SUMMARY AND CONCLUSION

1. Zirconium phosphate, one of the important high exchanging, acid resistant inorganic cation exchanger has drawn the attraction of many scientist because of its application in various fields.

In the present investigation Zirconium phosphate hydrogel having different molar ratios of ZrO₂ : P₂O₅ in the composition were synthesised by the wet interaction of pure grade ZrOCl₂ and H₃PO₄ solutions. For this purpose only molar ratio of ZrO₂ : P₂O₅ was varied in the compositions keeping the other parameters such as concentration of the ingredients, sequence of addition, temperature etc. fixed. Variation in the molar ratio resulted in the generation of product having different ratios of ZrO₂ : P₂O₅ which covered a range from 2 : 1 to 1 : 2. At higher proportion of PO₄ the excess of the anions was found to be depleted and passed out in the solution phase.

Zirconium is rarely found in dilute solutions as simple Zr⁺⁴ or as Zirconyl ZrO⁺² ion but is generally present in either complexed or hydrolysed form in which the polymeric ion may predominate. Thus the structures of the product depend on the nature of the ions from which they are formed.

Here the hydrogel was formed in acidic condition and all the characteristics of the gel were noticed including the syneresis liquid on aging. The consistancy of the gels was semisolid and optically they were translucent.
Gels were properly processed to remove the extraneous soluble impurities and dried at low temperature. Although the mole ratio of ZrO$_2$ : P$_2$O$_5$ in the product followed a relation with the batch ratio but significant deviation from batch ratio was observed at higher P$_2$O$_5$ content.

X-ray pattern indicated the amorphous nature of all the synthetic hydrogels. Bulk and true densities followed direct relationship with ZrO$_2$ content.

2. Single endothermic peak in the DTA diagram showed the homogeneity of the hydrogels with respect to hydrate formation. This peak temperature changed inversely to P$_2$O$_5$ content in the composition which might be correlated with the structural rigidity of the formed hydrogel. The size, number and disposition of channels are the controlling factors for expulsion of water which in other ways followed a relationship with the composition of the hydrogel. Again the sharp exothermic peak at higher temperature due to conversion into crystalline Zirconium phosphate was also influenced by the molar ratio as revealed through the nature and height of the peaks.

3. Cation exchange capacity which is one of the important characteristics of this type of hydrogel varied significantly with the molar composition. CEC values increased with increase in P$_2$O$_5$ content in a parabolic path within the range as studied in the present investigation. In this type of exchanger the practical CEC
value was always lower than the theoretical one which was due to the blocking of the exchanger sites in the gel structure.

Cation exchange in Zirconium phosphate occurs in two stages. In the first hydrogen ions are displaced from P-OH groups which are bonded to water molecules. Then the hydrogen ions are replaced from P-OH groups which are bonded to adjacent layers leading to an increase in spacings. Variation in IR spectra indicated some difference in the nature of bonding which might have supplemented the difference in CEC value.

4. The significant influence of molar ratio of \( \text{ZrO}_2 : \text{P}_2\text{O}_5 \) on the DTA curves and the total water content on the hydrogel structure have led to the study of equilibrium dehydration-rehydration on progressive heat treatment. Magnitude of dehydration increased upto 800°C but not in a linear path. The nature of the curves was more or less same in that they were not well defined and the inflexion zone was within 400-500°C. The magnitude of dehydration followed an inverse relationship with \( \text{P}_2\text{O}_5 \) content upto certain minimum following which it turned in a reverse way.

5. Rehydration of the heat treated samples as calculated on the basis of the dehydrated weight, was found to be a direct function of humidity and the temperature of heat treatment influenced in a reverse way. The reversibility was maintained upto certain region and a sharp reduction was observed from 600°C which
might be correlated with the lattice shrinkage and pore elimination.

6. The residual exchange capacity was found to be dependent on the thermal history of the hydrogel. During heat treatment flexibility of dehydration—rehydration was maintained within a certain zone and the retention of CEC was closely dependent on it. The residual CEC of the different samples heated at 700°C clearly indicated that complete structural collapse did not occur at this temperature. Removal of water decreases the magnitude of hydration of the cation and the resultant increase in the electrostatic force of attraction which is responsible for reduction of CEC.

Comparison of dehydration curves and the related properties showed that the latter was dependent on the water content in the hydrogel structure which was controlled by the molar ratio of ZrO₂ : P₂O₅.

7. For getting an understanding into the mechanism of the dehydration process kinetic study was undertaken. Temperature range was selected in accordance to the dehydration peak in the DTA curves. The results of isothermal dehydration experiments have been plotted using Guggenheim

\[
\log \Delta L = \frac{-kt}{2.303} + \log \left[ L_\alpha (1-e^{-k\Delta t}) \right]
\]

Linearity of plots of \( \log \Delta L \) vs. time indicated the applicability of First order kinetics irrespective of the nature of the
hydrogel. The general observations were

(i) Major portion of the dehydration curves of all the hydrogel having different molar ratio of ZrO₂ : Al₂O₃ followed first order kinetics. This suggested that the dehydration was essentially controlled by the mutual interaction of the water molecules encaged in the gel structure.

(ii) The total course of the reaction did not follow the first order kinetics. The deviation as observed in this case appears to be due to the increasing probability of randomness in the orientation of water molecules. The extent of validity of first order law followed a direct relationship with temperature. Significantly lower values were observed at 70°C. This might be due to the fact that the supplied thermal energy was not sufficient enough to dislodge the water molecules. In this respect compositional effect was so much significant.

(iii) The reaction rate constant for dehydration reaction were determined both at the initial and final stages of the reaction i.e. K₁ and K₂. In the final stage of dehydration the concentration of water molecules decreased significantly and the mutual interaction of the structurally isolated water molecules would require a higher energy as a result of which K₂ values were always found to be higher than the corresponding K₁ value. The observed particle size effect was in conformity with the other diffusion controlled solid-gas type heterogeneous reaction. Due to highly porous structure of the hydrogel the escaping water...
molecules face very little diffusion barrier which minimized the compositional effect.

(iv) The equilibrium weight loss due to expulsion of water ($L_\alpha$) in the early stage of dehydration was found to be a direct function of temperature indicating thereby that the bonding of water molecules covered a range. The variation of $L_\alpha$ values with particle size was insignificant and as such the average values have been reported. The $L_\alpha$ values followed a direct relationship with $P_2O_5$ content in the composition from ratio $1:1.68$ onwards. The activation energies at the initial and final stages of dehydration were calculated from the usual Arhenius relationship. In the early stage the dehydration mostly involved the channel water and the energy requirement for expulsion was not of high order. In all cases $E_1$ values were lower than the corresponding $E_2$ values. Upto mole ratio $1:1.84$ activation energy values increased progressively but afterwards a descending trend was observed. This clearly indicated that in this type of phosphate hydrogel structure an optimum ratio of the ingredients was responsible for proper orientation of water molecule in the charged lattice pronounced by hydrogen bonding. Beyond this anionic framework is affected which decreased the diffusion path.

The effect of particle size was in conformity with classical heterogeneous phase reaction. Because of the extremely porous structure of the synthetic phosphate hydrogel the variations were not of very high order. All the kinetic parameters including the activation energy both at the initial and final
stages of dehydration exhibited relationship in accordance with the activity relationship with the exposed surfaces.

8. The cation exchange capacity of the synthetic Zirconium phosphate hydrogels was found to be dependent on the composition. The selectivity of cations followed the usual sequence as derived from the ionisation, activity coefficient and ionic potential.

9. The rate of ion exchange is determined by diffusion process which may be controlled by either particle or film diffusion. The rate law was derived by applying the diffusion equation to the ion exchange system such as

\[ \frac{Q_t}{Q_\infty} = \frac{6}{\pi} \frac{D_t}{r} \]

Here \( D \) was taken to be the diffusion coefficient of the entering cation. Since in each case the starting Zirconium phosphate was taken in hydrogen form it might be assumed that although \( D \) was related to inter diffusion of ions entering and leaving the exchanger the variation of \( D \) would be the same if \( D \) were the diffusion coefficient of the entering ion alone. For a fixed concentration of exchanging cations the order of diffusion coefficient followed the sequence \( \text{Ca}^{2+} > \text{Ba}^{2+} > \text{Mg}^{2+} \). It has been observed that the plots of \( Q_t/Q_\infty \) exhibited linearity up to 60-70% beyond which flattening occurred. This might be due to fall of electrolytic concentration in the pores of the exchanger which leads to a decrease in the diffusion coefficient at the latter
stage of exchange. Activation energies for diffusion of the cations calculated from the slopes of Arrhenius plots of log D against 1/T decrease regularly with decrease in hydrated ionic radius of the cations.

Thus Zirconium phosphate as synthesised in the present investigating through wet interaction process appears to revive the interest of the inorganic exchangers because of high exchange capacity and conversion into hydrogen form. Though the materials possess a single phase hydrated structure but the compositional effect played a vital role with respect to important physico chemical characteristics. Thus the application of this active synthetic material will be manifold e.g. as catalyst, adsorbate and also as additives and aggregate in many high temperature reactions. The phase stability at elevated temperature appears to open up newer fields of application.

4. Results and Discussion
   a. Dissociation of hydrogen ion means release of loosely bound H\(^+\) in the aqueous phase and as such core structure became negatively charged.
   b. Thermal analysis results were related to ratio of ZrO\(_2\)\(\cdot\)P\(_2\)O\(_5\) and could not be correlated with the structure because of amorphous nature of the sample. In case samples having molar ratio ZrO\(_2\) : P\(_2\)O\(_5\) = 1 : 0.91 to 1 : 1.68 two steps dehydration was observed. The second break in the 400-700°C might be due to dehydroxylation of the gel product.
5. **Kinetics of dehydration**

Kinetics of thermal dehydration of the hydrogel is basically a heterogeneous discontinuous process following mostly first order kinetics.

This is diffusion controlled reaction and the diffusion of water molecules from the reaction interface is determining for the rate of dehydration of the samples. As the sample was used in granular form for kinetic study and 500 mg sample was spread in thin layer in the crucible the back pressure was not effective.