CHAPTER 4

ZEOLITE MOLECULAR SIEVES

4.1 NATURAL ZEOLITES

"Rarely in our technical society the discovery of a new class of inorganic materials result in such a wide scientific interest and kaleidoscopic development of applications as had happened with the zeolite molecular sieves". The starting line of Donald Breck's famous book 'Zeolite Molecular Sieves' [1] throws ample light on the importance of zeolite in today's world.

4.1.1 Classification and Nomenclature :

Zeolites were first suggested by Cronstedt[2] as a new group of minerals consisting of hydrated aluminosilicates of the alkali and alkaline earths with his discovery of stilbite in 1756. The mineral exhibited intumescence when heated in a blow pipe flame which led him to name it as zeolite. The early investigations on zeolites did not lead to any significant progress in the understanding of the structure of zeolites. In the year 1956 Read and Breck reported the structure of synthetic zeolite 'A' which marked the beginning of the systematic study of the zeolite structures. From later studies it was inferred that all zeolites are framework of aluminosilicates and all of the zeolite structures are three dimensional.

With the development of the experimental techniques, the zeolites continued to receive attention in regard to their characterisation and identification. For many years these minerals were identified and characterised on the basis of chemical composition, optical properties, certain physicochemical properties and morphology. Modern methods used in the characterisation and identification of zeolites include X-Ray diffraction, which is based on the crystal structure, for identifying the fine-grained materials. Zeolite minerals were classified as highly acid species (i.e. high silica content) followed by metasilicates and orthosilicates. Winchell defined a mineral species as a crystalline phase found in inorganic nature[3]. He proposed that a mineral should not be defined in terms of a simple formula because the formula assigned to most minerals give an approximate composition. Minerals cannot be defined in terms of composition alone. A mineral species may vary in composition and different minerals may have nearly identical chemical composition. For example, the three different feldspar minerals, adulari, sanidine and microcline have essentially the same composition, $K\,Al\,Si_3\,O_8$. Twenty two different phases of the simple oxide SiO_2, have been defined[4]. It appears that many zeolites are metastable toward other more stable phases such as analcine or feldspars, and many transform during long periods of geological time.

Although well crystallized, zeolite minerals vary considerably in chemical composition. Conflicting experimental results have been reported on the same mineral by various investigators. These are due, in part, to structural differences caused by the presence of different metal cations. Zeolite minerals occur in igneous rocks as well-developed, single crystals which may be as large as several millimeters. In some instances, the zeolite crystals in igneous rocks may be found as dense polycrystalline aggregates. These hard aggregates resist weathering and, as the matrix rock disintegrates, the zeolite module is left as a pebble.

Zeolites occurring in sedimentary rocks are found in different environments like saline, alkaline nonmarine deposits and fresh water and marine deposits.

Pure zeolites are colorless, some mineral specimens may be coloured because of the presence of finely divided oxides or iron or similar impurities. The density of zeolite range between 2 and 2.3 g/cc. The density primarily depends on the basic frame work structure like openness and void volume, but exchange cation does also affect density.

Table 4.1 gives a list of important natural zeolites alongwith their chemical composition.[5]

Table 4.1 : A List of Natural Zeolites

Sr. No.	Name	Structure group	Occurance	Unit cell content
1.	Analcime	1	Ireland New Jersey Wyoming	$Na_{16}\ Al_{16}\ Si_{32}\ O_{96}\ 16H_2O$
2.	Bikitaite	6	Rhodesia	$Li_2\ Al_2\ Si_4O_{12}\ 2H_2O$
3.	Brewsterite	7	Scotland	$Sr_2\ Al_4\ Si_{12}\ O_{32}\ 10H_2O$
4.	Chabazite	4	Nove Scotia, Arizona Ireland, Nevada, Italy	$Ca_2\ Al_{14}\ Si_8\ O_{24}\ 13H_2O$
5.	Clinoptilohite	7	Wyoming, Western US	$Na_6\ Al_6\ Si_8\ O_{24}\ 13H_2O$
6.	Dachiardite	6	Elba, Italy	$Na_5\ Al_5\ Si_{19}\ O_{48}\ 12H_2O$
7.	Edingtonite	5	Scotland	$Ba_2\ Al_4\ Si_6\ O_{20}\ 8H_2O$
8.	Epistilbite	6	Iceland	$Ca_3\ Al_6\ Si_{18}\ O_{48}\ 16H_2O$
9.	Erionite	2	Oregon, Nevada, USSR	$Na_2\ K_2\ Mg_{0.5}\ Ca_2\ Al_9\ Si_{27}\ O_{72}\ 27H_2O$
10.	Faujasite	4	Germany	$Na_{12}\ Ca_{12}\ Mg_{11}\ Al_{58}\ Si_{134}\ O_{384}\ 235H_2O$
11.	Ferrierite	6	British Columbia, Italy, Utah, Nevada	$Na_{1.5}\ Mg_2\ Al_{5.5}\ Si_{30.5}\ O_{72}\ 18H_2O$
12.	Garronite	1	Ireland, Iceland	$Na\ Ca_{2.5}\ Al_6\ Si_{10}\ O_{32}\ 14H_2O$
13.	Giamondine	1	Italy	$Ca_4\ Al_8\ Si_8\ O_{32}\ 16H_2O$
14.	Gmelinite	4	Nova Scotia	$Na_8\ Al_8\ Si_{16}\ O_{48}\ 24H_2O$
15.	Gonnardite	5	France, Italy	$Na_4\ Ca_2\ Al_8\ Si_{12}\ O_{40}\ 14H_2O$

16. Harmotome	1	Scotland	$Ba_2\ Ca_{0.5}\ Al_5\ Si_{11}\ O_{32}\ 12H_2O$
17. Yugawaralite	1	Japan	$Ca_2\ Al_4\ Si_{12}\ O_{32}\ 8H_2O$
18. Heulandite	7	Iceland, New Zealand	$Ca_4\ Al_8\ Si_{28}\ O_{72}\ 24H_2O$
19. Laumontite	1	Nova Scotia, Fareo Islands New Zealand, USSR	$Ca_4\ Al_8\ Si_{16}\ O_{48}\ 16H_2O$
20. Mesolite	5	Nova Scotia	$Na_{16}\ Ca_{16}\ Al_{48}\ Si_{72}\ O_{240}\ 64H_2O$
21. Mordenite	6	Nova Scotia	$Na_8\ Al_8\ Si_{40}\ O_{96}\ 24H_2O$
22. Natrolite	5	Ireland, New Jersey	$Na_{16}\ Al_{16}\ Si_{24}\ O_{80}\ 16H_2O$
23. Offretite	2	France	$KCa_2\ Al_5\ Si_{13}\ O_{36}\ 15H_2O$
24. Paulingite	1	Washington	$(K_2\ Na_2\ C_a\ B_a)_{76}\ Al_{152}\ Si_{520}\ O_{1344}\ 700H_2O$
25. Phillipsite	1	Ireland, Sicily Western US, Africa	$K_2\ Ca_{1.5}\ Na\ Al_6\ Si_{10}\ O_{32}\ 12H_2O$
26. Scolecite	5	Iceland Colorado	$Ca_8\ Al_{16}\ Si_{24}\ O_{80}\ 24H_2O$
27. Stilbite	7	Iceland Ireland Scotland	$Na_2\ Ca_4\ Al_{10}\ Si_{26}\ O_{72}\ 34H_2O$
28. Thomsonite	5	Scotland, Colorado	$Na_4\ Ca_4\ Al_{10}\ Si_{26}\ O_{88}\ 24H_2O$
29. Wairakite	1	New Zealand	$Ca_8\ Al_{16}\ Si_{32}\ O_{96}\ 16H_2O$

Natural zeolite have not found any substantial industrial application even though a few like analcime, chabazite, clinoptilolite, erionite, and mordenite occur abundantly in sediments.

Japan is the largest user of natural zeolite Mordenite and Clinoptilolite which are used in adsorbent applications including air separation and in drying and purification. Natural zeolites are used as fillers in paper, cement and concrete, in fertilizer and soil conditioners and as dietary supplements in animal husbandry.

4.1.2 Occurrence of Mineral Zeolites :

Zeolite minerals have been used in many investigations of zeolite structures and properties (adsorption, ion exchange etc.). These investigations have contributed considerably to the present state of knowledge about zeolites. Zeolite minerals occur in miniscule quantities as a result of which the investigators have, sometimes, been required to use for research purpose milligram quantities of mineral zeolites. The naming of minerals is thoroughly discussed by Fleischer[6] and McConnel[7]. Zeolite minerals were considered as typically occurring in cavities of volcanic rocks and basaltic rocks. During the last fifty years, a number of brief descriptions of zeolite minerals found in sediments and as alteration products of volcanic ash and other pyroclastic materials have appeared. Ross[8] speculated in 1928 that analcine in the Wickieup, Arizona lake sediments was formed by the action of saline lake water on volcanic ash. More recently the use of X-Ray diffraction for the examination of very fine-grained submicroscopic particles that occur in sediments has resulted in the identification of several zeolite minerals[9]. In 1891, the Challenger expedition found phillipsite in red clay at the bottom of the central pacific ocean south of Sandwich island[10]. The metastable formation of zeolites in sedimentary environments probably takes place by a natural process. Although all of the zeolite minerals are known to have been found in igneous rocks, only a few occur in sedimentary environments. Complete summary of zeolites in sedimentary rocks is given in the excellent reviews by Hay[11] and Sheppard[12].

4.1.3 Structure of Zeolites :

The fundamental unit is a tetrahedral complex consisting of small cations such as Si^{4+} , in tetrahedral co-ordination with four oxygens as in Fig. 4.1 (Pauling's first rule). The Al

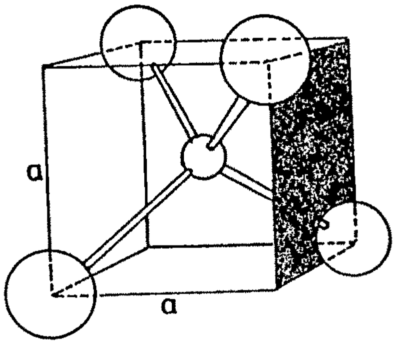

Fig . 4.1 The tetrahedrom of oxygen coordinated with silicon.

ion commonly coordinates tetrahedrally as well as octahedrally with oxygen in silicates. This has a profound effect on aluminosilicate structures and their composition. The complexity of silicate structures occur because of the various ways in which the tetrahydral groups may link by the common sharing of oxygen ions to form polynuclear complexes. The substitution of aluminum for a silicon produces a deficiency in electrical charge that must be locally neutralized by the presence of an additional positive ion within the interstices of the structure. Different types of aluminosilicates result from differences in the way in which the tetrahedra may link in space in one, two or three dimensions and from the types of other ions that substitute within the interstices. In some structures the tetrahedra link to form infinite chains which results in fibrous needlelike crystals. In other structures the tetrahedra are linked in layers or sheets as in mica minerals. These layers or sheet structures do not have three-dimensional stability and may expand if the layers are forced apart by water, other molecules, or ions. If SiO or AlO tetrahydra are linked in three dimension by a mutual sharing of oxygen alone, it results in a framework structure.

Classification of zeolite structures :

Structural classifications of zeolites have been proposed by Smith[13] and Fisher and Meier[14,15] and Breck[16]. The classification consists of seven groups; within each group, zeolites have a common structure which is a specific arrary of (Al, Si)O_4 tetrahedra. In the classification, the Si-Al distribution is neglected. For example, the two simplest units of four tetrahydra (4-rings) and six tetrahedra (6-rings) are found in many other framework aluminosilicates. These subunits have been called Secondary Building Units (SBU) by Meier[17]. The primary units are SiO_4 and AlO_4 tetrahedra. The secondary building units proposed by Meier is shown in Fig. 4.2. The classification which follows is

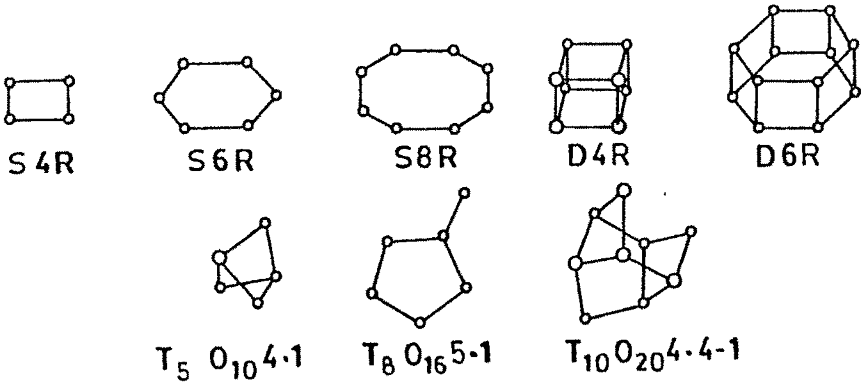

Fig. 4·2 The secondary building units (SBU) in zeolite structures according to Meier.

based on seven groups, they are as follows :

GROUP	SECONDARY BUILDING UNIT (S.B.U.)
1	SINGLE 4-RING : S4R
2	SINGLE 6-RING : S6R
3	DOUBLE 4-RING : D4R

4	DOUBLE 6-RING : D6R
5	COMPLEX 4-1, $T_5 O_{10}$ UNIT
6	COMPLEX 5-1, T_8O_{16} UNIT
7	COMPLEX 4-4-1, $T_{10}O_{20}$ UNIT

4.1.4 Physical Properties :

Thermal Expansion :

The thermal expansion of fully hydrated zeolite Sodium A had been studied by the determination of the unit-cell dimension from X-Ray patterns over the temperature range of -183 degree C and 25 degree C. The thermal expansion coefficient based on the change in unit cell dimension with change in temperature is about the same as for quartz.

Density :

The density of zeolites is low, ranging from about 1.9 to 2.3 g/c.c. Cation exchange with heavy ions increased the density; some barium zeolites have densities as high as 2.8 g/cc. The density depends on the openness of the zeolite structure and the cation.

Hardness :

The hardness of zeolite minerals ranges from 4 to 5 on the Mohs scale. A hardness of 4 is typical of the mineral fluorite and measures 163 on the knoop scale. The value of 5 is characteristic of apactite (knoop 430) and is less than the hardness of feldspar[18].

Colour :

Zeolites in pure state are colourless. Crystals of some mineral specimens are so transparent that it is difficult to see them in matrix rock. In other instances, small amount of impurities account for the colour of minerals, such as iron in pink chabazite as is found in Nova Scotia.

Electrical Conductivity :

Zeolites contain mobile cations which are located within sites in cavities, on the channel walls, and free within the channels coordinated with water molecules. The electrical conductivity exhibited by zeolites is ionic and arises from the migration of cations through the zeolite framework[19]. The conductivity was found to depend strongly on the cation size and the size of the channels within the zeolite structure. The activation energy decreases due to a diminishing coulombic attraction between the cation and the cation site. Each divalent cation must be associated with two negatively charged sites in the framework structure. The calcium ion should have twice the activation energy for conduction as the sodium ion if only electrostatic interactions are considered and provided that the calcium ion site is completely equivalent to two sodium sites. The calcium ion is situated between or near one of the widely separated negatively charged sites in the framework and the bond strength must accordingly be reduced. The sharp increase in the activation energy with increasing size of divalent atoms reflects the greater ease of bonding to two separate sites by the larger, more polarized cations. The addition of water molecules to the dehydrated zeolite structure produces a pronounced change in the electrical conductivity. A change in conductivity with the adsorption of nonpolar molecules in zeolites has been determined. A higher electrical conductivity obtained for the absorption of nitrogen indicates that the nitrogen molecules are more strongly bound to the structure than oxygen molecules. The adsorption interaction energies of nitrogen and oxygen with the zeolite are attributed to cation quadrupole interaction[20].

4.2 SYNTHETIC ZEOLITES

4.2.1 Review of Early Work :

As it is not always possible to obtain natural zeolites in large quantities required for industrial applications, a lot of work has been done to develop synthetic zeolites. Attempts to synthesize silicates under hydrothermal conditions began with the experiments conducted by Schafhautle in 1845 for preparation of quartz by heating silica with water in an autoclave. St Claire Deville reported the synthesis of 'levynite' by heating aqueous solutions of potassium silicate and sodium aluminate in glass tubes at 170 degree C in the year 1882. The synthesis of 'analcime' was reported by De Schulten in 1882. The hydrothermal alteration and synthesis of silicates carried out till 1937 has been reviewed in a paper by Morey and Ingerson[21]. During this period identification of the various products obtained was based upon chemical analysis or optics. As the products in most instances were very small in particle size, the results were not very accurate. Until identification of polycrystalline materials by means of X-Ray powder data became common, accurate identification of products as zeolite was not possible.

The results of a series of experiments for the hydrothermal synthesis of silicates by Baur in 1911 is reported by Barrer[22]. Solutions of soluble compounds prepared to produce the necessary ratios of Na_2O, K_2O, Al_2O_3 , SiO_2 and CaO were placed in a steel drum which was hermetically sealed and heated in a furnace for the required duration to obtain crystalline products. In 1936, Straub described the preparation of analcime by the hydrothermal treatment at 282 degree C for 46 hours[23]. The first synthesis of an analcime type zeolite substantiated by X-Ray diffraction analysis was by Barrer and White[24].

Many unsubstantiated reports on the synthesis of chabazite type zeolite were published, but Barrer has questioned the reliability of the reported chabazite preparations[25] as the attempts to reproduce them failed. The first substatiated synthesis of a mordenite-type zeolite was made by Barrer[26]. An aqueous sodium aluminate solution which contained sodium carbonate was used to produce a gel composition similar to mordenite. Crystallization was obtained by heating the gel with water in an autoclave at 300 degree C.

Baur reported the formation of potassium faujasite and stilbite by hydrothermal synthesis[21]. Mixtures of silica and potassium aluminate or silica, potassium aluminate and aluminium hydroxide gave a product reported to be potassium faujasite. However, Baur stated that there was some uncertanity regarding the identification.

The discovery of a hydrothermal method to convert minerals such as analcime, leusite or various aluminosilicate gels into zeolite by treatment at high temperature with concentrated solutions of barium chloride, barium bromide or similar salts was reported by Barrer.[27]

4.2.2 Synthesis of Zeolite :

Since many decades, scientists have been extremely interested in reproducing the formation of minerals in the laboratory by methods which were believed to be similar to natural processes. Early hydrothermal investigations were confined to temperatures above 200 degree C and correspondingly elevated pressures. Reaction mixtures composed of the various components corresponding to the desired product were maintained at constant temperature and pressure for required period in the presence of excess water. The water itself was not usually considered a reactant. Some degree of success might have been achieved in these early experiments, but positive identification of the products was not reported.

Most of the synthetic zeolites are produced under nonequilibrium conditions and are considered to be in metastable phases. In the four component system Na_2O - Al_2O_3 - SiO_2 - H_2O, at 1000 atmospheres pressure and excess water, synthetic phases related to albite, analcime, mordenite, hydroxycancrinite etc. are formed at temperature ranging from 290 degree C to 700 degree C[28]. In the same system, from identical or similar chemical compositions, widely different zeolite species may be formed as metastable phases in closed systems at temperatures lower than 200 degree C.

A new approach to zeolite synthesis was initiated by R.M. Milton and associates in the Union Carbide Corporation. This approach was to start with very reactive components in a closed system and employing temperatures for crystallization which are close to temperatures required for synthesis of organic compounds[29,30]. Many of the synthetic zeolites are formed at temperatures ranging from room to boiling water.

Early attempts to synthesize zeolites were based upon the then prevalent notion regarding their formation in bastaltic rocks. Recent information on the formation of zeolite minerals in sediments and ocean bottoms is consistent with the relatively lower temperatures used in laboratory synthesis. The low temperature synthesis is well suited for large scale manufacturing in the industry.

In the commercial manufacture of Molecular Sieve, sodium silicate, alumina trihydrate and sodium hydroxide are automatically batch weighed into mix tanks and stirred until it becomes homogeneous[31]. The resulting gel is pumped into a crystallization tank where it is maintained under closely controlled conditions. The progress of crystallization is usually monitored by several quality control techniques including X-Ray diffraction. After crystallization is complete, the crystal slurry is filtered and washed. If calcium or other cations are to be substituted for sodium in the crystal, the filter cake is transfered to a heated tank where it is mixed with a solution of the appropriate metal salt. As in the original crystal slurry the exchanged form is washed and filtered.

To form the commercial 1.5 mm and 3 mm pellets, crystals from the filter (mostly in the 0.1 to 10 micron range) are mixed with specially selected clay binders and fed through an extruder. The pellets are then dried, screened and fired in a rotary kiln to drive out the water and activate the Molecular Sieve. The pellets are immediately packaged to prevent any moisture pickup.

4.2.3 Adsorption by Dehydrated Zeolites :

In 1840, Damour observed that zeolites could reversibly dehydrate without any apparent change in their transparency or morphology[32]. Dehydrated chabazite crystals were observed to rapidly adsorb the vapours of water, methyl alcohol, ethyl alcohol and formic acid, but it did not adsorb acetone, ether or benzene[33]. It was later deduced that zeolites adsorbed molecules smaller than the pore opening and due to this the term 'Molecular Sieves' originated.

Molecular Sieves retain adsorbates by strong physical forces rather than by chemical absorption. This means that when the adsorbed molecule is desorbed, it leaves the crystal in the same state as when it entered. In adsorption by Molecular Sieves the amount of a given compound adsorbed increases rapidly to the saturation value as the pressure and concentration in the external phase increases. Any further increase in pressure at constant temperature causes no further increase in the amount adsorbed. This equilibrium saturation value corresponds to a complete filling of the internal void volume with the adsorbate.

Desorption from Molecular Sieve powders shows no hysteresis. The adsorption and desorption are completely reversible with the respective isothermal curves coinciding completely. With the pelleted material, some further adsorption may occur at pressures near the saturation vapour pressure through condensation of liquid in the pellet voids external to the zeolite crystals.

The external surface area of the Molecular Sieve crystal is available for adsorption of molecules of all sizes, whereas, the internal area is available only to molecules small enough to enter the pores. The external area is only about 1% of the total surface area. Materials that are too large to be adsorbed internally will commonly be adsorbed externally to the extent of 0.2 to 1 weight per cent.

Molecular Sieves separate molecules based on size and configuration, but they will also adsorb preferentially based on polarity or degree of unsaturation. In a mixture of molecules small enough to enter the pores, the less volatile, the more polar or the more unsaturated a molecule, the more tightly it is held within the crystal. The very strong adsorption forces in Molecular Sieves are due primarily to the cations which are exposed in the crystal lattice. These cations act as sites of strong localized positive charge which electrostatically attract the negative end of polar molecules.

4.2.4 Basic Types of Synthetic Molecular Sieves :

While there are over thirty types of synthetic Molecular Sieves developed mainly by the Union Carbide team, four basic types called 3A, 4A, 5A and 13X have found the maximum commercial utility. Table 4.2 gives the important specifications of these zeolites[31].

Table 4.2 : Important Synthetic Zeolites and their Specifications

Basic Type	Nominal Pore Diameter Angstroms	Common form	Bulk Density (gm/l)	Heat of Adsorption (max) (Kcal/kg H2O)	Equilibrium H2O capacity % wt
3A	3	Powder	480	1000	23
		1.5 mm Pellets	750		20
		3 mm Pellets	750		20
		8 x 12 Beads	705		20
		4 x 8 Beads	705		20
4A	4	Powder	480	1000	28.5
		1.5 mm Pellets	720		22
		3 mm Pellets	720		22
		8 x 12 Beads	720		22
		4 x 8 Beads	720		22
		14 x 30 Mesh	705		22
5A	5	Powder	480	1000	28
		1.5 mm Pellets	690		21.5
		3 mm Pellets	690		21.5
13X	10	Powder	480	1000	36
		1.5 mm Pellets	640		28.5
		3 mm Pellets	640		28.5
		8 x 12 Beads	640		28.5
		4 x 8 Beads	640		28.5

As can be seen the 13X has the highest water adsorption capacity of 28.5% and has 10 A pore diameter. The isotherms for adsorption of water in 13X powder at temperatures of 25 degree C and 100 degree C are given in Fig. 4.3.

The adsorption capacity of 13X pellets would be about 20% lower than the pure powder due to the binding material used in the pellets. The adsorption isotherms for the pellets is shown in Fig. 4.4 [34].

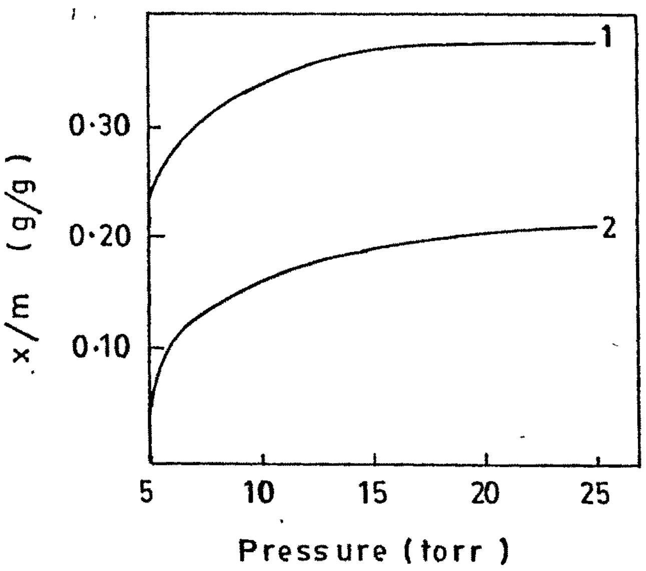

Fig. 4·3 Isotherms for the adsorption of H_2O in 13X powder
(1) 25 °C (2) 100 °C

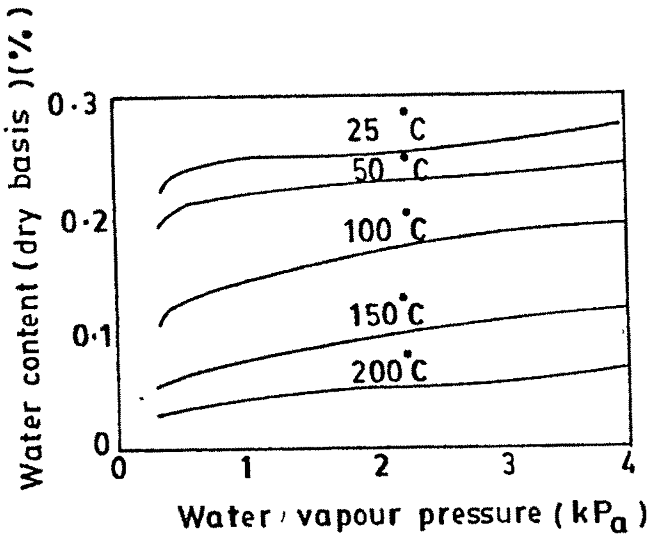

Fig. 4·4 Adsorption isotherms of water vapour on zeolite 13 X pellets

The structure of 13X is similar to that of Faujasite and the ratio of Si to Al is 1 to 1.5. It is a stable crystal with a pore volume of about 0.36 CC per gm. The X-Ray Diffraction data is given in Table 4.3[1].

Table 4.3 : X-Ray Diffraction data of Molecular Sieve 13X

h k l	d(A)	I
111	14.465	100
220	8.845	18
311	7.538	12
331	5.731	18
333	4.811	5
511		
440	4.419	9
531	4.226	1
620	3.946	4
533	3.808	21
622	3.765	3
444	3.609	1
711	3.500	1
551		
642	3.338	8
731	3.253	1
553		
733	3.051	4
822	2.944	9
660		
751	2.885	19
555		
840	2.794	8
911	2.743	2

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