as well as extent of self-reliance desired in nuclear fuel cycle technology [6].

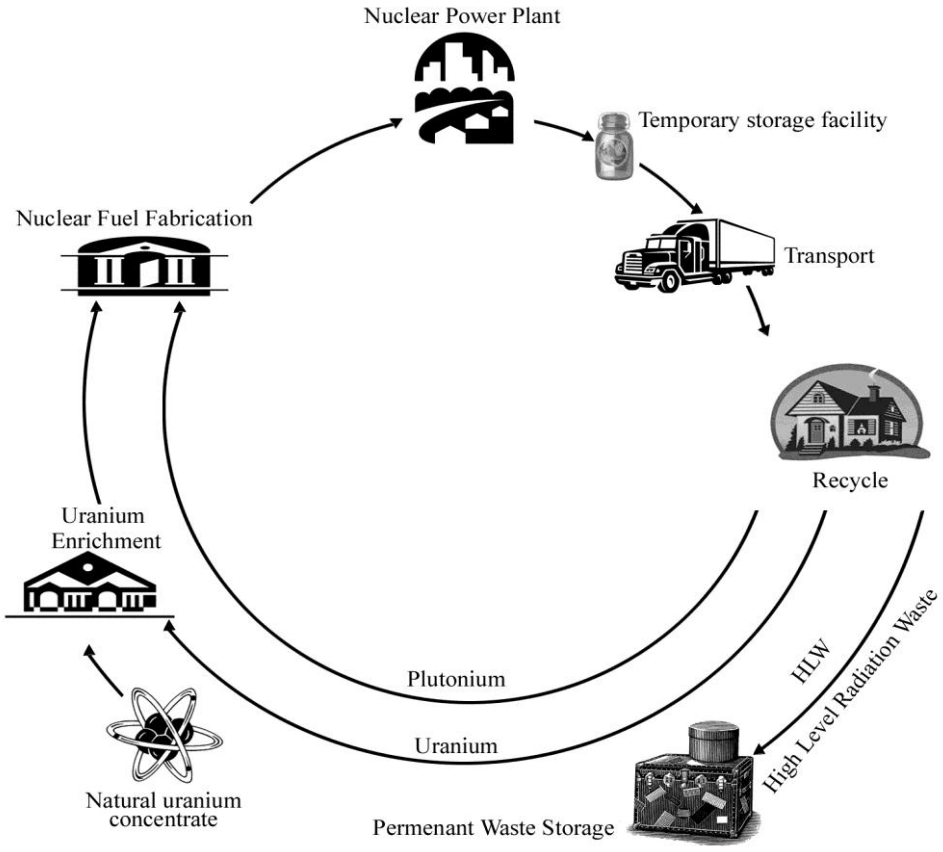

Fig. (1.1): Simplified nuclear fuel cycle.

1.3. Milling and Yellow Cake Production

Extraction of uranium from its ores generally involves the following unit operations, figure (1.2) [7]:

i- Size reduction: The ore is crushed and ground to provide a suitable range of particle sizes required for effective leaching and to produce a material that can be slurried and pumped through the processing circuits.

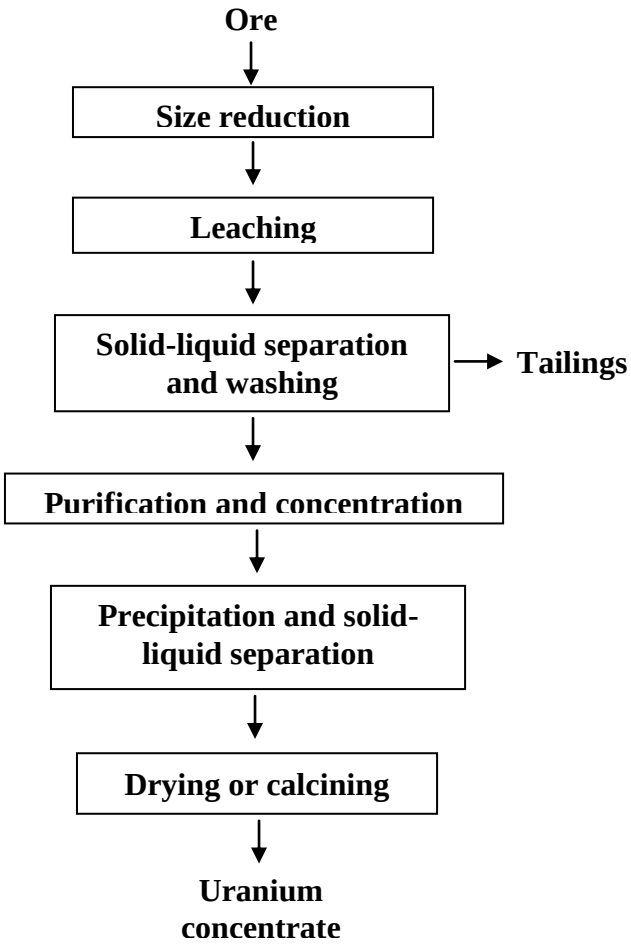

Fig. (1.2): Generalized process for production of uranium concentrate from ore.

ii- Leaching: Uranium is leached from the ground ore using either acid or alkaline (carbonate) solutions with or without heating and with or without addition of oxidants.

iii- Solid-liquid separation and washing: The pregnant liquor is separated from the leached ore, which is then washed to remove any remaining dissolved uranium.

iv- Purification and concentration: The pregnant liquor contains a low concentration of uranium (usually in the order of 1 g/L) and many impurities; it must, therefore, be concentrated and purified using either ion exchange resins or solvent extraction, or both.

v- Precipitation and solid-liquid separation: Uranium concentrate (yellow cake) is precipitated from the pregnant solution in one or two stages using a common base; the product is either filtered or dewatered by settling and centrifugation.

vi- Drying or calcining: The concentrate is dried or calcined and packed in steel drums lined with polyethylene.

vii- Tailing disposal: The process should also include adequate provision for treating and impounding the tailings and for recovering and recycling some, or most, of the water used.

These unit operations are combined to constitute actual industrial processes.

1.4. Yellow Cake Purification

Although in mining and milling operations uranium has been separated from majority of other elements and radionuclides (such as radium, radon, and thorium) present in original uranium ore, it still contains impurities detrimental to its final use and needs further purification to reach nuclear grade. Yellow cake is refined by either dry or wet process. The former is based on the anhydrous fluoride volatility process; where uranium hexafluoride product is purified by distillation.

All commercial yellow cake refiners use the classical wet process, in this process uranium dissolution in nitric acid produces an aqueous solution of uranyl nitrate $UO_2(NO_3)_2$, containing excess nitric acid and variable amounts of nitrates of metallic impurities present in the concentrates. The next step in the purification is separation of uranyl nitrate from the other metallic impurities in a dissolver solution by a liquid-liquid extraction (solvent extraction). Practically, all uranium refineries now tributyl phosphate (TBP) dissolved in an inert hydrocarbon diluent. Solvent extraction process depends on association between the uranyl and nitrate ions to produce a neutral complex with TBP in the extraction section. In the scrubbing section, all nonuranium metallic impurities and some uranium are removed from the organic phase by counter flowing dilute nitric acid, which is returned to the extracting section. In stripping section, purified uranium in organic phase leaving the scrubbing section is transferred to an aqueous phase by back-extraction with suitable stripping agents.

1.5. Uranium

1.5.1 Some aspects of uranium chemistry

Uranium was discovered by Klaproth (Germany) in 1789[8] in the course of an examination of pitchblend mineral originating in Saxony. Historically, it is the oldest known of all actinides with atomic number 92, and its ground state electronic configuration is [Rn] $5f^3$ $6d^1$ $7s^2$. It shows the +3, +4, +5 and +6 oxidation states and compounds of U(IV) and U(VI) being of major importance.

The occurrence of uranium in outermost layer of earth's crust is about 2.7ppm [9]. About 155 minerals containing uranium as an important constituent are known, with about 50 others containing minor amounts of uranium or containing uranium as impurity [10, 11]. Uranium minerals can be divided into two broad classes, primary and secondary. Primary uranium minerals are found in magmatic hydrothermal veins and in pegmatites. They include uraninite, pitchblende, and a large number of complex multiple oxides such as uranium-bearing lanthanides, niobates, tantalates, and titanates [12]. Secondary mineral being produced by alteration , hydration, metathesis, and/or oxidation and possibly including transport and redeposition of the uranium away from its original place of occurrence, secondary minerals usually contain hexavalent uranium and are bright yellow-green through red. As expected from the importance of uranium as an energy source, there is a very extensive literature dealing with all aspects of uranium mineralogy and geology [10,11,13 -20].

Because of the complexity of many uranium ores and the usual low concentrations of uranium present, recovery of uranium often has a difficult problem for chemist. Physical concentration methods (floatation, gravitational, electromagnetic, etc.) have met only limited success. Chemical methods used for uranium recovery from ores have to be designed to economically treat large ore volumes. Because of this and because uranium is a very electropositive metal, most direct pyrochemical methods are not applicable and processes usually involve modern aqueous extractive metallurgy [21].

Uranium ores vary in chemical complexity from the relatively simple pitchblendes, which are accompanied by perhaps ten other minerals, to exceedingly complex and refractory uranium-bearing titanates, niobates, and tantalates containing rare earths and many other metals. As mentioned previously, all methods that have been commonly used comprise the following steps: first, preconcentration of ore; then a leaching operation to extract uranium into an aqueous phase; and finally recovery of uranium from pregnant leach liquors by ion exchange, solvent extraction, or direct precipitation [22-26].

U(III) is unstable in aqueous medium and slowly evolves hydrogen from aqueous solution, but otherwise it is similar to trivalent rare earths. Fluoride and oxalate precipitate U(III) from acid solution; while sulfide, sulfate, chloride, bromide, iodide, nitrate, and perchlorate do not.

U(IV) is chemically similar to Ce(IV); iodate, substituted arsenates, and cupferron precipitates it, even from strong acid solutions. Oxygen slowly oxidizes U(IV) to U(VI), a process which is rapidly accelerated by several catalytic species.

Pentavalent uranium disproportionates in solution to uranium (IV) and (VI). Solutions of U (V) are most stable in pH range of 2.0 to 4.0, with a disproportionation half life of at least two hours at room temperature. Uranium (V) is precipitated as a potassium salt form strong carbonate solution.

U (VI) is the main stable state in solutions contacting air. The familiar test for sodium, precipitation of sodium uranyl acetate, is useful for qualitative identification of the uranyl ion (UO_2^{2+}). Peroxide precipitates U (VI) and also oxidizes and precipitates U (IV) from moderately acid solutions [27].

Hydroxides of all valence states of uranium, except zero, are insoluble. A dimeric species has been identified for uranium (VI)-hydroxide system. The order of stability for anionic complexes of different valency states is:

$$U^{4+} > UO_2^{2+} > U^{3+} > UO^{2+}$$

This also is the order of hydrolytic reaction. The formation of stronger complexes with uranyl ion than with trivalent species is attributed to the higher charge on uranium atom in the uranyl entity. The order of stability of anionic complexes is [28]:

fluoride > nitrate > chloride > bromide > iodide > perchlorate;

carbonate > oxalate > sulfate

This is the same as the order of such cations as Al(III), Fe(III), Zr(IV), and Cu(II), but is the reverse of that of Ag(I), Cu(I), Hg(II), and Pb(II).

Uranium is the fourth element in the actinide series and its analytical chemistry shows characteristic differences between the earlier actinides and lanthanides. The analytical chemistry of uranium is fairly extensive, and includes gravimetric, coulometric, polarographic, spectrophotometric, and other modern methods.

Gravimetric method is usually proceeded by precipitating hexavalent uranium from solution with ammonium hydroxide, and this gives a good separation of uranium from several elements. Carbonate-free ammonia is essential for complete precipitation because of the strong complexation of uranyl ions by carbonate ions. Gravimetric determination is completed by igniting the precipitate to U_3O_8 at 875 ± 25 ^oC for a period of about 16 h [29]. A number of organic reagents have been proposed as precipitants for uranium, and the full extent of their use has been discussed [30]. The reagents include cupferron, arsanilic acid, and others.

It is well known that, in alkaline carbonate medium, most interfering elements are precipitated whereas U(VI) forms a soluble carbonate complex [31,32]. Vast majority of the elements are precipitated as carbonates or hydroxides by the carbonate of alkali metals or ammonium, while uranium forms mainly soluble carbonate complexs of the structure $[UO_2(CO_3)_3]^{4-}$ and/or $[UO_2(CO_3)_2]^{2-}$ and stays in solution [33-38].

Uranium(VI) can be selectively extracted from nitrate medium with polar solvents, such as methylethyl ketone in CCl_4 [39], mesityl oxide [40], ethyl acetate [41], TBP [42], TBP in isooctane [43],TBP in xylene [44], and TOPO in cyclohexane [45]. Also, it has been extracted from nitrate medium with triphenylarsine oxide in chloroform[46], and as the tetrapropylammonium uranyl nitrate complex, into methyl isobutylketone [47].

In presence of amines, uranium can be extracted with non-polar solvents from hydrochloric, sulphuric, and acetic acid media [48].

Thiocyanate and uranyl ions in acid medium form a stepwise series of yellow complexes such as $[UO_2SCN]^+$, $[UO_2(SCN)_2]$, and $[UO_2(SCN)_3]^-$. Higher concentration of thiocyanate displaces the equilibrium towards the last-mentioned and more intensely colored complex. The absorption maximum of this complex lies in near ultraviolet, at 350 nm. At wavelengths shorter than 360 nm, thiocyanate ions begin to absorb. Uranium thiocyanate complex may be extracted with diethyl ether, amyl alcohol [49], or TBP in CCl_4 [50,51] or kerosene [52]. Extraction of this uranium complex from weakly acidic medium in presence of EDTA prevents interference by iron (III) and many other metals. The interference of iron (III) can also be eliminated by addition of a reducing agent such as stannous chloride or ascorbic acid. The uranium thiocyanate ion-association complex with crystal violet was extracted into chloroform [53].

1.5.2. Basic aspects of uranium radiochemistry

The value of uranium has become that associated with its use in nuclear power reactors. Uranium is one of the important elements in nuclear field. Nuclear power based on uranium fuel is used in generating electricity owing to the need to reduce the usage of fossile fuels. Uranium is also used in atomic dating and powering nuclear submarines. Detailed nuclear, physical, and chemical properties of uranium are addressed in many textbooks and references due to its nuclear importance [27, 54-57].

All electrical energy that has been generated from nuclear reactors has come indirectly from uranium. It is important to mention that the energy yield per atom of uranium 235 is about 200 MeV. The majority of reactors use natural, slightly enriched or highly enriched uranium. Even plutonium fuelled systems contain depleted uranium have had to rely on uranium at some earlier stages for generation of initial uranium inventories [58].

A fuel element must be capable of resisting temperatures considerably, about 1000 ^{o}C, without either any physical or chemical deterioration due to heat or to radiation effects. The cost of uranium constitutes only a smaller fraction of the total cost of nuclear power [9]. Most power reactors today use ceramic enclosed pellets of UO_2, PuO_2 or ThO_2 as a fuel [58]. The use of uranium as a reactor material is limited by presence of certain elemental impurities with high neutron absorption cross-section e.g. boron, cadmium, hafnium and several rare earth elements.

The build-up of fission products as a result of neutron fission contributes to the decrease in reactivity in reactors. This requires their removal which represents a major reason for reprocessing of fuel. The quantity of fission products depends on the reactor power and the burn-up [9].

Prior to development of nuclear industry, present applications of elements in nuclear field depend on the nuclear properties of the elements rather than their chemical properties or compounds used. The major use of uranium in nuclear power industry is well known [57].

The naturally occurring uranium isotopes [8, 59] are U-238 (99.275%), U-235 (0.72%) and U-234 (0.0054%) with half-lifes of $4.468X10^{9}$, $7.038X10^{8}$ and $2.45X10^{5}$ years, respectively. All these radionuclides are alpha-emitters. U-235 is the only naturally occurring fissile material [60]. The nuclear properties of these naturally occurring radionuclides together with other uranium isotopes are given in Table (1.1) [59].

Table (1.1): Nuclear properties of some uranium isotopes [59]

Mass number	Half life	Mode of decay	Main radiations (MeV)	Method of production
232	68.9 y	α	α 5.320 (68.6%), 5.264 (31.2 %), γ 0.058	^{232}Th (α,4n)
	8 X 10^{13} y	SF		
233	1.592 X 10^{5} y	α	α 4.824 (82.70%), 4.783 (14.9 %), γ 0.097	^{233}Pa daughter
	1.2 X 10^{17} y	SF		
234	2.47 X 10^{5} y	α	α 4.777 (72 %), 4.723 (28 %)	nature
	2 X 10^{16} y	SF		
235	7.1 X 10^{8} y	α	α 4.397 (57 %), 4.367 (18 %), γ 0.186	nature
	3.5 X 10^{17} y	SF		
236	2.342 X 10^{7} y	α	α 4.494 (74 %), 4.445 (26 %)	^{235}U (n,γ)
	2 X 10^{16} y	SF		
237	6.75 d	β^-	β^- 0.519	^{236}U (n,γ)
			γ 0.060	^{241}Pu daughter
238	4.51 X 10^{9} y	α	α 4.196 (77 %), 4.149 (23 %)	nature
	8.19 X 10^{15} y	SF		
239	23.5 min	β^-	β^- 1.29, γ 0.075	^{238}U (n,γ)

U-238 is the longest-lived member and the parent of the 4n+2 radioactive decay series, which includes U-234 as a member. U-235 is the natural parent of the 4n+3 series and it is the longest-lived member. The principal radioactivities of these two series are given in Table (1.2) [61].

Uranium is the only nuclear fuel which occurs naturally and contains 0.72 % of the fissionable isotope U-235. The more abundant isotope U-238 may be converted to plutonium Pu-239 by a neutron capture and decay processes, Table (1.3) [62], and Pu is readily fissionable. Thorium occurs abundantly and forms fissionable U-233 through a neutron capature and decay processes, Table (1.3). Hence there is one basic fuel, uranium, and two other elements, thorium and plutonium, which enter the fuel cycle through breeding processes [63].

Table (1.2): Principal radioactive decay products of ^{238}U (A) and ^{235}U (B) chains [61].

Nuclide		Half-life		Radiation	
A	**B**	**A**	**B**	**A**	**B**
^{238}U	^{235}U	4.51×10^9 y	7.1×10^8 y	α (γ)	α, γ
^{234}Th	^{231}Th	24.1 d	25.5 h	β(γ)	β(γ)
^{234}Pa	^{231}Pa	1.17 min	3.25×10^4 y	β, γ	α, γ
^{234}U	^{227}Ac	2.47×10^5 y	21.6 y	α (γ)	α, β(γ)
^{230}Th	^{227}Th	8×10^4 y	18.2 d	α (γ)	α, γ
^{226}Ra	^{223}Fr	1602 y	22 min	α (γ)	α, γ
^{222}Rn	^{223}Ra	3.821 d	11.43 d	α	α, γ
^{218}Po	^{219}Rn	3.05 min	4.0 s	α	α, γ
^{214}Pb	^{215}Po	26.8 min	1.78 ms	β, γ	α
^{214}Bi	^{211}Pb	19.7 min	36.1 min	β, γ	β, γ
^{214}Po	^{211}Bi	164 μs	2.15 min	α	α, β(γ)
^{210}Pb	^{207}Ti	21 y	4.79 min	β(γ)	β, γ
^{210}Bi	^{207}Pb	5.01 d	Stable	β	
^{210}Po		138.4 d		α	
^{206}Pb		Stable			

Table (1.3): Principal fissionable nuclides [62].

Nuclide	Fission Threshold (neutron energy in Me V)	Average Energy Available from Thermal Fission (Me V)
Fertile ^{232}Th	1.4	…
Fissile ^{233}U	0	198
Fissile ^{235}U	0	202
Fertile ^{238}U	0.6	…
Fissile ^{239}Pu	0	210
Uranium-Plutonium Cycle: $^{238}U + n \xrightarrow{\gamma} {}^{239}U \xrightarrow{\beta} {}^{239}Np \xrightarrow{\beta} {}^{239}Pu$		
Thorium-Uranium Cycle: $^{232}Th + n \xrightarrow{\gamma} {}^{233}Th \xrightarrow{\beta} {}^{233}Pa \xrightarrow{\beta} {}^{233}U$		

Uranium can be used in a number of different forms as nuclear fuels: generally as metals and alloys or as ceramic compounds such as oxides and carbides. These fuel forms may be introduced into the fuel element in bulk, e.g. cast metal rods or sintered oxide pellets, or they may be dispersed in a nonfissionable metal or ceramic matrix [24, 63].

1.6. Radioactive Waste

Nuclear waste is any waste material-gas, liquid or solid its radioactivity exceeds certain limits. From the global point of view, pollution of the earth's air, water and soil is the threat to all life. During the last century man used nuclear energy resources and created hazardous radioactive isotopes through nuclear explosions that were injected into air, water and soil.

The total radiation in environment which originates from radioactive decay, comes from three sources:

i) natural radiation due to presence of natural radioactive substances.

ii) radionuclides produced by interactions of cosmic rays.

iii) man-made nuclear releases such as nuclear reactors, reprocessing plants, radiochemical laboratories as well as the application of different radionuclides in research and development. The radioactive remaining materials after these activities are called radioactive wastes.

1.6.1. Radioactive waste management

The management of these wastes means all activities, administrative and operational, that are involved in handling, conditioning, transport, storage and disposal of waste [64]. It also includes the radiological control during all these activities to provide an efficient protection of biosphere and consequently man from the radiological hazard in both short and long –term [65]. Therefore, waste management includes collection, sorting, treatment, conditioning, transportation, storage and eventual disposal.

The intention of regulations limiting the release of radioactive material from nuclear installations is to keep the radioactivity concentration in ground and surface water or in air well below the level recommended by the international commission for radiological protection (ICRP). The regulations may follow the limitation of the total amount of radioactivity associated with a certain material that may be released over a given period of time [66].

As a consequence of this limitation, most of the radioactivity arising as waste from nuclear technology has to be isolated from the environment by some storage or final disposal technique. The first step toward this is usually a volume reduction, preparing the waste for storage as a liquid or solid. This is considered part of the waste-generation technology rather than of the waste management.

1.6.2. Physical classification of radioactive wastes

Various classification systems can be used to categorize radioactive wastes [66, 67]. Classifications can be based on specific activities, dose-rates or radiotoxicities. Other classification criteria might be the origin of waste, physicochemical natures or types of radiation and half-lives of the radionuclides. Each of these classifications may have its advantages and disadvantages depending on the purposes of classification. The International Atomic Energy Agency (IAEA) has suggested a classification system based upon specific activity [68].

The specific activities defining high, intermediate and low-level are often different in various countries and are even different in various establishments of the same country. According to the physical nature, three types of radioactive wastes are to be considered, namely; solid, liquid and gaseous wastes [68].

1.6.2.1. Solid wastes

The main characterization for radioactive solid wastes produced from nuclear power plants, nuclear research centers, medical institutions and fuel reprocessing plants [69, 70] are shown in Table (1.4). On the basis of the treatment and immobilization processes, which are appropriate, the solid wastes are usually classified and segregated as either combustible or non- combustible; sometimes they are segregated for compaction.

Table (1.4): Characteristics of typical radioactive solid wastes [69,70].

Characteristic	Combustible		Non-combustible	
Waste Category	**Non-alpha**	**Alpha Bearing**	**Non-alpha**	**Alpha Bearing**
Main sources	Nuclear power plants, nuclear research centers, medical institutions	Fuel reprocessing plants, nuclear research centers, medical institutions	Nuclear power plants, nuclear research centers	Fuel reprocessing plants, nuclear research centers
Physical type:	Paper, clothe, and polymeric Materials	Metal, glass, masonry, polymeric material	Metal, glass, masonry, polymeric materials	Metal, glass, masonry, polymeric materials
Bulk density, Kg/m^3	100 - 400	100 - 400	200 - 3000	200 - 3000
Compressibility, %	50 - 85	50 - 85	0 - 60	0 - 60
Chemical:				
Ash content:				
(wt%)	2 - 15	2 - 15	--	--
(vol.%)	2 - 15	2 - 15	--	--
Radioactivity: Nuclides	Activation products, fission products	Fission products transuranics	Activation products, fission products	Fission products transuranics
Specific activity:				
β -γ (Ci/m^3)	0 - 0.5	0 - 0.1	0 - 0.1	0 - 0.1
α (Ci/m^3)	0 - 0.01	0 - 5	0 - 0.01	0 - 100

1.6.2.2. Liquid wastes

In many nuclear power plants, one of the largest sources of liquid wastes are the demineralizer regenerator. Sulphate wastes result from regeneration primarily in boiling water reactors (BWRs) also in pressurized water reactors (PWRs). Borate wastes result from the boric acid used in the primary coolant system of PWRs.

Three categories of low and intermediate-level liquid wastes are identified based on their specific activities and are shown in Table (1.5) [69]. For example in Egypt, low-level waste is defined as materials with activity no greater than 10^{-6} Ci/m^3 with salt content less than 0.7 Kg/m^3. Intermediate-level waste is defined as materials with activity less than 10^{-4} Ci/m^3 with salt content less than

25 Kg/m^3. The chemical and radiochemical composition of low and Intermediate level liquid wastes are summarized in Tables (1.6) and (1.7) [71].

Table (1.5): Classification of radioactive liquid wastes [69].

Category	Activity(m^3)	Remarks
	Mixed β/γ-emitters[a]	
Exempt waste	< 37 K Bq	No treatment required; release after measuring[b] treated, no shielding required
Low-level waste (LLW)	37 K Bq 37 M Bq to 3.7 G Bq	Treated, shielding sometimes required according to radionuclide composition
Intermediate-level waste (ILW)	3.7 G Bq to 370 T Bq	Treated, shielding necessary in all cases

[a] Concentration of alpha activity is negligible.
[b] Related to the release rates, licensed by the respective component authority.

Table (1.6): Chemical composition of Inshas low and intermediate level liquid wastes [71].

Name	Concentration range (g/L)	
	LLW	ILW
Dry residue	0.42-0.7	10-100
Suspended matter	0.01-0.03	0.15
Ratio Ca:Mg	1:1	1:1
Sulphate ion	0.03-0.06	0.06-0.10
Chloride ion	0.02-0.05	0.04-0.12
Nitrate ion	0.06-0.12	0.007-0.07
phosphat ion	0.001-0.04	0.01-0.02
Oxalate ion	0.001-0.04	0.02-0.10
Detergent	0.01-0.02	0.01-0.03

Table (1.7): Radiochemical composition of low and intermediate level liquid wastes [71].

Name	Quantity			
	LLW		ILW	
	Bq/m^3	Ci/L	Bq/m^3	Ci/L
Σ β-including	3.7×10^{7}	1×10^{-6}	3.7×10^{9}	1×10^{-4}
Cesium-137	1.48×10^{7}	4×10^{-7}	1.85×10^{9}	5×10^{-5}
Cobalt-60	1.85×10^{5}	5×10^{-9}	3.7×10^{7}	1×10^{-5}
Strontium-90 + Yttrium-90	2.22×10^{6}	6×10^{-8}	7.4×10^{8}	2×10^{-5}
Ruthenium-106 + Rhdium-106	7.4×10^{5}	5×10^{-8}	3.7×10^{8}	1×10^{-5}
Iodine-131	1.85×10^{5}	5×10^{-9}	3.7×10^{7}	1×10^{-6}
Europium-154	1.1×10^{6}	3×10^{-9}	3.7×10^{8}	1×10^{-5}
Zirconium-95 + Praseodymium-144	1.11×10^{6}	3×10^{-9}	3.7×10^{8}	1×10^{-5}
Cerium-144 + Praseodymium-144	7.4×10^{5}	2×10^{-8}	.....	.....
Σα-	3.7×10^{5}	1×10^{-8}	3.7×10^{8}	1×10^{-5}

1.6.2.3. Gaseous wastes

Nuclear power reactors are the main sources of radioactive gaseous wastes. Gases quantities depend largely on the type of reactor. The range of activity is restricted and methods of treatment are few, but never the less, there still exist some differences in activity levels and composition of gaseous effluents that justify the classification of gaseous wastes into several categories as shown in Table (1.8) [68].

Table (1.8): Proposal for categories of radioactive gaseous wastes [68].

Category	Activity Level A (Ci/m^3)	Remarks
1	$\leq 10^{-10}$	Usually not treated effluents
2	$10^{-10} < A \leq 10^{-6}$	Effluents usually treated by filtration
3	$> 10^{-6}$	Effluents usually treated by different methods

1.6.3. Sources and quantities of radioactive waste from nuclear activities

Compared to the previously described sources and quantities of radioactive wastes mainly generated in developed countries with an extensive nuclear program, a relatively small volume of exclusive low-level wastes are generated at small nuclear research centers, universities, industries and other nuclear research establishments [72].

In small nuclear research centers a great number of radioisotopes are produced in research reactors for different purposes by irradiation of special targets or in a particle accelerator from which the desired isotopes are subsequently extracted or processed in nearly connected hot cells or laboratories. Beside the above mentioned institutions in a nuclear research center, some other installations are located where radioisotopes in tracers levels are used and handled. The volume of liquid and solid radioactive wastes produced by individual users of radioactive materials is not likely to be large. Most of the radioactive wastes, solid and liquid are contaminated with short-lived radioisotopes, and are directed for decay, dilution and subsequent discharge. Waste containing long lived fission products including transuranic nuclides, are not produced within the vast majority of laboratories in small nuclear research centers of developing countries. Only a small part of radioactive waste, is contaminated with long-lived radioisotopes like ^{14}C and ^{3}H from limited laboratory experiments or uranium and thorium from processing investigations in laboratory and pilot plant scale.

The application of radioactive materials in medical diagnosis and therapy is extremely important and continually expanding. In many instances alternative methods are not available. The main areas of application are: radioimmunoassay, radiopharmaceuticals, diagnostic techniques, radiotherapy, and research.

Volumes and activity-concentrations of radioactive waste are relatively low. A completely different type of solid waste represents an encapsulated quantity

of certain radionuclides housed in shielded assemblies which are extensively used for various purposes in hospitals. Individual radionuclide is present in a very concentrated form with high activity level.

Certain industrial establishments use particular forms of radioactive material like sealed sources, luminous devices and specialized electronic valves for scientific measurements, non-destructive testing, quality control, the evaluation of plant performance and, development as well as evaluation of their products and processes. The quantities of this type of work depend largely on the development and level of the countries technology.

Users of radioactive materials in research establishments and universities are most commonly involved in monitoring the metabolic or environmental pathways associated with a large range of compounds as diverse as drugs, pesticides, fertilizer and minerals. The range of useful radionuclides is normally fairly restricted and the activity content of the labeled compounds is low, but at some research establishments rather exotic radionuclides may also be used. The radionuclides most commonly employed in studying the toxicology of many chemical compounds and their associated metabolic pathways are carbon-14 and tritium, as they can be incorporated into complex molecules with considerable uniformity.

1.7. Aim of the Work

In the Nuclear Material Authority, uranium is purified from its mineral ores concentrate (impure yellow cake) by a liquid-liquid extraction process to separate the bulk of uranium from the associated impurities in the leach liquor or after dissolution of the impure cake in nitric acid solution. The obtained raffinate solution contains about 1500 ppm of uranium together with the other impurities. The main aim of this work is to develop a selected process for removal of this uranium from the raffinate solution before their safe disposal. Within this objective, two approaches were investigated for this purpose. The first is based

on a chemical precipitation procedure while the second is based on a solvent extraction procedure. The different parameters affecting the removal of uranium from this raffinate by precipitation or solvent extraction were studied. Further the best conditions for uranium removal were obtained and assessed.

1.8. Main Separation Methods for Decontamination of Radioactive Waste

Radioactive waste is mainly generated from the nuclear fuel cycle (front and back ends), industrial applications of radioisotopes as well as uncontrolled release of radioactive materials from nuclear accidents. In milling operations, the radioactive wastes are mainly solid rock materials representing the tailing below the cut off level of the ore materials. In the subsequent milling and purification of yellow cake processes, the radioactive wastes are represented by the ore residue tailing or solution stream, respectively. Separation of metal contaminants from liquid wastes involves operations intended to benefit safety and/or economy. There are several ways that can be used in treatment of radioactive liquid wastes. Among these are chemical precipitation, solvent extraction, ion exchange, adsorption, and others.

1.8.1. Chemical precipitation

Precipitation is one of the most widespread methods of separating elements from solutions and is based on the difference in solubility of the various metal compounds. It involves two steps: nucleation and crystal growth. The factors favoring increased rate of nucleation are concentrated solution, high speed of agitation, and presence of finely divided solid in solution which act as nucleating agent. If the rate of nucleation is high, the precipitate will be finely divided. On the other hand, if the rate of nucleation is slow, the precipitate will have large particle size. As a result, finely divided precipitates are obtained from concentrated solutions and coarse precipitates are obtained from dilute solutions. Rate of precipitation may also decrease as a result of presence of certain metal ions or organic compounds in solution [73, 74].

Usually, precipitation is carried out under strict conditions to achieve the necessary separation from the other constituents. In general, the following factors control a precipitation process [75]:

i-Precipitation should be conducted within a certain pH range, since most precipitates are redissolved outside this range. For example, $Al(OH)_3$ precipitates from dilute solution at pH 4 but redissolves at pH 8.

ii-Precipitation should be conducted at an optimum temperature since most precipitates are more soluble in hot than in cold solution.

Coprecipitation is the contamination of a precipitate by substances that are normally soluble under the conditions of precipitation. It can be used to precipitate an ion that is difficult to precipitate due to its very low concentration, e.g., radioactive trace amounts in leach solution. In the first case, a co-precipitator is added deliberately and is called a collector or carrier.

The choice of a precipitant for certain metal ions depends, beside the economic factor, on the following factors:

i- It should be specific as far as possible so that pure precipitates can be obtained.

ii- It should form a very insoluble precipitate so that quantitative recoveries are possible.

It is comparatively rare to find a precipitant having all these requirements, and it is often that the precipitate obtained is only a crude concentrate which has to be redissolved and purified.

Presence of a complexing ion in solution may prohibit the precipitation of an ion. For example, AgCl precipitates readily from silver nitrate solution on adding a chloride ion but not from a cyanide solution since silver in such solution is complexed as $[Ag(CN)_2]^-$. This principle is often utilized to make separations. For example, by adjusting the pH of a solution to 10, using sodium carbonate, uranium remains in solution as a complex sodium uranyl carbonate,

while aluminum and manganese are precipitated as hydroxides. If NaOH were added, then uranium together with other impurities would precipitate.

Change in valency by adding an oxidizing or a reducing agent to the solution is sometimes exploited to affect selective precipitations. For example, both Co^{2+} and Ni^{2+} ions precipitate as hydroxides at pH 6.7, but Co^{3+} precipitates at pH 3. Therefore, to precipitate cobalt selectively from a mixture with nickel, oxidation of Co^{2+} to Co^{3+} prior to precipitation is conducted.

Presence of a reducing agent may also be necessary for formation of a precipitate. For example, most of tetravalent uranium salts are insoluble in water while the hexavalent salts are soluble. Therefore, uranium (VI) in leach solutions may be reduced to uranium (IV), as recovery of uranium from low level liquid wastes was achieved by reduction of uranium (VI) to uranium (IV) using Fe(II) in sulphuric and phosphoric acid media followed by uranium (IV) precipitation as fluoride [76]. Similarly, cuprous salts are less soluble than cupric and therefore they can be precipitated by adding a reducing agent. Cuprous ion may undergo hydrolysis to be precipitated as an oxide, undergo disproportionation to produce a metal, or in presence of certain ions, e.g., Cl^- or CN^-, precipitate to form an insoluble salt.

1.8.1.1. Precipitation of metal hydroxides

Hydroxide systems have an extensive application in hydrometallurgical processing. A strongly alkali such as sodium hydroxide is generally unsatisfactory as a precipitating agents for metal hydroxides. The pH is difficult to control even when a dilute alkali solution is used, and the precipitates formed are very gelatinous and voluminous. They are usually flocculated colloids and are highly prone to adsorption. As a consequence, filtration is slow and often unmanageable. Washing is difficult and the precipitate is usually far from pure. Strong alkalis, including lime, are mainly used in scavenging operations to recover metals present in small concentrations as in the recovery of metals from

effluents. To control a solution at a specific pH requires the use of a suitable buffer or an appropriate metallic oxide, hydroxide or carbonate. Buffers are effective but are usually costly for hydrometallurgical processes and are mainly used in analytical separation. An example is the use of a benzoic acid-ammonium benzoate mixture to control a solution at pH 4 [73].

The existence of the two oxidation states of iron provides alternative selective hydrolysis routes for the separation of iron from other metals. Thus several metals can be precipitated preferentially as hydroxides in presence of iron (II). This method is used in the extraction of titanium by the sulphate process where titanium (IV) is selectively hydrolysed at pH 2 with iron (II) held in solution. Alternatively, iron (III) in small amounts can be precipitated selectively as hydroxide from several other metals. For example, in extraction of nickel, iron is oxidised and separated as $Fe(OH)_3$ using nickel hydroxide as a hydrolyzing agent [73].

1.8.1.2. Precipitation of metal carbonates

None of the carbonates is stable below pH 1.5 and the likelihood of obtaining clear-cut, selective precipitation of metal carbonates by pH control is difficult but the preferential precipitation should be possible in some situation. Thus $CdCO_3$ should precipitate preferentially to $ZnCO_3$, and $CoCO_3$ to $NiCO_3$. Such reactions may be of use for purification purposes in circumstances where the second metal is the minor constituent [73].

1.8.2. Solvent extraction

In the early nineteenth century it was observed that many metals reacted with organic compounds to form colored complexes, which were soluble in organic solvents. These complexes, later, called chelates [77], the metal atom is bound to at least two donor atoms linked together through a hydrocarbon chain. The specific significance of cyclic structure of metal chelates was discussed in 1904

by Ley [78]. Chelating agents can be highly selective for certain metals through variation of donor atoms, donor strength and ring structure. This has led to their extensive use in analytical chemistry for separating different metals, which is the subject of several excellent monographs [79-82]. The first publication on chelate extraction is probably that of Cazeneuve in 1900 [83], who extracted aqueous Cr (III) by a solution of diphenylcarbazide in benzene.

Solvent extraction is well known as one of the most effective techniques for the separation and purification of elements on industrial scale [84]. A large number of liquid-liquid extraction processes have been proposed for metal waste recovery and recycling [85, 86]. Solvent extraction separation is based on the difference in solubilities of elements and their compounds in two immiscible liquid phases. Usually, the initial phase is aqueous and the second phase is organic solvent immiscible with each other. Solvent extraction is usually fast and demands only very simple equipments. It lends itself to multistage operation without increase of heat consumption and chemicals which make it particularly useful when either extreme purification is necessary or when the metals are so similar in their properties that a single precipitation or crystallization would not give the required degree of separation. It is preferable when large amounts of metal ions are found.

The first large-scale industrial solvent extraction process was used in the production of ton amounts of high- purity uranium in 1942 by the Mallinckrodt Chemical Company in St. Louis, where ether was employed to extract uranyl nitrate selectively from impure aqueous solutions [87]. Ether was later replaced by dibutylcarbitol (DBC, Butex) and methyl isobutyl ketone (MIBK), hexone for uranium purification [88].

There are several mechanisms by which a metal containing species may transfer from an aqueous phase to organic one and they have been classified in different arbitrary ways [89]. The metal species in solution must change to form a compatible species with the organic solvent.

There are some general requirements for successful solvent extraction operation,these main requirements are [91];

i- the ability of the extractant to transfer the metal to the organic phase,

ii- the ability of the extractant to provide a pure product stream free from harmful impurities,

iii- high solubility in the chosen organic diluent of both the extractant and the metal complex. Also, low aqueous solubility of the extractant in the aqueous phase to minimize losses during operation,

iv- reasonable kinetics for extraction and stripping,

v- good coalescing properties of the aqueous and organic phases after contacting either in extraction or stripping,

vi- the extractant should have a consistent quality with little batch to batch variation, and

vii- the extractant and diluent should be non toxic and biodegradable.

Liquid- liquid extraction is based on the physiochemical property of the relative solubility of elements in selective solvents [90]. Liquid- liquid extraction processes can performed using conventional mixer-settlers or the pulsating columns. In the nineties of the last century the interesting liquid membranes has been introduced with the advantage of achieving both extraction and stripping in one step.

Organic extractants used for metal extraction can be divided, in general, into the following three classes; acidic extractants, basic or anion exchange extractants and solvating extractants [90].

1.8.2.1. Acidic extractants

These extractants possess ionizable hydrogen atoms that can be replaced by metal ions to form neutral complexes which are soluble in organic phase. The extent of extraction depends on acidity of aqueous phase, nature of metal,

ionization constant, pKa, of extractant and its concentration, as well as any interactions between the metal and extractant [90].

The simple extraction equilibrium is generally represented by:

$$M^n + n\overline{RH} \rightleftharpoons \overline{MR_n} + nH^+ \quad \text{.....(1)}$$

where, M^n refers to metal ion in aqueous phase,

RH refers to extractant in organic phase,

and bars refers to organic phase.

1.8.2.2. Basic (anionic) extractants

These extractants are normally protonated form of high molecular weight amines or quaternary ammonium compounds [84]. The extraction depends on the ability of metal ions to form anionic species in aqueous phase which are then extracted as ion-pairs by amine salts in an ion exchange process:

$$\overline{(p\text{-}n)R_3HN^+} + MX_p^{(p-n)} \rightleftharpoons \overline{(R_3HN^+)_{p-n}\,(MXp^{(p-n)})} \text{.....(2)}$$

where, R_3HN^+ is the extractant in organic phase,

$MX^{(p-n)}$ is the metal species in aqueous phase.

In general, extraction by amine salts follows the order of quaternary ammonium salts > tertiary > secondary > primary amines [90].

1.8.2.3. Solvating extractants

Solvating extractants compete with water in the primary solvation shell of metal atom. The extraction generally proceeds by replacement of water molecules by these reagents, which often contain suitable donor atom to metal extractants which facilitates the transfer of metal complex into a non polar organic phase [90].

$$MX_p(H_2O) + \overline{qS} \rightleftharpoons \overline{MX_pS_q} + qH_2O \text{.....(3)}$$

or

$$HMX_{(n+1)} + \overline{xS} \rightleftharpoons \overline{HS_x^+MX^-_{(n+1)}} \text{.....(4)}$$

where MX is the metal species in aqueous phase,

S is the extractant in organic phase.

Metal extraction by solvating extractants depends on the extent of complex formation in the aqueous phase [90]. The nature of extracted complex is determined by a balance between electropositivity of metal and polarity of solvating ligand compared to water.

1.8.3. Ion exchange

The term ion-exchange is generally understood to mean the exchange of ions of like sign between a solution and a solid highly insoluble body in contact with it. This technique can be used for removal of undesirable cations and/or anions from waste water or aqueous solutions.

Solid ion exchangers may be synthetic or natural and insoluble ionic macromolecules that are able to exchange ions with the outer surrounding solution. Ion exchanger contains either positive or negative net charges which are neutralized by the movable ions in solution. Ion exchange process is generally carried out by the column technique. The size of column is selected according to the quantity of ions to be retained in the column. The behavior of elements such as chromium on strongly acidic cation exchanger in hydrofluoric acid can be eluted using 1M HF or retained on Dowex 50 then eluted with 4M HNO_3. The properties of rare-earth metals are so similar that separation of them is a difficult task. The classical methods of separation such as fractional crystallization and fractional precipitation are very time consuming. The situation is greatly improved when a complexing agent such as citrate or EDTA are present in solution using ion exchange chromatography.

Effects of eluent concentration, pH, presence of complexing agents, and column length should be studied when using such technique as a mode of separation. This method is preferable when small quantities or low concentrations are found [92]. Ion exchange materials have several applications

in numerous fields such as in nuclear industry, water treatment, metal recovery and analytical chemistry.

1.8.4. Adsorption

Adsorption is a significant phenomenon in many natural, physical, biological and chemical processes. The material that is concentrated or adsorbed to surface is called the adsorbate while the adsorbing phase is termed the adsorbent (solid-liquid, solid-gas, liquid-liquid or liquid-gas) [93]. There are many substances, natural and artificial which can be used as adsorbents such as humic substances, clays, sand, fly ash, active carbon as natural adsorbents and magnesia cement, hydroxides, metal oxides, zeolites as artificial adsorbants. Beacause of their large surface area and their high degree of surface reactivity, they have several applications in radiochemistry, environmental chemistry, analytical chemistry and biochemistry.

1.8.5. Other methods

Other methods such as electrochemical and dialysis methods are also used for decontamination purposes. The electrolysis of dilute sulphuric acid solutions with mercury cathode results in the deposition of a variety of elements such as Cr [94] (from liquid wastes) as example. Uranium may be deposited electrochemically at cathode from acetate, oxalate, formate, fluoride, chloride and phosphate solutions[95-101].

Dialysis method is based on the relative rates of diffusion of substances through membranes. There are other methods of separation related to the dialysis such as electrodialysis which is carried out in an electric field and ultra filtration which is filtration under pressure through large pored dialyzing membrane. The principal factors which govern passage of substances through membrane are mainly diffusion coefficient of substances and size of pores in the membrane. Recovery of chromium (VI) from liquid wastes was achieved by this method [102,103].

1.9. Literature Survey

Kulkarni [104] has used the emulsion liquid membrane (ELM) technique for selective separation and recovery of low concentrations of uranium, generated during uranium purification and processing, from acidic wastes using tri-n-octylphosphine oxide (TOPO) in paraffin as a carrier and sodium carbonate as a stripping agent. The waste used as the feed phase, have a composition of nearly 600 ppm U(VI), 360 ppm Fe(III), 325 ppm Ca(II), 390 ppm Mg(II) at an acidity of 1.2 M HNO_3. In presence of various metal ions, selective permeation of uranyl ions through liquid membrane was observed to be more than 70%. Batch type extractions of U (VI) by the ELM method were performed to simulate two-stage counter extraction and the experimental findings suggest that U (VI) concentration in the final raffinate can be lowered to below 50 ppm.

EL-Dessouky et. al. [105] have used natural inorganic exchangers to precipitate radioactive elements for treatment. In this work, improvement the removal of caesium, cobalt and europium with zinc sulfate as a coagulant, different clay minerals and parameters affecting the precipitation process have been investigated.

Silicon (IV) antimonate was used as a cation exchanger (Aly et. al. [106]) to recovery of some radioactive nuclides from acidic radioactive waste, silicon (IV) antimonite was prepared by dropwise addition of antimony pentachloride and sodium silicate. This product shows excellent thermal and chemical stability. Distribution coefficient, selectivity and separation factors for recovery of metal ions were calculated. Further, effective separation and recovery of metal ions have been achieved with column technique from nitric acid media.

Barbette et. al. [107] studied the efficiency for extraction of uranium (VI) by new modified silica gels, namely N-tripropionate (or N-triacetate)-substitude tetraazamacrocycles-bound silica gels. Effects of nature of ligand, pH and temperature were studied both in batch experiments as well as in continuous

extraction. This silica gel is a good candidate for extraction of uranium (VI) when compared to a commercially available acid-type chelating resin. The breakthrough and regeneration tests showed that the total removal of uranium (VI) from a contaminated solution can be achieved using a column packed with such tetraazamacrocycles-bound silica gels. Finally, use of a modified silica gel in a pilot device allowed total decontamination of $50m^3$ of real effluents containing traces of uranium, plutonium, and americium.

Two types of alumina/zirconia composite systems using MgO and Y_2O_3 stabilizers were prepared applying the polymeric sol-gel route method using metal chloride precursors. The prepared composite materials, ceramic powders, were tested for removal of Co(II), Cd(II), Pb(II), and U(VI) ions from liquid waste. Factors affecting sorption behavior e.g. particle size, contact time, temperature, initial concentration of solute, mass of adsorbent and competing ions were studied. Adsorption capacity of prepared composite materials for removal of Co(II), Cd(II), Pb(II), and U(VI) ions from liquid waste was measured and found to be 209, 183, 33 and 67 mg/g, respectively [108].

Equilibrium measurements on the sorption of uranium and thorium ions from nitric acid solutions by di(2-ethyl hexyl) phosphoric acid (HDEHP) – impregnanted activated carbon have been done using batch technique [109]. Experimental isotherms evaluated from distribution coefficients of both ions were fit to Langmuir, Freundlish, and Dubinin-Radushkevich (D-R) isotherm models. Of the models tested, D-R expression was found to represent isotherms of both ions better over the entire concentration range investigated than either Langmuir or Freundlish model. The changes in standard thermodynamic quantities (viz. ΔH, ΔS, and ΔG) were calculated and maximum adsorption capacity of HDEHP impregnanted carbon together with the mean free energy of both studied ions were determined using D-R approach.

A bench scale electrolytic cell made from plexiglas was used for electrochemical separation of ^{137}Cs and ^{60}Co from simulated aqueous radioactive

solutions [110]. In this cell, a stainless steel plate represented the anode. The electrochemical treatment technique used depends on forcing the radioactive cations of solution ($^{137}Cs^{+}$ and $^{60}Co^{++}$) towards the opposite electrode under influence of applied current, where they highly sorbed in pottery body. Highest removal for ^{137}Cs and ^{60}Co was in alkaline medium, especially at pH > 9. It was found that at pH 11, applied voltage 30 V and current 100 mA, the highest removal of ^{137}Cs is 99.8 % after 2.5 hours, and 99.3 % for ^{60}Co after 1.25 hour.

A rapid and selective method was developed for separation of uranium from multicomponent mixture containing Ce, Sc, Y, Hf, Cs, and Pb. Uranium was extracted with DC-18- crown-6 in chloroform from 6-8.5 M HCl, and stripped with 0.5 M HCl [111].

Rajan and Shinde [112] have proposed a solvent extraction method for separation of uranium using TOPO dissolved in toluene as an extractant. Various parameters affecting extraction conditions have been studied. The method permits separation of uranium from some metals in binary mixtures.

Batch experiments were done on sorption of uranyl ion from nitric acid solution using Amberlite XAD 4 resin impregnated in di (2-ethylhexyl phosphoric acid (HDEHP) or dihexyl N,N- diethyl carbamoyl methyl phosphonate (DHDECMP). Various factors affecting sorption of this ion were studied. Also the column technique was applied to study sorption of uranyl ion. The sorption capacities were found to be 0.38 X 10^{-3} and 1.79 X 10^{-3} mole/g for HDEHP/ Amberlite XAD 4 and DHDECMP/ Amberlite XAD 4, respectively. A solution of 2M HNO_3 was found to be a good eluent for leaching uranyl ion. Addition of TBP to the solvent shows no enhancement in sorption process [113].

Deacidification of radioactive liquid waste was studied using supported liquid membrane (SLM) impregnated with 1 % Alamine-336-benzene. Two main systems based on HNO_3 or HCl as acid feed solutions were studied. The strip solution used was NaOH at different concentrations. It was found that the

permeability coefficient of H^+ transfer for the two systems is 2.5 X 10^{-5} $cm.s^{-1}$ [114].

A process has been developed for immobilization Cs, Sr, Ce, Pb, and Cr in forms that is non-dispersible and could be safely immobilized. The simulated radioactive wastes of Cs, Sr, and Ce, and hazardous wastes of Cr, and Pb were immobilized in a stable form of sulfur polymer cement (SPC). In this process, the contaminants (in a single form) were added to the sulfur mixture of sulfur and aromatic / or aliphatic hydrocarbons that used as polymerizing agents for sulfur (95 % S, and 5 % organic polymer by weight). The leach index for investigated metals from the prepared SPC matrices was in the range of 9-11. The order of release of investigated metals was Sr > Cs > Pb > Cr > Ce for the aliphatic polymer, and Sr > Cr > Pb > Cs > Ce for the aromatic one [115].

Treatment of radioactive solid waste containing mainly radium ^{226}Ra produced from oil and gas production industry in Egypt was studied. The treatment process has been carried out by suspending the clay fraction content in solid waste in suitable leaching solutions. Factors affect the treatment process have been investigated and discussed. The removal of ^{226}Ra was found to depend on the clay fines content in solid waste [116].

Amorphous titanium vanadate has been prepared with TiO_2/V_2O_5 ratio of 4:1. The ion exchange capacities of prepared exchanger have been investigated for Cs^+, Co^{2+} and Sr^{2+} ions separation. Nitric acid could be used to elute Cs^+, Co^{2+} ions from their column [117].

Bilharzial host snails were converted into useful sorbent materials either in form of oxidized animal charcoal or snail ash. These sorbent materials could be used for removal of $^{(152+154)}Eu$ from aqueous waste solutions through a batch technique study. It was found that removal of europium ions was more than 95 % for both sorbent materials at pH = 4. The data obtained showed that snail ash and oxidized animal charcoal can be used for removal of $^{(152+154)}Eu$ from low level liquid radioactive waste solution [118].

Potential use of a new cellulose sorbent (Egy-sorb) loaded with TBP/kerosene solution for removal of U(VI), Th(IV) and Co(II) with CYANEX-301/kerosene from nitrate medium has been investigated using batch technique. Effect of the different parameters affecting uptake of these metal ions such as acidity, metal and extractant concentrations, diluent as well as temperature were separately studied. Thermodynamic parameters are also calculated. The results are used to assess the conditions for maximum removal and separation of uranium, cobalt and thorium from nitrate waste solutions using Egy-sorb [119].

Ali et al. [120] investigated sorption of Th and U from nitric acid by ammonium molybdophosphate (AMP), which was found to be insoluble in water or nitric acid solutions of different concentrations. The authors reported that the capacity of AMP decreases by increasing the nitric acid concentration.

Triphenylphosphine oxide (TPPO) was chosen as an extractant for uranium from nitric acid medium. Different procedures and parameters were systemized to judge its feasibility. Executed experiments were carried out testing the following variables: TPPO and nitric acid concentration, time of shaking, temperature, pH, different diluents, aqueous to organic phase ratio (A/O) and different interfering ions. The factors studied were followed by investigation related to apply the extraction system of TPPO to extract and determine uranium content from certain international and reference geologic samples with application on local igneous and sedimentary samples [121].

Immoblization of low and intermediate level radioactive liquid wastes in different matrices: ordinary Portland cement and cement mixed with some industrial by-product: by-pass klin cement dust, blast furnace slage and ceramic sludge was studied. Effects of these industrial by-product materials on the compressive strength, water immersion, radiation and leachability were investigated. The compressive strength increased after immersion in different

leachants for one and three months for samples with liquid LLW higher than those obtained for liquid ILW. The cumulative fractions released of cesium-137 and cobalt-60 of solidified waste forms of liquid LLW was lower than those obtained for liquid ILW [122].

Cyanex extractants are commercial solvent extraction reagents available by Cyanamid Canada Inc., and have been applied in treatment of radioactive waste [123].

Serag et al. [124] studied use of solvent extraction technique for selective separation of uranium matrix from the yellow cake solution. Several extraction procedures were investigated using TBP/carbon tetrachloride, trioctylphosphine oxide TOPO/cyclohexane and tris(2-Ethylhexyl)phosphate (TEHP)/cyclohexane system. The latter exhibited the best extraction selectivity towards uranium.

Snyder et al. [125] reported removal of radioactive contaminants from some metals mainly; nickel, cobalt, chromium and iron, by the electrolytic processes. In this process, contaminants were extracted by a mixture of DEHPA, TOPO and alkane before electrodeposition of the metal.

Huang et al. [126] investigated the kinetics of synergistic extraction of U(VI) with TOA-TOPO in n-hexane by using the single drop technique. Extraction rate was found to increase with addition of TOPO. Effects of the concentrations of U(VI), H^+, TOA, TOPO, and temperature on extraction rate were studied and the apparent activation energy was calculated. The rate controlling step and a kinetic equation were also suggested.

In presence of TOPO, 3-phenyl-4-benzoyl-5-isoxazolone (PBI) was found to be a promising chelate extractant for partitioning of actinides from acidic nuclear waste solution [127]. Quantitative extraction of Pu and U was possible in nitric acid concentration range 1-6 M.

Daoud et al. [128] studied extraction of U(VI) by di-2-ethylhexylphosphoric (HDEHP) and TOPO mixture and of U(IV) by HDEHP and octylphenyl acid phosphate (OPAP) from phosphoric acid. They investigated kinetics of

extraction of U(IV) by HDEHP using the lewis-cell technique and the mechanism of extraction was proposed.

Tows et al. [129] reported complexation and transport of uranyl nitrate in supercritical carbon dioxide with organophosphorus reagents. Ligands investigated include trioctyl phosphine oxide (TOPO) and others. It was found that TOPO shows reasonsable extraction efficiency for uranyl nitrate but the resulting complexes were difficult to transport, presumably due to solubility limitations. Kinetics of extraction were rapid, with quantitative extraction being achieved in 30 – 40 minutes.

Shaoning-Yu et al. [130] studied synergistic extraction of U(VI) and Th(IV) from nitric acid solution by TOPO in toluene, the ability to extract U(VI) and Th(IV) was seriously improved.

Kohler et al. [131] studied extraction of uranium, thorium, and plutonium with TOPO in hexane from nitric acid medium, reextracted by ammonium hydrogen carbonate and sodium sulfate solutions under addition of alcohol to organic phase and electroplated from sulfuric acid medium onto polished stainless steel disks. This method was used in determination of isotopes of the above elements in environmental samples and a method for separation of uranium and thorium was also given.

Sarkar et al. [132] studied synergistic effect on the equilibrium extraction behavior of uranium with chloroform solution of TOPO. Effects of aqueous phase, pH and bulk organic phase concentration of TOPO on extraction have been investigated.

Extraction of U(VI) by mixtures of 2-ethylhexyl phosphonic acid and TOPO in cyclohexane and xylene from aqueous sulfuric acid medium had been investigated [133].

Extraction kinetics of U(VI) by 20 % TBP in kerosene from 3 M nitric acid has been investigated using a stirred Lewis cell. Effects of concentration of

uranium, TBP, H^+, nitric acid, and nitrate as well as temperature were separately studied. Reaction rate was found to be first order dependent on the TBP concentration and slightly affected by variation in temperature. A mechanism of extraction in which chemical reaction at interface controls the transfer rate was proposed [134].

Kinetic investigations indicated that stripping rate (using dilute nitric acid) increases by increasing TBP and uranium concentrations while variation in temperature slightly affect stripping rate. Stripping by precipitation with ammonia solution was also carried out under different stirring rates. The results of stripping U(VI) by the two methods were compared and discussed [135].

Combined extraction of Cr(VI) and U(VI) using 30 % solution of TBP in dodecane from nitrate aqueous medium was studied. Under HNO_3 < 1 M concentration in organic phase, Cr(VI) was found to be in the form of chromate while at HNO_3 > 3 M in the form of dichromate and presence of U(VI) varied essentially the Cr(VI) spectra in the organic phase [136].

Effects of selected fission products as well as stabilizing and reducing agents on kinetics of extraction of U(VI) under the purex conditions were investigated using a stirred Lewis cell. Effects of different concentrations of U(VI), Ce(VI), Zr(VI), and Mo(IV) on extraction were separately studied as well as when mixed together. When separately added to U(VI), the rate of extraction was found to decrease with addition of U(IV) while addition of Zr(IV), Ce(IV), and Mo(VI) had a negligible effect. When these ions were mixed together, the extraction rate of U(VI) was found to increase [137].