INTRODUCTION

INTRODUCTION

The global energy consumption has steadily increased as civilization evolved. This demand accelerated sharply about 1900 as some nations moved into the age of modern technology. The renewable energy sources can contribute only a small fraction to the future world energy demand. Through many years, nuclear energy has created a revolution in our daily lives as well as in our knowledge of our physical world. It is not unlikely that in the next several years nuclear energy will lead to even further advances in our understanding of nature and to even greater benefits to society.

Nuclear fuels consist of fissile materials, which produce a net increase in neutrons when they absorb neutrons, and fertile materials, which produce fissile material when they absorb neutrons. The principal fissile materials are ^{235}U, ^{239}Pu, and ^{233}U; ^{241}Pu is also of some importance. The principal fertile materials are ^{238}U and ^{232}Th; ^{240}Pu, and ^{234}U also plays a role as fertile materials.

^{235}U is the only fissile material that occurs in nature in a significant quantity. Natural uranium consists of 0.711%weight percent ^{235}U, 99.283 % ^{238}U, and 0.0058 % ^{234}U as a negligible trace constituent. Until now, most power reactors have been fueled with either natural uranium or slightly enriched uranium containing from 2 to 5 % ^{235}U, produced from natural uranium in a gaseous diffusion plant.

As the fuel in a nuclear reactor is irradiated, it undergoes nuclear transmutations that cause its composition to change as fissionable material is consumed, neutron absorbing fission products are formed, and heavy nuclides, mainly isotopes of uranium and plutonium, are formed. This change in composition brings about changes in reactivity of the fuel, which eventually decreases to such an extent that the reactor will no longer be critical unless the spent fuel is replaced with fresh fuel.

One of the principle objectives of fuel-cycle analysis is to follow quantitatively the changes in concentration of fissile and fertile nuclides and fission products during neutron irradiation. Another important objective is to follow the changes in reactivity that take place as fissile nuclides are depleted or formed from fertile nuclides, and as neutron poisons are formed through buildup of fission products or burned out through reaction with neutrons. A third important objective is to follow the shifts in flux and power density distribution that take place in a reactor as a result of spatially non uniform changes in fuel composition and reactivity.

Reactivity decreases with increasing burnup because the increase in ^{239}Pu and ^{241}Pu content is not sufficient to compensate for the decrease in ^{235}U content, and because ^{236}U, ^{240}Pu, ^{242}Pu, and fission products, whose content increases, are neutron-absorbing poisons. Another very important effect of irradiation on fuel, which is the change in physical properties that take place. Fuels often change dimensions and swell, blister, or crack. Fission-product gases may be released and build up appreciable pressure inside the cladding. Physical properties, such as thermal conductivity, may be changed. In many cases important physical properties or intolerable dimensional changes limit the amount of heat that can be obtained from fuel rather than loss of reactivity, Fig, (1) shows a schematic flow sheet of the fuel cycle.

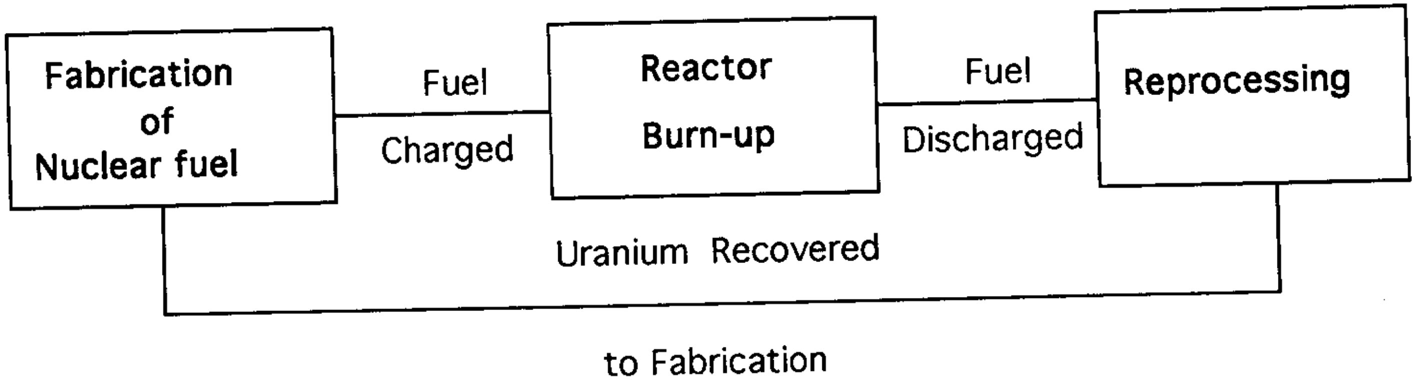


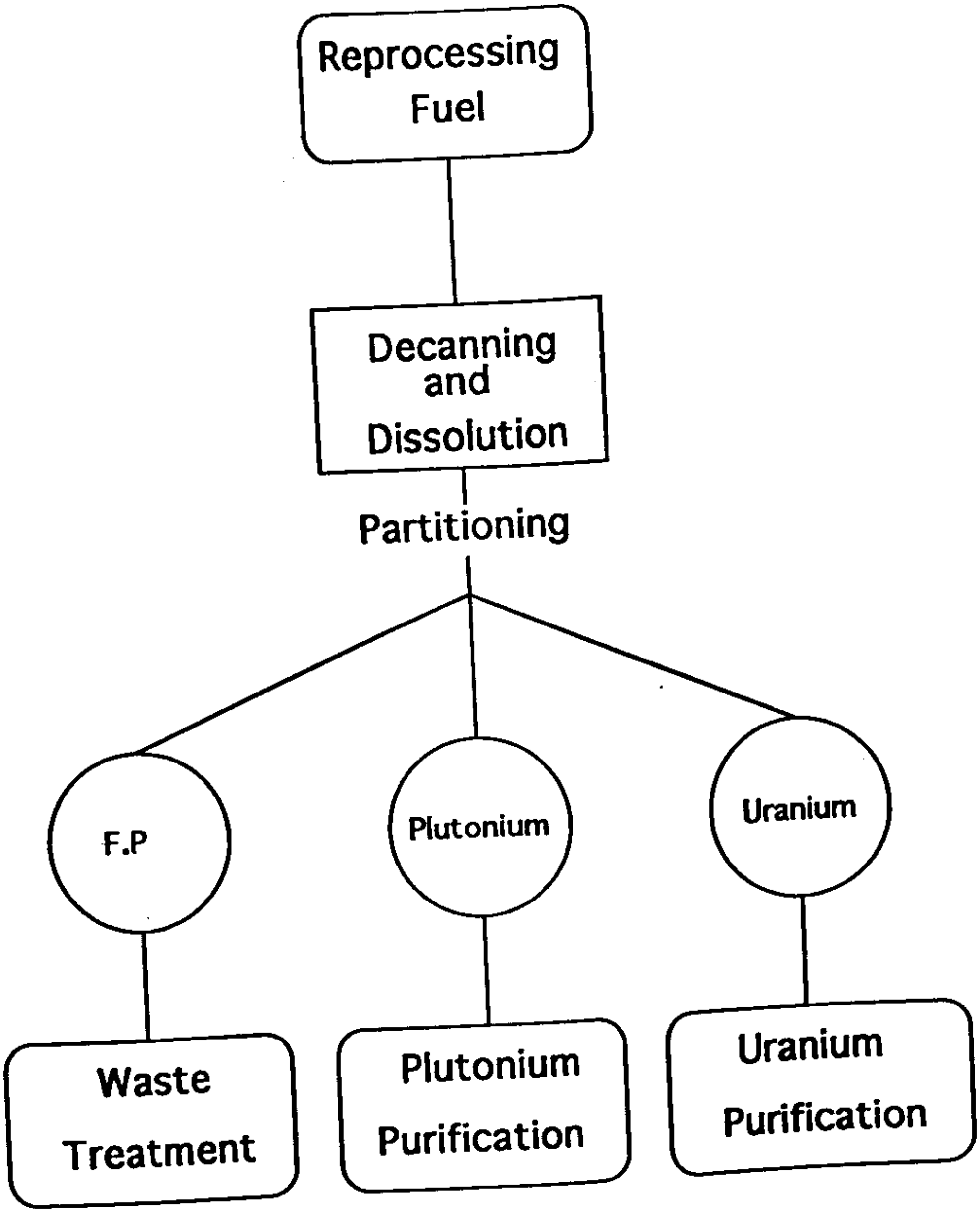
Fig. 1: Schematic flow sheet of fuel cycle.

The reprocessing of the spent reactor fuel elements is considered advantageous for saving resources as well as for economic and safety reasons. Fig, (2) shows the main steps in the reprocessing of spent reactor fuel.

Synthetic inorganic ion exchangers have been developed in recent years[1]. This is mainly because of their greater power to withstand higher radiation doses and temperatures than the commonly-used organic-based resins. In addition to this they sometimes exhibit highly specific properties which might permit improved separations under ordinary conditions.

A large number of synthetic inorganic substances which exhibit ion-exchanging properties has been described. The large classes of ion exchangers useful in nuclear field may be classified as follows:

A- Natural ion exchangers.
   1- Clay minerals.
   2- Zeolites
B- Synthetic inorganic ion exchangers.
   1- Hydrous oxides
   2- Acid salts of polyvalent metals.
   3- Salts of heteropolyacids.
   4- Insoluble ferrocyanides.
   5- synthetic aluminosilicates.
   6- Certain other substances e.g. synthetic apatites, sulfides, alkaline earth sulfates etc.



Fig(2) : Main steps in reprocessing of spent reactor fuel.

A- Natural ion exchangers:

1- Clay Minerals

The clay minerals consist of complex series of aluminosilicate structures of a number of basic types. Aluminosilicate type of clay consists of alternating parallel two dimensional layers derived from silicate tetrahedra and aluminate octahedra [2]. At the edges and corners there are normally free hydroxyl groups. The ion exchange properties of clay minerals may be explained from the above structure. The selectivity of clay minerals increases as the hydrated ionic radii of metal ions decreases, e.g. for the alkali metals the orders is $Li^+ < Na^+ < K^+ < Rb^+ < Cs^+$.

2- Zeolites

Zeolites, commonly known as molecular sieves, are a group of hydrous crystalline aluminosilicates, built up of tetrahedral units of AlO_4^{5-} and SiO_4^{4-} in such a way that the corners, edges and faces of the tetrahedra are shared to give compact porous structures. Depending upon the structure and bonding, zeolites may exist as fibrous, lamellar, or rigid three dimensional structures. It is the latter type [three dimensional network] which has been extensively investigated for ion exchange properties [3].

B- Synthetic inorganic ion exchangers:

1- Hydrous oxides:

Adsorption properties of alumina, silica and iron oxides have been known for a long time, and the processes taking place have been often described in terms of ion exchange. Most of these hydroxides shows the properties of both cationic and anionc ion exchangers that make them especially interesting. These substances are mainly amphoteric ones and their dissociation could be schematically represented as follows:

$$\mathrm{MOH} \rightleftharpoons \mathrm{M^+ + OH^-} \qquad \mathrm{I}$$

$$\mathrm{MOH} \rightleftharpoons \mathrm{MO^- + H^+} \qquad \mathrm{II}$$

M is the central ion.

In recent years a great number of these compounds have been studied. Special emphasis was placed on elucidating the mechanism of the process as well as on the application of these substances for isolation, removal, and treatment of radioactive materials and purification of water.[4].The ion exchange properties of these exchangers was found dependent essentially on the dimention of the unite cell.

1.1- Hydrous oxides of divalent and trivalent metals:

Hydrous oxides of Mg^{2+}, Be^{2+}, Zn^{2+} and their mixtures with ferric hydroxide and alumina have been studied as ion exchangers. Hydrous BeO of composition $BeO.1.7H_2O$ exhibits both anion and cation exchange properties[5-7].

Hydrous magnesium hydroxide shows anion exchange property The mixed oxide $Mg(OH)_2$-$Fe(OH)_3$[7] has been studied. The mixed oxide $Zn(OH)_2$ and $Al(OH)_3$ was employed for decontamination of ^{35}S and ^{32}P from waste solutions [8].

The acid salt of tirvalent group has been extensively studied. The ion exchange properties for the group III elements (aluminum and iron) shows the peoperties of both cationic and anionic ion exchange [4]

1.2- hydrous oxides of quadrivalent elements:

Generally, the oxides of the group IV are obtained by adding an excess of base to solutions of their salts. The gelatinous precipitates so obtained, although often represented as SiO_2, SnO_2, TiO_2, ThO_2 and ZrO_2, are not realy well defined solids. Their chemical composition and properties depend on the method of preparation as well as on the further treatment of the fresh gelatinous precipitate. Amorphous products are most often obtained from these precipitations, but it is also possible, in some cases, to obtain crystalline forms [9-11]

Hydrous silica:

A large variety of products can be obtained by different methods of preparation. These vary in their sorption behaviour, specific surface area, and porosity. Hydrous silica was used in the separation of of Na-Rb-Cs-Fr [12] and Tl-Bi [13] as well as the separation of uranyl ion from aqueous solution [14].

Stannic oxide:

hydrous stannic oxide is prepared by the acidification of sodium stannate solution or by the reaction of nitric acid with tin metal [15].

Titanium oxide

It is prepared by mixing titanyl oxalate or $TiCl_4$ solution with sodium hydroxide [16,17]. Hydrous titanium oxide was used for removal of Pu and certain fission products e.g Ru, Zr, Nb[25] and for separation of U, Ni, Co, Cu, and Fe (II) [19]. Selectivity of hydrous titanium oxide as ion exchanger for alkaline metal has been studied [20,21]. A layered hydrous titanium oxide has been prepared [22].

Thorium oxide

Thorium oxide has been prepared by treating soluble salts of thorium with alkali[16]. Hydrous thorium oxide behaves both as anion and cation exchanger[16]. The selectivity series for alkali metals is Cs > Rb > Na and for transition metals is Cu > Ni > Co[17].

Zirconium oxide:

Hydrous zirconium oxide is prepared by mixing a zirconium salt with alkali[23]. It shows both anion and cation exchange capacity[24]. It is highly selective towards phosphate[25]. Hydrous zirconium oxide has been used for adsorption and separation of different anions [26-29].

Manganese dioxide.

Hydrous manganese oxide has been prepared [30]. The ion exchange selectivity towards the alkaline earth metal has been studied [31]. It is more selective towards alkaline earth metals than the alkali metals[32]. A number of separations on hydrous manganese dioxide have been described; retention of ^{51}Cr and separation of ^{60}Co-^{59}Fe from neutron activation analysis of Fe-Cr alloy [33].

1.3- Hydrous oxides of pentavalent and hexavalent metals :

Antimonic acid:

Hydrous antimonic oxide both amorphous and crystalline has been prepared by thermal polymerization and subsequent acid treatment [35].It is also prepared by digesting of $K_2H_2Sb_2O_7.4H_2O$ in HNO_3 at 25°C for 18 h [36]. It acts as a cation exchanger. The affinity series for alkali and alkaline earth metal ions depends on whether it is amorphous or crystalline and on the solution in which the exchange reaction occurs. The series: Li < Na < K < Rb < Cs in acid solution and in ammonia solution, Li < Na ≈ Cs < K = Rb are found for the amorphous and glassy solid. The kinetics exchange of Cs , Sc and Eu on crystalline antimonic acid was studied [37]

Phosphoantimonic acid :

It is prepared by mixing $SbCl_5$ and phosphoric acid or by treating Sb[V] salt solution with phosphoric acid, then neutralizing with ammonia solution [38]. It is also prepared by mixing $NH_4H_2PO_4$, KNO_3, and Sb_2O_3 at 200°C for 4h. [39]. A layered structure of phosphoantimonic acid has been prepared. The structure and the ion exchange properties were studied [40]

2- Acidic salts of polyvalent metals :

Acidic salts of polyvalent metals are the most widely studied inorganic ion exchangers. The metals studied are zirconium, thorium, titanium, cerium(IV), tin(IV), tantalum, aluminium, iron(III), chromium, uranium(VI), etc. The anions employed are phosphate. arsenate, antimonate, vanadate, molybdate, tungstate, tellurate, silicate, oxalate etc. These salts act as cation exchangers.

Tin (IV) based ion exchangers :

Both amorphous and crystalline stannic phosphate are prepared by mixing stannic chloride and sodium hydrogen phosphate or phosphoric acid solution[41-56]. Amorphous stannic arsenate is prepared by mixing stannic chloride solution and sodium hydrogen arsenate or arsenic acid[46,48-52]. The crystalline variety is prepared by refluxing the amorphous material with arsenic acid. Stannic molybdate is prepared by mixing stannic chloride and ammonium molybdate solutions[53,54]. Stannic antimonate is prepared from potassium pyroantimonate and stannic chloride solution, the product is a glass like substance and highly resistant to mineral acids[55-58]. Stannic antimonate is also prepared by mixing antimony pentachloride and tin tetrachloride solutions[1], whereas Varshney and Gupta [57], were prepared tin(IV) antimonate from tin (IV) chloride and potassium antimonate.

Ion exchange equilibria of alkali metal ions on Sn/Sb ion exchanger had been studied[58-60]. Tin(IV) antimonate has been prepared as a lead selective cation exchange material. Stannic tungstate is prepared by mixing stannic chloride and sodium tungstate solution[53]. Thermally stable stannic selenite is prepared by mixing stannic chloride with sodium selenite as discussed by Qureshi et. al. [62]. The equilibrium exchange of cesium and strontium ions with the hydrogen form of tin(IV) antimonate have been studied at different temperature. Also thermodynamic parameters have been calculated [61].

Cerium based ion exchangers :

Cerium(IV) phosphate has been prepared under various conditions of precipitation. It is synthesized by mixing a ceric salt solution with phosphoric acid under different conditions[63-80]. Crystalline cerium arsenate is prepared by Alberti et. al. by refluxing cerium(IV) sulphate solution with arsenic acid[81]. Cerium(IV) antimonate is prepared by treatment of ceric ammonium sulphate with potassium pyroantimonate solution[82]. Ceric tungstate is prepared by mixing ceric ammonium sulphate and sodium tungstate solution[83]. The anion exchange properties of ceric oxide has been studied.[84]

Titanium based exchanger :

Titanium phosphate, arsenate, antimonate, molybdate, tungstate vanadate and selenite has been prepared [85]. A comparative study of titanium based ion exchangers was also reported by Qureshi et. al. [86]. The ion exchange properties of titanium-zirconium oxide has been studied [87].

Zirconium based exchangers :

Amorphous and crystalline forms of zirconium phosphate have been prepared [88, 89]. The crystal structure α-ZrP has been solved by Clearfield [90].

A great variety of ion exchange studies and ion separations have been carried out with amorphous ZrP [85,91-93]. The ion exchange properties of crystalline ZrP as well as the amorphous has been studied [4]. Zirconium pyrophosphate, polyphosphate, hydrophosphate have been reported as ion exchangers[94-100]. Zirconium arsenate is prepared by mixing zirconium salt solution with arsenic acid, the crystalline variety is prepared by refluxing the amorphous form with the arsenic acid[101-103]. Zirconium antimonate is prepared by mixing $ZrOCl_2$ with an excess of Sb_2O_5 solution in hydrochloric acid[104-106]. The product is amorphous. Crystalline zirconium antimonate was prepared by Tandon and Mathew[107].

Zirconium tungstate is prepared by mixing zirconium salt with sodium tungstate solution or by passing sodium tungstate solution through hydrous zirconium oxide column. It is obtained in amorphous form [108-112]. The ion exchange properties of zirconium silicate and zirconium oxalate have been reported[113-115].

Thorium based ion exchangers :

Thorium phosphate of different compositions, prepared under various conditions, has been reported. The exchanger, when precipitated at room temperature, shows low exchange capacity and low stability towards hydrolysis but when precipitated at 100°C, the exchanger shows high exchange capacity[116-118].

Thorium arsenate both amorphous and crystalline varieties is prepared by refluxing thorium nitrate and arsenic acid solution[119, 120]. Thorium molybdate is prepared by mixing thorium nitrate and sodium molybdate solutions[122]. Thorium tungstate, both amorphous and crystalline varieties have been reported. It is prepared by mixing thorium nitrate and sodium tungstate solution[122, 123].

3- Salts of heteropoly acids :

The first systematic study of the ion exchange properties of the heteropoly acid salts was carried out with phosphomolybdate as reported by Baxter and Griffin and Buchwald and Thistlethwaite[124-125]. The parent acid of this series is 12-heteropoly acid of general formula $H_mXY_{12}O_{40}.nH_2O$ [m=3-5] where X is phosphorus, arsenic, silicon, germanium, selenium and boron, etc. and Y is element such as molybdenum, tungsten, vanadium, etc.

4- Insoluble ferrocyanides :

Quite a large number of insoluble ferrocyanides of various metals e.g Ag, Zn, Cd, Cu, Ni, Co, Sn, Pb, Mn, Ce, Fe, Bi, Ti, Zr, V, Mo, W, and U etc. have been studied for their ion exchange property. These exchangers are prepared by mixing metal salt solutions with $H_4Fe[CN]_6$.

$Na_4Fe[CN]_6$ or $K_4Fe[CN]_6$ solutions. The ferrocyanides with varying composition are formed depending upon the experimental conditions. The limiting composition $M_2(II)[Fe(CN)_6]$, $M_2(I)M(II)[Fe(CN)]_6$ and $M_2(I)M_3(II)[Fe(CN)_6]_2$ with various amounts of water of crystallization are reported for ferrocyanides of bivalent metals. The exchangers act as cation exchangers with a high affinity for alkali metal ions especially for Cs^+ [126-137]. The separation of lanthanides and cesium on zinc hexacyanoferrate has been studied [134-136]

5- **Synthetic aluminium silicates** :

This class represents quite a large family of inorganic ion exchangers. It may be divided into three main groups on the basis of their structure: amorphous, two dimensional layered aluminosilicates and aluminosilicates with rigid three dimensional structure. The first two groups have been studied extensively over many years. Now attention has been concentrated on the third group of synthetic zeolites[142-152].

6- **Miscellanious ion exchangers** :

Ion exchanger properties have been found in many synthetic apatites. The structure of apatite contains some anionic and cationic components which are exchangeable. Apatite may be represented as

$$M_{10}[XO_4]6Y$$

where M= Ca, Sr, Ba, Cd, and Pb

X= P, As, V, Cr, Mn, Si, Ge

Y= F_2, Cl_2, Br_2, $[OH]_2$, O^{2-} and CO\O(2-,3)

The following insoluble sulphides Ag_2S, FeS, CuS, CdS, ZnS, PbS, NiS, As_2S_3 and Sb_2S_5 have been studied for their ion exchange properties. These exchangers are selective towards cations forming insoluble sulphides. Some alkaline earth sulphates show adsorption properties. Barium possesses enhanced sorption activity especially for Sr^{2+}[127].

Japanese workers continue to show interest in the extraction of uranium from sea water and the conceptual design and cost estimation for two types of commercial plants have been discussed by Kanno[152]. A pilot plant with an annual capacity of about 10 Kg U was due to start construction in 1980[153]. Kelmers[154] has also discussed the status of technology for the recovery of uranium from sea water. Driscoll and Best[155] have summarized all the work carried out during 1981 at the Massachusetts Institute of Technology on the extraction of uranium from sea water. This comprehensive systems study deals with a powered organic ion exchanger and with hydrous titanium oxide; the former appears to be favoured. The extraction of uranium from sea water has also been reported by Gregg and Folkendt[156].

Hydrous titanium oxide has been studied as an absorber for uranium for many years and studies on the mechanism[157-159] of uptake and on physical properties[160] have been reported by Yamashita et. al., distribution coefficients for the adsorption of a range of metal ions on hydrous titanium dioxide have been reported by Inoue and Tusuji[161]. Nineteen absorbents were tested by Sastry et. al.[162] and the preferred one was titanium oxide.

The distribution of cobalt(II) ion between crystalline hydrous titanium dioxide fibers and aqueous solutions has been investigated [163]. Hydrous titanium dioxide in amorphous form was prepared in a state, demineralized as much as possible, through different processes. The equiadsorption point [EAP] for anions and cations was determined at an ionic strength of 0.1 with the use of alkali metal chloride solutions [164]. Other titanium based absorbents have been shown to have the ability to absorb a large amount of uranium from sea water [165].

Yamashita et. al.[166] have described the extraction of uranium from sea water using magnetic exchangers, and the magnetic properties of hydrous Ti(IV)-Fe(II) oxide composite absorbents have also been studied by Ozawa et. al.[167]. The main disadvantage of the use of titanium oxide as an absorber for the removal of uranium from sea water lies in its susceptibility to attrition. Schenk et. al.[168] have therefore carried out studies on the absorbents. They examined about 200 organic ion exchangers and concluded that of the resins examined the most suitable were poly[acrylamidooximes] which could give uranium loadings ranging from a few hundred to a few thousand parts per million. The uptake of U(VI) from seawater by metal hydroxides dispersed in polyacrylamide gel particles has been examined by Shigetomi, Kojima and Shinagawa[169], but of the five hydrous oxides examined only titanium hydroxide showed useful adsorptive properties. Aluminium-activated carbon composites and aluminium hydroxide have been studied by Katoh et al[170].

Titanium tungstophosphate shows a high selectivity for Th(IV) and its use as a thorium selective ion exchanger has been described by Rawat and Khan[171]. Another inorganic ion exchanger, stannic phosphate, has been shown to be potentially useful in removing uranium from a U-Pu-fission product mixture in nitric acid. The uranium is less strongly absorbed than the Pu + fission products. Mayankutty and Nadkarni [172] have suggested the use of stannic phosphate to remove traces of Pu+F.P's from Purex process stream. The selective separation of thorium and uranium from lanthanides using sulphonic acid exchangers[173] and chelate ion exchangers[174] has been reported by Hubicki and his coworkers. The chelate ion exchangers were of the anion acid, phosphate, mercaptide or polyphenol types and the best separation of U, Ni, Ca, Th and Fe from the rare earth elements was obtained with amino type exchangers; for U+Th separations a phosphate type exchanger was the best. Quantitative separation of Th, Pu and U from fission products has been studied using ion exchange and solvent extraction[175] and the separation of thorium from uranium [in 5% tri-n-butyl phosphate Shell T] using the macroreticular cation exchanger Amberlyst-15 has been described by Nadkarni et. al.[176].

By far the greatest amount of interest in fission product separation has been in the behaviors of cesium and strontium and most of the work has been carried out on inorganic absorbers. Cesium can be taken up by a variety of inorganic absorbers e.g. ammonium phosphomolybdate[177-179], ammonium phosphotungstate, titanium phosphate[180,181] zirconium antimonate[182]. Ammonium phosphomolybdate was selected by Suess and Pfrepeer[177] from a variety of inorganic absorbers to separate cesium from synthetic purex type wastes and it has also been used by Murthy et. al.[178] to separate Cs from other fission products. In Murthy's studies cesium was absorbed onto ammonium phosphomolybdate or phosphotungstate from about 2M HNO_3 and it was eluted with 3M NH_4NO_3 at 40-50°C ,after washing the column; high purity cesium was produced. Murthy et. al.[183] has also examined the use of manganese dioxide for the uptake of Cs, Ce, Ru, Sr, Zr, and Nb.

In the search for materials having larger pores the basic concept of pillared clays gradually emerged. Layered naturally occurring and synthetic smectites such as bentonite, montmorillonites and chlorites may be visualized as a sandwich of aluminum octahedra between layers of silicate tetrahedra as shown in Figure 3. These sandwiches or platelets are stacked one upon the other to yield a clay particle.

Clays are distinguished by the type and location of cations in the layered framework. An important property of the smectite is their ability to swell by intercalation of water, alcohols, or amines. The extent of the swelling depends upon the layer charges, the interlayer cation and the nature of the swelling agent [184]. The negative charge on the clay layers, arises when the trivalent cation in the octahedral layers is partially replaced by a divalent cation, creating a negative charge. The electrical charge on the layer is balanced by the charge balancing cations between the layers. These cations illustrate the origin of the cation exchange

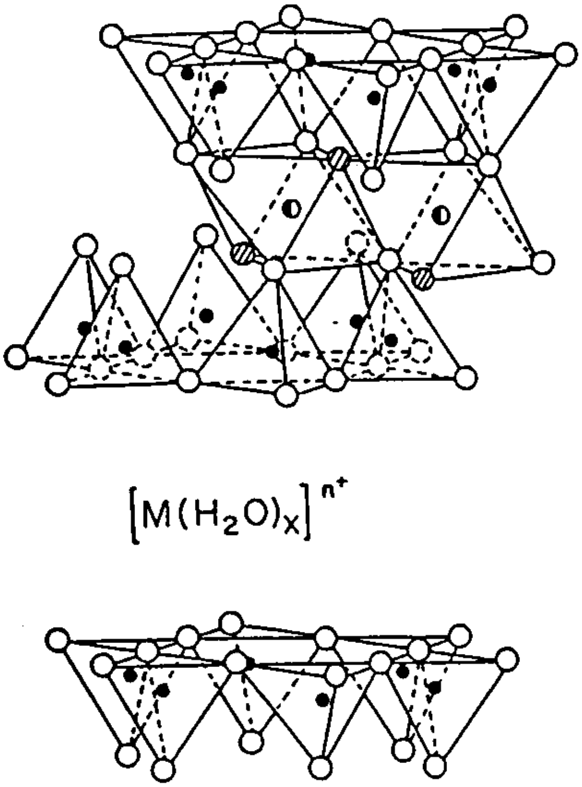


Fig. 3: Schematic Drawing of smectite clay; ◐: octahedral; ●: tetrahedral coordination ion; O: oxygen; ▨: OH group.

properties of the clay minerals. However, these interlamellar cations can be exchanged with large polymeric cations forming pillared clays. Figure 4. shows a description of the pillaring process. As a result of pillaring, and after calcination, the clay layers will contain oxide cluster pillars which prop open the clay sheets increasing surface area and the acidity is high enough for catalytic reaction.

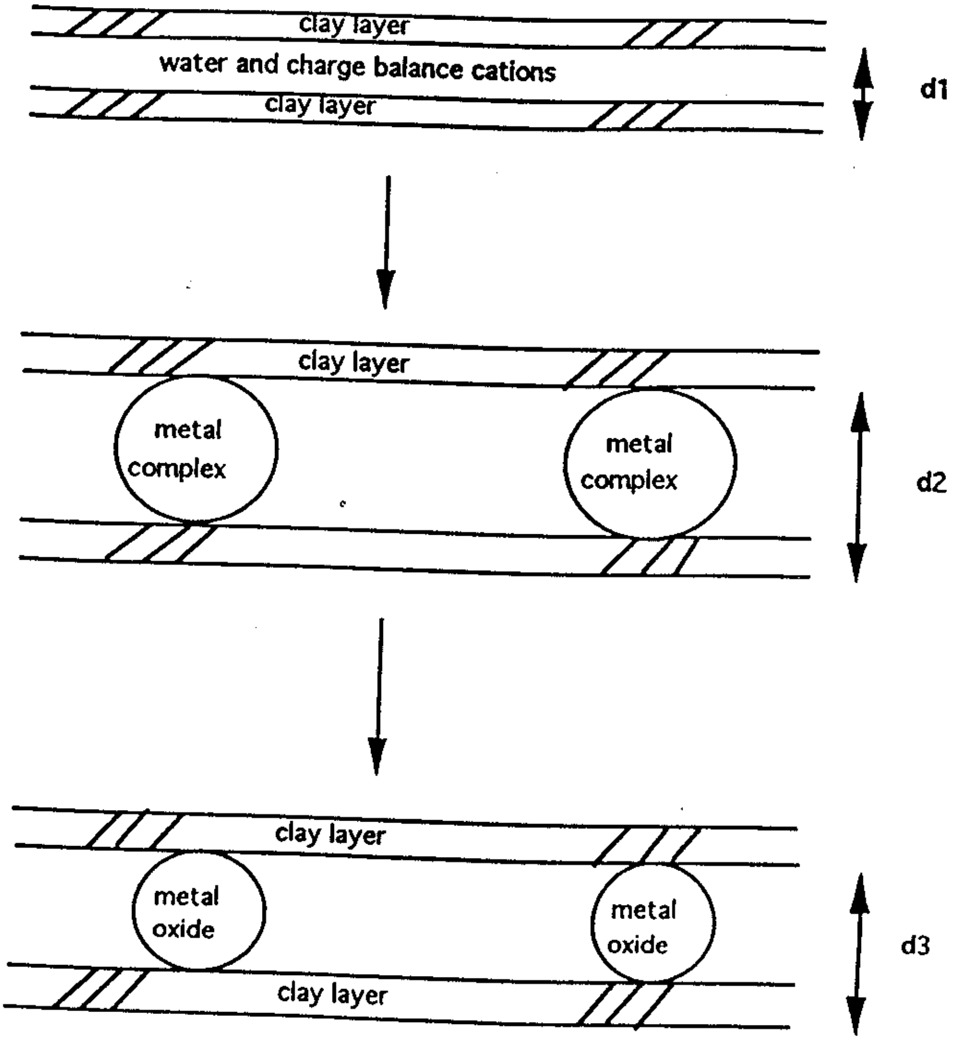


Fig. 4: Schematic diagram of pillaring. d1<d2>d3.

In the preceding two decades a new class of two dimensional molecular sieves has been synthesized from certain types of aluminosilicate clay minerals. The general procedures is to incorporate a large inorganic cation between the layers to prop them open [185]. The props, or pillars, are thermally cross linked to the layers. It has long been known that various organic molecules such as amines and alkyl ammonium ions readily intercalated between clay layers [186], and that porous structures can be formed from such complexes [187]. In general these organically pillared structures suffer from thermal instability of the organic component, although relatively stable complexes have been formed with cage-like amines [188-190]. Table 1, [191], shows different pillared species used to intercalate between the clay layers.

The intercalation by aluminum hydroxy cations has been studied in detail, and the chemistry of the solutions is well known. Using small angle X-Ray scattering, Rausch and Bale [192] suggested, for OH/Al ratios between 1 and 2.5, the formation of polymer species $[Al_{13}O_4(OH)_{24}(H_2O)_{12}]^{7+}$, the structure of which has been previously described in the solid state by Johansson [193]. This polymer species is composed of 12 octahedral aluminum atoms and a central aluminum tetrahedral as illustrated in Fig. 5.

The analysis of these solution by ^{27}Al NMR gives a signal that is shifted 63 ppm with respect to all $Al(H_2O)\backslash O(^{3+},_{6})$ and is assigned to tetrahedral Al in Al-13 [194,195]. The failure to observe a signal due to octahedral Al- is explained by the existence of a strong quadrupole coupling constant which broadens the line.

Table 1: Different cationic solutions used as intercalation to pillared clay.

Solution of intercalation	d(001)* (Å)	Specific surface area (m^2/g)
Al-13	18.4	211
Zr-4	17.4	309
BO^{3+}	12.7	---
Cr^{3+}	18	---
Nb_6Cl_{12} or Ta_6Cl_{16}	19	70
Fe_{3+}	13.9	100 (calc. 300°C)
$ZrOCl_2$	15.7	---
Ti4+	23.8	---

d(001) is the value after calcination above 400°C

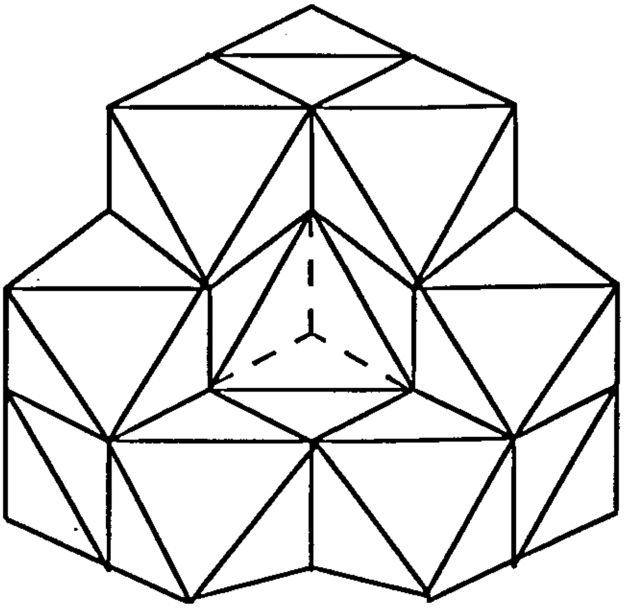


Fig 5: Schematic representation of the Al-13 Keggin ion

The chemical process involved in intercalation is ion exchange. Accordingly, chemical and physical factors will have an influence on the degree of exchange and distribution of the cation within the particle of the clay. These factors are the concentration of cations, on one hand, and diffusional limitation on the other hand. The selectivity is higher for highly charged cations.

Generally many ionic species are present in the solution, including Al\O($^{7+}$,$_{13}$,) Al^{3+}, Al\O($^{4+}$,$_{2}$), $[Al2(OH)_x(H_2O)^{10\text{-}x}]^{(6\text{-}x)+}$, and H^+. The process must then be described as a competition between these ions and the original cations of the clay. The selectivity of cation exchange in silicates depends on both the charge and size of the cations [196,197], and the rate of the exchange is expected to be lower for the bulkier species. It is then expected that, at thermodynamic equilibrium, $[Al\text{-}13]^{7+}$ and $[Zr\text{-}4]^{8+}$ cations will be exchanged specifically; however, the intermediate situation may be different since these cations have such a large size that they should initially be excluded from the clay.

Therefore, the Al or Zr content at the steady state is not expected to depend critically on the experimental conditions, except for the pH, which controls the distribution of the ionic species in solution [198-202].The influence of the distribution of the pillars within the clay on the thermal stability of the Pilc (Pillared Inorganic Layered Compound) is readily explained by the fact that the average distance between the pillars, and thus the facility of sintering, depends on this distribution. It can then be hypothesized that the thermal stability is an indirect determination of this distribution, which depends on many experimental conditions of the ion exchange. The influence of method used for drying the pillared clay has been studied. Pinnavaia et. al [203] compare these different methods and it appears to be more important than the choice of the pillaring agent or the clay layer change in determining the porosity of the final product.

Dyer et. al studied the ion exchange pH dependent processes on aluminum and zirconium pillared clays [204]. They found the dependence of the exchange properties on the pH to be similar to that of the hydrous oxides.

The effect of phosphorus compound on the Al-pillared clay has been studied. It shows a significant effect on the thermal stability, specific surface area, acidity and catalytic properties [205,206]. Aluminum pillared montmorillonite stable up to 500°C was prepared. The basal spacing of the samples whose values reached about 19Å usually decreased to about 17Å during the heat treatment used to convert oligomeric cations to Al_2O_3 pillars [200,207].

Many attempts have been carried out to prepare pillared clay with modified pore structure, surface area, acidity and interlamellar spacings. Sterte et. al [208] found that the hydrothermal treatment of the Al-montmorillonites at 750°C for 18h resulted in increased average layer distances in the materials primarily due to a collapse of micropores. The acidity retention of the Al-montmorillonites, measured by pyridine adsorption, were approximately proportional to the corresponding surface area retention.

Sakurai et. al found that the pillared mica catalysts, modified by fixed interlayer cations, were considered to be useful for designing pillared clay catalysts at the molecular level, since the method can incorporate in order various types of cations, which function as the active sites, onto a clay surface or into the layer structure [209,210].

Aim of Work

Nuclear activities over the past four decades have produced a tremendous amount of radioactive waste. Through these years many attempts to overcome this enormous problem have been tried.Recently work with inorganic ion exchangers has shown good ion exchange results and selective properties. Also layer compounds seem to be promising materials in attempts to solve this huge problem.

According to the previous introduction our work was designed to be in two parts:

A- First part:

Work done in the Arab Republic of EGYPT, at Atomic Energy Authority and Faculty of Science-Benha, concerning the inorganic ion exchange material "Tin-Antimonate".

Inorganic ion exchangers exhibit a high selectivity for some elements or group of elements and their exchanging properties are often connected with fairly good stability toward high temperature and ionizing radiation. Now, synthetic inorganic exchangers are being applied in the fields of nuclear energy and water desalination. From the prementioned introduction and literature survay it is found that a limited work was done on tin(IV) antimonate in the ion exchange field. This jusify present programe directed to investigate double salts of antimonate as ion exchangers. The proposed program includes:

i-Preparation of tin(IV) antimonate.

ii-Characterize the matrix properties on the basis of XRD, Thermal Analysis and IR Spectroscopy.

iii-Besides the present study was under taken to obtained further information on the adsorption behavior of UO^{2+}_2, Eu^{3+} and Co^{2+} ions on the material under different conditions. The cation diffusion rates and adsorption isotherms are also to be determined.

iv-Another very important line of studies on the adsorption is their use in practical separations on columns.

B- Second Part:

The Work done in The Laboratory of Professor Abraham Clearfield, Chemistry Department Texas A&M University, USA. Concerning the layer compounds. The program includes:

i- Preparation of aluminum pillared clay.

ii- Properties characterized on the basis of XRD, DTA, FTIR, SA, EDAX.

iii- Studies the ion exchange behavior on this material.

This is very important in view of the expected use of inorganic exchangers in the nuclear fuel cycle utilities such as waste disposal, recovery of actinides from various sources of nuclear plant effluent.

PART I