Chapter - V

THE IONEXCHANGE PROPERTIES OF ZEOLITES
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References
5.1 INTRODUCTION:

This chapter deals ionexchange properties of zeolites. Influence of ionexchange on the thermal and structural properties of heulandite crystals has been described, discussed and illustrated. Use of natural zeolites for the extraction of NH₄/NH₃ from highly polluted water has also been reported in this chapter.

5.2 IONEXCHANGE IN ZEOLITES:

Zeolites are capable of exchanging their non-framework cations and this is one of their outstanding characteristic properties. Ionexchange has been observed to take place under an aqueous medium at normal pressure and normal temperature to boiling temperature. At higher temperature and pressure in aqueous medium, tetrahedral cations may also be exchanged.

Cations in the structure of the zeolite compensate for the framework charges arising from substitution of silicon by aluminium. The ionexchange capacity is basically a function of the degree of substitution of aluminium for silicon in the framework structure. The greater the substitution, greater the charge deficiency and greater the number of alkali or alkaline earth cations, required for electrical neutrality.

The cation exchange behaviour of zeolites
depends upon:

i) The nature of cation species

ii) Cation size

iii) Temperature

iv) Concentration of cation species in solution

v) Anion species associated with cation in solution

vi) Solvent

vii) Structural characteristic of a particular zeolite.

Due to the ionexchange properties, zeolites are widely used as ionexchangers in areas such as purification of water for removal of ammonium ions, heavy metals from potable and waste water, ionexchange reactions in soils, treatment of radioactive waste, ionexchange in cracking processes etc. are reported.3'6

5.3 INFLUENCE OF ION EXCHANGE ON THERMAL & STRUCTURAL PROPERTIES OF HEULANDITE CRYSTALS:

To use zeolite as catalyst, the thermal stability of zeolite plays predominant role in various catalytic reactions, such as petroleum cracking, hydrocarbon conversion reactions etc. The thermal stability of zeolite framework7 depends on
the type of cation, their distribution among the non-framework sites and the cation exchange. Several workers have studied the thermal stability of heulandite.8-10

The present study deals with the investigation of structural and thermal properties of K⁺, NH₄⁺ and Mg²⁺ cation exchanged heulandite crystals by X-ray diffraction, infrared spectroscopy and thermal analysis [TGA/DTA].

5.3.1 EXPERIMENTAL:

The crystals were collected from Ajantha ranges and areas surrounding Aurangabad city of Maharashtra. Crystals of heulandite are shown in Plate 5.1. The collected crystals were separated from geodes, cleaned, crushed and sieved to get 106μm sized crystals. The powdered sample was washed repeatedly and dried.

The sample was cation exchanged with 0.5M aqueous solutions of chloride salts of potassium, ammonium and magnesium at boiling temperature for 24 hours. The cation exchanged samples were washed repeatedly till free from chloride ions and dried. For convenience parent heulandite sample has been labeled as P-Heu and cation exchanged heulandite samples as K-Heu, NH₄-Heu and Mg-Heu. All samples have been characterized by X-ray diffraction, infrared spectroscopy, thermal analysis (TGA/DTA)
Chemical contents (Si & Al) of the parent sample were determined by wet chemical analysis method. The Na, K, Ca and Mg contents of the parent and the cation exchanged samples have been determined by atomic absorption spectroscopy. From the results of chemical analysis the unit cell formula for the parent heulandite sample on the basis of 0/2 has been determined as...

\[
Ca_{2.03} Na_{0.79} K_{0.14} [Si_{2.14} Al_{1.88} O_{7.2}] 24 H_2O
\]
giving Si/Al ~ 3.8

5.3.2 RESULTS AND DISCUSSIONS:

i) X-RAY DIFFRACTION:

The XRD patterns of the samples are depicted in figure 5.1 (a), (b), (c), (d) confirm the earlier data published for the heulandite.\textsuperscript{11} The XRD pattern of the samples reveals the crystalline nature and phase purity. The 'd' values and corresponding intensities are listed in table 5.1. It has been found that intensities of the peaks are changed with the cation exchange. This may be due to the difference in scattering factor of the exchanged cations.\textsuperscript{12}
Fig. 5.1(a): X-ray diffractogram of P-Heu.

Fig. 5.1(b): X-ray diffractogram of K-Heu.
Fig. 5.1(c): X-ray diffractogram of NH₄-Heu.

Fig. 5.1(d): X-ray diffractogram of Mg-Heu.
Table No. 5.1

XRD data for Cation Exchanged Heulandite

<table>
<thead>
<tr>
<th>2θ</th>
<th>d(Å)</th>
<th>P-Heu</th>
<th>K-Heu</th>
<th>NH₄-Heu</th>
<th>Mg-Heu</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>I/I₀%</td>
<td>I/I₀%</td>
<td>I/I₀%</td>
<td>I/I₀%</td>
</tr>
<tr>
<td>09.80</td>
<td>8.978</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>11.10</td>
<td>7.964</td>
<td>06</td>
<td>12</td>
<td>10</td>
<td>05</td>
</tr>
<tr>
<td>19.00</td>
<td>4.667</td>
<td>28</td>
<td>19</td>
<td>17</td>
<td>23</td>
</tr>
<tr>
<td>23.30</td>
<td>3.984</td>
<td>28</td>
<td>39</td>
<td>50</td>
<td>28</td>
</tr>
<tr>
<td>22.80</td>
<td>3.987</td>
<td>27</td>
<td>25</td>
<td>36</td>
<td>25</td>
</tr>
<tr>
<td>26.00</td>
<td>3.424</td>
<td>11</td>
<td>10</td>
<td>13</td>
<td>08</td>
</tr>
<tr>
<td>28.10</td>
<td>3.172</td>
<td>11</td>
<td>14</td>
<td>11</td>
<td>08</td>
</tr>
<tr>
<td>28.50</td>
<td>3.129</td>
<td>10</td>
<td>15</td>
<td>14</td>
<td>16</td>
</tr>
<tr>
<td>29.90</td>
<td>2.985</td>
<td>60</td>
<td>45</td>
<td>46</td>
<td>53</td>
</tr>
<tr>
<td>31.90</td>
<td>2.803</td>
<td>21</td>
<td>08</td>
<td>10</td>
<td>10</td>
</tr>
<tr>
<td>32.80</td>
<td>2.728</td>
<td>19</td>
<td>16</td>
<td>17</td>
<td>18</td>
</tr>
<tr>
<td>45.80</td>
<td>1.979</td>
<td>--</td>
<td>05</td>
<td>06</td>
<td>05</td>
</tr>
</tbody>
</table>
ii) **INFRARED STUDY**:  

Infrared spectra of the samples were scanned in the region of 400-4000 cm⁻¹ as shown in figure 5.2 (a), (b), (c), (d). It is established that the infrared spectra of zeolites reflect the framework and the fundamental building units in the structure. Infrared spectra of zeolites are modified by the presence of cations in the framework structure. The influence of exchangeable cations i.e. non-framework cations on the framework vibrations of zeolites has been investigated by Maxwell et al. and Shiralker et al.¹³

From the table 5.2, the heulandite exhibits bands¹⁵-¹⁶ at 1015, 770, 640, 510 and 424 cm⁻¹. The band at 510 cm⁻¹ is characteristics of Si-O vibrations. The bands at 770 cm⁻¹ and 424 cm⁻¹ correspond to the vibrations of Al-O bend.¹⁷

The frequencies of structure sensitive and insensitive bands minorly change with the type of cation. The intensity of 770 cm⁻¹ (inter. sym. stretch.) is considerably changed with the type of cations.
Fig. 5.2(a): IR spectra of P-Heu.

Fig. 5.2(b): IR spectra of K-Heu.
Fig. 5.2(c): IR spectra of NH₄-Heu.

Fig. 5.2(d): IR spectra of Mg-Heu.
### Table No. 5.2

**Infrared Spectral Data for Cation Exchanged Heulandite**

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>Internal Tetrahedra (cm⁻¹)</th>
<th>External Linkages (cm⁻¹)</th>
<th>Double Ring (cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Asymmetric Stretch</td>
<td>Symmetric Stretch</td>
<td>Asymmetric Stretch</td>
</tr>
<tr>
<td></td>
<td></td>
<td>T-O Bend</td>
<td></td>
</tr>
<tr>
<td>P-Heu</td>
<td>1015(ms)</td>
<td>640(ms)</td>
<td>1255(s)</td>
</tr>
<tr>
<td>K-Heu</td>
<td>1005(mw)</td>
<td>640(ms)</td>
<td>1255(s)</td>
</tr>
<tr>
<td>NH₄-Heu</td>
<td>1020(ms)</td>
<td>626(ms)</td>
<td>1251(s)</td>
</tr>
<tr>
<td>Mg-Heu</td>
<td>1015(ms)</td>
<td>640(ms)</td>
<td>1257(s)</td>
</tr>
</tbody>
</table>

s-strong ; ms-medium strong ; m-medium; w-weak; mw-medium weak; vw-very weak; sh-shoulder
iii) THERMAL ANALYSIS:

Open framework zeolites have broader, low-temperature endothermic effect on DTA curves, whereas small-pored zeolites are characterized by high temperature effect and produce sharper peaks.\(^{18}\)

The structure collapse is an exothermic process in zeolites and a high temperature exothermic peak is considered as a measure of thermal stability.\(^{19}\)

From the DTA curves as depicted in figure 5.3, it has been cleared that the first endothermic peak of P-Heu which is centered at 190°C shifts towards 150°C due to potassium exchange (K-Heu). Here the peak area increased. In case of Mg-Heu, there is an increase in area of this peak but temperature has not changed. In NH\(_4\)-Heu there is broadening in first endothermic peak and the position is at 130°C. All these endotherms are attributed to the desorption of zeolitic water.

The first exotherm in these heulandites are related to the phase change to heulandite B. In P-Heu and Mg-Heu exothermic
Fig. 5.3(a) : TGA/DTA curves of P-Heu.

Fig. 5.3(b) : TGA/DTA curves of K-Heu.
Fig. 5.3(c): TGA/DTA curves of NH$_4$-Heu.

Fig. 5.3(d): TGA/DTA curves of Mg-Heu.
peak at 500°C indicates the structural collapse. This type of exothermic peak is absent in K-Heu and NH₄-Heu. In NH₄-Heu an exotherm occurs at 400°C associated, to decomposition of ammonium ions. After 400°C due to evaporation of ammonia, NH₄-Heu has been converted into H-heulandite.

TG curves as shown in figure 5.3 reveal that the dehydration of heulandite is in steps. All zeolites except K-Heu show maximum weight loss due to dehydration at 250°C and which is supported by an exotherm on DTG curves. The rate of dehydration depends on the nature of cation present. The loss of water form P-Heu and Mg-Heu is faster as compared to that form K-Heu. This indicates that a stronger bonding of water molecules exists with K⁺ than with Mg²⁺ and Ca²⁺ in Mg-Heu and P-Heu respectively.

The TG curve of NH₄-Heu consists of three distinct steps. The step upto 320°C is due to loss of physically sorbed water, the second step upto 400°C to ammonia evolution and third step upto 1000°C is due to dehydroxylation.

5.4 NATURAL ZEOLITES - AS AN ANTIPOLLUTION DEVICE:

Due to wide spread use of artificial fertilizers and contamination of effluents with industrial wastes, the concentration of nitrogen compounds in lakes has increased considerably. These compounds, in particular ammonium, adversely
affects the purity of water, lowering its quality, increasing algae and contaminating lakes, ponds and rivers. According to existing norms, in drinking water ammonia concentration should not exceed 0.5 ppm.

Extraction of nitrogen compounds from wastes can be performed using physico-chemical methods. This includes adsorption by activated carbon, chlorination, ionexchange, chemical coagulation etc. These methods have both advantages and defects. Use of coagulants decrease organic nitrogen, but the concentration of ammonia does not change. Ionexchange resins were used for ammonium ion extraction from domestic wastes. But the high cost and problems in regeneration made the purification of effluents, practically difficult.

Since few zeolites, particularly platy varieties possess a high selectivity towards NH₄/NH₃, in Japan, U.S.A and some European countries, natural zeolites have been widely utilized for the treatment of waste water and purification of drinking water.²⁴,²⁵ Such type of work has not been reported from India so far.

Taking the advantage of large deposits of natural zeolites available in Marathwada region of India, an attempt has made to test the utility of these zeolites for the treatment of highly polluted liquid for the extraction of NH₄/NH₃.
5.4.1 EXPERIMENTAL:

A few natural zeolite varieties have been collected and characterized for their zeolitic nature. Zeolite crystal were crushed and sieved to get 200µm sized crystals. Highly polluted liquid samples collected from different localities have been used for the study. Each zeolite powder has been treated with the highly polluted liquid sample for 12 hrs at room temperature with constant steering. In each case ppm level of NH₃, before and after treatment has been determined by Nesslerization technique. The regeneration of the zeolites were done by using 0.5M NaOH solution, treated at boiling temperature for 6 hrs.

i) METHOD FOR ESTIMATION OF AMMONIA IN SOLUTION

The ammonia from waste water was estimated by colorimetric method, with the help of colorimeter. 100ml of sample (pre and post treated Liquid) was taken. 1ml of zinc sulfate and 0.5 ml NaOH were added to obtain pH of 10.5. The sample was filtered with the help of 'Whatman 42' filter paper. 1 drop of EDTA and three drops of Nessler's reagent were added to filtrate and percentage transmittance was noted after 10 minutes. The concentration of ammonia was determined from the calibration curve.
ii) **RESULTS:**

Pre and post treatment results are presented as follows:

<table>
<thead>
<tr>
<th>Cation exchanger</th>
<th>Before Treatment</th>
<th>After Treatment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Heulandite</td>
<td>24</td>
<td>06.00</td>
</tr>
<tr>
<td>Clinoptilolite</td>
<td>25</td>
<td>03.40</td>
</tr>
<tr>
<td>Stilbite</td>
<td>25</td>
<td>11.30</td>
</tr>
<tr>
<td>Natrolite</td>
<td>23</td>
<td>22.00</td>
</tr>
<tr>
<td>Scolecite</td>
<td>24</td>
<td>21.00</td>
</tr>
</tbody>
</table>

From the above tabular form it has been confirmed that the zeolites particularly clinoptilolite and heulandite are useful for the treatment of polluted liquid.

5.5. **CONCLUSION:**

i) Different ionexchange forms of heulandite can be obtained easily.

ii) Effect of different ionexchanges are not identical.

   a) Ionexchange with K⁺, makes the structure more open than parent heulandite and imparts more thermal stability to the structure for higher temperature.

   b) Ionexchange with magnesium does not effect
the stability of the parent heulandite but it makes the structure comparatively more open.

c) Ionexchange with ammonium makes the structure appreciably more open and thermal stability also increases to larger extent.

Such ionexchanged forms can be used for specific applications.

From the section 5.4 it has been inferred that the platy zeolites particularly heulandite and clinoptilolite are useful for the removal of NH₃/NH₄ from waste water due to their ionexchange property.
REFERENCES


Plate 5.1 : HEULANDITE