# CHAPTER-1

# INTRODUCTION

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## 1.1. Introductory Outline

Interest in the industrial use of inorganic exchangers has increased rapidly since the mid 1980's. Increased environmental awareness has resulted in strict regulations for waste releases and more effective treatment methods are required to meet these conditions. The need for waste releases is especially urgent in nuclear industry, which generates large amounts of radioactive effluents in almost all phases of the nuclear cycle, and from reprocessing of the waste for further use of some of the radioactive elements. Ion exchange as a separation process is relatively facile and energy-efficient compared to other common solution phase separation procedures used in industry (e.g. solvent extraction and precipitation). The challenge in nuclear waste treatment is the efficient separation of the radionuclides present in trace amounts from complex solutions, which contain high concentrations of interfering inactive components, or extreme acidity or alkalinity. Therefore the method for effective separation in such conditions must be selective only for the trace ions in question. The major attraction in the use of inorganic ion exchangers in such applications is their good chemical and thermal stability, and the possibility for obtaining very high selectivity's and thus, good separation efficiencies.

## 1.2. History of Ion Exchanger

History of ion exchange was originally discovered to take place in soils, such as clays and zeolites. These materials found application as water softeners, over many years ion exchange has widely used for water softening, demineralization, and removal of nitrates in the preparation of drinking water(1,2). Furthermore, the use of ion exchange for controlling contamination of water systems with heavy metal ions seems to be promising (3). But the first commercially available ion exchangers were amorphous aluminosilicate gels. They were of low chemical stability and a need for alternatives led to the development and synthesis of organic ion exchange resins in the 1930's. However, the beginning of nuclear technology in the 1940's demanded materials with still better thermal stability (>150°C). The application of an exchanger in the treatment of nuclear waste solutions also requires good resistance of the material to ionizing radiation, which is a property the organic resins tend to lack. Therefore, the focus of researchers returned to inorganic ion exchangers(1,2).

Acid salts of metal oxides, such as phosphates, silicates and antimonies proved to be superior to many organic resins in this respect. These materials also had other important and advantageous properties needed in efficient separation of ions, such as high selectivity and capacity. However, these sorbets were mostly amorphous in nature and elucidation of the ion exchange mechanism, and their physical and chemical properties was very difficult and limited. The discovery of a crystalline phase of zirconium phosphate in 1964 made it possible to explain its observed ion exchange behavior in structural terms (4,5). The increased knowledge of the crystalline structures of many inorganic compounds since then allows for more in-depth studies of the correlation between the structure and observed ion exchange properties of a compound. Although originally the intent of the studies involving inorganic ion exchangers such as hydrous oxides, salts of polyvalent acids and zeolites was to explore their suitability for the treatment of nuclear waste solutions and purification of water, another approach in the search for efficient ion exchangers may now be taken. Traditionally the development of new materials for specific, desired conditions by the 'trial and error' approach has required a great deal of experimental effort and time. With the understanding of the origin of selectivity in inorganic ion exchangers, one could achieve greater control over the properties of the materials through synthetic design, and thus the ion exchange properties for highly selective separation applications for almost any desired conditions. However, because the origin of selectivity in these materials is not yet adequately understood, this approach requires that more fundamental research be carried out with most of the crystalline exchangers known today. By slightly altering the composition or the three-dimensional structure of the compound through systematic changes in synthetic variables and framework cation substitution, exchangers with desirable properties may be developed. During the past few years, a wide application of inorganic ion exchangers in liquid waste treatment has been investigated for fission and activation product elimination and for alpha emitter removal. The use of small amounts of inorganic ion exchange materials in conjunction with ultra filtration has been shown to be a very effective decontamination process. A wide range of exchangers exist, so the proper selection of appropriate inorganic exchangers could lead to good decontamination for the actinides, fission and activation products. Inorganic ion exchangers, due to their resistance to radiation and chemical attack and their compatibility with potential immobilization matrices, find wide applications in industries, including waste treatment, hydrometallurgy, preparation of high purity materials, water purification and several environmental applications. Due to growing environmental awareness, chemists are trying to restrict the use of hazardous compounds or organic solvents as far as possible. The mandate of green chemistry is to reduce the use of such organic solvents. Separation with an inorganic ion exchanger does not involve organic solvents and in that way is cleaner than a conventional liquid–liquid extraction (LLX) process. The advantage of solid phase extractants to be used for practical purposes like ‘water purification’ and 'decontamination' lies in the fact that the extracting does not require further treatment after taking up the desired element from its matrix. For an effective application, the inorganic ion exchangers are supposed to contain ions that are exchangeable with others present in a solution in which it is considered to be insoluble. During the past few years, a wider application of inorganic ion exchangers in nuclear waste treatment has been investigated for fission and activation product elimination.

## 1.3. Comparison of Organic and Inorganic Ion Exchangers

Inorganic ion exchangers are in general superior to organic exchangers in some aspects as they are resistant towards high ionizing radiations (6,7) and can be used at elevated temperatures without any danger of decomposition (6,9). Moreover, they often exhibit specificity towards certain metal ions. It is for these reasons that there has been a revolutionary growth in the field of synthetic ion exchangers (10,13). Studies have been conducted for their preparation, properties and analytical applications to simple binary and ternary separations of metal ions have been performed by different chromatographic techniques (14–17). However, their analytical and industrial applications in diverse fields are yet to be explored. A general comparison between organic and inorganic ion exchangers is given in Table (1). Therefore organic resins are limited due to its breakdown in aqueous systems at high temperatures and in presence of ionizing radiation; for these reasons there has been a resurgence of interest in inorganic exchangers in recent years, since they are particularly stable under these conditions (17-19). Applications which have bee suggested include the ion-exchange absorption and fixation of highly active waste solutions on clays, and the use of other inorganic exchangers for water treatment at high temperatures and for chemical processing of highly active solutions(20,21).

**Table (1): General comparison of organic and inorganic ion exchangers.**

| Property | Organic exchangers | Inorganic exchangers | Comments |
|---|---|---|---|
| Thermal stability | Fair to poor | Good | Inorganic are especially good for long-term stability. |
| Chemical stability | Good | Fair to good | Specific organics and inorganic are available for any given pH range. |
| Radiation stability | Fair to poor | Good | Organics are very poor in combination with high temperatures and oxygen. |
| Exchange capacity | High | Low to high | The exchange capacity will be a function of the nature of the ion being removed, its chemical environment and the experimental conditions. |
| Selectivity | Available | Available | For some applications, such as cesium removal, inorganic can be much better than organics, owing to their greater selectivity. Ion selective media are available in both organic and inorganic forms. |
| Regeneration | Good | Uncertain | Most inorganic are sorption based, which limits regeneration. |
| Mechanical strength | Good | Variable | Inorganic may be brittle or soft or may break down outside a limited pH range. |
| Cost | Medium to High | Low to high | The more common inorganic are less easily than organics. |
| Availability | Good | Good | Both types are available from a number of commercial sources. Inorganic can be converted to equivalent mineral structures; organics can be immobilized in a variety of matrices or can be incinerated. |
| Handling | Good | Fair | Organics are generally tough spheres, inorganic may be brittle; angular particles are more friable. |
| Ease of use | Good | Good | If available in a granulated form both types are easy to use in batch or column applications. |