SYNTHESIS AND CHARACTERIZATION OF ZIRCONIUM PHOSPHOBORATE AND ITS CONVERSION INTO GRANULAR SHAPE

A

Thesis Submitted

in partial fulfillment of requirements for the

Degree of

Master of Science in Chemistry

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Candidate's Declaration

I, hereby declare that the work presented in the dissertation entitled, **"Synthesis and characterization of Zirconium phosphoborate and its conversion into granular shape"**, in partial fulfillment of the requirements for the award of the degree of Masters in Chemistry, of Thapar University, Patiala, is my own work during the period of Jan 2010 to June 2010, under the supervision of Dr. Susheel Mittal and Dr. Rajeev Mehta. I have not submitted the matter embodied in this dissertation for the award of any other degree.

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This is to certify that the above statement made by the candidate is correct and true to the best of our knowledge.

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This is to certify that the project entitled, **"Synthesis and characterization of Zirconium phosphoborate and its conversion into granular shape"**, submitted by Mr. Ashok Sharma in partial fulfillment of the requirement for the award of degree of Master of Science in Chemistry of Thapar University, Patiala, is a bonifide work carried out under the supervision of Dr.Susheel Mittal (Head of Chemistry Department) and Dr. Rajeev Mehta (Associate Professor in Chemical Engineering Department). The work embodied in this dissertation has not been submitted for the award of any other degree.

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Abstract

ZrPB is reported as inorganic ion exchanger, highly selective for Er^{3+} ions over other lanthanides. This material was selected for its granulation. The material was synthesized by the reported procedure and characterized for its ion exchange properties like ion exchange capacity, pH titrations, thermal stability and morphology using XRD and SEM techniques. Preparation of granular ion exchanger was tried by a number of methods like sol-gel method, epoxy resin as a binder using different solvents. However these attempts were not successful.Then another method of synthesis by using Nylon-66 as a binder was tried which resulted in the preparation of granular zirconium phosphoborate. The material has been characterized as a granular material by XRD and SEM technique.

Chapter-1

Intoduction

1.1 What are ion exchangers?

Ion exchange materials are insoluble substances containing loosely held ions, which are to be exchanged with other ions in solutions, which come in contact with them. These exchanges take place without any physical alteration to the ion exchange material. Ion exchangers are insoluble salts of acids or bases, which can exchange either with positively, charged ions (cation exchangers) or negatively charged ones (anion exchangers). Synthetic ion exchange materials based on coal and phenolic resins were first introduced for industrial use during the 1930's. A few year later resins consisting of polystyrene with sulphonate groups to form cation exchangers or amine groups to form anion exchangers were developed. These two kinds of resins are still the most commonly used resins today. There are several features of inorganic exchangers which commend their use in a number of applications. We have already mentioned their temperature stability and resistance to high radiation fields. The most important property of inorganic ion exchangers is their high selectivities. As a result, separation factors tend to be much larger than those exhibited by organic exchangers. The reason why the inorganic materials have not achieved widespread commercial usage is that most of these materials are obtained as fine powders unsuited for column operation. A concerted effort has not been made to develop suitable binders to convert them to granular form of some zeolites.

1.2 Preparation of ion exchangers

Many natural and synthetic substances are capable of ion exchange. For technical purposes, however, only those substances, which have adequate mechanical and chemical properties, are suitable. Three most important groups in the order of their development include inorganic, natural organic base and synthetic resin ion exchangers. Amongst these, the aluminosilicates, both natural and synthetics are suitable for technical purposes. Zeolites are naturally occurring cation exchangers. In their crystal lattice some SiO_4^{4-} groups placed in the tetrahedral form are substituted by AlO_4^{5-} groups. Every AlO_4^{5-} group means a free negative charge, which binds by coulomb forces some easily moving uni or bivalent cations. Synthetic silicate based ion exchangers were produced for technical purposes by fusing soda, potassium carbonate, falspar and kaolinite and later from aluminium sulphate solution containing sodium silicate by precipitation with sodium hydroxide solution (Gelpermutite). Since then artificial, crystalline zeolites have also been successfully synthesized. Zirconium phosphate, zirconium tungstate and zirconium molybdate gels have recently been placed in the market (Bio-Rad Lab, U.S.A.). They have a better stability against nuclear radiation and against higher temperature than resin based materials. Therefore, they can be used advantageously in reactor technology. In the laboratory they can be used for the chromatographic separation of alkali and alkali earth ions. Aluminium, iron (III), and zirconium hydroxide hydrate gels act as synthetic inorganic anion exchangers.

1.3 Operation of ion exchange columns

If a portion of sodium chloride solution is poured on to a column of a strongly acidic resin in the hydrogen form, on the upper part of the column the hydrogen ions are entirely replaced by sodium ions, while below there is a part of the column where both hydrogen and sodium ions are present. If one plots the concentration distribution after pouring on a certain volume of sodium chloride solution, the S shaped curve is obtained. The ratio of sodium ion concentration to the total ion concentration of the resin is plotted along the horizontal axis, while the distance from the top of the resin column is plotted along the vertical axis. The concentration distribution can be represented by an S-shaped curve. By pouring on further sodium chloride solution the S-curve (front of the Na^+) ions reach the end of the column and break through. Sodium ion appears in the effluent inspite of the fact that hydrogen ion are still present in the column. The amount of sodium ions absorbed by the column until the break through gives the break through capacity of the resin column, which is one of the characterstics data for the operation of column. This value is naturally always lower than the value of total capacity. The changes takes place on an ion exchange resin can be registered in several ways according to which the variable of concentration (C) length of the column (L) and time (t) is considered as constant. Instead of concentration the equivalent fraction, instead of the length of the column the volume of the column (x), proportion to the former, instead of the time the volume (v) of the solution poured on or that of the effluent, which is proportional to the time (supposing a constant flow rate) can be plotted. If a concentration at a given point of time is plotted against the length of the column, the so-called isochrones is obtained.

1.4 Nature of inorganic ion exchangers

It is not generally recognized that a very large number of inorganic compounds possess the property of ion exchange. It is common knowledge that clays and zeolites are ion exchangers, but so are many phosphates, titanates, heteropoly acid salts, and layered double hydroxides (anion exchangers) also posses ion exchange properties. In a review article (Clearfield, 1988), there are 14 classes of compounds with significant ion exchange capacity. Many more types have been described by (Vesely and Pekarek, 1972), and others are being discovered all the time (Abe et al., 1991). Only a few of the major types are briefly discussed below.

1.4.1 Hydrous oxides

The hydrous oxides may be divided into two main types: those like ZrO_2 and SnO_2 for which ion exchange occurs only on the surface and others, such as the hydrous oxides of antimony and manganese, that contain cavities or tunnels much like zeolites. The former oxides have been termed particle hydrates while the latter have been referred to as framework hydrates (England et al., 1980).

1.4.2 Layered ion exchangers

(a) Oxides: The ternary oxides are generally highly crystalline so that their structures can usually be determined from single crystal analysis or, in failing to obtain suitable crystals, from powder data. We note that the interlayer distance is small and many of them have a limited swelling capacity. As a result, the ion exchange process may be followed by taking X-ray diffraction (XRD) patterns. The extent of exchange can be determined visually by estimating the amount of the exchanged phase relative to the amount of starting phase in the XRD pattern.

(b) Group 4 and 14 Phosphates: The ion exchanger in these element groups were first prepared as amorphous gels. Phosphated hydrous oxide compound has the composition $Zr\text{-}(HPO_4)_2.H_2O$ and has a layered structure. The metal atoms lie slightly above and below a mean plane drawn through the center of the layer. The metal atoms are bridged by phosphate group located alternately above and below the mean plane. Three phosphate oxygens bond to Zr atoms while the fourth bonds to a proton and extends into the interlayer space. The layers are staggered forming a network resembling a hexagonally shaped cavity. The water molecule resides in a pocket of the cavity formed by three P-OH groups. Only van der Waals forces hold the layers together as the water molecules are hydrogen bonded to the P-OH in the top side of one cavity or the bottom side in an adjacent cavity. The calculated and measured ion exchange capacity is 6.63 mequiv/g as both protons are exchangeable. The exchange reactions are represented by the following equations:

$$\underset{(7.6\ \text{Å})}{\mathrm{Zr(HPO_4)_2.H_2O}} + \mathrm{Na^+\ (aq)} + \mathrm{4H_2O} \longrightarrow \underset{(11.8\ \text{Å})}{\mathrm{ZrNaH(PO_4)_2.5H_2O}} + \mathrm{H^+\ (aq)}$$

$$\underset{(11.8\ \text{Å})}{\mathrm{ZrNaH(PO_4)_2.5H_2O}} + \mathrm{Na^+\ (aq)} \longrightarrow \underset{(9.8\ \text{Å})}{\mathrm{Zr(NaPO_4)_2.3H_2O}} + \mathrm{H^+} + \mathrm{2H_2O}$$

The stepwise nature of the ion exchange is shown by the titration curve (Clearfield et al., 1969; Clearfield, 1982). In the first stage of exchange, the H-form of the exchanger is converted to the half-exchanged phase that, because of the increase in water content, expands its interlayer spacing. Exchange takes place by diffusion of ions from the outer surface inward with advancing phase boundary (Alberti, 1978). Thus, as the sodium ions are exchanged beyond the surface, a half-exchanged phase is formed in small pockets near the intersection of two faces. Crystallization of the gels is a slow process requiring days of refluxing in strong phosphoric acid. The shapes of the titration curves change with increasing crystallinity. That is, they exhibit more than one slope (Clearfield, 1990). X-ray powder patterns show that a change of slope signifies a change of phase. A gel that had been refluxed in 0.8 M H_3PO_4 exhibited a single phase up to $X_{Na} = 0.25$, a second phase from $0.25 < X_{Na}$ to $X_{Na} > 0.75$, and a third phase at still higher Na^+ ion loading. One other feature of these phosphate exchangers is of interest and importance is that it is possible to prepare materials of the type $Zr(OH)x(HPO_4)_2.1/2x$. These compounds are generally amorphous gels whose selectivities are modified by the creation of larger spaces between the phosphate groups.

(c) Layered double hydroxides: Layered double hydroxides constitute an interesting and extensive class of layered compounds (Reichle, 1986a,b). Their general composition may be represented as $M^{II}_n.M^{III}\ (OH)_{2n+2}X$, where n = 2-5 and X is a charge balancing anion. The layers have the $Mg(OH)_2$ structure in which the trivalent metal is isomorphously substituted for the divalent one (Allmann, 1970; Brown and Gastuche, 1967). This substitution creates positively charged layers balanced by anions in the interlamellar space.

One of the major impediments to the use of inorganic ion exchangers is the fact that they are not available in granular form suitable for column use. Several of the fine powdered exchangers have been pelletized. Several groups in the former Soviet Union have produced the gel type exchangers as small beads in several mesh sizes. Some of the exchangers have been produced on a large scale in Russia and the Ukraine and utilized for removal of heavy elements from industrial effluents. Given the stress on environmental factors at the present time, it would appear prudent to enlarge the options available by use of inorganic exchangers. For example, many of these inorganics can be used in hot organic solvents or corrosive media. Because of their very high selectivities, they can remove traces of metals where ultrapure solutions are required or effect separations that are difficult to achieve with organic resins. Many of the inorganics can be incorporated into organic resins to make interesting composite exchangers. Among other applications carbon based inorganic exchangers have been prepared in the former Soviet Union for oral administration to livestock and humans for the purpose of sequestering ingested radioactive species.

1.5 Characteristics of ion exchangers

The most important features characterizing an ideal exchanger are:

1. A hydrophilic structure of regular and reproducible form
2. Controlled and effective ion exchange capacity
3. Rapid rate of exchange
4. Chemical stability
5. Physical stability in terms of mechanical strength and resistance to attrition
6. Consistent particle size and effective surface area compatible with the hydraulic design requirements for large-scale plant.

1.6 Types of ion exchangers

The types of ion exchange materials are:

1.6.1 Cation exchanger

Ion exchange resins are classified as cation exchangers, which have positively charged mobile ions available for exchange. They differ in the ionizable groups attached to the polymeric network. It is this functional group that determines the chemical behavior of the exchanger. Exchangers can be broadly classified into four groups:

(a) Strong acid cation exchangers: Strong acid resins are so named because their chemical behavior is similar to that of a strong acid. The resins are highly ionized in both the acid and salt forms. They can convert a metal salt to the corresponding acid by the reaction, e.g.,

$$2(\mathrm{R\text{-}SO_3H}) + \mathrm{NiCl_2} \longrightarrow (\mathrm{R\text{-}SO_3})_2\mathrm{Ni} + 2\mathrm{HCI} \tag{1.1}$$

Where, R is polymeric chain to which functional groups like SO_3H are attached. The hydrogen and sodium forms of strong acid resins are highly dissociated and the exchangeable Na^+ and H^+ are readily available for exchange over the entire pH range. Consequently, the exchange capacity of strong acid resins is independent of solution pH. These resins would be used in the hydrogen form for complete deionization; they are used in the sodium form for water softening (calcium and magnesium removal). After exhaustion, the resin is converted back to the hydrogen form (regenerated) by contact with a strong acid solution, or the resin can be converted to the sodium form with a sodium chloride solution. For equation 1.1, hydrochloric acid (HCl) regeneration would result in a concentrated nickel chloride ($NiCl_2$) solution.

(b) Weak acid cation resin: In a weak acid resin, the ionizable group is a weakly acidic group like- (COOH) as opposed to the sulfonic acid group (SO_3H) used in strong acid resins. These resins behave similarly to weak organic acids that are weakly dissociated. Weak acid resins exhibit a much higher affinity for hydrogen ions than do strong acid resins. This characteristic allows for regeneration to the hydrogen form with significantly less acid than is required for strong acid resins. The degree of dissociation of a weak acid resin is strongly influenced by the pH of solution. Weak acid resin has limited capacity below a pH of 6.0 making it unsuitable for deionizing acidic metal finishing wastewater.

(c) Strong base anion resin: Strong base anion are highly ionized and can be used over the entire pH range. The resins are used in the hydroxide form for water deionization. They will react with anions in solution and can convert an acid solution to pure water, e.g.,

$$R—NH_3OH + HCl \longrightarrow R\text{-}NH_3Cl + HOH$$

Regeneration with concentrated sodium hydroxide (NaOH) convert the exhausted resin to the hydroxide form.

(d) Weak base anion resin: Weak base resins are like weak acid resins. The degree of ionization is strongly influenced by pH in weak base anion resin. Consequently, weak base resins exhibit minimum exchange capacity above a pH of 7.0. These resins merely sorb strong acids and they cannot split salts. The weak base resin does not have a hydroxide ion form, as does the strong base resin. Consequently regeneration needs only to neutralize the absorbed acid: it need not provide hydroxide ions.

1.6.2 Inorganic ion exchanger

Organic ion exchange dominated the field because of their uniformity, chemical stability and the ability to control resin properties by synthetic procedures. A new direction was applied to the field of inorganic ion exchangers when Clearfield and Stynes[1] demonstrated that zirconium phosphate could be crystallized and hence it become possible to know the structure of this polymorph of zirconium phosphate[2-5]. With this knowledge, the observed ion exchange behavior could be explained in structural terms[6]. Principal classes of inorganic ion exchangers are shown below.

Table 1. Some examples of inorganic ion exchange materials with ion exchange capacity

Sr.No	Types	Examples	Exchange capacity (equiv/g)
1.	Smectic clays	Montmorillonites	0.5-1.5
2.	Zeolites	$Na_x(AlO_2)_x(SiO_2)_y.zH_2O$	3-7
3.	Substituded aluminium phosphates	Silicoaluminophosphate,metal substituted aluminophosphate	Depends upon value of x
4.	Other phosphates	U,V and Sb phosphates	8

5.	Condensed phosphates	$NaPO_3$	4-7
6.	Group iv phosphates	$Zr(HPO_4)_2H_2O$, $Sn(HPO_4)_2H_2O$	4-8
7.	Hydrous oxides	SiO_2xH_2O,Polyantimonic acid	1-2
8.	Heteropolyacid salts	$M_nXY_{12}O_{40.}xH_2O$	0.2-1.5
9.	Ferrocyanides	$M_{4/n}{}^{n+}Fe(CN)_6$	1.1-6.1
10.	Titanates	$Na_2Ti_nO_{2n+1}(n=2-10)$	2-9
11.	Apatites	$Ca_{10-x}H_x (PO_4)_6(OH)_{2-x}$	Cation and anion exchange
12.	Anion exchangers	$Mg_6Al_2(OH)_{16}CO_3.4H_2O$	2-4
13.	Miscellaneous type	Alkaline earth sulfates	1.5-3
14.	Fast ion conductors	$Na_{1+x}Al_{11}O_{17\_x/2}$, $Na_{1+x}Zr_2Si_xP_{3-x}O_{12}$	2-7

1.7 Granular inorganic exchangers

Many different methods have been proposed for preparing granules of inorganic ion exchangers and for improving granular strength of these materials. On the basis of the preparation method used, the resulting ion exchangers can be classified in three groups:

1. Intrinsic inorganic ion exchangers
2. Supported ion exchangers
3. Composite ion exchangers

1.7.1 Intrinsic inorganic ion exchangers

Intrinsic inorganic ion exchangers represent a group of ion exchangers prepared without use of any additives. These are also called intrinsic sorbents. These are of two types:

(a) Natural inorganic ion exchangers: Natural inorganic ion exchangers are usually modified for use in column packed beds by crushing and followed by sieving to obtain particles of the required size. In the last step the, fine particles are washed by flushing the absorber by water, e.g., clinoptilolite, mordenite.

(b) Synthetic inorganic ion exchangers: These are insoluble inorganic compounds prepared by precipitation in aqueous solutions. The precipated inorganic ion exchangers must be separated by filtration and the undesirable chemical admixtures washed out. Suitable granules are obtained by sieving the dried, crushed filtration cake to obtain a fraction with requested grain size. The finest particles are washed out of granules before application. Vesel and Pekarek state[7,8] that many granular inorganic ion exchanger are prepared by this method. In some cases it is not possible to produce an absorber with sufficient mechanical strength. For this reason the special methods of modification of inorganic ion exchangers are slow growth method, high temperature treatment, freeze thaw method and sol gel method.

1.7.2 Supported ion exchangers

Supported ion exchangers represent a group of inorganic ion exchangers, in which the active inorganic component is deposited in a suitable supporting material. The simplest way to prepare supported sorbents is to either mix the fine grained or amorphous precipitate of the ion exchanger with an inert support material or induce it to precipitate directly on a suitable support materials. Initially used as supports are asbestos, filtration paper, alumina, charcoal, glass wadding and other porous materials[7-8]. Later, Caletra et al[9-11] used silica gel as the support for various inorganic ion exchangers.

1.7.3 Composite ion exchangers

Composite ion exchangers[12] represent the group of inorganic ion exchangers modified by a binding material to prepare larger particles with higher granular strength. Possible inorganic binding materials include, e.g., clay minerals, cements, silica gel, alumina, which may be mixed with the powdered inorganic ion exchanger and water to form a paste of suitable consistency. The paste is then used to form pellets, which are dried and calcined to improve their mechanical strength. The required properties of binding materials are-sufficient aggregation force, ample chemical stability, no adverse impact on the ion-exchange properties of the inorganic ion exchanger, no ion exchange property of their own, high permeability of the aqueous solutions of the targeted ions, and an ability to produce granules with a high quantity of the active component of the absorber.

Chapter-2

Literature Survey

The first commercially available ion exchangers are amorphous aluminosilicate gels[13,14]. These gels later become known as permutites but their instability toward acid solutions and their variability of behavior led chemists to seek alternatives. This search eventually led to the synthesis of organic ion exchange resins[15]. These resins soon dominated the field because of their uniformity, chemical stability and the ability to control resin properties by synthetic procedures. The advent of nuclear technology initiated a search for ion exchange materials that would remain stable above 150^0C and in high radiation fields. Early attention was focused on hydrous oxides since it was known that they sorbed coprecipitated many ions. It was soon discovered that hydrous oxides combined with anions such as phosphates, vanadates, molybdates and antimonates produced superior ion exchangers[16-19]. Much attention paid to the synthesis of zirconium phosphate which actually had been discovered earlier[20]. These materials are amorphous in nature and not resistant to alkaline hydrolysis.

Zeolites and calcium phosphates are commercially available and well developed inorganic ion exchangers. Inorganic ion exchangers have immense importance because of their temperature stability, good chemical stability, compatibility with matrices used for their immobilization, resistance to high radiation field, high selectivity exhibited for many ions and large separation factor. Instead of their wide importance, the inorganic ion exchangers have not achieved widespread commercial usage because many of the compounds are obtained as fine powders which is unsuited for column beds. Many different methods have been proposed for preparing granules of inorganic ion exchangers and for improving granular strength of these materials. On the basis of the preparation method used, the resulting ion exchangers can be classified in three groups-intrinsic, supported and composite inorganic ion exchangers.

Various scientists improved the strength of inorganic ion exchangers by using different methods to prepare granular materials. Some of these are given below:

i. Under normal circumstances, ammonium salts of heteropolyacids may be prepared only in the form of very small crystals (200 mesh). A procedure for preparing larger particles (0.4 nm) described by Smith[21] consists of contacting crystals of molybdophosphoric acid with a concentrated solution of ammonium nitrate. Relatively strong agglomerates of ammonium salt result.

ii. Zinc or nickel hexacyanoferrate (ii)[22,23], crystals has also been used to prepare by slow growth method. In this method local growth occurs on sodium or potassium ferrocyanide crystals placed in concentrated zinc or nickel solution to produce hollow spheres. Particles of 0.1 to 0.5 nm can easily be prepared. The chemical stability for zinc ferrocyanide in solutions from pH 1 to 10 and for nickel ferrocyanide from pH 0 to 12.

iii. The various granulatede hydrous oxides have been prepared by freeze thaw method. e.g., SnO_2, SiO_2, MnO_2, TiO_2, ZrO_2, and mixed absorbers[24]-nickel hexacyanoferrate + $Ni(OH)_2$, PbS + $Pb(OH)_2$, NiS + $Ni(OH)_2$. The freeze thaw method is used to produce granules from inorganic ion exchangers yielding amorphous precipitate that settle and filter poorly. The method make use of the fact that water is irreversibly separated when a gel is frozen and the absorber become granular. After thawing, the granules are separated from the solution and air dried at ambient or elevated temperature.

iv. The use of sol gel method to prepare spherical particles of inorganic ion exchangers is a significant contribution to developing procedures for modifying their granulometric and mechanical properties. This method making use of converting a sol dispersed in an organic solvent to hydroxidic gel[25-27] . From the principle of the method it follows, that it is possible to prepare uniform spheres of hydroxidic gels from only polyvalent hydrolysable cations, e.g., Al^{3+}, Fe^{3+}, Cr^{3+}, Si^{4+}, Ti^{4+}, Zr,$^{4+}$ or their mixtures. The conversion of a sol into a gel may be accomplished by either internal or external gelation[25-27]. Internal gelation is generally used to prepare intrinsic absorbers. Sols may be dispersed in media that are immiscible with water (paraffin or silicon oils, kerosene etc.) in chemical reactors equipped with good stirring capabilitry, or in continuous gelation column by dripping from capillaries[27]. The disadvantage of sol gel method is the great shrinkage of particles after drying of hydrogels, or their conversion to xerogels. The procedure is not universal because it is not possible to prepare zinc or nickel hexacyanoferrates by sol-gel method[27].

v. Caletka et al.[9-11] used silica gel as the support for depositing several hexacyanoferrates on different types of silica gel[9] of suitable grain size. The simplest way to prepare supported sorbents is to either mix the fine grained or precipitates of the ion exchanger with an inert support material or induce it to precipitate directly on a suitable support. The materials initially used for supports are asbestos, charcoal, alumina, filtration paper, glass fibres, glass wadding and other porous materials can be used. The main disadvantage of this procedure is a considerable increase in volume and problems with the loading larger columns. The sorption properties of the resulting column are too low and the ion exchangers may be washed out of the bed when they are used for longer periods.

vi. Porous stainless steel membrane[28] were used for support of hydrous titanium and zirconium oxides. TiO_2 ans ZrO_2 were precipitated within the porous metal matrix using tetraisopropyl orthotitanate or zirconium propoxide and LiOH solution. Such stainless steel might be impregnated with TiO_2 up to 7% of their weight. Impregnated steel membrane is used as a means of removing radionuclides from the primary coolant used in pressurized water reactors.

vii. Water et al**.**[29] used organic polymers as a support for inorganic ion exchangers[16]. They were the first to describe the preparation of copper hexacyanoferrate–loaded anion exchange resin. Harjula et. al. also studied possible applications of IRA-400 and IRA-904 anion exchange resins, chelex-100 chelating resin as supports for potassium–cobalt hexacyanoferrates. Harjula selected granular potassium cobalt hexacyanoferrate for separating ^{137}Cs from concentrates at Lovissa NPP.

viii. Granulated wood cellulose, cotton cellulose and pine wood saw dust were proposed as supporting matrices in a patented procedure for manufacturing sorbents with transition metal hexacyanoferrates[30]. The supporting material is treated with the suspension of freshly precipitated metal hexacyanoferrate and dried at 90 to 110^{o}C. The volume of inorganic ion exchanger in total volume of the produced sorbent is 1% to 30%. The suspension of transition metal hexacyanoferrate reacts with the surface of the supporting material. Due to this interaction, the resulting sorbents exhibit improved properties. The sorbents with granulated wood as a support are produced under the trademark, Fezhel.

ix. Krishnaswami et. al.[31] used fibrous polymers as a support for inorganic ion exchangers. He developed the procedure for impregnating acrylic fibres with iron hydroxide. Iron treated fibres were used for the insitu extraction of various elements from seawater.

x. Powdered and microcrystalline inorganic ion exchangers may also be converted to granular form by using suitable binding material. Both inorganic and organic materials may be used as binding materials to prepare such composite sorbents. Possible inorganic binding material include e.g., clay minerals, which may be mixed with the powdered inorganic ion exchanger and water to form a paste of suitable consistency. This paste is then used to form pellets, which are dried and calcined to improve their mechanical strength. Cement has also been used as a binding material for granulating nickelhexacyanoferrate[32]. At first a dry mixture of cement and hexacyanoferrate salt (3:2 or 4:1) was prepared and then mixed with water. The resulting dense grout was moulded into desired form. After 3-7 days of curing, the product was crushed and sieved. Granules obtained from both of these mixtures exhibited ample long-term stability in contact with solution.

A sol gel procedure[33] was used for granulating powdered inorganic ion exchangers into a matrix of SiO_2. Urea and hexamethylenetetramine are added to the sol of silicic acid and upto 70% (w/w) of exchanger. This mixture was dispersed into an organic medium such as silicon oil at elevated temperature. A composite sorbent containing ammonium molybdophosphate (AMP) prepared by this procedure[34] contained 65% (w/w) of the active component in the dried residue and had a sorption capacity of 0.22 mmole Cs ml^{-1}. Hydrophilic polyacrylic hydrazide was used for granulating hydrous titanium oxide[35,36]. Titanium oxide powder was homogenized with an aqueous solution of PAH and dried at 60°C. The granular sorbent was obtained by crushing the resulting solid, washing it with water and sieving.

Spherically granulated[37] sodium aluminophosphatesilicate was prepared by a gel method. According to this method H_3PO_4 solution, 1M $Na_2SiO_3.SiO_2$ solution and $NaAI(OH)_4.NaOH$ solution were mixed efficiently in a mixer. The reaction mixture obtained was dispersed into a vertical column filled with an organic solvent (aliphatic hydrocarbons C_9H_{20}-$C_{11}H_{24}$, ambient temperature). In the column the formation of spherical granules of hydrogel took place. After separation from the organic solvent the granules of gel were thoroughly washed with water, and then dried in an air oven at 100°C. The APS was mechanically strong (crush strength 240-260 kg/cm^2), glass-like, colourless spherical beads with diameters in the range of 0.2-2 mm. The proton form of the APS (APS-H) was prepared by treatment with an excess of a 0.1 M solution of nitric acid. Crystalline silicotitanate[38] (CST) an inorganic ion exchange material, marketed commercially by UOP Inc, for selective cesium and strontium removal from alkaline systems. The CST purchased from UOP is normally in the acid form or $H_2NaSi_2(Nb_{0.3}Ti_{0.7})_4O_{13}(OH).4H_2O$ utilizing $Zr(OH)_4$ as a binder to produce a granular product suitable for use in a packed bed[39,40]. Since the binder is a hydroxide, the material would suffer some degradation when used with an acidic feed material[41]. Preliminary testing indicated the CST to have acceptable cesium removal properties, but showed 16–18% binder degradation based on dissolved zirconium in the combined column effluent.

Tetravalent metal acid salts are a widely studied group amongst the known inorganic ion exchangers due to their excellent thermal stability, chemical resistivity and unique selectivity toward certain metal ions[42-48]. They are cation exchangers possessing the general formula $M(IV).(HXO_4)_2.nH_2O$,where M(IV) = Zr, Ti, Sn, Ce, Th etc. and X=P, W, As, Mo, Sb etc.. The material was broken down to desired particle size (30-60 mesh ASTM) by grinding and sieving, and then the acid treated, TIP was obtained as white granules. Its Na^+ IEC was determined by the column method[49]. A sol gel method[50] has been suggested for obtaining zirconium (IV) phosphate in the form of spherical grains with high mechanical strength[51]. This method consists of the following main stages: synthesis of a sol of zirconium (IV) hydroxide by electrolysis of a $ZrCl_4$ solution, drop dispersion of the sol into an ammonia solution to give gel-spheres of $Zr(OH)_4$, conversion of gel-spheres of $Zr(OH)_4$ into zirconium (IV) phosphate, and washing and drying of gel-spheres of zirconium (IV) phosphate. The basic stage of the method is the conversion of gel-spheres of zirconium (IV) hydroxide into gel spheres of zirconium (IV) phosphate. This is due to the layered structure of zirconium (IV) phosphate and hydroxide. Zirconium (IV) hydroxide layers are formed by tetrameric ions bound together by hydroxide groups lying above and below the layer plane. As a result, each zirconium (IV) ion is surrounded by eight hydroxy groups forming a distorted cube. The hydroxy groups lying above and below the layer of zirconium (IV) ions are replaced with hydrophosphate ions without any significant change in the positions of zirconium (IV) ions in the layer, with the result that the integrity of the gel spheres is retained.

Several granulated titanium silicate [52] precursors with different Si:Ti molar ratios (from 0.5 : 1 to 2 : 1) were prepared via the sol gel method. Granular titanium silicate xerogels (0.25-0.5 mm particle size) were used as precursor for one preparation of the crystalline alkali metal titanium silicates. A typical procedures includes hydrothermal treatment of precursor with NaOH solution autoclaved at 180°-190ºC and autogenous pressure for 48 h. The product obtained were separated, washed with water and dried at 60-70ºC. Now a days, scientist give more stress on the formation of hybrid ion exchangers. In this case there is incorporation of polymer material into an inorganic ion exchanger take place.

Many scientists have introduced organic-inorganic hybrid ion exchangers consisting of inorganic ion exchangers and organic binding matrices[53-57]. This inorganic ion exchanger refers to a composite group of inorganic ion exchangers, which are modified by some binding polymeric materials for the preparation of some large size particles with granular strength[58]. Inorganic ion exchange materials may be encapsulated through immobilization with porous polymeric materials such as alginate, agar, polyacrylamide, carrageenan, cellulose acetate and polyvinyl alcohol[59,60]. The porous structure of polymers allows metal ions to diffuse into the internal pores and exchanged with the internal ion exchanger. Organic-inorganic hybrid ion exchanger (e.g. zirconium vanadate) prepared by homogenous technique was mixed thoroughly with an aqueous solution of PVA containing sodium alginate using the homogenizer at 14000 rpm. This mixture was pumped by a peristaltic pump at 10 ml/min and then dropped into a gently stirred 6% boric acid solution containing 3% $CaCl_2$ to form spherical beads.[54] In order to complete gelation inside beads these beads were stirred gently in the boric acid $CaCl_2$ solution for 24 h. The beads were then removed and washed with distilled water. Finally the washed beads were dried at 40ºC for 24 h.

Doping[61] of inorganic ion exchange material tin silicate with zirconium ion by sol-gel technique was conducted for the production of a novel granular inorganic ion exchanger. Various solid samples of zirconium doped tin silicate were prepared by the reaction of tin tetrachloride with sodium silicate and different concentrations of zirconium chloride solutions with a volumetric ratio equal to 1:2:1. The reaction carried out in water bath for 4 hours during which white gelatinious precipitates formed. After overnight standing, the precipitate was separated by centrifugation and washed with HNO_3 to remove the excess Cl^- ions and impurities and rewashed with distilled water to remove NO_3^- ions and dried at 60ºC. The granular solid was poured in near boiling water (70-80ºC) to remove the trapped air and finally dried, grained, sieved and stored at room temperature. Tin silicate[61] used in the process was synthesized by slow addition of stannic tetrachloride with sodium silicate up to a molar ratio Sn to Si equal to 1:2 in 4 hours in a water bath thermostat at 60ºC with continuous stirring. During the addition process, white gelatinous precipate formed. After complete addition process, the precipitate is left standing overnight to allow particles to grow. The precipitation was separated by centrifugation and washed with HNO_3 to remove the excess Cl^- ions and impurities and rewashed with distilled water to remove NO_3^- ions and dried at 60ºC. The granular solid was poured in near boiling water to remove the trapped air and finally dried, grained, sieved and stored at room temperature.

Yasushi Nakazima and Isao Yoshida[62] formed granular zirconium phosphate (NZP-P) by mixing hundred grams of zirconium phosphate (NZP-P) with 40 g of 30% silica sol and made into spherical granules by Marumerizer (Fujii Paudal Co. Ltd). V.K.Gupta et.al.[63] formed granular zirconium (iv) selenoiodate. The inorganic ion exchanger zirconium (iv) selenoiodate sample were prepared by adding zirconium (iv) oxychloride gradually to a mixture of potassium iodate and sodium selenite in different ratios and concentrations with intermittent shaking of the mixture and maintaining the pH at one throughout mixing. The resulting white gelatinious precipitate was left to stand for 24 hour in the mother liquor. It is decanted and washed with dimineralized water (DMW), filtered and dried at 40 ± 2ºC. The dried white and opaque product was broken into small granules when it was immersed in water and the granules obtained were converted into H^+ form. Finally the exchanger was washed with DMW to remove excess acid and then again dried at 40 ± 2ºC.

Chapter-3

Materials and methods

3.1. Apparatus

A digital pH-meter (Denver Instrument Co., U.S.A.) was used for pH measurements, a temperature controlled electric oven was used for drying the sample. A thermo gravimetric analyzer TGA (Shimadzu TGA-50, Japan) were used for Thermal stability. X-ray Diffractometer of (PANlytical's X' Pert Pro) for X-ray diffraction. For FTIR (Perkin Elmer FTIR spectrometer), scanning electron microscope (JEOL JSM 6510LV, Japan) and Muffle furnace (Carbolite, Aston Lane, England) for heating were used.

3.2. Synthesis of Zirconium Phosphoborate

Zirconium (iv) phosphoborate[64] (ZrPB) was prepared by adding zirconyl oxychloride (0.1 M) solution (containing hydrofluoric acid, 12 ml/L) to a continuously stirred equimolar mixture of boric acid (0.1M) and orthophosphoric acid (0.1 M) solution at 60ºC in a volume ratio of 2:1:1. Gelatinious white ppt were obtained and pH of the gel was adjusted to 1.0 by adding either HCl or precipitate NaOH solution. Precipitates were filtered, washed until free from halides and phosphates and then dried at 40ºC. The dried product broke down into small granules when immersed in water. The material was converted into H^+ form by keeping it in HCl (0.1 M) for 24 hours with intermittent changing the acid and finally dried at 40ºC. The product was washed with deionised water in order to remove excess acid.

3.3. Ion exchange capacity

Ion exchange capacity of the different samples of zirconium phosphoborate was determined by column operation. The exchanger (0.5 g) in the H^+ form was put in a glass column with glass wool support. Eluted 50 mL of each electrolyte solution through the column at the rate of 5-8 drops per minute. The librated protons in each different solutions were titrated against standard sodium hydroxide solution. The ion exchange capacity was determined with respect to some monovalent and divalent cations.

3.4. Thermal stability

ZrPB exchanger (0.8 gm in H^+ form) was taken in three prewashed silica crucibles. Placed crucibles containing samples in the furnance at 100°, 200° and 500ºC one by one. After three hours of ignition at respective temperatures weighed all the samples again and noted the loss in weight by the sample at different temperatures. Ion exchange capacity of all the heated samples was determined for sodium ions by the same procedure as described above by using phenolphthalein as an indicator. Ion exchange capacity for sodium ions has been plotted as a function of the square root of the temperature (Figure 1).

3.5. pH Titration

pH titrations with potassium hydroxide (0.1 N) and sodium hydroxide (0.1 N) were performed by the added salt method. 0.2 g of the exchanger was kept in contact with varying volume of the base and the salt solutions for 24 hours. The pH of the solutions was noted by using pH meter.

3.6. XRD studies

X-ray powder diffractometry was carried out using X-ray diffractometer with CuK_α radiation beam (λ= 1.54060). Fine powdered sample of the ion exchanger was packed into a flat aluminium sample holder. X-ray source was a rotating anode operating at 45 kV and 40 mA with a copper target. Data were collected between 5° and 80°.

3.7. Infrared Spectroscopy

IR spectrum of the prepared ion exchange material was measured using FTIR spectrometer. The disc technique using KBr as a matrix was found to be suitable. In this concern, the ion exchanger was thoroughly mixed with KBr and the mixture was ground and then pressed to give a disc of standard diameter. The IR spectrum was scanned over the wavelength range 500 cm^{-1}-4000 cm^{-1}.

3.8. Thermal Analysis

The thermal stability of the prepared ion exchanger was evaluated by TGA and DTA. Measurements were carried out with a heating rate of $10^\circ C$/min under flow of N_2 starting from ambient conditions upto $700^\circ C$.

3.9. Scanning electron microscopy

The ground ion exchanger was stocked over a holder. Then, it was gold-sputtered before examination. The samples were scanned to identify the structure and estimate the particle diameter at different magnifications.

Chapter-4

Results and discussion

Synthetic inorganic ion exchangers offer definite advantages over their organic counterparts in terms of intrinsic properties like selectivity, chemical and thermal stability. Limitations associated with these materials are their poor mechanical strength and are difficult to be transformed into granular beads, suitable for column operations. A double salt of zirconium with phosphate and borate is synthesized as per the reported procedure[64] and converted it into the granular form by a number of methods. Zirconium phosphoborate is characterized as a weakly acidic cation exchanger and to check its reproducibility, a number of lots were synthesized. Ion exchange characterstics like workable ion exchange capacity, spectroscopic analysis and thermal analysis were carried out to establish the reproducible nature of the material**.**

4.1. Characterization of ion exchanger

1. **Ion exchange capacity**

   The working capability of zirconium phosphoborate, i.e., the ion exchange capacity was determined for some mono and bivalent cations. The results are given in Table 1. Ion exchange capacity for alkali and alkaline earth metal ions, is found in the order $K^+ > Na^+$ and $Ca^{2+} > Mg^{2+}$. These results suggest that the ion exchange capacity decreases as the radii of the hydrated alkali metal ions increases, but the same is not followed by alkaline earth metal ions.

2. **Reproducibility**

   In order to check reproducibility of the material, spectroscopic studies like IR, SEM and TGA were carried out on all samples of different lots. The IR and SEM analysis of these samples were same and representative records of these results are shown in Figure 5 and Figure 8.

3. **Infra-Red analysis**

   Infrared spectra of zirconium phosphoborate samples dried at various temperatures were recorded in KBr pellet medium. The IR spectrum shows the following absorption peaks. The broad bands[65] at 3420 cm^{-1} and 2320 cm^{-1} are due to –OH group of interstitial water (or free water) and P-OH (acidic) stretches, respectively. The sharp band at 1630 cm^{-1} is due to –OH deformation mode. A broad band[66] in the region 900-1200 cm^{-1} might be due to mixing of group vibrations in the range 1250-1150 cm^{-1}, 1090 cm^{-1} and 900 cm^{-1} for P=O (Hydrogen bonded), P-OH and P-O-P groups, respectively. Weak absorption bands[65,67] at 600 cm^{-1}, 520 cm^{-1} and 420 cm^{-1} are probably due to P-O, B-O and Zr-O vibrations. On heating zirconium phosphoborate above 100°C it becomes hard, this is probably due to the loss of interstitial water molecules. It is, therefore, obvious that zirconium phosphoborate contains free water as well as –OH groups. This fact is further supported by the IR spectra. The bands at 3420 cm^{-1} and 1630 cm^{-1} also start diminishing as the drying temperature is increased.

4. pH titrations

pH titrations were performed by the added salt method. The titration curve (Figure-2) shows that zirconium phosphoborate exhibits bifunctional behavior for Na$^+$ and K$^+$ ion- exchange. It gives the information about the type and strength of the acidic group. Zirconium phosphoborate was found to be weakly acidic and cation uptake is higher at higher pH.

5. Thermal analysis

The thermogravimetric analysis results show loss in weight due to water molecules. From the TGA curve, it is shown that heating of exchanger above 100°C suffers a loss of 3% of the weight while upto 200°C, it loses 9% of the dry weight (Table 2 and Figure 7) indicating the presence of hydroxyl groups which are lost on heating due to coalescence.

6. XRD analysis

In the X- ray diffraction experiments, Ni filtered CuK$_\alpha$ radiation was employed. An X-ray diffraction powder patteren is taken for the H$^+$ form of the exchanger and for the granular exchanger. Diffused spectrum (Figure 3 and Figure 4) with 1-2 peaks in the 2θ range of 20°-30° indicate that the exchanger is a poorly crystalline material with some degree of crystallinity. The d-values can be compared with those of zirconium phosphate[68]. By analogy[69,70] zirconium phosphoborate may be considered to be a layer of zirconium atoms with phosphates and borate groups making bridges alternately above and below the plane.

7. Effect of heating on ion exchange capacity

The sample after heating at 100°C lose about 60% of its ion exchange capacity while heating at 200°C increases the capacity to 90% of its original value which may be due to the reason that on heating at 200°C, the exchanger organizes its functional group. Most of the ion exchange capacity was due to interstitial water molecules (Figure 5, ν = 2320 cm^{-1}, OH stretches of interstitial water) and not due to bonded –OH group (Figure 6, weak band at ν = 3420 cm^{-1}) as the loss of interstitial water at 100°C results in 60% loss of its ion exchange capacity. A recovery in ion exchange capacity at 200°C to its 90% of the original value can be related to the loss in weight of exchanger by about 10%.

4.2 Preparation of granular ion exchanger

Different methods were used to convert the powdered exchanger material in the form of granules. All procedures are given below:

(a) **Composite ion exchanger:** A number of mixing ratios of Nylon-66 : ZrPB were tried. But the one with a nylon-66 : ZrPB ratio 3:7 was found to give good mechanical as well as exchange properties. Samples prepared with other combinations of binder : exchanger ratios either gave too brittle powder or were too sticky and resulted in forming sheets rather than granules. Nylon-66 was mixed in the m-cresol to make 30% solution (w/v) at room remperature. The inorganic ion exchanger was mixed with nylon-cresol solution with constant stirring using magnetic stirrer at 140°C upto half an hour. Evaporated the m-cresol on oil bath and dried the sample which resulted in a granular inorganic exchanger. The granular material was analysed by SEM and XRD analysis (Figure 4 and Figure 9). SEM images (Figure 9a and Figure 9b) when compared with those of ZrPB in powder form (Figure 8) very clearly indicates granulation of the material. A comparision of XRD patterns of ZrPB powder form (Figure3) and granular form (Figure 4) indicates no change in the semicrystalline behavior of the material. Hence no loss in characteristics of the material are expected, after its granulation.

(b) **Epoxy as a binder:** Powdered exchanger was mixed with a paste of ‘resin’ and ‘hardener’ of araldite. After their proper mixing the exchanger became hard and tough. Then the hardened material was crushed into pieces and then ground in pastle mortar and sieved. The fine granules of exchanger were obtained.

(c) Sol-gel metod: Equimolar solutions of boric acid and phosphoric acid were mixed and zirconyl oxychloride solution was slowly added in 1:1:2 ratio (v/v). After complete addition, digestion for one hour at a slightly raised temperature ($70^{\circ}C$) was carried out. The gel so obtained was washed by decantation and made free of chloride and phosphate ions. The thick gel was then filtered under water suction to make the gel more thick and viscous. This gel was then poured through a column of 50 cm length and 2 cm diameter filled with solvent paraffin. The exchanger gel was collected in a petridish in the form of very fine droplets. Petridish containing the gel was then heated ($150^{\circ}C$) under vaccum to remove the solvent paraffin. Fine granules of the exchanger were obtained in the petridish (Figure 10). Although the exchanger material could be prepared in the form of granules but the sample was too small to carry out further analysis.

(d) Synthesis of exchanger using acetone as a solvent: The gel obtained in procedure (c) was poured dropwise into a petridish containing acetone. The idea was to remove water from the hydrated gel with the water removing property of acetone. After some time acetone evaporated and we could get very fine granules of the material. The morphology of the granules was studied by using microscopic techniques, which showed fine granules of regular shape.

(e) Synthesis of exchanger using acetonitrile as a solvent: The thick white gel was tried to convert it into granular form by replacing acetone with acetonitrile as detailed above. The granules of exchangers were obtained after evaporating the solvent. The morphology of the granules was studied by using microscopic techniques.

Table2: Ion exchange capacity of zirconium phosphoborate

Sr.No.	Metal ion	Salt solution used (1M)	Ion exchange capacity (meq/g)
1	Na^+	Sodium chloride (1 M)	0.58
2	K^+	Potassium chloride (1 M)	1.17
3	Ca^{2+}	Calcium chloride (0.5 M)	0.52
4	Mg^{2+}	Magnesium chloride (0.5 M)	0.32

Table3: Effect of heating on ion exchange capacity of zirconium phosphoborate for sodium ions

Sr.No.	Temperature (°C)	Ion exchange capacity (meq/g)	Loss in wt. (%)
1	RT	0.58	0.0
2	100	0.25	3.0
3	200	0.50	9.0
4	500	0.17	14.0

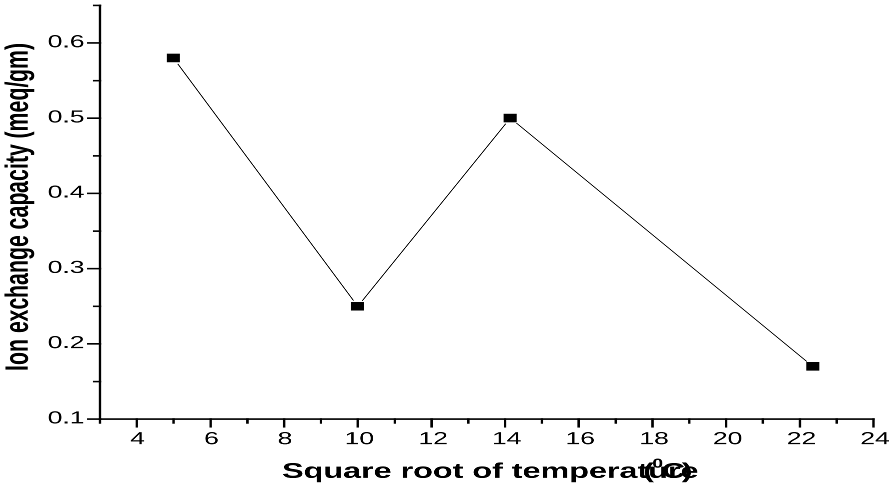

Figure 1: Ion exchange capacity as a function of square root of temperature

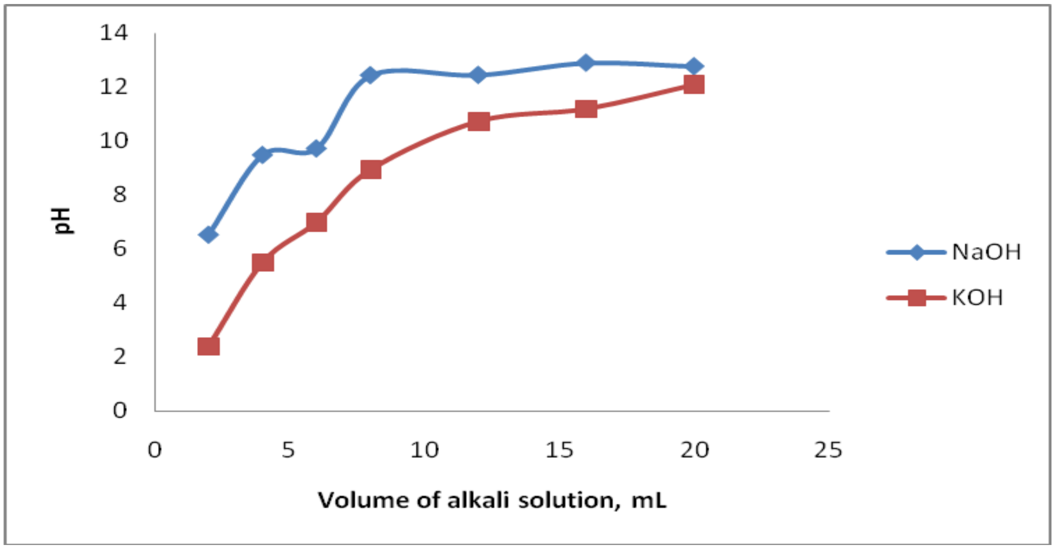

Figure 2: pH titration of alkali solution by added salt method

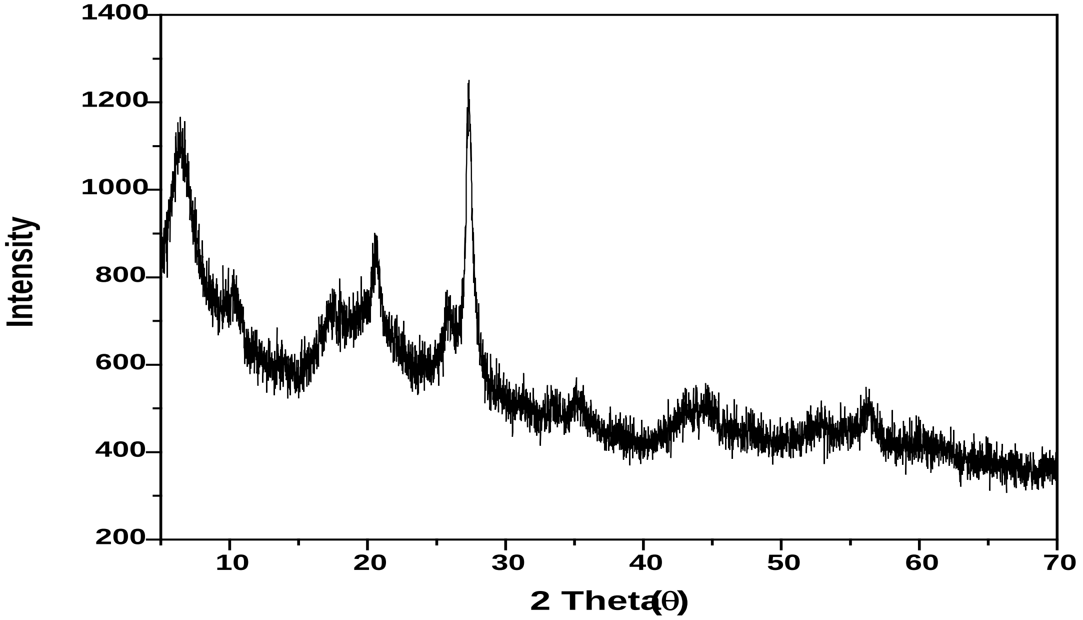

Figure 3: XRD patterens of zirconium phosphoborate in H^+ form (powder)

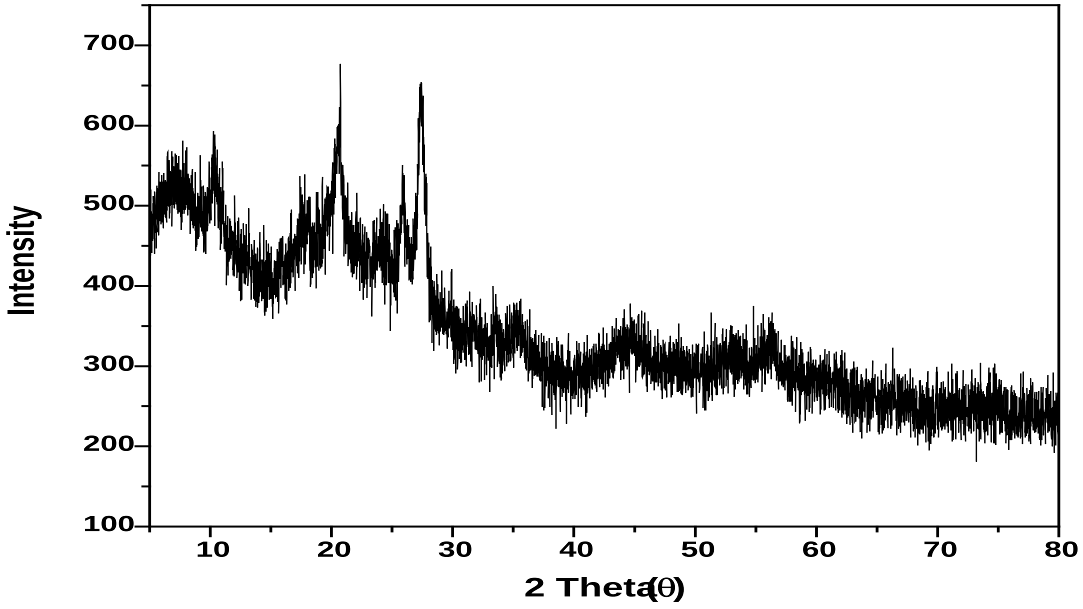

Figure 4: XRD pattern of zirconium phosphoborate (granular)

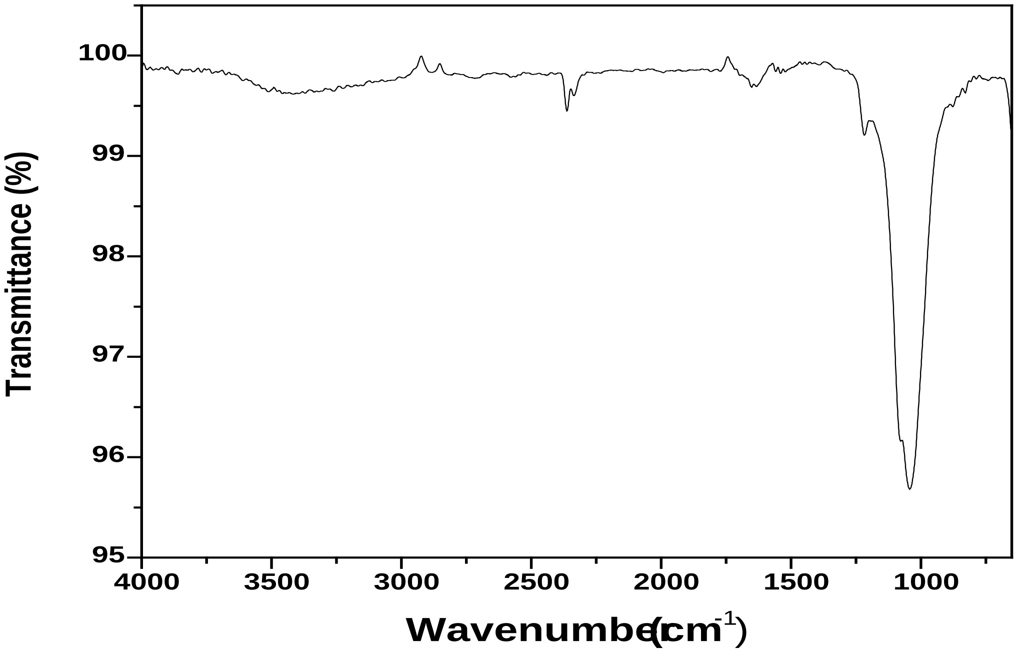

Fig 5: FTIR of zirconium phosphoborate (without H^+ form)

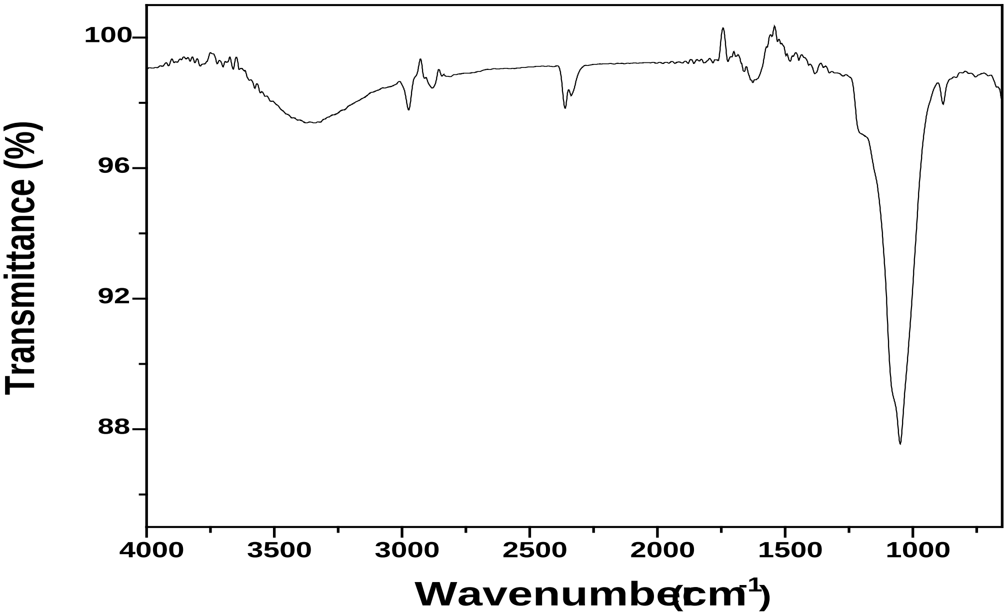

Fig 6: FTIR of zirconium phosphoborate in H^+ form

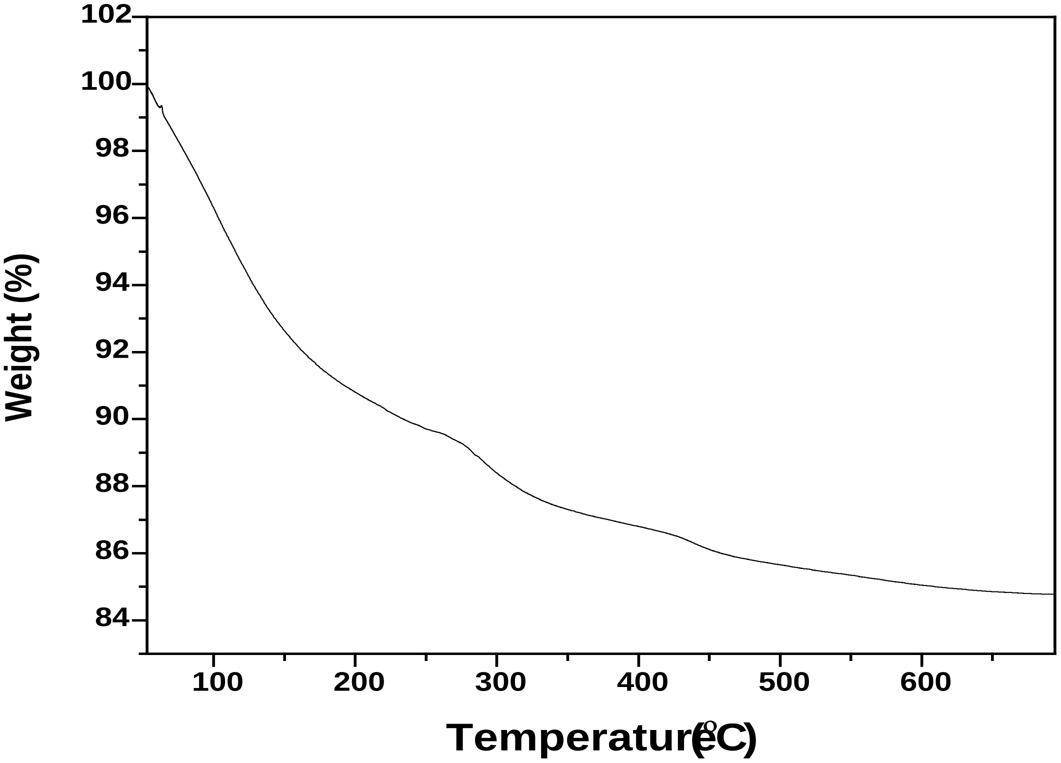

Figure 7: TGA of zirconium phosphoborate in H^+ form

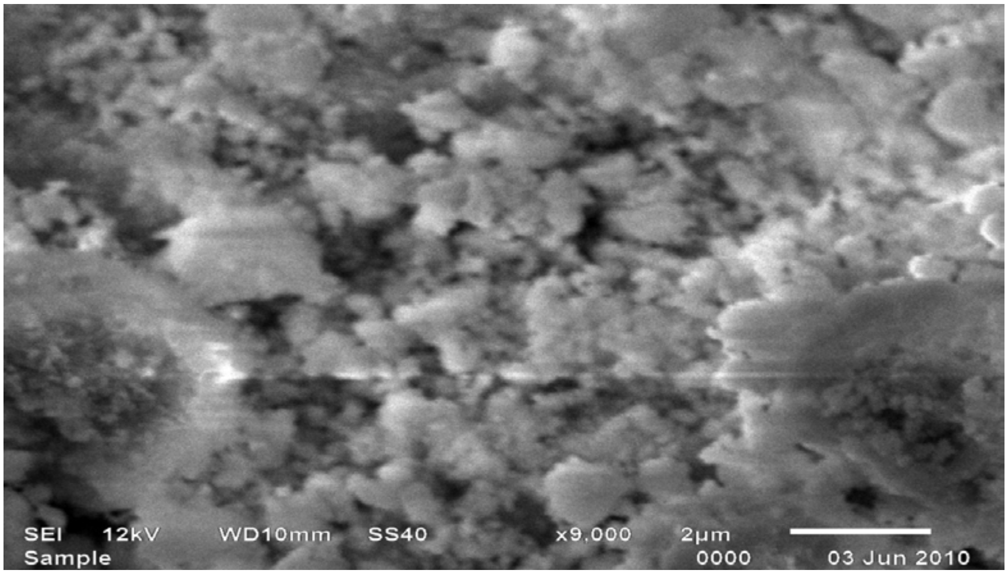

Figure 8: SEM images of zirconium phosphoborate exchanger (H^+ form)

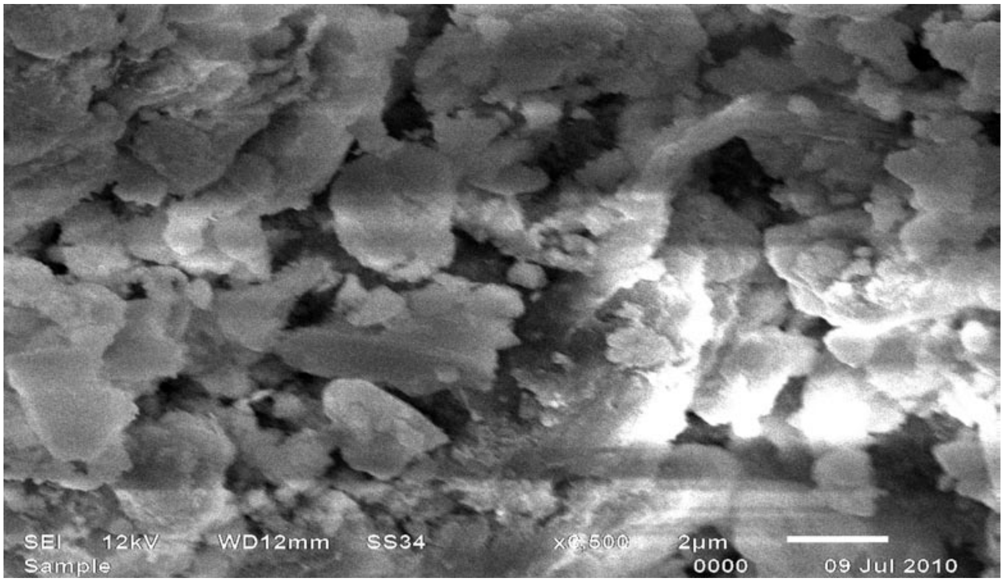

Figure 9 (a): SEM images of zirconium phosphoborate exchanger (granular) with nylon-66 as a binder at 6500 x magnification

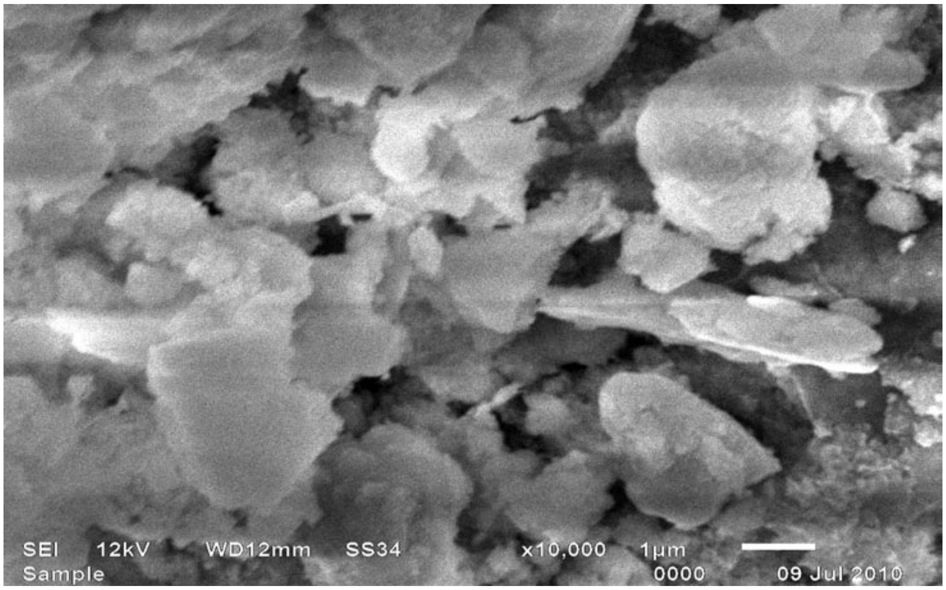

Figure 9 (b): SEM image of ZrPB exchanger (granular) with nylon-66 as a binder at magnification 10,000 x

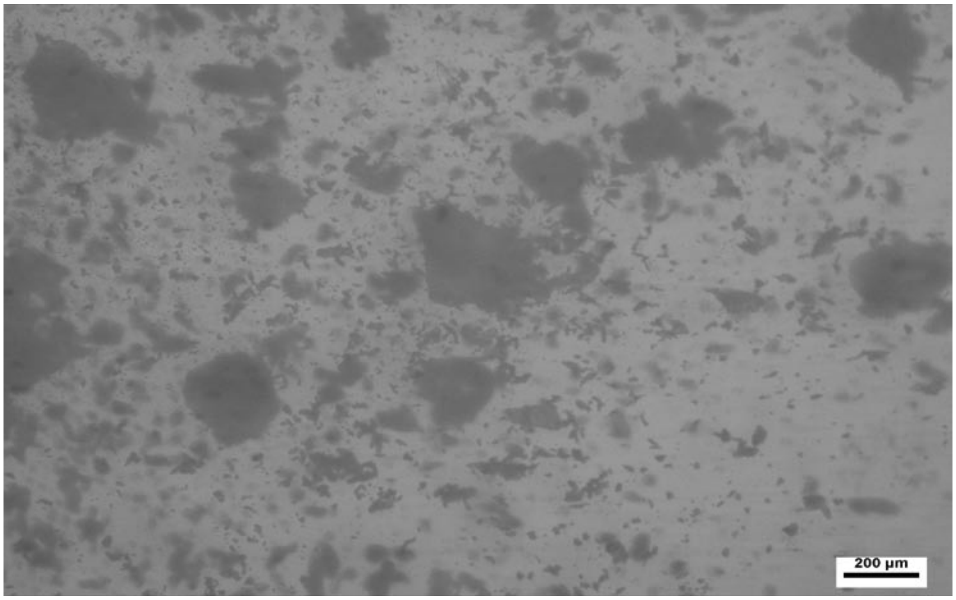

Figure 10: Microscopic image of the zirconium phosphoborate (granular) at 50x

Chapter-5

Conclusion and future scope

Following conclusions can be drawn from the work accomplished in the dissertation:

1. Synthetic inorganic ion exchanger zirconium phosphoborate has been synthesized as per reported procedure. The material is characterized for its ion exchange characteristics and found to possess the reported properties.
2. Five different methods were tried to prepare the exchanger in the granular form. The method using Nylon 66 as a binder and m-cresol as a homogeniser was successfully used to prepare granules of the material.
3. The exchanger material was characterized for its granular shape by SEM studies.
4. XRD studies confirmed that the material did not change its crystallinity during the process of granulation.
5. The exchanger was also converted into granules by sol-gel method as well, as indicated by microscopic image of the product.
6. For future scope, the material should be prepared in bulk quantities and tested for its flow characteristics in column operations.
7. The exchanger should be used for the separation of Er^{3+} from other lanthanides through column operation.

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