INTRODUCTION

Inorganic ion exchange materials :

The term "ion exchange" covers an almost limitless list of chemical reactions and fundamental processes where it is based on empirical experimence as a method for removing salt from sea water. Ion seiving is included under the broad heading of ion exchange because this process usually involves an exchange of ions. Some of the more obvious examples of ion exchange are the softening of hard water, the purification of blood in living organisms, the collection of radioactive metal ions from the coolant water used in nuclear power plants and the ultra-purification of chemicals[1,2]. Inorganic ion exchangers are both the oldest and the newest ion exchange materials[2]. The first commercial synthetic inorganic ion exchanger (alumino silicate),was synthesized[3]. The discovery and development of the theory of ion exchange was reflected in practical applications. ***Harm and Rumpler***[3] proposed the use of natural and artificial alumino silicates. ***Kressman***[4,] who developed the methods and theoretical basis of adsorption chromatographic analysis, by using both oxides and hydrated oxides of metals, various types of soils, silicates, and other inorganic substances as adsorbents[3-5]. At the begining of the 20th century, ***Gans***[6] developed the basis for the synthesis and technical application of inorganic cation exchangers. He termed the cations exchangers would find broad applications. However, the usefulness of the permutites prepared at that time, based on alumino silicates, was limited by their low chemical and mechanical stability. They were useful only for exchange in neutral media and their exchange capacity was low[5, 7]. The first synthetic organic ion exchange resins were synthesized in 1935[8]. During the following two decades, the emphasis was on the development of the organic resins.

At 1950, there was a need for new ion exchange materials and processes useful at high temperatures in presence of high ionizing radiation doses, and high acidic or oxidizing media. Common organic ion exchange resins were found to be inadequate under these conditions, as they were greatly degraded and lost their ion exchange properties [5]. One of the possible ways of solving this problem involved replacing the organic skeleton of the ion exchanger by an inorganic skeleton[5]. The earlier research on the sorption properties of some hydrated oxides silica gels and alumina was neglected and intense research was carried out on the ion exchange properties of oxides, hydrated oxides[7, 9-12]. Pioneering work was carried out in this field by the research team at the ***Oak Ridge National Laboratory*** led by ***kraus***[12], and by the english team led by ***Amphlett***[1]. Potentially suitable ion exchange sorbents that were studied included not only the oxides and insoluble salts of polyvalent elements, but also the salts of heteropoly acids, hexacyanoferrates, alumino silicates and zeolites [5,7,9].

Choice of sorbent :

For more than 30 years, inorganic ion exchange materials have attracted the attention of analytical chemists. A great variety of suitable inorganic compounds are available that can be used as sorbents for ions from aqueous solutions[4, 5]. In this concern, more than 400 of different inorganic substances have been prepared over the last 40 years and their sorption and other properties have been studied. These compounds constitute the basic range of inorganic ion exchange materials. Various crystal modifications of these substances, mixed sorbents, ...etc have also been prepared.

In addition to those synthetic sorbents a large group of natural and synthetic aluminosilicates are available which are utilized primary in the analysis of organic or biochemical substances and in gas analysis [5]. In spite of the wide variety of compounds that can be used as inorganic ion- exchanging materials, they have a number of more or less common properties that assist the chemist analyst in orientation in this very large number of compounds and help him to select the most suitable for a given analytical problem [5]. Inorganic ion-exchange materials can be employed as cation exchangers, and some act as amphoteric exchangers, the properties of some are similar to those of organic oxidants [5]. The selection and usefulness of a suitable sorbent also depends on its stability in the medium employed. The concentration of free acid or base in the solution can be a decisive factor [5]. Sorption on some substance occurs in a very wide range of acid concentration, while some inorganic ion exchange materials are sensitive to the increase in concentration of ammonium or alkaline hydroxides in the analyzed solution. Exchange on some types of sorbents is possible in only a very narrow pH range. Suitable sorbents can be chosen for applications in presence of high concentrations of strong oxidizing or complexing agents. On the other hand, other sorbents are very sensitive to these reagents [4,5]. The concentrations of H^+ or OH^- ions in solution or the presence of various complexing agents can affect the solubilities of some sorbents. The properties of some inorganic ion exchange materials can also be affected by the time elapsed from their preparation. Long term storage in the air can result in a number of changes connected with the sorption properties of the material, its crystal structure, stability, selectivity and exchange capacity[5].

A further important property of inorganic sorbents that plays an important role in the selection of a suitable exchange material is its selectivity for the analyzed element or for a small group of elements to be analyzed. Very high selectivity of a sorbent for a given elements permits it to be separated from a number of other elements, but it is usually rather difficult to elute this elements from the sorbent when radioisotopes emitting gamma radiation are employed[5], this disadvantage can be avoided by quantitatively determining the test element directly on the exchanger. A number of analytical methods are based on this phenomenon and are used in the analysis of various biological materials or mixtures in substances of high purity using neutron activation analysis[5].

Classification of inorganic ion exchange materials :

Synthetic organic ion exchangers can be classified on the basis of the exchangeable species, functional group, skeleton types, and the rigidity of the polymeric structure[5]. A similar classification of inorganic ion exchange materials is practically impossible. The chemical variety of these materials, characteristic properties for ion exchange, and the general inhomogeneity of the structure of sorbents with ion exchanging sites with various selectivity, all made it very difficult to find a single classification system. Consequently, classification of these materials on

Ion exchange synthetic zeolites act as catalysis for many chemical reactions, most importantly, for reactions involving organic compounds[25]. These zeolites are of interest to the petroleum industry. ***Barrer*** [9] has reviewed much of the early research of molecular sieve action of solids with liquids, in particular, various organic liquids. He discussed adsorption as a function of pore size and as a function of the complexity of the adsorbing molecule. These factors lead to the practicality of the separation of hydrocarbons by zeolites. Investigation by infrared spectroscopy of the adsorption of gaseous molecules can provide information about the nature of surface molecular groups such as hydroxyl groups.

2- Non alumino silicate :

Synthetic inorganic ion exchangers comprise a somewhat different class of ion exchange material. Most of these are gelatinous solids which do not have exactly reproducible stoichiometric properties or exchange characteristics.

a- Insoluble ferrocyanides :

The ferrocyanides were fairly intensively studied during the mid 1960's[26]. It was found that there are two types of ferrocyanide compounds can be formed. One type forms with various transition metal ions, such as vanadium and titanium [27, 28]. ***Lehto et al.***, [29] found that potassium cobalt hexacyano ferrate (II) is synthesized with the composition $K_{1.7}\ Co_{1.12}\ Fe(CN)_6 \cdot H_2O$. Ion exchange properties of these compounds were found to be stoichiometric, the exchangeable ions being potassium and cobalt in the ratios presented for the corresponding phases. The effective capacity for cesium on potassium cobalt hexacyano ferrate (II) was 0.33 meq g^{-1}., which is only 6% of the theoretical capacity. ***Lehto et al.***, [30], also, studied the cesium uptake by K_2 [Co Fe $(CN)_6$], the exchange process is assumed to involve only the outer most surface layer of their crystals which have cubic lattice, i.e. only potassium (or cobalt) ions inside the elementary cubes closest to the surface of the crystals are exchanged for cesium ions. ***Lehto and Co Workers*** [31], prepared potassium cobalt hexacyano ferrate (II), and studied it for the separation of Cs^{137} from nuclear waste solutions. Separation of Cs^{137}, Cs^{134} from nuclear power plant low -level waste solutions by ion exchange with potassium cobalt hexacyano ferrate (II) and ammonium phosphomolybdate was studied by ***Lehto and Harjula*** [32], similar investigations were carried out by ***Marie et. al.***, [33] in this respect, the authors prepared potassium zinc hexacyano ferrate (II) $K_2 Zn_3 [Fe (CN)_6]_2$. and used it for the uptake of ammonium ion (NH_4^+). The obtained equilibrium data indicated higher selectivity for ammonium ion relative to potassium ion and much lower to cesium ion.

b- Salts of heteropoly acids :

The second subclass of non-aluminosilicate synthetic inorganic exchangers is that of heteropoly acids. The best known of these are the various cation salts of phosphotungstic and phosphomolybdic acids [34] The most intensively studied heteropoly acid is ammonium 12-molybdophosphate. The first systematic study of ion exchange on this exchanger was reported in 1958 [35]. The cation exchange of the alkali metals on this exchanger was studied [36-38], as well as the exchange of bivalent and trivalent ions [39]. Ammonium 12-phosphotungstate was used to achieve the separation of rubidium from cesium [40], and ammonium 12- phoshomolybdate was used to separate sodium and potassium from other ions and from each other [41].

The effect of the size of the exchangeable cations on the ion exchange properties of a number of heteropoly salts was investigated[42]. A comparative study of the exchange behaviour of pyridinium, picolinium, lutidinium and collidinium salts of tungstophosphoric as well as of molybdophosphoric acid has been made [42]. The exchange isotherms of both tungstophosphates and molybdophosphates against NH_4^+, K^+, Na^+, and Li^+ clearly indicate that the exchangeability decreases with the increase in the size of the exchangeable ion in the heteropoly salts.

C- Hydrous oxides of polyvalent metal ions :

Hydrous oxides act as anion exchangers and as cation exchangers; their ion exchange properties depend upon the pH of the solution in which they are placed, these amphoteric solids act as cation exchangers in solutions which have pH values above their isoelectric points (the pH at which the concentrations of cation and anion exchangers are equal, and the average charge of the solid exchanger is zero) but as anion exchangers when the pH value is below their isoelectric points. The isoelectric points vary from 4.8 for stannic dioxide to 9.8 for thorium dioxide [43]. The isoelectric point for zirconium dioxide (zirconia) is about 7.0 .***Clearfield*** synthesized crystalline hydrous zirconia [44], and the thermodynamics of ion exchange on hydrous zirconia were studied[45]. where rapid exchange can occur if the particles are small enough [45]. All diffusion processes require an activation energy, Ea, to