1. INTRODUCTION

1.1. Introductory Outline:

The increasing concern towards protection of the environment and optimization of a wide range of industrial activities in both nuclear and non-nuclear fields imposes the need to find and synthesis new highly selective ion-exchangers materials resistant to high temperature and ionizing radiation.

Ion exchange is an important tool for separation of metal ions from liquid wastes and immobilizing in a stable solid matrix which is a promising means for the nuclear fuel cycle (1-3). The ion exchange process is an effective method to remove of radioactive nuclides and fission products from a large volume of liquid waste.

Many inorganic ion – exchanger materials have been shown to exhibit good thermal and radiation stability, and for this reason considerable interest for these materials has arisen in recent years, particularly in processes used in the nuclear fuel cycle and in the application of radionuclide in research, medicine and industry.

Compared with the organic resins, many inorganic ion-exchangers are much more selective for certain ions or groups of ions and most of them are easily and cheaply prepared than the organic resins (4-5). They undergo little or no swelling upon immersing in aqueous solutions. Although organic resins are commercially available, these materials suffer from two vermiculite for cesium removal from effluents (9). One of the big potential advantages of natural materials is their relative cheapness, but if they need to be processed after mining this advantage is reduced. All these exchangers are normally discharged when exhausted and replaced with new materials.

1.3.2.2. Synthetic inorganic ion exchangers:

Synthetic inorganic ion exchangers have been developed in recent years (9). This is mainly because of their greater power to withstand higher radiation doses and temperatures than the commonly used organic resins.

Classification of these materials according to the chemical characteristics of the ion exchange species were carried out (3). The synthetic inorganic ion exchangers can be classified into the following groups (3, 10):

1- Hydrous oxides
2- Acidic salts of multivalent metals
3- Salts of heteropolyacids
4- Insoluble ferrocyanides
5- Synthetic aluminosilicates
6- Certain other substances, e.g., synthetic apatite, sulphides, alkaline earth sulphates,…etc.

1.3.2.2.1 Hydrous Oxides:

The adsorptive properties of hydrous oxides, such as alumina, silica and ferric oxide have been known for many years and it has been established that the adsorption of ions by these material is presumably by ion – exchange (10). In that sense the hydrous oxides are of particular interest because most of them can function as both cation and anion exchange. These substances are mostly amphoteric and their dissociation may be represented as follows:

$$\text{M-OH} \;===\; M^{+} + OH^{-} \qquad \text{Scheme (1)}$$

$$\text{M-OH} \;===\; \text{M-O}^{-} + H^{+} \qquad \text{Scheme (2)}$$

Where M, represents the central atom.

Scheme 1 is favored by acid conditions, when the substance can function as anion exchanger and scheme 2 by alkaline conditions, when the substance can function as a cation-exchanger. Near the isoelectric point of the oxide (11), dissociation according to both schemes can take place and both types of exchange may occur simultaneously.

In recent years, a number of review papers were written in which the ion exchange properties of hydrous oxides as SiO_2, TiO_2, ThO_2 and ZrO_2 were described (11-14). Hydrous zirconium oxide in alkaline media work as a cation exchanger. It is capable of the sorption of alkali and alkaline earth metal ions. In addition, it has very good sorption properties towards hydrolysable metal ions, such as Fe^{3+}, Cr^{3+} and Ni^{2+}. Amphelt et al.(13), gave a method for separating micro amounts of radioactive cesium and radio-strontium nuclides from fission products. Kraus and Philips (14), using the same exchanger eluted Cs^{+} ions from the column with 0.5M HNO_3 solution.

Other authors have reported data on the other hydrous oxides (15, 16). The results showed that among the investigated materials, the best properties were exhibited by hydrous titanium oxide.

Hydrous manganese oxide can be employed for the separation of various elements from fission products (17). The ion exchange capacity of such material is 0.73 m mol/g and that the selectivity order for alkali metals is $Cs^+ > NH_4^+ > K^+ > Na^+ > Li^+$ (18, 19). ^{99}Mo adsorbed on manganese dioxide from ammonium molybdate solution (20). The adsorption capacity of manganese dioxide for ^{99}Mo was very low.

For determining the amount of transition elements in hydro-organic media, a hydrous tin oxide ion exchanger was applied by Meloni and Brandone (21). The same hydrous oxide was used in a fully automated process for determining impurities in high purity iron metal (22).

The hydrous oxides of multivalent metals, such as Nb, Ta, Sb, Mo and W, have cation exchange properties. Among them, hydrous antimony (V) oxide, antimonic acid has been the most intensively studied. The adsorption of K^+ on antimonic acid studied by different authors. It has been reported that the adsorption and desorption of K^+ ions on antimonic acid is due to the exchange between the H^+ ions of the acid and K^+ ions in the external solution (23, 24). A systematic study of the distribution coefficients, K_d, for various metal ions on crystalline antimonic acid has been reported (25). The retention of 20 trace elements on a column, with a diameter of 1 cm and a length of 3cm, containing hydrated antimony pentoxide, using HCl, HNO_3 and H_2SO_4 of various concentrations as eluents have been studied (26).

1.3.2.2.2. Salts of hetero polyacids:

The first systematic study of the ion exchange properties of the hetero polyacids was carried out with phosphomolybdate as reported by Baxter et al.(27, 28). 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 or boron, etc. and Y is element such as molybdenum, tungsten, vanadium, etc.

The salts of hetero polyacids with small cations are relatively soluble (e.g. K^+, NH_4^+, Rb^+,Cs^+,Sr^{2+}, Ba^{2+} and alkyl ammonium). Hydrolytic degradation occurs in strongly alkaline solutions.

Ammonium molybdophosphates [AMP = $(NH_4)_3MO$ or $(NH_4)_2HMP$] are the most common salts and have satisfactory mechanical properties for column applications techniques. The tungestophosphate constitutes the second most widely studied group of hetero polyacids that exhibit strong exchange properties. Other hetero polyacids and their salts have been described in the literature (29-35).

1.3.2.2.3. Acidic Salts of Multivalent Metals:

A wide range of compounds of this type has been described as ion exchangers. Among the metals studied have been zirconium(IV), thorium(IV), titanium(IV), cerium (IV), tin (IV), aluminum(III), silicon(IV) etc. and the anions employed include phosphate, arsenate, antimonite, molybdate, tungstate, silicate etc (36). These salts, acting mostly as cation –