CHAPTER II

LITERATURE
The earliest systematic studies in which ion exchange properties were described are concerned with base exchange in minerals present in the soil. Many hypotheses have been proposed to explain the phenomenon of base exchange in soil. Since then various inorganic ion exchangers have been developed side by side with the organic exchangers. But most of the fundamental studies including the kinetics, selectivity and the different models have been proposed for organic exchangers only. Amongst the inorganic exchangers Zirconium phosphate is going to occupy a key position because of its superiority with respect to resistance towards acids, temperature and radiation.

Zirconium phosphate may be prepared either by precipitation with phosphoric acid, or, solutions of soluble phosphates, from acid solutions of suitable Zirconium salts (e.g. Zirconyl chloride or nitrate) or, by treatment of Zirconium oxide with phosphoric acid. In the later cases the uptake of phosphate is irreversible and is considerably in excess of anion exchange capacity of the oxide. The former method of preparation is the one usually employed.

The physical form of Zirconium phosphate prepared by precipitation varies according to the method employed, but two principal types may be distinguished. A finely divided microcrystalline form in which the ratio of phosphate to Zirconium is approximately 2 : 1 [corresponding to Zirconyl dihydrogen

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phosphate $\text{ZrO}_2 (\text{H}_2\text{PO}_4)_2$ is produced by slowly adding the reactants (zirconyl nitrate solution and phosphoric acid to a well stirred, heated, dilute sulphuric acid solution\textsuperscript{4}. In the slow precipitation where neither reagent is greatly in excess of the other and where solubility of product is high relative to room temperature condition leads to the growth of fine crystals which are too small themselves to be used in ion exchange column, but which may be pelleted under pressure without a binder and then granulated\textsuperscript{7}.

If, however, the reagents are mixed rapidly at room temperature, rapid precipitation ensures that a gelatinous precipitate is formed which settles extremely slowly until it has been thoroughly washed by decantation to remove the stabilising counter ions which prevent coagulation of the precipitates\textsuperscript{8}. It is known that hard, glassy product tend to be formed from dilute zirconium solutions and that concentrated solution produce a softer, chalklike material. Similarly, although nitrate solution in general favour the formation of opaque, granular material, sulphate solutions keep glassy product in which the rate of uptake of cations particularly polyvalent ions is much lower. In general, the granular products formed by rapid precipitation have a phosphate : zirconium ratio less than 2 : 1\textsuperscript{6} and are of rather indefinite composition. The ratio in the solid increases towards a limiting figure of 1.7 as the corresponding ratio in the reacting solution is increased, and at low values of latter (0.5 to 1.0) it is possible to precipitate solid which still contain in addition to phosphate the anion present in the zirconium
solution. The original anion may be reversibly displaced by other anions, the product thus exhibiting both cation and anion exchange properties.

Vesely and Pekarek have shown that under conditions where phosphate considerably in excess the composition of the product may depend upon the conditions of the preparations. Samples prepared by them by precipitation from 6N HCl solutions were found to contain upto 2.9% of chlorides, which could be removed by repeated washings with water, presumably by replacement with hydroxyl group; conversely, samples of high phosphate content (PO₄ : Zr = 1.8 - 2.0) prepared in absence of HCl were found after digestion with 4N HCl to have a lower phosphate content and to contain appreciable quantities of chloride. The findings of Vesely and Pekarek do not however, completely explain the differences in composition observed by other authors, since in many cases ratios of 1.7 - 1.8 are obtained for products in which no anions other than phosphate can be detected.

Zirconium phosphate may also be prepared in the form of spherical beads by adopting the techniques used to produce various spherical cracking catalyst such as Thorium phosphate and sodium aluminosilicate. In one of the methods Zirconyl nitrate solution and phosphoric acid are mixed rapidly and sprayed into a coloumn of mineral oil; precipitation takes place within the spherical droplets as they fall through the oil phase, and by careful choice of conditions precipitation is complete and the droplet gelled by this time it passes to an aqueous layer at the foot of the coloumn.
After washing and drying in air at 300°C beads of 2 mm diameter are obtained. In another method the rate of precipitation was controlled by complexing Zirconium with citrate ion before mixing with phosphoric acid and spraying into an oil column. By selecting suitable proportions of citrate and Zirconium the onset of precipitation may be delayed for any chosen period. Ion exchangers containing phosphate groups can be produced by using R₃PO₄ to treat the Zirconia gel or, polyphosphates. Galkin et al. studied the effect of aging conditions of Zirconium hydroxide cogel, obtained by a sol-gel method, on its reactivity with H₃PO₄. In general, the aging decreases the reactivity. Drying at 90 or 150°C results in conversion of the hydroxy to oxybridges and reduces strongly the reactivity. Zr(HPO₄)₂ and Zr(HPO₄)₂·H₂O are produced by refluxing Zirconium phosphate with orthophosphoric acid in an aqueous 2 M solution. Mackawa and Sugiura et al. manufactured the crystalline Zirconium phosphate. Aqueous solution of phosphoric acid containing NH₄ and/or, alkali metal ions and aqueous solutions of Zirconium compounds containing SO₄²⁻ are mixed to form a precipitate that is hydrothermally treated to give high purity crystal. Zirconium phosphate compound AZr₂(PO₄)₃nH₂O (A=NH₄ and/or alkalimetals). The products are used as inorganic ion exchangers. Preparation of α-Zirconium phosphate with controlled degree of hydrolysis via delamination procedure was studied by Alberti and Marmottini. The hydrolysis of α-Zr(HPO₄)₂·H₂O has an appreciable influence on its ion exchange, intercalation proton
conduction and catalytic properties. It is further more of importance for the preparation of pillard porous material. Direct hydrolytic attack in alkaline media can be carried out only for the surface phosphate groups of the layered crystals. To overcome this difficulty the crystals delaminated by a intercalation of methyl amine, the colloidal dispersion was left 24 hours to hydrolyse at fixed pH value and finally after regeneration in H-form by acidification the hydrolysed material was separated from solution. The selectivity of inorganic ion exchange materials such as Aluminium silicate, Zirconium phosphate, hydroxy apatite, heteropolyacids, hydrotalcite etc. has been interpreted by crystallographic structure determined by XRD, IR, DTA, NMR.

Preparation of silver ion modified phosphate intercalation compound was carried out by Takehisa and Hayama. In preparation of silver ion modified phosphate intercalation compounds by modifying lameller phosphate cation exchanger with Ag ions via ion exchange, H⁺ ion produced as by product during ion exchange are slowly and simultaneously neutralised by Bronsted base (As proton acceptor) to facilitate the reaction. The compounds are useful for antibiotic agents, adsorbents, catalysts, solid electrolytes and functional material for sensors. Lameller phosphates AlH₂P₂O₁₀, Zr(HPO₄)₂ and Ti(HPO₄)₃ were treated with AgNO₃ aqueous solution to form the compounds respectively.

Mixed Ti-Zr, Sn-Zr and Sn-Ti phosphates containing different atoms of 4th group elements were synthesized by Bortun and Budovitskaya et al and their ionexchange properties towards
Co\(^{2+}\), Ni\(^{2+}\) and Cr\(^{3+}\) ions were studied. The values of the equilibrium constant of the ion exchange reactions of the d-metal sorptions from acetate and chloride solutions were calculated. The sorbents affinity to transition metal ions greatly depended on their chemical composition, enriching of tin containing samples with Zirconium and specially with Ti increases the affinity of Co\(^{2+}\) ions. The observed changes in the selectivity of the inorganic ion exchangers are connected with the possibility of creating in their structure adsorption centres with different geometrical parameters depending on the dimensions of the 4th group elements.

Krylov, V. N. and Larina, K. P.\(^{20}\) studied the influence of synthesis conditions on the properties of Zirconium phosphates modified with glycolic or, diglycolic acids. Introduction of glycolic or, diglycolic acid during preparation increases the phosphorus content in the sorbent which increases the overall ion exchange capacity. The use of diglycolic acid as a modifier gives a sorbent with Am (iii) or, Eu (III) distribution coefficient increased by 1 or, 2 orders of magnitude respectively. Tsunako, Mitsutomo and Takehisa Eiji\(^{21}\) manufactured layered crystalline Zr-phosphate in high pressure steam. ZrO\(_2\) or, Zr(OH)\(_2\) and phosphoric acid are heated under 5-30 atmosphere steam to give Zirconium phosphates. The compound is useful as ion exchangers, filters, catalysts etc. Thus a mixture of ZrO\(_2\) and 85% phosphoric acid was heated at 200\(^{\circ}\)C for 5 hours under 10-11 atmosphere steam to give Zr(HPO\(_4\))\(_2\).H\(_2\)O.
Granular Zirconium phosphate as obtained by rapid precipitation method exhibited amorphous nature and as such opinion on the structure of this material is based largely on analogy with data on the structures of complex Zirconium ions present in aqueous solution. X-ray studies on hydrous granular Zirconia show that as the drying temperature is increased the structure begins to show signs of crystallinity at $300^\circ\text{C}$ and the pattern is identical with the reported monoclinic Zirconia when it is heat treated at $1000^\circ\text{C}$. Similarly the amorphous structure of Zirconium phosphate persists until at least $500^\circ\text{C}$ but that at $1000^\circ\text{C}$ the pattern is characteristic of Zirconium pyrophosphate, $\text{ZrP}_2\text{O}_7$. These changes are accompanied by irreversible loss of water from the material. In the phosphate the constitutional water is lost above $300^\circ\text{C}$ presumably due to the condensation of acid phosphate groups to pyrophosphate.

Although the details relating to loss of water on heating vary for different samples from one author to another the salient features are that neither oxide nor phosphate gives evidence of the existence of discrete hydrates.

Evidence in favour of the condensation of the acid phosphate groups to pyrophosphate on heating is furnished by the infrared spectra of different samples of Zirconium phosphate. Spectra of materials with ratio $\text{PO}_4 : \text{Zr}$ equal to 1.7 and 1.95 after heating to $1000^\circ\text{C}$ for 24 hours are similar to that of cubic Zirconium pyrophosphate while material with $\text{PO}_4 : \text{Zr} = 1 : 1$ gives a pattern resembling that from a product formed on heating $\text{ZrO}_2$. 

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and ZrP$_2$O$_7$ to 1200°C which may be ascribable to Zirconyl pyrophosphate (ZrO)$_2$P$_2$O$_7$. Condensation of the acid phosphate groups was followed at different temperatures for Zirconium phosphate with P$_4$O$_{10}$ : Zr = 1.95 by examining the characteristic P-O-P frequency range of 958-983 cm$^{-1}$. The spectra showed that condensation is not only complete at 850°C but that it commences at a temperature which is at least as low as 260°C. Comparison of the spectra with those of mixtures of phosphates and pyrophosphates suggests that about 20% of the phosphate groups are condensed at 260°C and about 60% at 450°C. Thus it can be concluded that at least part of the weight loss is due to constitutional water formed on condensation of acid phosphate groups. When Zirconium phosphate is converted to the sodium or potassium form and heated to 1000°C the characteristic P-O-P frequency is strongly suppressed indicating that the substitution of Na$^+$ or K$^+$ for H$^+$ on the acid phosphate groups hinders condensation of the latter.

The analysis of IR and Raman spectra of the ion exchanger α-Zr (HPO$_4$)$_2$.H$_2$O and its half and fully exchanged phases ZrKH(PO$_4$)$_2$ and Zr(NH$_4$PO$_4$)$_2$.H$_2$O are reported by Mathew and Nayar. The splitting of the degenerate and non degenerate modes indicates the presence of two crystallog, distinct anions in these compounds. HPO$_4^{2-}$ has stronger P-O bond in ZrKH(PO$_4$)$_2$. One of the three crystallog distinct H$_2$O molecules in α-Zr(HPO$_4$)$_2$.H$_2$O can be considered as a free H$_2$O molecule. The H$_2$O molecules have significantly different hydrogen bond strengths. In
Zr(NH$_4$PO$_4$)$_2$.H$_2$O bonds indicate the presence of two distinct NH$_4^+$ and H$_2$O molecules. PO$_4^{3-}$ in ZrK$\left(PO_4\right)_2$ is linearly distorted.

In fairly dilute solutions pH titration and ultracentrifuge studies have shown\textsuperscript{26} that Zirconium exists as hydrolysed species such as ZrOOH$^+$ while in the more concentrated solutions in HCl trimeric and tetrameric ions such as $\left[(ZrO)\_4(OH)\_3\right]^{3+}$ and $\left[(ZrO)\_4(OH)\_4\right]^{4+}$ have been observed. Other evidences based on coagulation of negative AgBr and AgI sols also supports the existence of highly charged, hydrolysed polymers containing upto three Zirconium atoms in each ion\textsuperscript{27}.

Direct evidence is provided by X-ray scattering studies on aqueous solutions of Zirconium and Hafnium oxyhalides\textsuperscript{28}. The structure postulated are similar to those found in crystalline oxyhalides\textsuperscript{29}. The existence of trimeric species in solution is also in accord with X-ray studies on basic salts of tetravalent metals such as Ti, Zr and Th\textsuperscript{30} prepared by hydrothermal synthesis at 50 - 250°C. This indicates the presence of polymers such as $\left[Zr_4(OH)_6 CrO_4\right]^{8+}$.

Chemical evidence from which deductions may be drawn regarding structure and composition, the dehydration isobars and thermogravimetric experiments reveal the absence of definite hydrates in the hydrous oxides, and we may assume\textsuperscript{31} that when the oxides are precipitated the ion ZrOOH$^+$ is incorporated as a repeating unit in the structure.

Chemical evidence in the case of Zirconium phosphate is conflicting and the structure and composition probably vary
according to the mode of preparation. Paterson\textsuperscript{91} has described a material in which the ratio of phosphate to Zirconium is 2 : 1, corresponding to diphosphato Zirconic acid\textsuperscript{92}.

\[
\begin{array}{c}
\text{HO} & \text{P} & \text{OH} \\
\text{HO} & \text{Zr} & \text{OH}
\end{array}
\]

This gives a smooth monofunctional titration curve, unlike the granular gels, and on continued washings only phosphate ion is found in solution, indicating a slow hydrolysis of the material.

The materials prepared by Bactslc and Pelscmaekers\textsuperscript{33}, although originally tending to a limiting ratio of phosphate to Zirconium of 2 : 1 in the freshly prepared precipitates when phosphate was in appreciable excess, tended on continuous washing to approach a limiting composition in which P\textsubscript{04} : Zr = 1.67. This suggests that the latter material may contain a trimeric unit based upon the structure [\((\text{Zro})_3(\text{OH})_3\)]\textsuperscript{3+} in which phosphate groups have replaced hydroxyl group. From the work of Nancollas and Paterson on thermogravimetric analysis\textsuperscript{34} it has been suggested that three water molecules are associated with each trimer.

From one of the studies it has been indicated\textsuperscript{35} how widely the properties may change when the condition of preparation are varied and they also give some indication of a possible structure for one form of crystalline Zirconium phosphate. Thermogravimetric analysis showed that the solid obtained from the interactions of Zirconyl chloride and phosphoric acid which
possessed the composition \( \text{ZrO}_2 \cdot \text{P}_2\text{O}_5 \cdot 2\text{H}_2\text{O} \), lost one moleule of water at 100 to 133°C and a second at 240 to 350°C. The original product was either amorphous or, poorly crystalline. On heating to 700°C poorly crystalline Zirconium pyrophosphate phase was identified by X-ray analysis. On annealing at 900°C the crystalinity of this phase was greatly improved. On refluxing the gel with phosphoric acid a well crystallised Zirconium phosphate was obtained, its composition being \( \text{ZrO}_2 \cdot \text{P}_2\text{O}_5 \cdot 2\text{H}_2\text{O} \). The crystalline Zirconium phosphate lost negligible amounts of phosphate on being washed with water.

The structures which have been tentatively proposed for the phosphate contain linear polymeric chains, whereas the physical stability, resistance to swelling and ionic sieve effects which are observed suggest that the structure is a robust three dimensional net work similar to that of cage like Zeolites. It may be that the unit is best represented by a cyclic polymer such as that of clearfield and Vaughan, rather than a linear one with oxygen or, hydroxyl bridges between pairs of Zirconium atoms.

Chemical and Infrared spectral evidence suggest that ion exchange in Zirconium phosphate involves replaceable Hydrogen atoms in acid phosphate grouping which play a role analogous to that of the sulphonic acid groups of strongly acid cation exchange resins. Zirconium phosphate behaves as an efficient cation exchanger in acid solution.
The compact structure of Zirconium phosphates, and the relatively small degree of swelling on conversion from the hydrogen form to other cationic forms suggest that it may exhibit ion-sieve properties similar to that of zeolites and this has been confirmed by a study of the uptake of substituted ammonium ions on the material. The heats of cation exchange reactions of alkali metals and amorphous Zirconium phosphate were measured calorimetrically at 298K. The dependence of thermodynamic functions on the ionic content of the sorbent were estimated. The selectivity of PZr is determined both by the enthalpic and entropic factor.

The ion uptake behaviour of the BuNH₂ intercalate of α-Zr (HPO₄).H₂O towards alkaline earth cations were examined by Peng and Clearfield. The rates of uptake are in the order of Sr²⁺ > Ca²⁺ > Ba²⁺ > Mg²⁺. Because of high pH afforded by the amine intercalat, the exchanged phase is always the fully exchanged one, Zr M(PO₄)₂.nH₂O. The values of n are 4 for Mg²⁺ and Ca²⁺, 3 for Sr²⁺ and 2 for Ba²⁺. Uptake of ion is about 6 equiv per gm. Sharply reduced loadings occur in the presence of excess of free amines. A solution containing equal amounts of Ca²⁺ and Mg²⁺ yielded a new solid solution phase with a 12.6Å spacing.

The uptake of cyclohexylamine by Zr(HPO₄)₂.H₂O was studied by pH titration cyclohexylamine was loaded ≤ 75% of the ion exchange capacity of α-Zr(HPO₄)₂.H₂O. Chemical analysis, thermal analysis, IR spectroscopy and XRD were used to characterize the product obtained at the final step of pH titration which was referred to as the cyclohexyl ammonium form.
The chemical composition can be represented as

\[ \text{Zr}(\text{C}_6\text{H}_{14}\text{NH}_3)_{1.5} \left(\text{H}\right)_{0.5} (\text{PO}_4)_{2}\cdot\text{H}_2\text{O} \]

The interlayer distances of the exchanger expanded to 18.4\(\text{Å}\) upon uptake of cyclohexylamine. The cyclohexylammonium ion was exchanged easily with \(\text{Ni}^{2+}\) ion in a solution.

The changes in water adsorption, MeOH adsorption and ion exchange capacity of Zirconium phosphate were studied by Karaseva et al. They are attributed to a reduction in the number of free hydroxyl group and to an increase in the number of P-O-P linkages.

The effect of solute ions on the thermal expansion of \(\text{ZrP}_2\text{O}_7\) solid solutions were studied by Ota and Yamai. The abrupt thermal expansion at the high-low inversion can be interpreted as due to the rotation of the polyhedra from the low temperature form in the partially collapsed state to the high temperature form in the fully expanded state. The replacement of Zr ions by larger ions and the stuffing of cations into the cavities of the framework stabilised the expanded structure and then depressed the abruptness of the expansion. Consequently the thermal expansion was reduced.

A possible method for determining the formation constant of both uranium and Antimony chlorocomplexes by cation exchange on Zirconium phosphate has been described by Aly and others. The distribution behaviour of U(VI) and Sb(V) between Zirconium phosphate and HCl was studied from acid solutions of different concentrations, 0.01 to 4.0 M. In both cases the molar ratio of the
omplexing agent to one mole of the metal ion was found to be about one in the acid range studied. The overall formation constants were calculated giving a mean $\beta = 39 \pm 4$ for Uranium and $\beta = 2.2 \pm 0.6$ for Antimony chlorocomplexes. The validity of the deduction presented was checked and the calculated $\beta$ values could be safely considered as apparent empirical constants rather than being the true thermodynamic formation constants.

Some Japanese scientists used Zirconium phosphate to prepare moisture sensors. Moisture sensors are composed of mainly of compounds prepared by heat treating crystalline or, amorphous $\text{Zr} (\text{M}'\text{PO}_4)_{2} \cdot \text{XH}_2\text{O} \ (\text{M}' = \text{Li, Na, K, Rb, Ce}; \ 0 \leq \text{X} < 20)$

The sensors are quick response and low impedance value at low humidity. Thus aqueous $\text{ZrOCl}_2$ was treated with excess HF, then with excess $\text{H}_3\text{PO}_4$ to give crystalline $\text{Zr(HPO}_4)_{2} \cdot \text{XH}_2\text{O}$ which was dispersed in water, mixed with LiOH to pH 11, filtered off, dried and heated three hours at 600°C.

Physical and chemical characterisation of a porous phosphate modified Zirconia substrate was studied by Schafer Wes A, Carr Peter W Parson K. A. A phosphate modification of a porous Zirconium oxide high performance liquid chromatog support was developed modification of the surface with inorganic phosphate alleviates the irreversible adsorption of proteins on the native oxide surface and make the surface more bio compatible.

The ion exchange properties of Zirconium phosphate phosphite a layered compound with asymmetric layers towards the alkaline earth cations were investigated and compared with those.
of α-Zirconium hydrogen phosphate. These cations were easily taken up in the phosphate regions of α-Zr(HPO₄)₉O₇(HPO₄)₈H₂O whereas only Ca²⁺ and Sr²⁺ are directly exchanged from α-Zr(HPO₄)₂·H₂O. The ion exchange mechanism involves a single phase transition and the solvation of the exchanged cations in the already formed phases. The interlayer distances and the water content of the exchanged forms of Zirconium phosphate phosphite and those of the corresponding phases of Zirconium phosphate were compared and discussed on the basis of structural features of the two hosts. Zirconium phosphate phosphite has a relatively low ion exchange capacity (2.5 meq/gm) compared to that of Zirconium phosphate (6.64 meq/gm) but is a more facile exchanger for large and hydrated cations.

X-ray photoelectron spectroscopy (XPS) were performed on α-Zirconium phosphate and on an organic derivative of Zirconium phosphate, Zirconium phosphate sulphophenyl phosphonate (ZrPS). The XPS result showed that the change of half of the phosphate groups in ZrP to sulphonyl phosphonate group in ZrPS changes the binding energy levels for some electrons in the solid. The XPS analysis also showed that upon intercalation of Lutheinum (2-2 bipyridine)₃⁺ into ZrPS, the binding energies of RU and N-atoms of the metal complex are unperturbed relative to the free complex. ZrP sample showed increased catalytic activity for dehydration of cyclohexanol with increased acidity of the sample.
An automatic titrator for easy measurements of slow reactions during ion exchange was prepared and tested using Zirconium phosphate. The instrument consists of an ion meter, autopiston burette, digital multimeter and a personal computer. The titration amount, the titration rate, measurement time and end point conditions were controllable. The results of each titration volume, pH and titration curves were recorded using the automatic titrator. The results for titration of Zirconium phosphate matched the theoretical values by using only little sample.

The sorption-selectivity properties of hydrated TiO₂, Ti-phosphate, Zr-phosphate or, MnO₂ for Li⁺ were compared. An ion exchange precipitation mechanism was proposed to explain the high sorption coefficient of Zr-phosphate. Trends in Li⁺ desorption were also studied. Exchangers based on Zr-phosphate were recommended for simplicity of regeneration and stability of sorption selectivity properties during cyclic operations in the purification of Li containing solutions or, waste waters.

The effects of the degree of sorbent transformation in the salt form and the concentration of Cd and base electrolyte of the efficiency of Cd adsorption by Ti and Zr-phosphate of low phosphorus content were determined. The thermodynamic exchange constants and free energies of the ion exchange reactions were calculated. Na exchanged Zr-phosphate are the most promising sorbents for the selective removal of Cd from aqueous solutions of complex compositions.
Alberti, G.; Costantino, V.; Marmottini, F. prepared colloidal dispersions of delaminated Zr-phosphate obtained as a result of intercalation of some amines which were sonicated and then put under a spray drying or freeze drying treatment. Highly dispersed and hydrated powders of Zr-phosphate were obtained. The water content of this new phases ranges from 1.2 to 3.5 mole/mole of Zr, as the relative humidity rises from 5 to 90%. Correspondingly, the interlayer distances changes from 8.0 to 10.5 Å. The ion exchange properties of the polyhydrated Zr-phosphate towards Na⁺, K⁺, Cs⁺, Ba²⁺ were determined and compared with those of α-Zr(HPO₄)₂·H₂O. Owing to the large interlayer distance these polyhydrated phases exhibits good ion exchange and intercalation properties specially towards large cationic or neutral species.

Benhamza H., Barboux P. et al. synthesized α-Zr(HPO₄)₂·H₂O from aqueous solution. Amorphous precipitates are obtained which crystallise slowly upon aging at 90°C in their mother liquor. Crystallisation could be much faster if alkoxide precursors are used. The sol-gel synthesis of α-Zr (HPO₄)₂·H₂O from both inorganic and metallo organic precursor was followed by solid state studies through NMR and X-ray diffraction condensation mechanism leading to the formation of a solid phase is important. Compared to ZrOCl₂ in aqueous solution, Zr(OP₃)₄ allows shorter reaction times and lower crystallisation temperature. This results in a material with smaller grains which should exhibit enhanced exchange properties.
The mineral concentrator of Zr and W (2.8 - 3.2 wt%) in W-Zr ore deposits of the Alder shield (USSR) is colloformic and crystalline baddeleyite (Bd). The presence of H$_2$O in Bd is probably due to incomplete dehydration of Zr (OH)$_4$ and the formation of ZrO$_2$ during the kinetic stages of low temperature hydrothermal process. The isobaric isothermal potential ($\Delta U$) of Zr(OH)$_4$ $\rightarrow$ cryst ZrO$_2$ + 2H$_2$O was calculated as -29.20 and -39.75 KJ/mol respectively at 25 and 200°C. The kinetics of dehydration of Zr (OH)$_4$ was studied at 100 - 400°C and PH$_2$O = 1 Kbar; the dehydration rate was related to the temperature, duration of experiment. With the dehydration two metastable phases are formed. The most rapid dehydration occurred at 200 - 400°C and PH$_2$O = 1 Kbar in H$_2$O.

Krylov and Larina showed that glycolic acid treatment does not improve the Eu(III) or Am(III) sorption properties of Zr-phosphate. Addition of diglycolic acid to the synthesis mixture for Zr-phosphate gives sorbents with enhanced dynamic sorption capacities since the sorption rates are increased.

Paper chromatography of metal ions has been performed on Zr(IV) phosphate strips in dioxane + 0.1 M HCl, butanol + 50% HNO$_3$ and several weak acid systems as tartaric acid, succinic acid, citric acid etc. As a result of these studies several important separations of metal ions have been achieved. A quantitative seperation of Bi(III) (1-10 µg) from several binary mixture has also been developed.
The catalytic activity of metallic Ag supported on Zr-phosphate was examined in the reaction of ethylene oxidation in terms of the average Ag-particle size, the surface area of the support. The activity decreased when the surface area of the support was increased. A maximum activity and selectivity was obtained with Ag particles about 480Å in average diameter supported on highly crystalline Zr-phosphate cations present in the ion exchange sites of the support have a strong effect on catalytic properties. Amongst the cations used Na⁺ gives the highest total conversion. K⁺ gives the best selectivity for ethylene oxide formation.

An aqueous mixture of a Zr-salt, H₂C₂O₄ and H₃PO₄ in which Zr, C₂O₄²⁻ and PO₄³⁻ were in proportion within a close range was reacted at pH ≤ 10 to precipitated crystalline Zr(HPO₄)₂·nH₂O (I) (n ≤ 8). Thus ZrOCl₂·8H₂O 11.6 in deionised water (total 74) was mixed with H₂C₂O₄·2H₂O 24.0 in hot water 235 g then with a mixture of commercial H₃PO₄ 13.2 and water 106.8 g sealed in a heat resistant plastic vessel with a small hole, heated at 96°C for 20 hours and decanted; the precipitate was filtered, washed until C₂O₄²⁻ was not detected and dried at 80°C.

During systematic research into the intercalation of alkylamines in layered α-[Zr(HPO₄)₂]H₂O some favourable cases were found in which the intercalate, in the presence of water, exfoleates giving rise to a colloidal dispersion of plate like particles of Zr-phosphate partially or totally neutralised by alkyl ammonium ions. This exfoliation occurs dramatically during...
the intercalation of propylamine. From this dispersion, very similar to that obtained with smectite clays, a suspension of very thin lamellae of highly hydrated $\alpha$ [Zr(HPO$_4$)$_2$]H$_2$O is formed after a deintercalation process. The thin lamellae can be easily recomposed in the form of films membranes by filtering the suspension on a porous plastic filter or, by spraying the suspension on a suitable support and leaving it to dry. This type of Zr-phosphate showed promise for application in the field of ion exchange, heterogeneous catalysis, chromatographic support and protonic conductors.

Synthesis of $\alpha$-Zr (HPO$_4$)$_2$ ion exchangers in the presence of Ru(bipy)$_{2+}$ (bipy = 2,2'-bipyridine) and HF at 335 K gives intercalates with excellent crystallinity. X-ray diffraction data consists of well resolved, narrow line. The Ru(bipy)$_{2+}$ was intercalated with interbasal distance dooz increasing from 0.756 mm to 1.59 mm and Ru(bipy)$_{2+}$ simply replaced H$_2$O in the interlamellar space. In the absence of HF, the Ru(bipy)$_{2+}$ was adsorbed on the surface rather than intercalated. The absorption bands of Ru(bipy)$_{2+}$ at 455 and 285 mm did not shift significantly on intercalation. These materials are potential heterogeneous photocatalysts for H$_2$O splitting.

In a study of X-ray diffraction spectrometry for analysis of lameller ion exchanger diffraction in the quant anal of crystalline solid phases were used. The areas of each phase with different ionic compositions were obtained. The use in materials of the $\alpha$ and $\gamma$-Zr-phosphate type, of a linear relation
between intensity and concentration for mixtures of phases with different counter ion content was proposed.

Polycrystalline samples of α-Zr(HPO₄)₂·H₂O, conditioned at various relative humidities were investigated at -20 to +20° by admittance measurement. The frequency response was fitted by complex nonlinear regression to an equivalent circuit consisting of a parallel combination of resistance, geometrical capacitance and a constant phase angle element. As a consequence of increasing surface hydration the d.c. conductance increased by 2/3 of magnitude as the relative humidity goes from 5 to 90%. The parameterisation of the d.c. conductance shows that these increments are essentially due to a change in activation energy from 12 to 6 Kcal/mol.

The sorption of NH₃ and H₂O vapour was studied on the sorbents prepared by the reaction of alkali metal (Li, Na and K) salts with Ti or Zr-phosphates.

The porous structure and properties were determined from Zr-phosphate ion exchangers T Katrina, LFTS and VFTS modified with complexon III, citric acid and tartaric acid respectively. The T Katrina and VFTS ion exchangers had sufficient porosity and high ion exchange property for Fe³⁺ (~1.9 meq/g) at short aging time of the freshly precipitated Zr-phosphate gel. The citric acid modified LFTS required extended aging and its ion exchange capacity deteriorate during operation.
The catalytic activities for ring opening isomerisation of cyclopropane and isomerisation of butene were examined on crystalline Zr(HPO₄)₂·Zr(HPO₄)₂ catalyst was highly crystallised during the dehydration of Zr-phosphate gel with concentrated H₃PO₄ solution under reduced pressure. This catalyst which was evacuated at higher temperature (above 770K), exhibited higher catalytic activities (based on surface area) than α-Zr(HPO₄)₂·H₂O catalyst or other conventional solid acid catalysts. The coisomerisation of d₀ and d₂-i-butene suggests that isomerisation would proceed on proton acid sites even after heat treatment at 110K. After evacuation at 773K most of the phosphate groups were removed, with consequent loss of water due to the condensation of phosphate groups between each Zirconium atom layer. However, a trace amount of residual phosphate groups still remained on the surface. After heat treatment at higher temperatures, the stretching and bending vibrations of P–O–P appeared in IR studies; their intensities increase with increasing temperature of evacuation. Even though the proton concentration decreased the reaction rates for isomerisation were drastically enhanced, because of the presence of P–O–P bonds which could withdraw the electrons from the residual phosphate groups on the surface. Intercalation of 2,2' Bipyridine, 2,9 dimethyl 1,10 phenanthroline has been studied with γ-Zr(HPO₄)₂·2H₂O. Indirect evidence, X-ray diffraction and IR spectroscopy indicate that the orientation to the amines in the interlayer are different from those in the α-Zr(HPO₄)₂·2H₂O analogs, probably due to the presence of H-bonding by the
interlayer water molecule. The materials exchange Cu\(^{2+}\). As expected, given its lower interlayer ligand compared with other materials \(\gamma\)-Zr(HPO\(_4\))\(_2\)(dmphen)\(_0.28\).2H\(_2\)O takes up Cu\(^{2+}\) most readily. Steric requirements alone and the uptake in all cases slower than that in the \(\alpha\)-Zr(HPO\(_4\))\(_2\).H\(_2\)O analogs both results indicating the importance of ligand matrix interactions. Spectroscopic evidence shows that Cu\(^{2+}\) coordinates to the amine ligands only in the bipy and phen cases whereas both dmphen-containing materials exchange Cu\(^{2+}\) into cavities widened without coordination to the intercalated ligands.

Electron microscopy and Hg porosimetry were used to study the porous structure of Zr-phosphate ion exchanger TFTS and LFTS modified with complexon III and citric acid respectively. Modification with complexon III led to the formation of a coarsely globules porous structure in the freshly precipitated Zr-phosphate gel whereas sufficiently porous Zr-phosphate ion exchanger modified with citric acid can be obtained only after 20 days aging of the precipitated gel. TFTS ion exchanger with coarse open pores were obtained by their treatment with EtOH by drying.

Multiple asymmetric layers of organic molecules were prepared that may be applicable to the fabrication of electro optical switching element and other second order nonlinear optical devices. The molecular layers thus formed are held together by Zr-phosphate and phosphonate bonds: Such multilayer films are constructed on both Au and oxidised Si-surfaces. The asymmetric orientation of the molecules in each layer is ensured by a three
The reaction of $\text{CCl}_4$ with $\text{Na.Zr(PO}_4)_9$ or $\text{KZr(PO}_4)_6$ was studied$^{67}$ in $\text{NaCl}$ or $\text{KCl}$ melt as a function of temperature gas flow and mass of phosphate solid phase transferred to the melt. Rate constants and activation energies were calculated.

$\text{NH}_3$, $\text{N}_2\text{H}_4$ and a range of simple amines were intercalated$^{69}$ into $\alpha-\text{Zr(HPO}_4)_2\cdot\text{H}_2\text{O}$. The phases that formed were characterised by X-ray diffraction and NMR studies. The position and intensities of isotopic $31\text{P}$ resonances depended on the type of amine present. With intercalation linear alkyl chain primary amines produced down field shifts of the phosphates group while secondary and tertiary amines produced upfield shifts. Water content had an important effect.

$\text{Zr-phosphate ceramics have been prepared}^{80}$ which contain 1-10 wt$\%$ group III B element compounds, 0.1 - 8 wt$\%$ group II B element compounds and the balance Zr-phosphate. The ceramics are prepared by mixing the ingredients and shaping the mixed mass. Final sintering was carried out at 1500 - 1650°C for a period of about 4 hours. These ceramics are heat resistant and are suitable for the manufacture of circuit boards, thermal insulators for space shuttles.

Singh and Singh$^{70}$ studied the membrane potential and solute separation on Zr-phosphate membrane. Zr-phosphate subjected to thermal treatment for various time intervals in presence of phosphoric acid was used for membrane formation. Membrane potential and membrane conduction measurements were used to study
the relation between the ion exchange capacity of Zr—phosphate and the electrochemical characteristics of the membranes using NaCl and MgCl₂ solutions of different concentrations. The results were used to establish solute separation characteristic of the Zr—phosphate membrane by using non-equilibrium thermodynamics.

Ishida examined the thermal conductivity and expansion of Zr—phosphate. The ceramics have thermal expansion co-efficient -1.5 x 10⁻⁶ per degree at 40 to 1200°C and strength 50 kg/mm² and this is specially suitable for manufacture of engine parts.

Giado and Ramos-Barrado et al carried out experiments on ion transport in Alumina pillard Zirconium phosphate. The AC conductivity of a novel large pore Alumina pillard Zirconium phosphate and some Li ion exchanged samples have been measured by an impedance method. These materials have a conductivity in the range of 10⁻⁵ to 10⁻⁹ Ω⁻¹cm⁻¹, higher than those of Alumina pillard Tin phosphate and its Li derivatives. The electrical behaviour of pillard Zr—phosphate fit and an equivalent circuit composed of two subcircuits in parallel with a condensor in the temperature interval of 200 to 500°C. Li ions are charged carriers and the conductivity increases when heating with activation energies between 0.99 to 1.22 EV.

Perekhozaeva concluded from a study on sorption of lead by oxide and phosphate sorbents that highest sorption capacity and best kinetics exhibited by Zr—phosphate containing 40% moisture.
The effect of salt anion nature on the sorption of cations of doubly charged metals by amorphous Ti and Zr-phosphates was studied by Kvashenko and Bortun\textsuperscript{74}. The influence of anions on divalent cation sorption by amorphous Ti or Zr-phosphate containing only small amounts of P was studied. Exchange constants were calculated and sorbent affinity series for divalent cations were established.

Sorption of transition metal ions on amorphous Zr-phosphate was observed by Bortun and Khryashchevskuu\textsuperscript{75} trends in sorption of Fe\textsuperscript{3+}, Pb\textsuperscript{2+}, Zn\textsuperscript{2+}, Cd\textsuperscript{2+},Cu\textsuperscript{2+}, Co\textsuperscript{2+} on amorphous Zr-phosphate were studied by using single salt aqueous solutions or, solutions of these cations containing KNO\textsubscript{3} as background electrolyte. Series of selectivities were determined for sorbents in H or, K form with P : Zr ratio 0.9 conversion to K-salt form increases the affinity for d-metal ions allowing their selective separation from background electrolytes containing macro amounts of alkali metal cations.

Boichinova and Nikolaeva\textsuperscript{76} studied the effect of modification on physico chemical properties of Zr-phosphate. The Zr (IV) phosphate was modified by adding EDTA during its preparation to achieve lower density, higher sorption capacity for a Fe\textsuperscript{3+} and better yield during synthesis. The effects of modification were studied by IR spectroscopy and X-ray phase analysis. Precipitation from EDTA solution at pH=8 gives an exchanger with higher pK values for functional groups. The more highly evolved porsche structure was due to retarding of
precipitation due to complexation of Zr (IV) which leads to the formation of a coarse globular structure.

Perekhozhaeva and Sharygin studied the kinetic characteristics of ion exchange process on Zr-phosphate prepared by sol-gel method. Internal diffusion coefficients were determined for a series of cations in Zr-phosphate of different moisture content. The structure and ion exchange characteristics of these samples were compared. The nature of ion retarding in sorbent has been discussed. The solution pH effects on the internal diffusion mobility of hydrolyzable and nonhydrolyzable ions were also examined.

Galkin and Sharygin studied physico chemical properties of spherical Zr-phosphate produced by the sol-gel method. In sol-gel preparation of spherical Zr-phosphate granules the stage of dehydration affects most significantly the formation of a porus structure. The adsorbent granules having P : Zr < 1.0 are microporous with specific surface area decreasing on the P : Zr ratio increases.

Paine, Blaha and Russell carried out experiment on polymeric material for metal ion separation. Although these solution techniques are adequate for many applications, there are numerous separation that would be improved by the development of advanced, solid supported organic extractants. Several approaches for the preparation of solid supported ligands suitable for lanthanide and Actinide separations have been reported and supports utilised include polystyrene and Zr-phosphate.
Kornyei, J and Szirtes, L. carried out experiment on chromatographic studies on mixed derivatives of Zr—phosphate and Dextrin gel. The mechanical stability of gels obtained from Zr—phosphate and its derivatives are not high enough for their use in column operation. To study their chromatographic properties the mixture of these gels with dextrin gels were prepared. For this mixture a neutral gel was prepared so that the Zr—phosphate part contained the functional group. Separations of Ga from Galium complexes of citrate EDTA were done by using a column filled with the above mentioned mixed gels.

Shakshooki, S. K. and Szirtes, L. studied the effect of γ-radiation on granular mixed Zr-Ti phosphates. Solid ZrOCl₂·8H₂O was added in a slow stream to solution of H₃PO₄ or to a solution of TiCl₄ in H₃PO₄ to obtain granules of amorphous Zr(HPo₄)₂·nH₂O or ZrxTi₁-x(HPo₄)·nH₂O where x = 0.95 to 0.8. Half of each product was soaked in C₂H₅OH to produce alcoholic solvated material. The particle size of the resulting material is very similar to that of ZrOCl₂·8H₂O in such a way that it may be controlled indirectly. These materials are suitable for ion exchange column operations. The relatively high γ-radiation did not alter the exchange properties. Some pH titrations were performed and the exchange capacities of alkali metal ions were determined by an isotopic tracer technique. The effect of drying temperature on ion exchange properties of Na⁺, K⁺, Cs⁺ on granular materials were studied. Other characteristics were made by chemical analysis and thermogravimetric analysis.
Schraut, A. and Emig, G. carried out investigations of the oxydehydrogenation of ethyl benzene. The reaction was carried out with an active coke deposited on hydrated Zr(HPO$_4$)$_2$ as catalyst. The active coke was a, c, H, O compound which acts as an organic redox system. The reaction system was described by five reaction equations.

1. Literature

Regarding the application Boyd et al demonstrated that the columns containing finely divided zirconium phosphate supported on silica wool could be used to separate uranium and plutonium from fission products by ion exchange process.

Krans has summarised a no. of applications in separation processes of this material. It is to be noted that alkali metals are held more strongly in zirconium phosphate than alkaline earth in zirconium phosphate and as such good separation is achieved.

A complete separation of the series of alkali metals in tracer level was achieved. Zirconium phosphate is used largely for selective separation and selectivity depends on drying temperature.

Paper chromatography using zirconium phosphate are now occupying an important position in separation processes. Zirconium phosphate possesses good physical rigidity for which they are used reactor water circuit operated at elevated temperature.

As a heterogeneous membrane zirconium phosphate was precipitated on a mat of glass wool fibers which are used for membrane separation process.